

## Thermoelectric Power of Single Crystal Bismuth Near the Melting Point

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By investigating directly the thermoelectric power of bismuth single crystals near the melting point a transition region is found in which the thermoelectric power changes gradually from that characteristic of the solid to that characteristic of the *final* liquid state. The region extends from the melting point to about  $8^\circ$  above it. As an explanation it is supposed that a definite crystal structure persists into the liquid state.

### INTRODUCTION

IN measuring the thermal e.m.f. of bismuth single crystals against constantan as a reference metal, Boydston<sup>1</sup> found certain irregularities in the e.m.f.-temperature curves in the region just beyond the melting point. As an explanation he says, "It appears, in fact, as if some crystalline arrangement still persists in the molten metal as shown by a transition region between the thermal e.m.f. of solid and liquid."

Goetz<sup>2</sup> makes use of a similar explanation for certain effects observed in his study of the factors influencing the growth and perfection of bismuth crystals. He found that if he used a seed crystal with regions of twinning to inoculate a molten rod he would invariably obtain a crystal which still showed the twin orientation unless he melted the seed back considerably beyond the region of twinning so that this region was at a much higher temperature than the melting point. He also found that a polycrystalline rod melted and raised to a temperature just slightly above the melting point, recrystallized, on cooling, into a rod which had the "same position and same orientation of the prominent crystal elements" as the original rod. If he heated the specimen considerably above the melting point, however, he found an entirely new arrangement on recrystallization.

Although Boydston observed only slight deviations of thermal e.m.f. from what is expected on the basis of an abrupt change at the melting point, it is obvious that these deviations must be accompanied by relatively large changes in the derived thermoelectric power curve. For this reason it seemed advisable to investigate directly the thermoelectric power of bismuth crystals over a temperature range extending on both sides of the melting point with the hope of definitely establishing the phenomenon foreshadowed by Boydston.

The method devised to do this consists in measuring the thermal e.m.f. over a small temperature interval at successive mean temperatures in the

<sup>1</sup> R. W. Boydston, *Phys. Rev.* **30**, 911 (1927).

<sup>2</sup> A. Goetz, *Phys. Rev.* **35**, 193 (1930).

desired region. The observed e.m.f. divided by the temperature interval gives directly the mean thermoelectric power at the mean temperature. By use of a small enough temperature interval the resolution can be made sufficiently high to justify considering this mean thermoelectric power as the actual.

#### APPARATUS AND METHOD

The experimental arrangement is shown in Fig. 1. The bismuth crystal, *BB*, has its ends fused to two copper blocks, *AA*. In fusing, the copper surface is cleaned with a flux ( $\text{ZnCl}_2$ ) and then with the end of the crystal pressed lightly against the block, the latter is heated until the bismuth just begins to melt. A little added pressure with the finger tip at this point insures a good contact. The crystal structure is not altered at the junction. Two holes *a*, *b* were drilled into the ends of each copper block, with the bottoms of the holes separated from the surface onto which the bismuth was fused by a thickness of copper of about 0.5 mm. Into the holes, *aa*, were inserted the two junctions of a constantan—copper thermocouple which measured the difference in temperature of the two ends of the bismuth rod. These junctions were en-

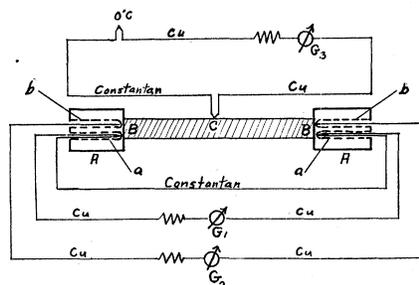


Fig. 1. Diagram of apparatus.

closed in small Pyrex glass tubes, the copper and constantan wires being separated by thin strips of mica. To the bottoms of the holes, *bb*, were silver soldered copper wires which completed the bismuth-copper thermal e.m.f. circuit. These wires were insulated from the side walls of the holes by small Pyrex tubes. This latter procedure was necessary in order to make sure that the effective junctions of this bismuth-copper couple should be at the surface of separation between the copper block and bismuth crystal. A second copper-constantan circuit had one junction placed at *C*, the other junction being maintained at zero degrees.

The electrical circuits are also pictured in Fig. 1. The reading of the galvanometer,  $G_1$ , is proportional to the temperature difference between the ends of the bismuth crystal, the reading of galvanometer,  $G_2$ , is proportional to the e.m.f. of the bismuth-copper circuit, and the reading of the galvanometer,  $G_3$ , is proportional to the mean temperature of the crystal.

