Memoirs of the College of Science, University of Kyoto, Series A, Vol. XXV, Nos. 3 & 4, Article 24, 1949.

Thermal Conductivities of Single- and Polycrystalline Bismuth*

By

Shigeka Nishioka

(Received September 7, 1949)

Abstract

Thermal conductivities of single- and polycrystalline bismuth were measured by using specimens in the form of a cube. The values found at 14°C were as follows:—

The thermal conductivity of polycrystal: 0.01914 cal./cm. sec. deg.

The thermal conductivity of single crystal parallel to the trigonal axis: 0.01269 cal./cm. sec. deg.

The thermal conductivity of single crystal perpendicular to the trigonal axis: 0.02252 cal./cm. sec. deg.

Linder's theory for the relation between the thermal conductivities of singleand polycrystalline bismuth was verified by applying the above values.

Measurements were also carried out on several specimens in the form of rectangular plates of single crystal, of which the orientation of the trigonal axis with respect to the normal to the plate ranges from 0° to 89° . The results showed that the Voigt-Thomson's relation is satisfied fully for thermal conductivities of bismuth.

Introduction

1-4

A number of investigators have measured the thermal conductivities of single- and polycrystalline bismuth by using specimens in the form of a plate or a cylinder. The relation between the thermal conductivities were studied by Kaye and Roberts³ and by Linder.⁵ Two entirely different formulae were given by them :—

Kaye and Roberts:
$$\frac{1}{k} = \frac{1}{3} \left(\frac{1}{k_{\perp}} + \frac{2}{k_{\perp}} \right)$$
,
Linder: $k = \frac{1}{3} (k_{\perp} + 2k_{\perp})$,

- 4. G. W. C. Kaye and W. F. Higgins, Phil. Mag., 8, 1056 (1929).
- 5. E. G. Linder, Phys. Rev., 39, 554 (1927).

^{*} Communicated by Professor K. Tanaka.

^{1.} Jaeger and Diegelhorst, Wiss. Abh. d. Phys.-tech. Reich., 3, 369 (1906).

^{2.} E. Giebe, Ber. d. deutsch. phys. Gesell. 5, 60 (1903).

^{3.} G. W. C. Kaye and J. K. Roberts, Proc. Roy. Soc. London, 104, 98 (1923).

Shigeka Nishioka.

where k is the thermal conductivity of polycrystal, and k_{\perp} and k_{\parallel} are two principal thermal conductivities of single crystal respectively.

The objects of the present work are (1) to measure the thermal conductivities of polycrystalline and single crystal bismuth by using the identical method, (2) to ascertain the previously reported values and the formulae of the relation between the thermal conductivities and (3) to check the Voigt-Thomson's law⁶ for the thermal conductivity. The method applied was one of a guard-tube type. The specimen used was in a form of a cube or a plate.

Preparation of specimens

Merch pure bismuth was employed in this experiment. Three kinds of specimens were prepared: (1) specimens of polycrystal in the cubic form, of which the length of one edge being about 0.93 cm, (2) specimens of single crystal in the cubic forms of which the length of the edge being about 0.93 cm and one plane being perpendicular to the trigonal axis of crystallization, (3) specimens of single crystal in the form of rectangular plate, 2 mm in thickness and 0.93 cm in width and length, of which the orientation of the trigonal axis with respect to the normal to the plane ranges from 0° to 89°. The method of growing the single crystal was one used ordinarily⁷.

Apparatus and experimental procedre

The apparatus was consisted essentially of the following parts (Fig. 1): a specimen S, a heating block B_1 , a cooling block B_2 and water jackets G_1 , G_2 , H_1 and H_2 . Heat supplied by a heater coil C_5 wound round B_1 was transmitted to B_1 , next to the specimen S and finally to the cooling block B_2 which was soldered to the upper surface of the water jacket G_1 . B_1 and B_2 were in the form of a rectangular parallelepiped with the same sectional area $0.94 \text{ cm} \times 0.94 \text{ cm}$ and 1.5 cm, 0.4 cm in height respectively. The doublewalled water jacket H_2 and the water jacket H_1 served to prevent the heat loss from the surface of B_1 by controlling the temperature of water circulating through them. Between H_2 and G_2 was inserted a hollow wooden block D with the same section as H_2 . B_7 controlling the temperature of water circulating through H_2 and G_2 , and the power supplied to the heater coil C_5 , the same temperature gradients could be established in S and in D. The tem-

^{6.} W. Voigt, Lehrbuch der Kristallphysik.

