PELTIER AND THOMSON EFFECTS FOR BISMUTH CRYSTALS

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Abstract

The Peltier and Thomson effects are directly measured (the former against copper) in single crystal rods almost covering the entire orientation range. For the first effect the Voigt-Thomson symmetry relation is definitely not substantiated, while for the latter the data do not provide an adequate test, though it appears likely that there is a deviation here also.

The following values are found: at a temperature of 27°C, $\pi(\| \text{vs.} \perp) = 13.8$, $\pi(45° \text{vs.} \perp) = 8.6$ microvolts; at a temperature of 48.5°C, $\sigma_{\|} - \sigma_{\perp} = 43$, $\sigma_{45} - \sigma_{\perp} = 26.5$ microvolts/°C. These values are all in fair agreement with values deduced from thermal e.m.f. temperature data of the writers and of previous observers.

Introduction

Bridgman[1] and Boydston[2] have recently measured the thermal e.m.f of bismuth crystals of various orientations[3] against a reference metal. From these results are deduced by the usual thermodynamic relations, values of the Peltier e.m.f. between the reference metal and a crystal of any orientation or between two crystals of different orientations; likewise the differences in the Thomson coefficients for the two parts of the above combination are deduced. In the investigation described below the Peltier e.m.f. against copper and the Thomson coefficient of bismuth crystals, covering most of the possible orientation range, were measured directly. Two sets of crystals were used, the first for measurement of Peltier coefficient, the other for all the other measurements, which included determination of specific resistance, mean thermoelectric power (between 0° and 100°C) against both copper and constantan, and the Thomson effect. From such data it should be possible to test the validity of the Voigt-Thomson symmetry relation for the directly observed Peltier e.m.f. and Thomson coefficient and to make comparison with the indirectly determined values of these same quantities.

Apparatus and Experimental Method

The method for determining the Peltier e.m.f. is essentially that of Caswell,[4] or Barker.[5] The two thermo-junctions (Cu-Bi and Bi-Cu) are isolated

[1] P. W. Bridgman, (a) Proc. Amer. Acad. of A. and S. **61,** 101 (1926); (b) Proc. Amer Acad. of A. and S. **63,** 351 (1929).

[2] R. W. Boydston, Phys. Rev. **30,** 911 (1927); also gives reference to earlier work.

[3] Orientation is used as usual to define the angle between the length of the specimen and the principal crystallographic axis, which for bismuth is perpendicular to the plane of best cleavage.

[4] A. E. Caswell, Phys. Rev. **33,** 379 (1911).

[5] H. C. Barker, Phys. Rev. **31,** 321 (1910).

from each other by placing them in separate Dewar flasks each containing the same amount of calorimetric fluid, a heating coil, a stirrer, and a copper-constantan thermocouple. See Fig. 1 (a). Current from the battery B_2 may be passed in either direction around the Bi-Cu circuit. The purpose of the heating coils is made clear below. By obvious manipulations of switches S_1 and S_2 it is possible to read the temperature in either flask, or to detect a very minute difference in temperature between the flasks. The heating coils, L and R, are wound of No. 36 constantan wire on thin mica sheets, while the leads, which go through the surface of the liquid and through holes in the flask covers, are of No. 2 constantan. The calorimetric fluid is "Finol," a light oil of low specific heat and high mobility. The amount contained in each

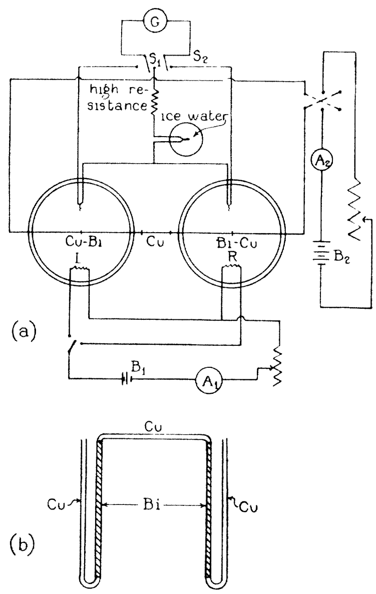

Fig. 1. Diagram of apparatus and electrical connections.

flask is about 150 cc. Stirring is done by glass propellors (not shown in Fig. 1) running at the rate of about 1 r.p.s.