The crystals were grown by a method similar to that described by Kapitza.<sup>3</sup> A groove<sup>4</sup> in an asbestos block was used for a mold. Crystals were

<sup>3</sup> P. Kapitza, Proc. Roy. Soc. **A119**, 358 (1929).

<sup>4</sup> The cross section was almost V-shaped, but with a rounded bottom.

grown of three brands of bismuth, Mallinckrodt C.P.,<sup>5</sup> a special silver-free<sup>6</sup> and Kahlbaum's best.

The results given below are for only the first brand, preliminary work<sup>7</sup> having shown no essential difference in the behavior of the others. The crystals were about 0.5 cm<sup>2</sup> in cross section and either 10 or 20 cm long. The longer ones were cut in half and a separate determination made on each piece.

In making a determination the crystal was put into an asbestos holder and placed in a horizontal furnace. The temperature gradient in the furnace was so controlled by auxiliary coils that the temperature difference between the ends of the crystal could be kept at about 1°C. The furnace temperature was allowed to pass slowly through the region under investigation. The time required to take the crystal through the desired temperature range (260° to 290°C) was about one hour.

#### RESULTS AND DISCUSSIONS

Measurements were made on six single crystals ranging in orientation<sup>8</sup> from 29° to 69°. These results are shown in Fig. 2. All crystals at a temperature sufficiently above the melting point, (i.e., in the region 280°–290°) showed a constant thermoelectric power against copper of 4.5 microvolts per degree (within 1 microvolt per degree). This has therefore been taken as a zero point and the ordinates of the curves depict the excess values above this constant level. While the curves are plotted against mean temperature, this is not obtained directly from the readings of the thermocouple, *C*, Fig. 1. This couple could not be placed in thermal contact with the crystal, and while for any one crystal it is believed that its readings give a correct measure of the rising temperature these readings may differ from the actual temperature of the center of the crystal by a presumably constant and small but undetermined amount. The observed curves have therefore been so adjusted in plotting Fig. 2 that they agree in mean temperature at the point where the final constant value is reached. This adjustment does not amount for any crystal to more than about 2° difference between the adjusted temperature scale and the indication of thermocouple, *C*, Fig. 1. The location of the melting point (271°C) as shown on the figure actually coincides with the reading of thermocouple *C* in the case of the 40° crystal. Moreover, it occurs, for this crystal, about 0.5° above the first sharp break which is then interpreted as coinciding with the beginning of the melting process. For no other crystal is the onset of melting so sharply marked. Even without such an adjustment,

<sup>5</sup> This is the same grade of bismuth that Boydston used and has the same stated analysis. Other work in this laboratory has shown that the silver content may be much less than the 0.04 percent maximum limit.

<sup>6</sup> The writer has to thank the U.S.S. Lead Refinery for this material. The analysis given with it shows: Pb 0.005 percent, Ag 0.0006 percent, Cu, Fe 0.000 percent.

<sup>7</sup> In this preliminary work about fifteen crystals were investigated, the experimental set-up being improved from time to time. As soon as a reliable arrangement was obtained the set of crystals reported on herein was grown and measured. The preliminary results were all in agreement with the final ones in their general characteristics.

<sup>8</sup> Angle between the trigonal axis and the length of the specimen.

however, the general character of the results is unchanged. To avoid confusion, the curves in Fig. 2 are plotted with an arbitrary displacement in the scale of ordinates between successive curves. Four of the crystals were sufficiently long for two determinations to be made, the circles indicating determinations made on the half onto which the nucleus had been fused during growth and crosses indicating the second half of the same crystal.

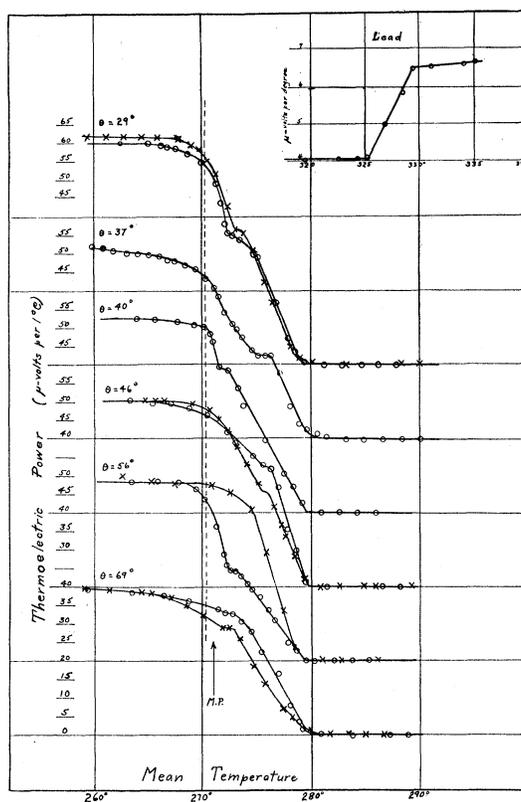


Fig. 2. Thermoelectric power as a function of temperature.

