Thermal Conductivity of HFC-32, HFC-125 and HFC-134a in the Solid Phase[1]

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ABSTRACT

The measurements of the thermal conductivity of HFC-32, HFC-125 and HFC-134a were carried out for the first time in the saturation pressure of the room temperature and in the temperature range from 120 K to 263 K, from 140 K to 213 K and from 130 K to 295 K in both solid and liquid phases, respectively. A transient hot-wire apparatus using one bare platinum wire with an uncertainty of less than 2% was employed to take the measurements. The experimental results demonstrated that the thermal conductivity of HFC-32, HFC-125 and HFC-134a in the solid phase showed a positive temperature dependence. As for HFC-32 and HFC-125, there were a big jump between the solid and the liquid thermal conductivity at the melting point. But for HFC-134a, the solid and liquid thermal conductivity at the melting point is almost continuous.

KEY WORDS: HFC-32; HFC-125; HFC-134a; melting point; refrigerant; solid phase; thermal conductivity; transient hot-wire method.

1. INTRODUCTION

Up to present, we have measured the thermal conductivity of the pure component HFC-32, HFC-125 and HFC-134a and their mixtures [1-5] in the liquid phase. In the present work, in order to obtain the solid thermal conductivity of these materials and to investigate the behavior of their thermal conductivity at the melting point, we measured the solid and liquid thermal conductivity of HFC-32, HFC-125 and HFC-134a in the saturation pressures of the room temperature 1.48 MPa, 1.29 MPa, 0.61 MPa, and in the temperature ranges from 120 K to 263 K, from 140 K to 213 K, from 130 K to 295 K, respectively.

2. EXPERIMENTAL APPARATUS

The measurements were carried out by the transient hot-wire method using one bare platinum wire with an uncertainty of less than 2%. Fig.1 shows a sectional diagram of the hot-wire cell with the pressure vessel. Considering the endurance of the hot-wire while the sample was under solidification at the melting point, the relatively thick platinum wire of 15 m in diameter was used. In order to compensate for the end effect of the hot-wire, two voltage potential leads of the same platinum wire were spot-welded at the positions nearly 10 mm far from each end of the wire. Between the two potential leads, the transient voltage rise, which corresponds to the temperature increase of the wire, was measured with the digital voltmeter directly. The measuring electrical system used in the present work was the same one as in the previous work [2].

Fig.2 shows a schematic diagram of the experimental apparatus. The temperature controlled thermostatic bath were composed of double layers. The pressure vessel was immersed completely in the inner layer of the bath. The heat transfer medium used was the liquid nitrogen, which was poured into the outer layer of the bath. Two electrical

heater twined about the upper and lower part of the pressure vessel respectively. By adjusting both the amount of the liquid nitrogen in the bath and the electrical power of the two heaters, we can regulate the temperature of the sample. To monitor the vertical temperature gradient of the sample, three CA thermocouples were fixed on the upper, middle and lower surface of the pressure vessel, respectively. The temperature of the sample was measured with a platinum-cobalt resistance thermometer calibrated on the ITS-90 with an accuracy of 0.05 K. In order to prevent the occurrence of the initial natural convection, the temperature in the upper part of the pressure vessel was always adjusted to be 12 K higher than that in the lower part. During the measurements, the temperature change rate of the heat transfer medium was regulated to be lower than 0.002 K/s in order to ensure the high accuracy of the measurements.

Considering that the accuracy of the temperature coefficient of the platinum wire is 0.3%, the accuracy of the temperature rise slope of the hot-wire is 0.5%, the accuracy of the heat generation of the hot-wire is 0.2%, and adding up the end effect of the hot-wire and so on, the accuracy of the experimental apparatus is ultimately estimated to be better than 2%.

3. RESULTS AND DISCUSSIONS

The functioning of the experimental apparatus was tested by taking the measurements of the liquid thermal conductivity of toluene, which agreed with IUPAC recommended values [6] within a deviation of 2~3% . During the experiment for HFC-32, HFC-125 and HFC-134a, the pressure vessel was always connected with the bomb of the sample, which remained the saturation in the room temperature. The measurements started from the room temperature, and the solid thermal conductivity was measured in succession following the measurements in the liquid phase. Near the melting point, the sample was

cooled for about 5 hours to ensure the complete solidification.

