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THERMO-ELECTRIC EFFECT IN SINGLE-CRYSTAL BISMUTH

By R. W. Boydston

Abstract

Thermal e.m.f., thermo-electric power, Peltier heat of single-crystal Bi against constantan as functions of crystal orientation.—Data are presented on the thermal e.m.f. against constantan of nine single-crystal wires of bismuth, of which the inclinations of the vertical axis, with respect to the wire axis, range from 23° to 83.5°. The temperature interval is from −182° to about 300°C. Some of the observed results are also referred to copper for the sake of comparison with results of previous workers. Data are also given on the thermal e.m.f. of liquid bismuth against various crystal orientations. The thermo-electric power, and Peltier heat, computed from the e.m.f.-temperature curves in the usual fashion, agree well with the Voigt-Thomson symmetry relation for temperatures above 0°C, but depart somewhat, though in no consistent fashion, from this relation for temperatures below 0°C.

Thermo-electric power, Peltier heat and difference of Thomson coefficients for $\mathrm{Bi}_{\perp}$ against $\mathrm{Bi}_{\parallel}$.—From the data are computed the Peltier heat and difference in Thomson coefficients for $\mathrm{Bi}_{\perp}$ against $\mathrm{Bi}_{\parallel}$. The location of certain maxima and minima in these curves are found not to occur in the region of rapid decline of atomic heat, though Grüneisen and Goens have found such a coincidence for Zn and Cd.

Thermal e.m.f. of polycrystalline specimens.—The thermal e.m.f. of polycrystalline specimens of both bismuth and zinc when determined experimentally agree surprisingly well with the result predicted by Linder's formula.

Introduction

SEVERAL papers have been published on various thermo-electric effects in single-crystal bismuth. Early work in this field, such as that of Perrot,[1] Lownds,[2] Jordan,[3] Borelius and Lindh,[4] seems to be confined to investigations of small single-crystal "slabs" which have been sawed or split from large single crystals. The angle between the longer dimension of the specimen and the principal crystallographic (vertical) axis has usually been either 0° or 90°. The properties of crystals prepared in the above way doubtless are affected by inevitable strains. Besides, on investigating strain-free crystals it seems desirable to investigate crystals of more than two orientations.[5] The only recent work done on bismuth, as far as the author is aware, is that done by Bridgman[6] who prepared single crystal rods of circular cross-section and presumably free from strain. He investigated the thermal e.m.f. against copper over the temperature interval between 20°C and 100°C of ten such

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[1] F. L. Perrot, Arch. des Science Phys. et Nat. **6**, 105, 229 (1898). **7**, 149 (1899).

[2] Louis Lownds, Ann. d. Physik **6**, 146 (1901).

[3] F. W. Jordan, Phil. Mag. **21**, 454 (1911).

[4] Borelius and Lindh, Ann. d. Physik **63**, 97 (1917).

[5] The term orientation is used to define the angle between the vertical axis of the crystal and the axis of the wire.

[6] P. W. Bridgman, (a) Proc. Nat. Acad. Sci. **11**, 608 (1925); (b) Proc. Amer. Acad. of Arts and Sci. **61**, 101 (1926).

specimens the orientations of which ranged from 68.5° to 90°. The present report covers an investigation of thermo-electric effects in single crystals of bismuth through temperatures ranging from −182°C to beyond the melting point. The crystal orientations are from 23° to 83.5°, inclusive. From data taken on these orientations, which are shown to follow the Voigt-Thomson law, the author has calculated the properties of crystals of both 0° and 90° orientation. Thus, the work covers the entire range of orientation from 0° to 90° for the above stated temperature interval.