^{7.} S. Ito, This Memoirs, A, XII, 97 (1924).

peratures of B_1 , G_2 and H_2 were measured by platinum thermometers C_1 , C_2 , C_3 and C_4 respectively. C_1 , C_2 , C_3 , C_4 and C_5 were 35 cm in length and 0.10mm in dia-

The middle part meter. $33 \text{ cm of the wires } C_5 \text{ and }$ C_1 were wound round B_1 , and C_2 around B_2 in the same way, and the both ending 1 cm of them were used as leads, the ends of which were soldered to copper leads in turn. The load W which is not described in Fig. 1, pressed B_1 through the support M, \mathbf{H}_1 and a hollowed wooden block A successively. The space enclosed by B_1 , H_2 and H_1 was filled with caolin powder. H_1 and H_2 were surrounded by a cotton wool to prevent heat loss.



Fig. 1. Diagram of apparatus.

The specimen S was coated at upper and lower surfaces with glyceline and was inserted between B_1 and B_2 . The water was flowed through H_1 , H_2 , G_1 and G_2 . When the steady state was reached, the temperatures of C_1 , C_2 , C_3 and C_4 were measured. Then the heater coil C_5 was supplied with power from batteries. The temperatures of the water flowing through H_1 , H_2 and G_2 were controlled so that the temperatures of H_1 and H_2 became equal to that of B_1 , and the temperature of G_2 to that of B_2 , and the same temperature gradient were established in the specimen S as in the hollow disk D. When the steady state was reached, the temperatures of C_1 and C_2 were measured. In order to calculate the resistance of the coil of the portion wound round the copper block, the resistance of the lead must be subtracted. This was done by using compensating wires as usual.⁸ The temperature drop in the specimen was calculated by applying the first correction as described in the following paragraph to the temperature difference between C_1 and

^{8.} For example, Handbuch d. Experimental Physik, VIII, 1 Teil, p. 62.

 C_2 . The intensity of the electric current through C_5 was measured with a standard resistance and a potentiometer. The power conducted through the specimen was calculated by applying the second and third corrections as described in the following paragraph to the power supplied to the heater coil C_5 .

Corrections

(1) Temperature correction. In order to obtain the temperature drop in the specimen, the sum of the temperature difference between C_1 and the upper surface of S, and that between the lower surface of S and C_2 , must be subtracted from the temperature difference between C_1 and C_2 . The value of this correction was estimated by the experiment of measuring the thermal conductivity as usual with a silver specimen. By subtracting the temperature drop in the silver specimen which can be calculated from the power conducted through it and the thermal conductivity of silver, from the temperature difference between C_1 and C_2 , the value of the correction was determined against the power conducted through the specimen. The results were as follows: the temperature drop which must be corrected was nearly proportional to the power conducted through the specimen, and was 2.16° C per cal/sec.

(2) Power correction. When the copper block B_1 was heated with an electric current through C_5 , the heat Q_2 produced in the platinum leads will enter B_1 also, besides the heat Q_1 which was produced in the



Fig. 2. B_3 , copper block with same sectional area as B_1 and 1 mm in height; W_1 , W_2 and W_3 , junctions of platinum leads with copper leads. portion of the coil C_5 wound round B_1 . For the purpose of measuring the ratio Q_2/Q_1 an experiment of measuring the thermal conductivity of bismuth was carried out, using the same arrangement of the apparatus as usual, except for a difference that a copper plate B_3 was inserted between B_1 and A. Platinum wires which are similar to the platinum leads of C_5 , were soldered at their ends to a point P on B_3 and to the ends of copper leads as is evident from the diagram in Fig. 2.

Supposing that, to an electric current through $W_1C_5W_2$ corresponds a temperature

difference T' between C_1 and C_2 , and also that, to the electric current of the same intensity through $W_2 P W_3$ corresponds a temperature difference T'' between C_1 and C_2 , we have