3.1 HFC-32

The measurements of the thermal conductivity of HFC-32 were carried out two times using two different hot-wire cells in the saturation pressure of the room temperature 1.48MPa and in the temperature ranges from 128 K to 223 K, from 120 K to 263 K in the solid and liquid phases, respectively. The sample of HFC-32 with the purity of better than 99.98wt% was supplied by Showa Denko Co., Ltd.. The experimental results for HFC-32 in the solid phase is listed in Table I. The thermal conductivity of HFC-32 in the solid and liquid phases is plotted as a function of temperature in Fig. 3. Above 193 K, the present results in the liquid phase agree very well with our previous work [1]. Because there is no previous measurement in the solid phase so that no comparison is possible. The experimental results between the measurements of the first and the second times agree well with each other within the accuracy of 2%. In the vicinity of the melting point, the solid and the liquid thermal conductivity of HFC-32 is not continuous. The thermal conductivity of HFC-32 in the solid phase is bigger than that in the liquid phase at the melting point. The thermal conductivity of HFC-32 in the solid phase shows positive temperature slope. During the measurement near the melting point, we observed that the reproducibility became worse sometimes, and the measured data were about 1040% bigger than the normal values. It is assumed that this is due to the latent heat generation during the liquid-solid phase transition. So these data were removed in the present work. The solid thermal conductivity of HFC-32 has been reproduced as a function of temperature by Eq. (1):

$$\lambda_S = \lambda_m + a \times (T - T_m)$$

$$= 0.2987 + 2.25 \times 10^{-3} \times (T - 136) \qquad (1)$$

$$(120K < T < 136K)$$

Where λ_S is the solid thermal conductivity, $Wm^{-1}K^{-1}$. λ_m is the solid thermal conductivity at the melting point, $Wm^{-1}K^{-1}$, T_m is the supposed temperature of the melting point according to the present experimental observation, K.

3.2 HFC-125

We have taken the measurement of the liquid and solid thermal conductivity of HFC-125 in the saturation pressure of the room temperature 1.29 MPa and in the temperature range from 140 K to 213 K. The sample of HFC-125 with the purity of 99.6wt% was supplied by Du Pont-Mitsui Fluorochemicals Co., Ltd.. Table II lists the experimental results for HFC-125 in the solid phase. The experimental results of HFC-125 in the solid and liquid phases are shown in Fig. 4. We have measured the liquid thermal conductivity in the temperature range from 193 K to 333 K in the previous work [2]. As shown in Fig. 4, the present results in the liquid phase above 193 K agree with our previous work within 2%. Different from the situation for HFC-32, though there is a big jump between the solid and liquid thermal conductivity of HFC-125 at the melting point, the thermal conductivity of HFC-125 in the solid phase is smaller than that in the liquid phase. The solid thermal conductivity of HFC-125 also shows a positive temperature slope similar to the HFC-32. With the same reason as in the case of HFC-32, the measured data near the melting point were removed here. The solid thermal conductivity of HFC-125 is correlated as linear function of temperature as the follows:

$$\lambda_S = \lambda_m + a \times (T - T_m)$$

$$= 0.1027 + 1.34 \times 10^{-4} \times (T - 172) \qquad (2)$$

$$(140K < T < 172K)$$

3.3 HFC-134a

The measurements for HFC-134a have been carried out at the saturation pressure of the room temperature 0.61 MPa in the liquid phase from 172 K to 295 K and in the solid phase from 130 K to 172 K. The sample of HFC-134a employed here was supplied by ICI Chemicals and Polymers, and its purity was confirmed to be better than 99.9wt%. Table III lists the experimental results for HFC-134a in the solid phase. Fig. 5 shows the temperature dependence of the solid and liquid thermal conductivity for HFC-134a. It is clear from Fig. 5 that the present results in the liquid phase above 193 K agree with our previous work [3] within the mutual uncertainties. No comparison is available in the solid phase because of no previous works. Contrary to the situation of HFC-32 and HFC-125, the solid and liquid thermal conductivity of HFC-134a at the melting point is almost continuous. Like the HFC-32 and HFC-125, the solid thermal conductivity of HFC-134a also shows a positive temperature slope. During the liquid-solid transition at the melting point, the measured data were removed in the present work because of the worse reproducibility due to the latent heat generation. The experimental data in the solid phase have been represented as a function of temperature by the following equation:

$$\lambda_S = \lambda_m + a \times (T - T_m)$$

$$= 0.1310 + 3.21 \times 10^{-4}(T - 170) \qquad (3)$$

$$(130K < T < 170K)$$

For the nonmetallic materials, the ratio of the solid to liquid thermal conductivity at the melting point is approximately expressed as [7]

$$\frac{\lambda_S}{\lambda_L} \cong \left(\frac{\rho_S}{\rho_L}\right)^{g_L} \qquad (4)$$

where λ_S and λ_L represents the solid and liquid thermal conductivity at the melting point respectively, ρ_S and ρ_L are the solid and liquid density at the melting respectively. g_L, which depends only on the thermal properties of the liquid phase, is defined as the variation of the liquid thermal conductivity λ_L with the volume at constant temperature near the melting point. For most of the nonmetallic substances, g_L is estimated to be in the range from 1 to 4. It can be assumed that the different behavior in the thermal conductivity of HFC-32, HFC-125 and HFC-134a at the melting point is responsible for different change in density during the solid and liquid phase change. In view of no solid and liquid density data at the melting point for HFC-32, HFC-125 and HFC-134a at present, the above-mentioned assumption remains to be verified yet by measuring the solid and liquid density in the near future.

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List of Figure Captions

Figure 1 The sectional diagram of hot-wire cell with the pressure vessel: 1, Pressure vessel (Duralumin); 2, Pressure vessel cap; 3, Platinum wire (15 m); 4, Platinum hook (0.5mm); 5, Cell frame (Titanium). 6, Pt-Co resistance thermometer well; 7, Sealing unit (Conax); 8, Metal O-ring.

Figure 2 The schematic diagram of the experimental apparatus: 1, Pressure vessel; 2, D.V. M; 3, Liq. N_2; 4, Heater; 5, Vacuum pump; 6, Pressure gage; 7, Sample bomb; 8, Cryostat; 9, Vacuum gage; 10, Thermocouples; 11, Pt-Co resistance thermometer.

Figure 3 The thermal conductivity of HFC-32 in the solid and liquid phases as a function of temperature.

Figure 4 The thermal conductivity of HFC-125 in the solid and liquid phases as a function of temperature.

Figure 5 The thermal conductivity of HFC-134a in the solid and liquid phases as a function of temperature.

Table I. Thermal Conductivity of HFC-32 in the solid phase.

Temperature (K)	Thermal conductivity, λ ($Wm^{-1}K^{-1}$)
135.0	0.2805
134.2	0.2882
133.1	0.2897
132.9	0.2882
133.0	0.2859
128.9	0.2872
128.6	0.2881
127.4	0.2845
127.6	0.2876
127.6	0.2881
120.3	0.2583
120.4	0.2523
120.5	0.2593

Table II. Thermal Conductivity of HFC-125 in the solid phase.

Temperature (K)	Thermal conductivity, λ ($Wm^{-1}K^{-1}$)
169.1	0.1034
169.0	0.1031
169.1	0.1021
162.2	0.1028
162.2	0.1007
160.4	0.1009
160.4	0.0996
160.5	0.1015
150.8	0.0997
151.0	0.0972
151.0	0.0991
140.7	0.0991
140.6	0.1004

Table III. Thermal Conductivity of HFC-134a in the solid phase.

Temperature (K)	Thermal conductivity, λ ($Wm^{-1}K^{-1}$)
166.5	0.1304
166.0	0.1310
166.1	0.1303
160.7	0.1282
160.9	0.1277
160.8	0.1269
150.9	0.1242
151.1	0.1240
150.4	0.1242
150.5	0.1242
151.0	0.1244
130.3	0.1168
130.6	0.1192
130.2	0.1182
130.8	0.1193
130.1	0.1187