METHOD AND APPARATUS

The general method and apparatus previously described by E. G. Linder[7] were used with only some slight changes. The first of these changes consisted in the substitution of carbon dioxide for air in the cooling blast in the crystal-growing apparatus. Thus the crystal-growing process took place entirely in an atmosphere of carbon dioxide and practically no oxidation occurred. In the second place, for orientations above 50° the growing crystal could be started on another single crystal which was bent near the end so that its basal plane was inclined at the desired angle with the surface of the melt. For lower orientations the temperature of the electric furnace had to be much higher, the cooling had to be considerably faster, and the crystal was grown at a more rapid rate. Thirdly, the thermal e.m.f.'s were measured against constantan instead of copper, the temperature of one junction of the bismuth-constantan couple being kept at 0°C while that of the other was varied from −182°C to 300°C, or slightly higher. Constantan was used because its thermoelectric power curve is much closer to that of bismuth (polycrystalline) than copper is. Thus, when the e.m.f. of the crystals is measured against constantan the effect for all orientations is much less than when measured against copper, but the differences between the different orientations are relatively much greater. This results in a better separation between the e.m.f. curves for the various orientations than is possible when copper is used as the reference metal. The thermal e.m.f. curve for the constantan wire was obtained against the same kind of copper wire used by Linder,[7] so that, where necessary, the results for bismuth are referred to copper. In the fourth place, the convention of the positive e.m.f. was changed. In this work e.m.f. is considered positive in the bismuth-constantan circuit if it is directed from the bismuth to the constantan at the junction of variable temperature. Lastly, the author found that for the purpose of splitting the crystal readily along the basal plane, immersing the crystal in liquid oxygen was better than amalgamation.

The bismuth used in this work was Mallinckrodt "C. P. Quality." According to their analysis the maximum impurities present were: Pb 0.00%, Cu 0.00%, Zn 0.01%, As 0.000%, and Fe 0.00%.

RESULTS

I. *Thermo-electromotive force, thermo-electric power, and Peltier heat as functions of crystal orientation.* In Figs. 1 and 2 are found the observed values

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[7] E. G. Linder, (a) Phys. Rev. **26**, 486 (1925); (b) Phys. Rev. **29**, 554 (1927).

of the thermal e.m.f. against constantan plotted against the temperature difference of the two junctions for each of nine single crystal specimens. The curves of Figs. 1 and 2 are continuous curves but are plotted separately for convenience in presentation. The curves cannot be represented by a second degree equation in t. Consequently, the thermo-electric power curves are not straight lines. The author did not try to find empirical equations to fit the above mentioned observed curves. Whenever derived quantities, such as the thermo-electric power, $e = de/dt$, appear their values have been obtained by the graphical method of drawing tangents and measuring the slopes. The dotted curves of those figures are calculated e.m.f. vs t curves for crystals of 0° and 90° orientations against constantan. These were obtained by extrapolation, making use of the Voigt-Thomson symmetry relation. The exact procedure is described in II, below.

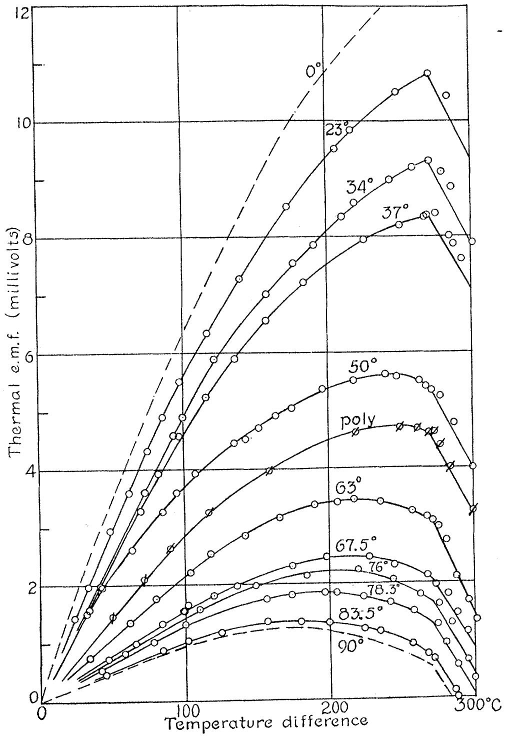

Fig. 1.

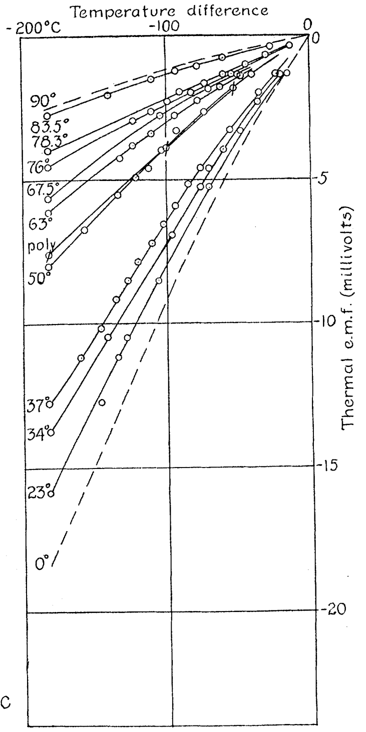

Fig. 2

Fig. 1. E.m.f. against temperature, for various crystal orientations, above zero degrees Centigrade. The orientation angle is shown above each curve.