The construction of the two bismuth copper junctions, in which the effect is measured, is apparent from the vertical section shown in Fig. 1(b). The two bismuth portions are parts of one crystal rod cut in two. The two ends adjacent to the cut are used to form the two Bi-Cu junctions in the flasks. The copper is No. 6 wire of commercial grade. The bismuth-copper connections are made without solder by fusing the bismuth directly to the copper, using zinc chloride as a flux. To take a reading a known constant current is sent in one direction through the bismuth-copper circuit. Heat is absorbed at the junction where current passes from bismuth to copper. To compensate for this loss of heat (and for the generation of heat at the other junction) current is passed through the appropriate heating coil. This current is continually so regulated that the flasks show no temperature difference. In about an hour no further adjustment is necessary. The reading of A_1 is then recorded. The current in the main (bismuth-copper) circuit is then reversed, but kept at the previous value, and the procedure above repeated. Caswell has shown that in this case the Peltier e.m.f. is given in volts by

$$\pi = \frac{i_R^2 R + i_L^2 L}{4I}$$

in which i_R, i_L = current (amperes) in right and left heaters, respectively; R, L = resistance (ohms) of right and left heaters respectively; I = current (amperes) in main circuit. This relation is valid provided the following conditions are satisfied.

1. The heat capacities of the two flasks and their contents are the same. This condition was met by making the two as nearly identical as possible.

2. The rate of loss of heat from each flask must be approximately the same. This was tested from time to time during the investigation and found to be satisfactory.

3. The temperature difference between the flasks and their surroundings must be small. The oil in the flasks never exceeded 2°C above room temperature at the end of any run.

For measuring the Thomson coefficient the method of Nettleton,[6] as modified by Ware,[7] was used. Measurements of the same specimen made on Ware's apparatus and the writers' agree well. The resistance of each crystal with one end at about 0° and the other at about 100°C is a necessary datum for determining the Thomson coefficient, and from it the specific resistance (at 48.5°C) can be computed. To do this the average cross section of a crystal is found from its measured mass and length, and assumed density (9.78 gm/cm^3). The crystals were from 6 to 10 cm long and from 5 to 10 mm^2 cross sectional area.

With the temperature gradient established along a crystal the thermal e.m.f. was measured with a potentiometer. The reference metal is copper, since the ends of the specimen were fused or soldered to copper blocks. Dividing this e.m.f. by the temperature difference gives the mean thermoelectric power. This is approximately the thermoelectric power at the mean temperature, 48.5°C. The thermoelectric power against constantan was measured in a similar fashion.

The two sets of bismuth crystals were grown by drawing them from a crucible full of molten bismuth. This method and the apparatus have been described by Linder.[8] The modifications in the procedure mentioned by Boydston and by Hoyem[9] and Tyndall were also followed. The crystals of

[6] H. R. Nettleton, Proc. Lond. Phys. Soc. **29**, 59 (1916–17).

[7] In connection with unpublished work in this laboratory by L. A. Ware on the Thomson Effect in zinc crystals.

[8] E. G. Linder, Phys. Rev. **29**, 554 (1927).

[9] R. W. Boydston, Phys. Rev. **30**, 911 (1927); A. G. Hoyem and E. P. T. Tyndall, Phys. Rev. **33**, 81 (1929).

one set (for Peltier Effect) were 30 cm long and from 2.5 to 3.0 mm in diameter. The others have been described above. The material used was Mallinckrodt C. P. bismuth with the following analysis:[10]

Zn 0.01%	Cu 0.00%	Fe 0.00%
Pb 0.00%	As 0.000%	Ag 0.04%

Results and Discussion

Measurements of Peltier e.m.f. against copper were made on fourteen single crystals ranging in orientation from 16° to 90°. For a majority of the crystals five readings were taken. For two, however, six readings were taken, while for three crystals, only four were taken. The arithmetic mean of all the readings on one specimen is the adopted value. The results are shown graphically in Fig. 2, in which the observed Peltier e.m.f. in millivolts is plotted

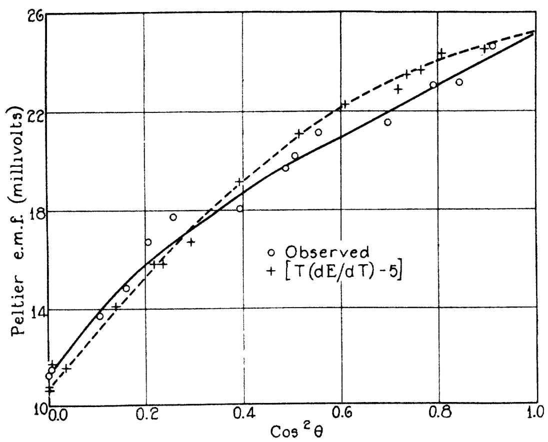

Fig. 2. Peltier e.m.f. as function of orientation angle.