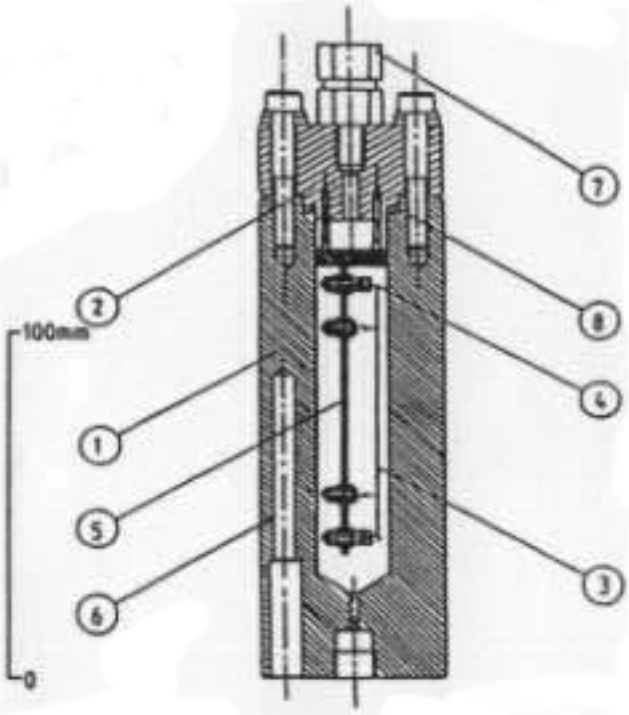


Figure 1