Fig. 2. Same as Fig. 1, except that temperatures are below zero degrees Centigrade.

So far, the only theory proposed to explain the thermo-electric properties of crystals is the thermodynamical theory of Voigt[8] and Thomson[9] according to which

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[8] Voigt, Lehrbuch der Kristallphysik.

[9] W. Thomson, Math. and Phys. Papers, I, 232.

$$e_\theta = e_\parallel \cos^2\theta + e_\perp \sin^2\theta = e_\perp + (e_\parallel - e_\perp)\cos^2\theta \tag{1}$$

where θ stands for the angle between the vertical axis and the axis of the wire, $e_\parallel$ and $e_\perp$ are the thermo-electric powers parallel and perpendicular to the vertical axis, respectively.

Authors disagree as to the validity of Eq. (1) as derived by Voigt and Thomson. Bridgman[6] considers that they have taken no account in their analyses of either the internal or surface Peltier heat and their results, therefore, can not be expected to hold for an actual thermocouple. His experimental work with zinc, bismuth, cadmium and tin tends to substantiate this view. On the other hand Linder,[7(b)] considering the equation as purely empirical, finds it valid for zinc crystals for the temperature range −150°C through 200°C, when tested experimentally. For bismuth Bridgman[10] obtains a nearly linear relation between a certain constant, a' (a' is proportional to Peltier heat and to the thermo-electric power at 0°C) and specific resistance. The latter obeys the Voigt-Thomson law so that a' should be a linear function of specific resistance if Eq. (1) is valid. Bridgman considers the departure from linearity real. The writer has tested Eq. (1) in the fashion described by Linder. In Fig. 3 are shown graphs for various temperatures of thermo-electric power against $\cos^2\theta$, where θ stands for the orientation. The points, except for the −100° curve, do not deviate from the expected straight line more than might be due to experimental errors. At −100°C the deviations are somewhat greater but the experimental errors are also thought to be slightly larger in this region. These deviations are not systematic and no smooth curve seems to fit better than the straight line which has been drawn through these points. Points for orientations measured

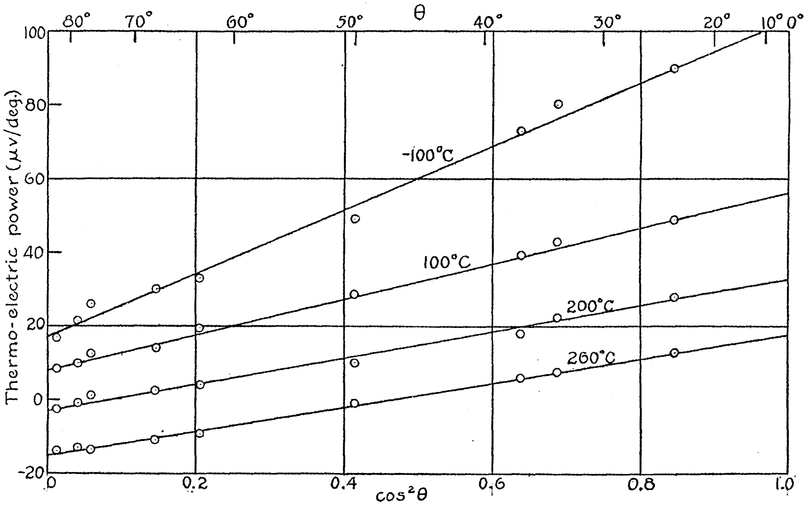

Fig. 3. Test of Voigt-Thomson Law. Thermo-electric power as a function of $\cos^2\theta$, for various temperatures of variable junction.

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[10] See Reference 6(b) Figure 7, page 119.

by Bridgman, if plotted in Fig. 3, would lie entirely in the interval between 0 and 0.15 for $\cos^2\theta$. The curved part of his line would lie perhaps between 0 and 0.02. The writer has only one point in that region, but owing to its coincidence with the straight line determined by all the other points, it seems unlikely that there is any considerable deviation from the Voigt-Thomson law.