$$\frac{Q_1 + Q_2}{Q_1 + 2Q_2} = \frac{T'}{T''}$$

Therefore

$$\frac{Q_2}{Q_1} = \frac{T'' - T'}{2T' - T''} \, \cdot \,$$

The results of the measurements were as follows :---

$$\frac{Q_2}{Q_1} = 0.0298 \cdot$$

(3)^{*} Power correction. In order to prevent the heat loss from the surfaces of B_1 and S, the temperature of B_1 was made equal to those of H_1 and H_2 . Despite of doing so, however, a portion of heat was still lost. This is attributed to the complex distribution of temperatures in the space between S_2 and H_2 owing to the leads laid in it. The heat loss was measured experimentally. Caolin powder was filled in place of the bismuth specimen. And then the experiment of measuring the thermal conductivety was carried out as usual. The power which was conducted through the caolin powder filled in the space between B_1 and B_2 was able to be calculated from the temperature difference between C_1 and C_2 , and the thermal conductivity of caolin powder which was measured by another experiment. The results were as follows: the heat loss was nearly proportional to the temperature difference between C_1 and C_2 , and was 0.000163 cal./sec. per 1° C of the temperature difference between C_1 and C_2 at 14° C.

Thermal conductivity of caolin powder

The thermal conductivity of caolin powder against its density was measured with a method similar to that used by Seeman.⁹ The results are given in Table 1.

TABLE 1. Thermal conductivity of caolin powderagainst the density at 14°C.

Density (gm/cm^3)	0.407	0.625	0.685	0.744
Thermal conductivity (cal./cm. sec. deg.)	0.000144	0.000272	0.000313	0.000325

9. H. E. Seeman, Phys. Rev., 29, 616 (1927)

Shigeka Nishioka.

Results

(1) Experiments using the cubic specimen. The experimental values of temperatures and heat quantities in detail are shown in Table 2, taking the measurements on the specimen No. 1 as an example. The lengths of its edge are 0.9114 cm, and the directions along these edges are denoted by X, Y and Z respectively, X being parallel to the trigonal axis of the crystallization.

TABLE 2. Results using specimen No. 1

Direc- tion		T_2	ΔT	T	$Q'\!\left(\frac{\mathrm{cal}}{\mathrm{sec}}\right)$	$\Delta Q_1 \left(\frac{\mathrm{cal}}{\mathrm{sec}} \right)$	$\Delta Q_2 \left(\frac{\mathrm{cal}}{\mathrm{sec}} \right)$	$Q\left(\frac{\text{cal}}{\text{sec}}\right)$	$k \left(\frac{\mathrm{cal} \cdot}{\mathrm{cnnsec.deg}} \right)$
X	$\begin{array}{c} 0.099 \\ 0.228 \\ 0.179 \\ 0.101 \end{array}$	2.879 2.002 2.843 1.929	$\begin{array}{c} 0.070 \\ 0.046 \\ 0.067 \\ 0.046 \end{array}$	$2.710 \\ 1.729 \\ 2.597 \\ 1.782$	$\begin{array}{c} 0.03224\\ 0.02046\\ 0.03092\\ 0.02094 \end{array}$	$\begin{array}{c} 0.00096 \\ 0.00061 \\ 0.00092 \\ 0.00062 \end{array}$	0.00046 0.00029 0.00042 0.00029	$\begin{array}{c} 0.03264 \\ 0.02078 \\ 0.03142 \\ 0.02127 \end{array}$	$\begin{array}{c} 0.01268 \\ 0.01265 \\ 0.01274 \\ 0.01259 \end{array}$

Mean 0.01265

	0.0361.122	0.045 1.041	0.02052	0.00061	0.00017	0.02096	0.02217
v	0.0621.757	0.071 1.624	0.03232	0.00095	0.00026	0.03302	0.02239
X	0.2961.399	0.046 1.058	0.02097	0.00061	0.00017	0.02121	0.02208
	0.1081.743	0.0691.566	-0.03122	0.00093	0.00025	0.03190	0.02244

Mean 0.02227

	0.0991.1	73 0.045	1.029	0.02050	0.00061	0.00017	0.02094	0.02224
7	0.1261.7	92 0.070	1.596	0.03204	0.00096	0.00026	0.03274	0.02242
11	0.2321.8	64 0.069	1.563	0.03145	0.00094	0.00025	0.03214	0.02244
	0.1081.1	87 0.046	1.033	0.02084	0.00062	0.00017	0.02129	0.02253

Mean 0.02241

 T_1 and T_2 , temperatures of C_1 and C_2 respectively; ΔT , correction with respect to temperature drop; T, temperature drop in the specimen; Q', power supplied to the heater coil; ΔQ_1 , correction of power with respect to the platinum lead; ΔQ_2 , loss of power; Q, power conducted through the specimen; k, thermal conductivity.