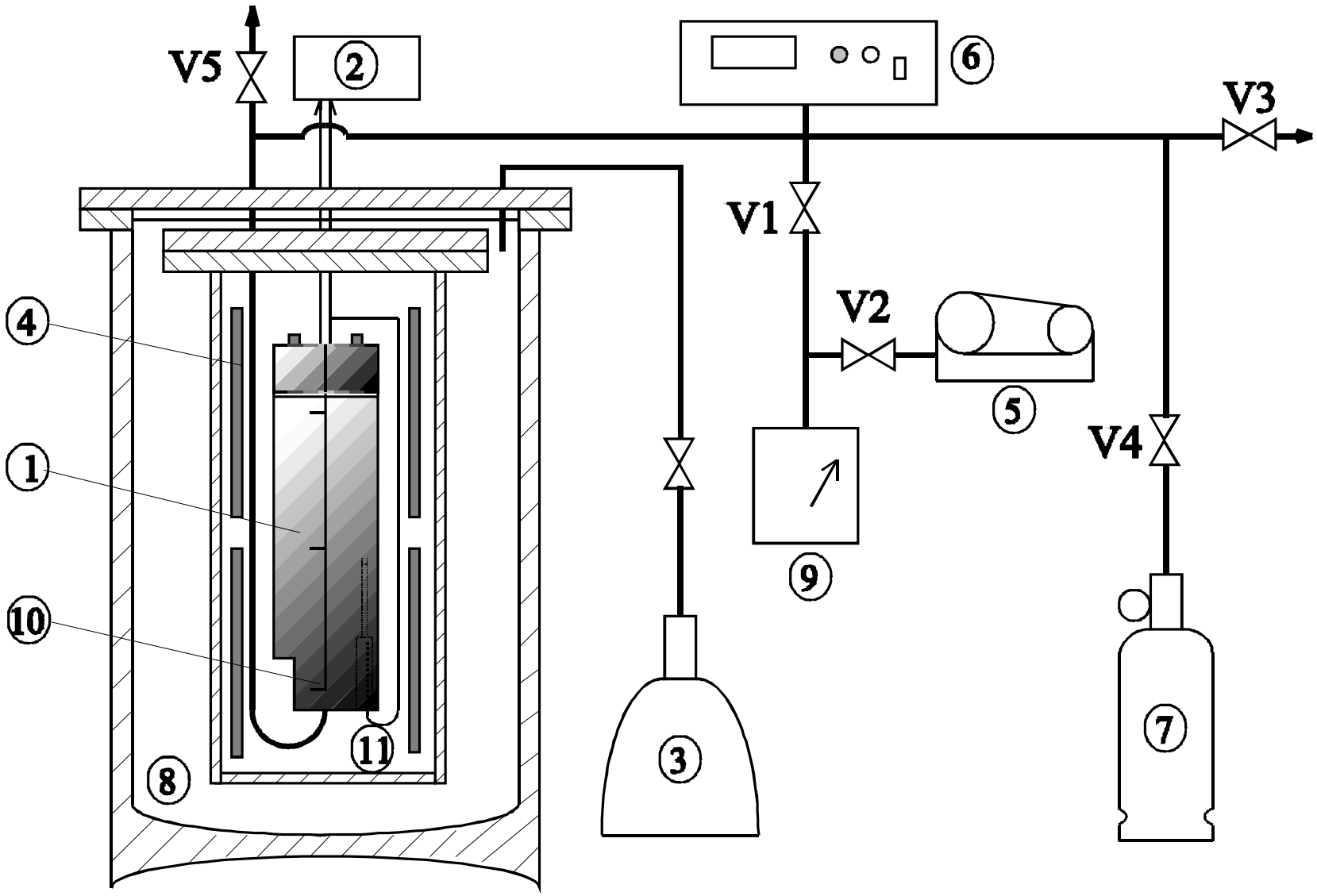
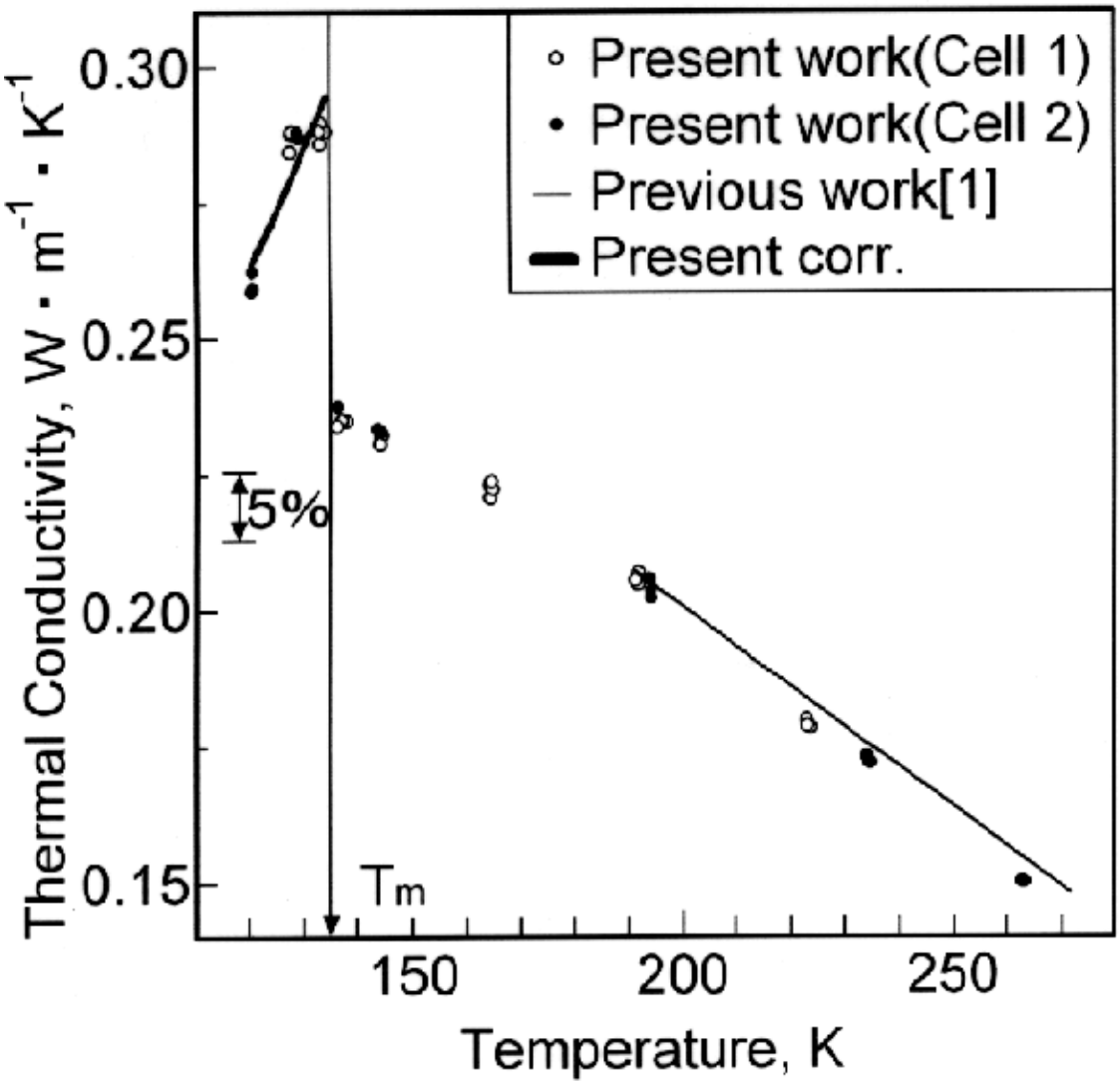