For the sake of comparing the writer's results with the results of other investigators, Tables I and II are given. Table I includes abstracted results from the earlier writers (above mentioned). The mean temperature is indicated by t_m. The thermo-electric power, e, is given in microvolts per degree (μv/deg). Table II compares the present results with Bridgman's.

TABLE I

Comparison of author's values for the thermo-electric power of single-crystal Bi with those of others.

Observer	t_m	e(μv/deg.)	Boydston e (μv/deg.)
	$\theta=0°$		
Lownds	56.4°C	118.35	109.
Borelius and Lindh	50.	92.	108.
Lownds	−35.	108.	119.
Lownds	−50.	94.	128.
	$\theta=90°$		
Jordan	20°C	53.1	52.
Perrot	55.	54.6	57.2
Lownds	50.6	61.94	55.3
Borelius and Lindh	50.	55.	55.3
Borelius and Lindh	100.	55.	50.5
Lownds	−33.5	28.3	48.
Lownds	−57.3	13.9	48.5

TABLE II

Comparison of present results with those of Bridgman.

θ	Bridgman Total e.m.f. (20° to 100°)	Ave. θ	Average total e.m.f. (20° to 100°)	θ	Boydston total e.m.f. (20° to 100°)
90°	4460μv				
90°	4540	90°	4500μv	90°	4200μv
85.5°	4610				
84.5°	4610	85°	4610	83.5°	4470
80°	5040	80°	5040	78.3°	4600
73.5°	5080			76°	4708
72°	5150	72.7°	5110	67.5°	4900
69.7°	5200				
68.5°	4900				
68.5°	5420	68.9°	5170	67.5°	4900

In both tables the reference metal is copper, the writer's values having been computed from the observed values by making use of the previously mentioned determination of the thermal e.m.f. curve of constantan against copper. The agreement in both tables is probably as good as can be expected in view of the great possible differences in both the material tested and the copper used as reference. The poorest agreement is with Lownds' data for temperatures below zero degrees. For the parallel orientation his values decrease with decreasing temperature, while the writer's increase.

If the usual thermodynamical relation, $\pi = TdE/dt$, for Peltier heat, π, is valid, Fig. 3 also shows how far Eq. (1) is capable of expressing the nature of variation of the Peltier heat with orientation.

II. *Thermo-electric properties of Bi⊥ and Bi‖.* The thermo-electric properties of bismuth may be obtained without reference to another metal by expressing the constants of one principal orientation, Bi⊥ ($\theta = 90°$), against the other, Bi‖ ($\theta = 0°$). Assuming the Voigt-Thomson law, which was shown at least to be very nearly true, one obtains, by integration,

$$E_\theta = E_\parallel \cos^2\theta + E_\perp \sin^2\theta \qquad (2)$$

where E_θ represents e.m.f., providing θ is independent of the temperature difference, t, of the junctions. $E_\perp$ and $E_\parallel$ may be calculated for any value of temperature difference, t, by substituting in Eq. (2) values for E_θ and θ from any two of the experimental curves of Fig. 1, preferably from curves lying far apart. Solving simultaneous sets of such equations yields $E_\perp$ and $E_\parallel$ against constantan for any desired value of t. Subtraction yields the value of the thermo-electromotive force of Bi⊥ against Bi‖. Fig. 4 and Table III contain values of this e.m.f. for various temperature differences.

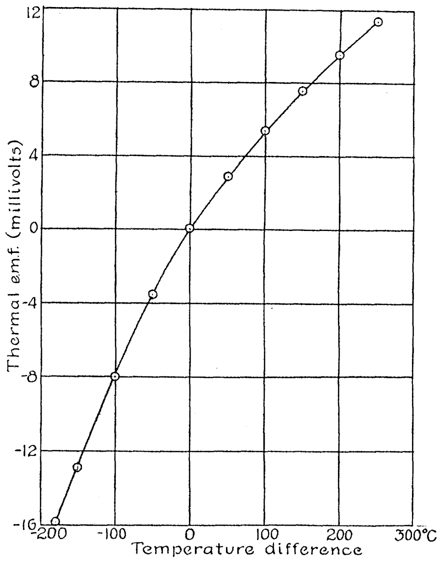

Fig. 4.