(circles) against the square of the cosine of the orientation angle. By substituting in $\pi = Te$, in which $T = 300°A$ and e is the mean thermoelectric power (at 48.5°C) against copper,* previously mentioned, it is possible to obtain values of the Peltier e.m.f. Values obtained in this way are plotted (as crosses) in the same figure. Before plotting, each value has been arbitrarily reduced by 5 millivolts, since any constant difference between the two sets of data can readily be ascribed to the use of different samples of reference metals (a copper block in one case and a copper wire in the other). These two curves are probably in agreement within experimental error. Such plots should yield straight lines to satisfy the Voigt-Thomson symmetry relation.

[10] The bismuth used by Boydston had this same stated analysis. The omission of Ag 0.04% is due to an oversight on his part. It seems certain, however, that the content of Ag in the crystals used in this investigation must be much less than 0.04%. This point is considered later.

* The value of e at 27°C should be used, of course, but it was not determined and probably does not differ much from the value at 48.5°C.

It is obvious that the experimental relation is not linear in either case. Moreover Bridgman[11] finds a very similar deviation from linearity for the thermoelectric power (as a function of $\cos^2\theta$) of bismuth crystals against copper, and therefore for the indirectly determined Peltier e.m.f.

TABLE I. *Peltier e.m.f. (millivolts) at 27°C.*

Junction	Directly * observed	$T(dE/dT)$*	$T(dE/dT)$* (Bridgman)	$T(dE/dT)$**	$T(dE/dT)$** (Boydston)
$M\text{–}Bi_0$	25.1	30.2	32.2	18.2	20.2
$M\text{–}Bi_{45}$	19.9	25.6	25.9	13.1	11.6
$M\text{–}Bi_{90}$	11.3	15.7	17.2	3.3	3.0
$Bi_0\text{–}Bi_{90}$	13.8	14.5	15.1	14.9	17.2
$Bi_{45}\text{–}Bi_{90}$	8.6	9.9	8.7	9.8	8.6

* Reference metal, M, copper.
** Reference metal, M, constantan.

Table I presents a comparison of previous work with the present, the subscript for Bi being the value of θ. The data in the second and third columns are obtained from the two curves in Fig. 2. To compute Bridgman's values use is made of his empirical formulas[12] for thermal e.m.f. as a function of temperature. The fifth column is obtained from a plot of the observations on thermoelectric power against constantan, previously mentioned. By interpolation in Boydston's Fig. 3 the thermoelectric power (against constantan) is found for 27°C, and from this the values in the last column are easily computed. All the results in this table are found to be in fair agreement, when allowance is made for the fact that in the upper 3 rows of data a different reference metal (or different specimen of the same metal) was used. In the lower two rows the results are typical of bismuth alone and an absolute comparison is allowable. It will be seen that the directly observed values are lower than those computed from $\pi = TdE/dT$. The agreement with this relation is, however, probably as good as is usually obtained. There seems little doubt that the deviation from the Voigt-Thomson symmetry relation is real for the Peltier effect in these crystals. Boydston finds no deviation (at 27°C) and one must conclude that the bismuth used by Boydston differed from ours in spite of having the same stated analysis

The specific resistance at 48.5°C is plotted in Fig. 3 against $\cos^2\theta$. The line drawn represents Bridgman's latest results, changed to 48.5° C, however, assuming a temperature coefficient of resistivity of 0.0044. With the exception of four points, the results are satisfactory and indicate that the crystals are not badly strained and that the bismuth is very pure, since both strains and impurities seem to affect the specific resistance seriously.[13] The three high points may be ascribed to slight accidental strains occurring during growth or in the subsequent handling of the crystals. This seems probable also because crystals of intermediate orientations are very easily deformed.

[11] Reference 1, (b),
[12] Reference 1, (b), p. 383.
[13] See discussion by Bridgman, reference 1, (b) pp. 386–389.