Figure 2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Present work(Cell 2)
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Present corr.
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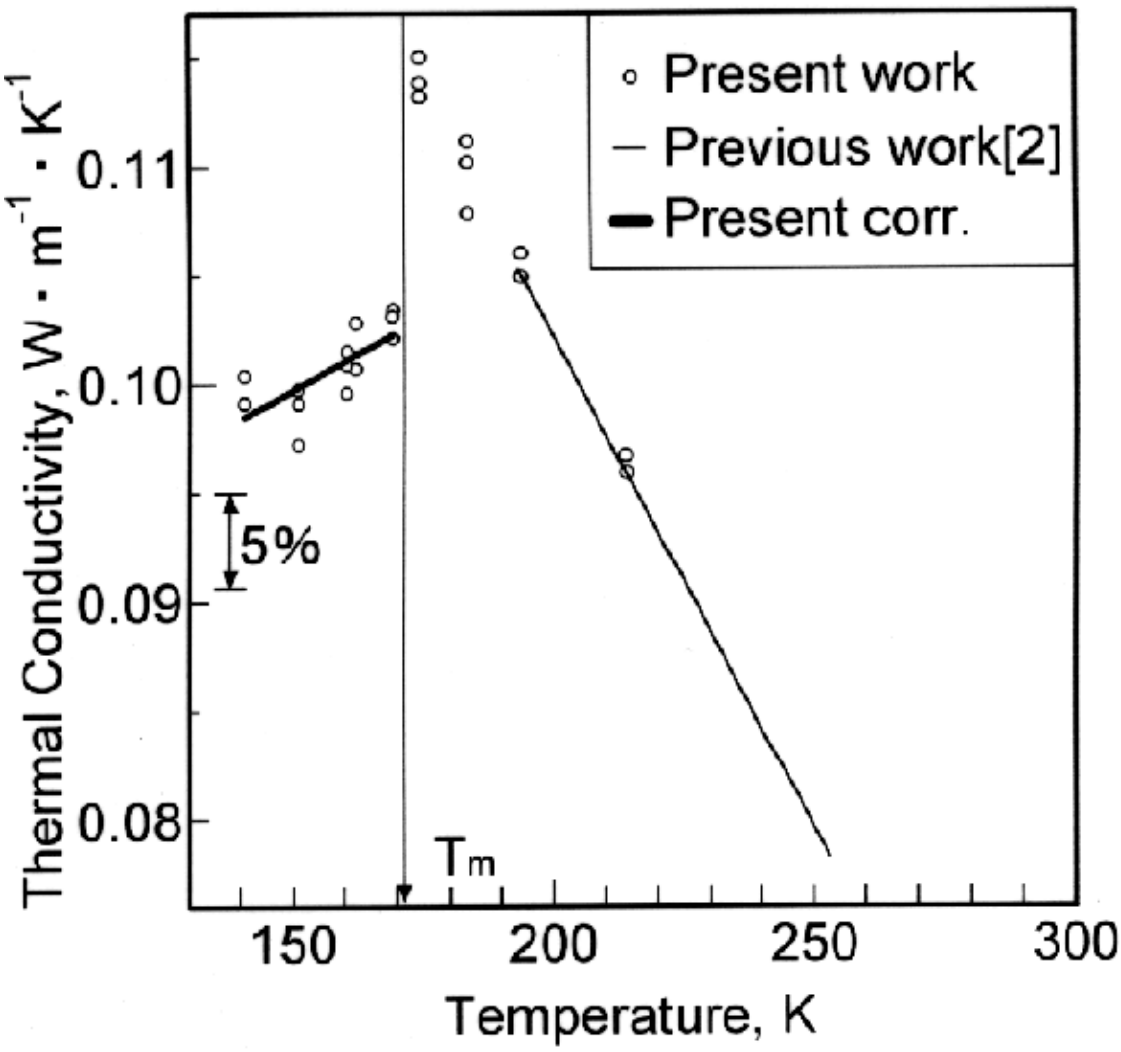
0.20
0.15
5%
Tm
150
200
250
Temperature, K