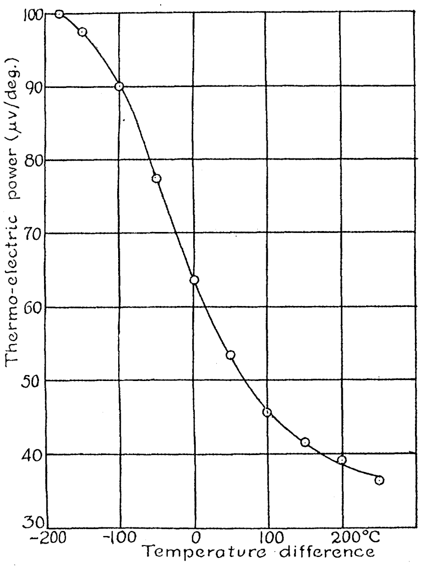

Fig. 5.

Fig. 4. Thermal e.m.f. for Bi⊥ against Bi‖.
Fig. 5. Thermo-electric power for Bi⊥ against Bi‖.

The thermo-electric power, $e = dE/dt$, can be obtained from Fig. 4 by measuring the slope of the tangents at various values of temperature, t. Fig. 5 and Table III contain the values obtained in this way.

TABLE III

Thermal e.m.f., thermo-electric power, Peltier heat, and difference between Thomson coefficients for $Bi_\perp$ against $Bi_\parallel$.

T	e.m.f. (μv)	e (μv/deg.)	π (μv)	$\sigma_\perp - \sigma_\parallel$ (μv/deg.)
−180°C	−15,876	100.	9,300	− 6.7
−150	−12,903	97.5	11,992	−13.3
−100	− 7,982	90	15,570	−32.7
− 50	− 3,537	77.5	17,282	−58.9
0	0	63.6	17,363	−66.6
50	2,910	53.5	17,280	−57.5
100	5,453	45.7	17,046	−38.4
150	7,593	41.7	17,639	−27.9
200	9,581	39.2	18,542	−25.7
250	11,402	36.4	19,037	−24.3

By Thomson's thermodynamical theory the Peltier coefficient is given by $\pi = TdE/dt = Te$, where T stands for the absolute temperature of the variable-temperature junction. Fig. 6 and Table III show the variation of the Peltier coefficient with temperature difference as calculated from this equation.

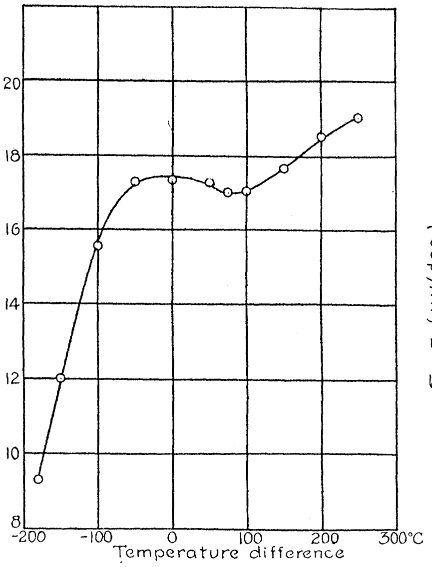

Fig. 6.

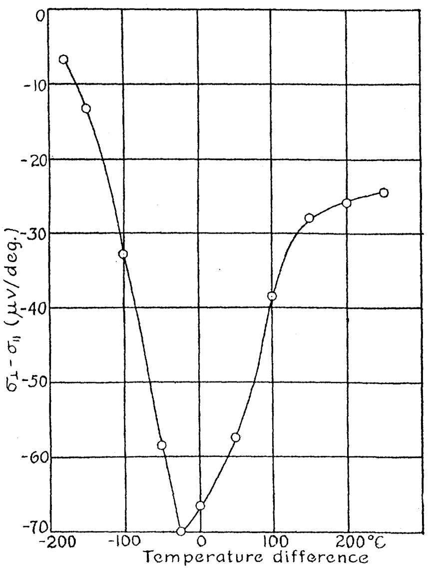

Fig. 7.

Fig. 6. Peltier coefficient for $Bi_\perp$ against $Bi_\parallel$.
Fig. 7. Difference in the Thomson coefficients for $Bi_\perp$ against $Bi_\parallel$.

According to the same theory the differences of the Thomson coefficients are given by $\sigma_\perp - \sigma_\parallel = Tde/dt$. By measuring slopes in Fig. 5, de/dt may be obtained. In Fig. 7 and Table III are given data on the relation between $(\sigma_\perp - \sigma_\parallel)$ and temperature t.