Ware has shown for zinc crystals that a deformation which is large enough to raise the specific resistance has a negligible effect on the Thomson coefficient. It might be expected, therefore, that the group of crystals of Fig. 3 would give consistent and satisfactory results for the Thomson coefficient. This is,

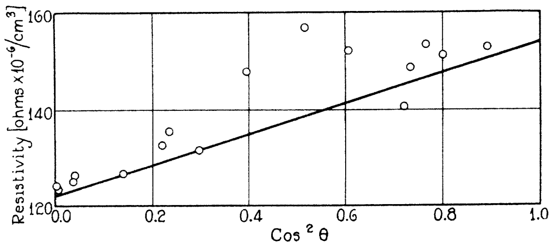

Fig. 3. Specific resistance as function of orientation angle.

however, not the case as is evident on reference to Fig. 4, particularly for orientations less than about 50°. These data, moreover, do not provide an adequate test of the Voigt-Thomson symmetry relation. In spite of this an attempt has been made to draw a smooth curve through the observations. Assuming that -8.5 microvolts/°C is a reasonably certain value for $\sigma_\perp$ (i.e. for $\theta = 90°$), it is possible to make comparison with Bridgman's latest data. The values of σ for $\theta = 45°$ and $\theta = 0°$ for a temperature of 48.5°C have

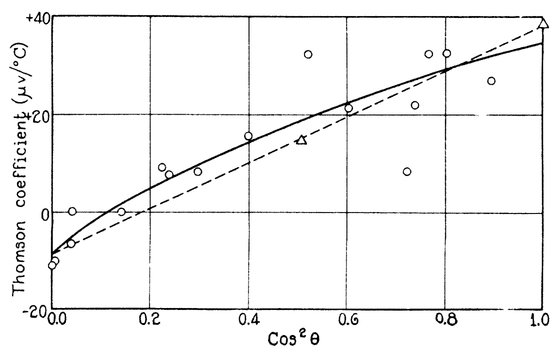

Fig. 4. Thomson coefficient as function of orientation angle.

been computed from formulas deduced by Bridgman[14] from his thermal e.m.f data. These values are plotted as triangles in Fig. 5. Our curve gives $(\sigma_\perp - \sigma_\parallel) = 43$ microvolts °C at 48.5°C, dependent on a very uncertain extrapolation to $\cos^2\theta = 1$. Boydston's data give $(\sigma_\perp - \sigma_\parallel) = 57.5$, and Bridgman's, 48. At 43.5°C Caswell[15] finds 58 microvolts/°C for polycrystalline bismuth, a value considerably in excess of what might be expected from the above stated values for crystals. Laws[16] finds a much lower value, 10 microvolts/°C.

[14] Reference 1, (b) pp. 384, 385.
[15] Caswell, Phys. Rev. **12,** 235 (1918).
[16] Laws, Phil. Mag. [6] **7,** 560 (1904).

It seems certain, from the investigations of the two writers just mentioned, that a small admixture of tin raises the Thomson coefficient to a very great extent. It therefore seemed desirable to make an analysis of the bismuth. This was done spectroscopically using the spark spectrum and the general procedure of Meggers, Kiess, and Stimson.[17] A small quartz spectrograph was used the dispersion of which was such that the length of spectrum between 3400 and 2600A was 1.5 cm. About 120 spectrograms were taken of three crystals[18] with normal, low, and high Thomson coefficients, respectively, as judged from the curve of Fig. 4. Between exposures a two millimeter piece was clipped from each of the two portions of the crystal between which the spark occurred. All of the spectrograms, except one, were identical and indicated a material of high purity. A very faint and diffuse line which might be the "raie ultime" of silver (3281A) was present in all the spectrograms. No trace of 3383A, another very sensitive silver line, was found. Moreover, comparison of these spectrograms with others taken in this laboratory of bismuth known to contain far less than 0.04 percent Ag, has led to the conclusion that the silver content is much lower than the figure stated in the analysis. Certainly the crystals examined showed no difference from each other and no detectable inhomogeneity in composition between different parts of the same crystal. In the one exceptional case mentioned above one of the electrodes consisted of a portion (one end) which had been accidentally fused and was probably contaminated with solder. Several lead and tin lines were easily identified in this spectrogram.

In conclusion the writers wish to express their thanks to Prof. E. P. T. Tyndall for suggesting this work and for his advice and interest during its prosecution.

[17] Meggers, Kiess and Stimson, Sci. Pap. Bur. Stand. **18,** 235 (1922–23).

[18] $\mathrm{Cos}^2\theta = .894$, $\sigma = 27$; $\cos^2\theta = .517$, $\sigma = 32.4$; $\cos^2\theta = .719$, $\sigma = 8.5$.