Figure 3


Present work
Previous work[2]
Present corr.
Thermal Conductivity, W · m-1 · K-1
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0.09
0.08
5%
Tm
150
200
250
300
Temperature, K

Figure 4

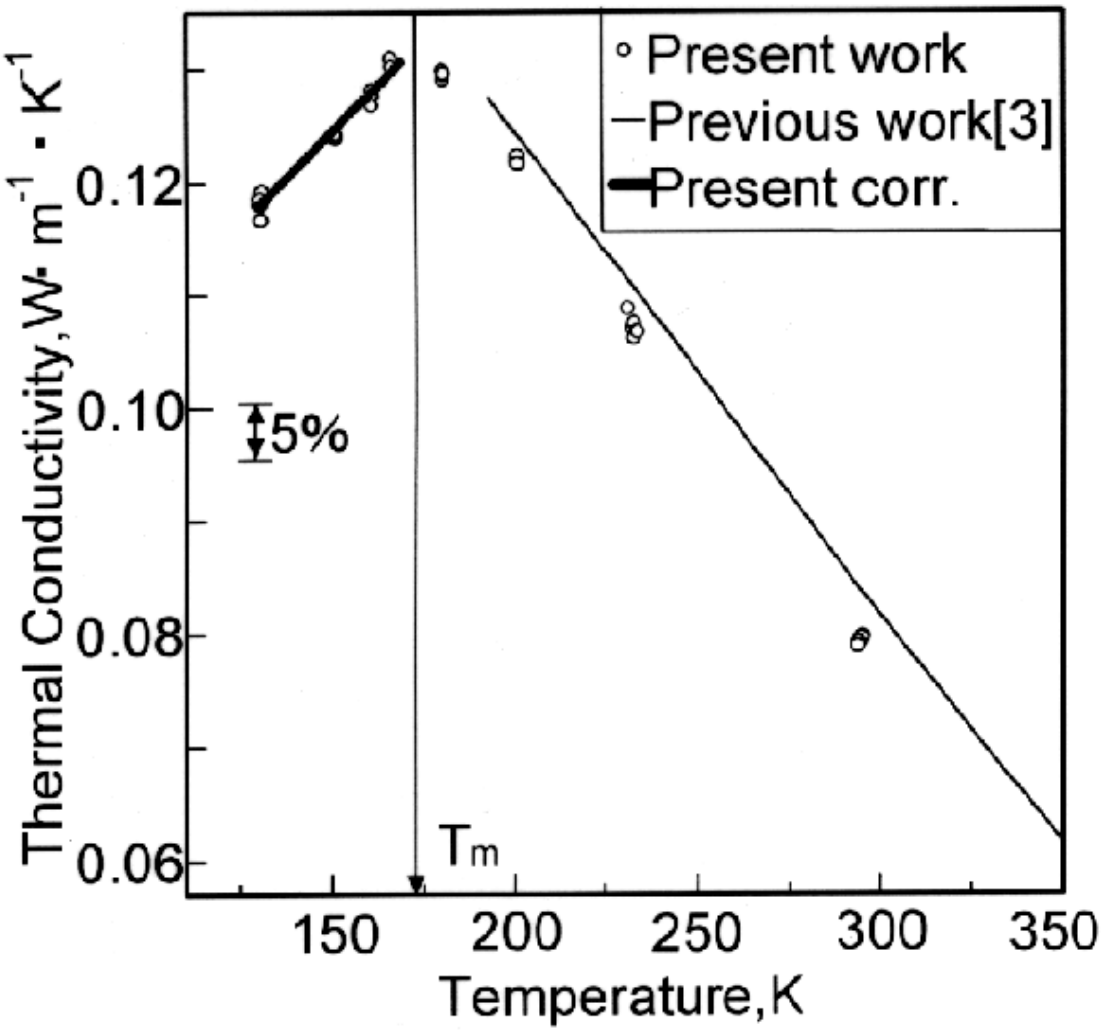
Present work
Previous work[3]
Present corr.
Thermal Conductivity, W· m-1 · K-1
0.12
0.10
0.08
0.06
5%
Tm
150
200
250
300
350
Temperature, K

Figure 5