It is clear from Fig. 2 that bismuth is abnormal in its thermoelectric behavior in the region just above the melting point. For most substances which melt at a definite temperature, the thermoelectric power changes abruptly at the melting point or the thermal e.m.f. curve suffers an abrupt change in slope.<sup>9,10</sup> For the crystals shown here, however, the curves before settling down to a practically constant final liquid value pass through a transition region which lasts for approximately 8°C. This is exactly the effect predicted by Boydston. This transition of thermoelectric power, of course, takes place entirely in the liquid state since the crystal is completely melted when the mean temperature (temperature at center of crystal) is 0.5° above 270°, since

<sup>9</sup> E. G. Linder, Phys. Rev. **29**, 554 (1927).

<sup>10</sup> T. R. Harrison and P. D. Foote, J.O.S.A. and R.S.I., **7**, 389 (1923).

the difference in temperature between the two ends of the crystal is only one degree.

On account of the doubt of the exact indication of thermocouple *C* and from the general appearance of the curves in Fig. 2 one might be inclined to believe that the melting process was not complete until the final constant value of the thermoelectric power had been reached and that the observed effect all lies in a region below the melting point and is, therefore, characteristic of the solid and not the liquid state. That this is not the case was verified by an independent experiment. A separate determination was made on a 90° crystal and as all of the curves show a small constant portion shortly after melting, the determination was stopped when that place was reached. The holder containing the crystal was then quickly taken from the furnace, tipped on its side and jarred a little. There was only one possible place where the liquid could seep out through the holder and this was at the position where the thermocouple *C* was inserted. It was found that the liquid had indeed forced its way out and on examining the material remaining in the holder, it was found recrystallized into a changed orientation<sup>11</sup> from what it was at the beginning. This seems conclusive evidence that the transition region belongs to the liquid state.

It seemed desirable also to make a check on the apparatus to be sure that the results obtained were not due to some peculiarity in the apparatus itself. To check this point a determination was made on a specimen of polycrystalline lead. The results of this determination are shown in the curve in the upper right corner of Fig. 2. Since the thermoelectric power of lead against copper is small, a temperature difference between the ends of the specimen of 4°C had to be used in order to obtain a conveniently large galvanometer deflection. This made the resolution much less than that for any of the bismuth crystals. The result obtained for lead, however, is the one to be expected on the assumption of no transition region existing. The thermoelectric power passes directly from the solid value to the liquid value without a change of slope in this region and the temperature interval of this change corresponds almost exactly to the temperature difference of the ends of the lead rod. The fact that the transition is not shown by a line parallel to the ordinate axis, is, of course, due to the finite resolution.

The above results yield incidently a value of 2.6 microvolts per 1°C for the thermoelectric power of solid against liquid lead at the melting point.

As a matter of interest a plot has been made, Fig. 3 of the thermoelectric power of the solid crystals just below the melting point against the square of the cosine of the orientation angle. To do this ordinates were read from Fig. 2 for the value of temperature shown by the dotted line. This is 0.25° below the temperature at which the hotter end of the crystals start to melt. The points lie on a straight line, confirming the Voigt-Thomson relation. This is in agreement with Boydston though at variance with the slight deviation from

<sup>11</sup> Doubtless from tipping and jarring. From Goetz's observation it should remain the same if undisturbed.

the law later found by Bridgman<sup>12</sup> and Fagan and Collins.<sup>13</sup> It does, however, give the writer considerable confidence in the method used to adjust the mean temperature scale. A numerical comparison<sup>14</sup> of Boydston's and the writer's data shows that at the melting point the former obtains:

$$e_{\parallel} - e_{\perp} = 70 \text{ microvolts/degree}^{15}$$

$$e_{\perp} - e_{\perp} = 29 \text{ microvolts/degree}$$

while the writer obtains:

$$e_{\parallel} - e_{\perp} = 65.5 \text{ microvolts/degree}$$

$$e_{\perp} - e_{\perp} = 31.0 \text{ microvolts/degree.}$$

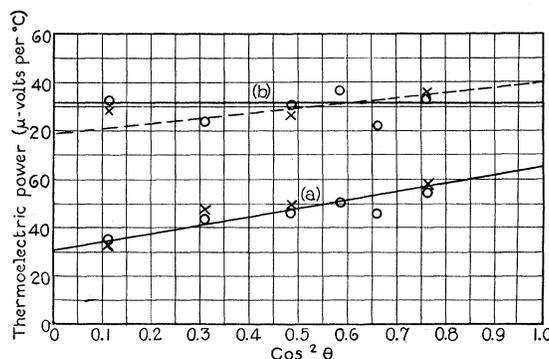


Fig. 3. Thermoelectric power as a function of  $\cos^2 \theta$ . (a) At the melting point. (b) At the *knee* of the curves of Fig. 2.

The results then show that the thermal e.m.f. curve of bismuth does not change its shape as abruptly and in as clearly defined a fashion as in the case of zinc, tin, lead and some other substances. The thermoelectric power before settling down to a final constant value passes through a transition region lasting for a temperature interval of about  $8^\circ\text{C}$  above the melting point. Moreover, this settling down is gradual. The curves for differently oriented crystals preserve their individuality for several degrees above the melting point. Although it is only quite close to the final liquid stage that the curves become practically identical there is within the transition region a feature common to all but one of the curves of Fig. 2, namely a slight *knee* or practically stationary value of thermoelectric power. This seems to indicate a definite phase, or intermediate liquid state, existing for a temperature range of about one degree. If this is the case it ought to occur at the same tempera-

<sup>12</sup> P. W. Bridgman, Proc. Amer. Acad. of A. and S. **63**, 351 (1929).

<sup>13</sup> H. D. Fagan and T. R. D. Collins, Phys. Rev. **35**, 421 (1930).

<sup>14</sup> Boydston's values for comparison were obtained by plotting his data for  $e_{\parallel} - e_{\perp}$  against  $\cos^2 \theta$  and then extrapolating the straight line to the ordinates of  $0^\circ$  and  $90^\circ$  crystals.

<sup>15</sup>  $e = dE/dT$ , the thermoelectric power,  $E$  being the thermal e.m.f.,  $e_{\parallel}$  = thermoelectric power of liquid bismuth,  $e_{\parallel}$  = thermoelectric power of crystal of  $0^\circ$  orientation,  $e_{\perp}$  = thermoelectric power of  $90^\circ$  crystal.

ture for all the crystals. Although it obviously does not do so its significance can be tested in another fashion. This is shown in Fig. 3b in which the value of the thermoelectric power at the knee is plotted against  $\cos^2 \theta$ . A definite intermediate liquid phase might be expected to give either (1) a straight line (dotted in the figure) with a positive slope indicating that the liquid is still very much like its *parent crystal* (2) a straight line (solid line in the figure) of zero slope, indicating that an identical state has been reached for all crystals. Unfortunately the observed data do not decide unambiguously between these two suppositions. In spite of this the existence of a knee at all strongly supports the idea of an intermediate state. It may be noted that this knee was also obtained for most of the crystals which were studied in the preliminary work previously mentioned.

The writer believes that the existence of a transition region extending from the melting point to about  $8^\circ$  above it, is established by the foregoing and that the explanation which has already been advanced is adequate to explain this phenomenon. Up to  $8^\circ$  beyond the melting point the liquid retains, but in decreasing measure, the organization of the crystal from which it is derived. Beyond that point the state of the liquid is independent of its previous history. It is practically impossible to think of any state or condition of the liquid, other than that postulated, which could give rise to such a transition region. It must be noted however, that the thermoelectric effect must be particularly well suited to observe this phenomenon as the appearance of a transition region for other properties which depend on crystal orientation has not been observed, so far as the writer knows. W. L. Webster's study<sup>16</sup> of the change in magnetic susceptibility in solidifying bismuth apparently shows no transition region for this quantity of the type shown here, but a sudden change occurring at the melting point. It may be, however, that a degree of organization suitable for modifying the thermoelectric effect may have little effect on susceptibility. Moreover, Webster was looking for an effect said to occur  $10^\circ$  below the melting point and not for one above.

It may be said finally that only x-ray diffraction can give positive and unambiguous proof of the explanation offered to explain the transition region.

The writer wishes to express his most sincere thanks to Professor E. P. T. Tyndall, who suggested the problem and under whose direction the work was carried out.

<sup>16</sup> W. L. Webster, Proc. Roy. Soc. **A133**, 162 (1931).