The results obtained on the specimens of the single crystal No. 1, No. 2 and the polycrystal No. 3, No. 4 are summarized in Table 3. In this table, k'_{\perp} and k''_{\perp} are the thermal conductivities in directions perpendicular to each other. k', k'' and k''' are those of the polycrystal in the directions parallel to each edges of the specimens.

Thermal Conductivities of Bismuth.

Specimen	Thermal	conductivity
Single crystal No. 1	$k_{\perp} = 0.01265$ $k_{\perp}' = 0.02227$ $k_{\perp}'' = 0.02241$	Mean $k_1 = 0.01269$
Single crystal No. 2	$k_{\parallel} = 0.01273 \\ k_{\perp}' = 0.02258 \\ k_{\perp}'' = 0.02281$	Mean $k_{\perp} = 0.02252$
Polycrystal No. 3	k' = 0.02101 k'' = 0.01973 k''' = 0.01621	Moon $k = 0.01914$
Polycrystal No. 4	k' = 0.01984 k'' = 0.02077 k''' = 0.01728	Incan k = 0.01314

TABLE 3. Thermal conductivities of bismuth at 14°C.

The values of k', k'' and k''' differ considerably from one another, which is attributed to the anisotropy of the specimen of polycrystal bismuth.

In order to discuss the validity of Linder's formula, the writer has calculated the thermal conductivity k of polycrystalline bismuth by putting the above values $k_{\perp} = 0.01269$ and $k_{\perp} = 0.02252$ into the said formula. This gives

$$k = \frac{1}{2} (2 \times 0.02252 + 0.01269) = 0.01924.$$

Thus, it is found that the value of k calculated by Linder's formula is nearly equal to that obtained experimentally for the polycrystalline bismuth.

The writer's values are compared with those obtained by other authors in Tables 4 and 5.

TA	BLE	4.	Thermal	conductivity	ot	polycrystalline	bismuth.
----	-----	----	---------	--------------	----	-----------------	----------

Author	Temperature	k
Jaeger and Diegelhorst ¹	18° C	0.0193
Giebe ²	18° C	0.0192
Nishioka	14° C	0.0191

· · ·						
TABLE 5.	Thermal	conductivities	\mathbf{of}	single	crystal	bismuth.

Author	Temperature	k_1	k_{\pm}	k_{\pm}/k_{\pm}
Kaye and Roberts ³	18° C	0.0159	0.0221	1.39
Kaye and Higgins ⁴	$27^{\circ}\mathrm{C}$	0.0129	0.0223	1.73
Nishioka	$14^{\circ}\mathrm{C}$	0.0127	0.0225	1.77

Shigeka Nishioka.

Table 5 shows that the writer's value for the polycrystal agree well with those obtained by other authors. The value of k_{\parallel} obtained by Kaye and Higgins is distinctly lower than that obtained by Kaye and Roberts, while the values of k_{\perp} agree well with each other. Kaye and Higgins explained this disagreement by the presence of fissures parallel to the principal cleavage plane.⁽¹⁾As⁽¹⁾the writer's experiment gave a low value like that of Kaye and Higgins, he examined the inner parts of the specimen if there were any fissures. But he looked out nothing.

(2)Experiments using plate-shaped specimens. The experimental procedure were similar to the case of using the cubic specimen. The results are given in Table 6 and shown graphically in Fig. 3, where θ is the orientation of the trigonal axis with respect to the normal to the plane of the specimen and k is the thermal conductivity. The value of the thermal conductivity k for $\theta = 89^{\circ}$ in Table 6 is about 4 % lower than k_{\perp} in Table 3, while the value of k for $\theta = 0^{\circ}$ in Table 6 agrees well with k_{\parallel} in Table 3. This is perhaps due to the fact that the temperature drops in glyceline films become larger as compared to that in the specimen by using a thin specimen, especially when the substance under test is of good conductivity, and consequently the error may be enlarged. However, the results are still capable of showing that the relation between the orientation and the thermal conductivity is linear, as this verifies the validity of Voigt-Thomson's law.

θ	$\sin^2 \theta$	k	~~		
00	0	0.0126	2.0	 	
14.7	0.064	0.0133			
27.2	0.209	0.0142	× 18	 	<
50.7	0.599	0.0177	1.6		
67.9	0.859	0.0203			
74.3	0.927	0.0210	14	 	<u> </u>
89.0	0.900	0.0217	<u> </u>		

Fig. 3.

TABLE 6.

154