It will be noticed from Figs. 6 and 7 that a distinct maximum in the Peltier coefficient and a maximum in the difference of the Thomson coefficients occur at a temperature slightly below 0°C. These curves are apparently of the same character as similar curves for zinc and cadmium, reported by Grüneisen and Goens.[11] These writers call attention to the fact that a maximum in the thermo-electric power, a maximum in the Peltier coefficient, and a minimum in the difference of Thomson coefficients, for perpendicular against parallel orientations, occur at the same temperature. For zinc this critical temperature is −225°C and for cadmium −255°C. They show further that this temperature in each case lies in a region in which the atomic heat falls off rapidly with decreasing temperature, thus showing a close connection between variation of atomic heat and thermo-electric constants.

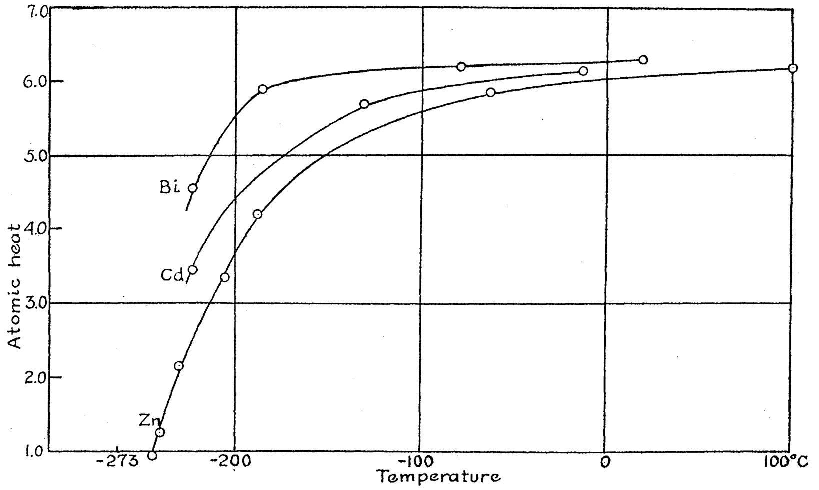

Fig. 8. Atomic heats of Bi, Cd, and Zn.

The facts for bismuth, unfortunately, do not support this supposition very well. No maximum of the thermo-electric power occurs in the region investigated, though it seems likely that a maximum lies about −200°C. The other maximum and minimum to be expected do occur but at a much higher temperature, as has been stated. They do not appear to coincide with a region of rapid decline in atomic heat, as may be seen from Fig. 8 which shows graphs of the atomic heats[12] of zinc, cadmium and bismuth. Perhaps the lack of agreement for bismuth is only another instance of its anomalous behavior.

III. *Behavior at the melting point.* Authors disagree as to whether there is a break in the thermo-electric properties of the various metals at the melting point. Darling and Grace[13] report no discontinuity for the thermo-

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[11] Grüneisen and Goens, Zeits. f. Phys. **37**, 378 (1926).

[12] Values used in plotting these curves were taken from Landolt-Börnstein Physikalisch-Chemische Tabellen (5th Ed.) and from Dewar, referred to in these Tables.

[13] Darling and Grace, Proc. Phys. Soc. London, **29**, 82 (1916).

electric power curves of lead, tin, cadmium, zinc, and aluminum. The curve for bismuth is quite generally conceded to have an abrupt break in it. Such writers as Koenigsberger,[14] Darling and Grace,[13] Pélabon,[15] call attention to this break. As may be seen from Fig. 1 the author finds a break at the melting point. It should be pointed out, however, that the change in slope is not so well defined and abrupt as that reported by Linder[7(b)] for zinc. The points immediately beyond the melting point lie above the straight line determined by the later points. It appears, in fact, as if some crystalline arrangement still persists in the molten metal, as shown by a transition region between thermal e.m.f. of solid and liquid. The effect is believed to be real as it occurs in every curve. To avoid confusion, not all of the points obtained beyond the melting point are plotted in Fig. 1, but the straight line portions of the graphs have been drawn to fit all of the observed points. These lines are practically parallel.

The experimental values obtained for the thermo-electric power of solid Bi, e_s, and of $e_l - e_s$, where e_l is the thermo-electric power of liquid Bi, are found, for the various orientations and for polycrystalline bismuth, in Table IV.

TABLE IV

Thermo-electric power of solid and liquid bismuth at the melting point.
$e_l = -49.8$ μv/deg.

θ	e_s (μv/deg.)	$e_l - e_s$ (μv/deg.)
23°	12.3	−62.1
34	8.25	−58.1
37	3.38	−53.2
50	− 5.8	−44.0
63	−13.7	−35.3
67.5	−15.5	−34.3
76	−16.6	−33.2
78.3	−17.7	−32.1
83.5	−20.6	−29.2
Poly.	− 6.17	−43.6

An attempt was made to calculate from Bernoulli's and Lorentz's formulas the value for $e_l - e_s$ of the polycrystalline specimen. No agreement could be obtained, however, between the theoretical values and the observed.

IV. *Verification of Linder's formula.* Linder[7(b)] has derived an expression for the thermo-electric properties of a metal specimen, composed of randomly oriented crystal grains. For metals, such as zinc and bismuth, the crystals of which contain a vertical axis of rotational symmetry, he computes 54.5° as the "equivalent orientation," that is to say, the polycrystalline specimen should give the same thermal e.m.f. temperature curve as a single crystal of the stated orientation. Linder's deduction is based on an assumption of the validity of the Voigt-Thomson symmetry relation for thermal e.m.f.

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[14] J. Koenigsberger, Ann. d. Physik **47,** 563 (1915).

[15] H. Pélabon, Ann. d. physique **13,** 169 (1920).

The electrical conductivities perpendicular and parallel to the vertical axis are moreover assumed equal, though they are actually slightly different. The only test, so far, of this law is Linder's own test of it in zinc. He found an experimental value of 65–70° for the equivalent orientation of the polycrystalline wire. The present writer has applied this law to bismuth and also again to zinc after preparing polycrystals by what he believes to be a better method than was used by Linder. Linder's preparation of his polycrystals consisted in melting unused single crystals in a Pyrex tube of small circular cross-section, and then cooling them, as rapidly as possible, by directing an air blast against the tube. It seems rather doubtful that random orientation can be produced by this method. A specimen of more nearly random orientation should be obtained if the specimen is cooled at a greater rate, and from all sides simultaneously. The author is indebted to Dr. Taylor, of the Chemistry Department, for providing a mold (of high conductivity) in which polycrystalline specimens could be prepared utilizing the above desired features. The specimens prepared in this mold showed a fine grained structure. Thermal e.m.f. data were then taken for two such polycrystalline specimens of bismuth and two of zinc. The thermo-electromotive force against temperature for one of the polycrystals of bismuth is plotted (ϕ) in Figs. 1 and 2. The data on the other specimen were nearly identical. The results for one specimen of each metal are summarized in Table V, in which may be found values of equivalent orientation (θ_{eq}), the thermal e.m.f.'s of which are, for the temperatures shown, identical with those of the polycrystalline specimens. The agreement of the average values with the theoretical value of 54.5° is exceedingly good in both cases.

TABLE V

Values of the equivalent orientations, θ_{eq}, of single-crystal Bi and Zn for which the thermal e.m.f is the same as for polycrystalline specimens.
θ(theoretical) = 54.5° for both Bi and Zn.

t		Bismuth θ_{eq}.	Zinc θ_{eq}.
−100°C		56.5°	52.6°
100		54.8	53.0
200		54.2	53.4
260		55.0	53.8
	Ave.	55.1°	53.2°

CONCLUSION

The results show that the thermo-electric properties of single crystal bismuth resemble very much similar properties found in zinc. The Voigt-Thomson symmetry relation for the thermo-electromotive force, Peltier heat, and thermo-electric power, as functions of orientation, appears to hold for both metals. Bismuth is found not to substantiate a connection between thermo-electric properties and variation of atomic heat with temperature which is reported for zinc and cadmium by Grüneisen and Goens.

In conclusion the writer wishes to express his appreciation to the members of the staff of the Physics Department for their friendly interest and cooperation. Mr. E. G. Linder deserves special mention in connection with the above statement. The writer wishes especially to express his thanks to Professor E. P. T. Tyndall for the assignment of the problem and for his criticisms, suggestions, and encouragement during the course of the investigation.

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UNIVERSITY OF IOWA,
July, 1927.