APRIL, 1927 PHYSICAL REVIEW VOLUME 29

THERMO-ELECTRIC EFFECT IN SINGLE CRYSTAL ZINC

By Ernest G. Linder

Abstract

Thermal e.m.f., thermo-electric power, Peltier heat of single crystal Zn against Cu as functions of crystal orientation.—In continuation of previous work data are presented on the thermal e.m.f. against copper of six single crystal wires of zinc, of which the orientations of the main crystallographic (hexagonal) axis with respect to the wire axis, range from 11.4° to 90°. (The average deviation from the mean for these observations is 0.8°.) The temperature interval is from $-182°$ to 475°C. The apparatus designed to enable measurements to be made above the melting point is described in detail.

Thermo-electric power, Peltier heat, and difference of Thomson coefficients for $Zn_\perp$ against $Zn_\parallel$.—From the data are calculated the thermo-electric power, Peltier coefficient, and difference of the Thomson coefficients for $Zn_\perp$ against $Zn_\parallel$. The data also provide a test for the Voigt-Thomson law for the variation of the thermo-electric power with crystal orientation. The law seems to be verified within the limits of experimental error for the low temperatures, but the deviations at the high temperatures (300°–400°) are greater than the experimental errors are thought to be.

Thermal e.m.f. of liquid Zn against single crystal and polycrystalline Zn.—Further, the thermo-electric powers of liquid Zn against solid single crystal Zn of different orientations, and against polycrystalline Zn are given. The value -7.89μv. per deg. for $e_l - e_s$ for Zn (polycrystalline) having been found. A theoretical discussion of the thermo-electric effect in polycrystalline substances having different properties along only two of the crystallographic axes, leads to the formula $\bar{e} = (1/3)(2e_\perp + e_\parallel)$, and indicates that such a polycrystalline metal wire should behave the same as a single crystal wire of orientation 54.5°, the experimental value found being between 65° and 70°. It appears from this formula that polycrystalline Zn may be considered as an alloy of two parts $Zn_\perp$ and one part $Zn_\parallel$.

Introduction

In 1925 the author published a preliminary account[1] of measurements which he was then making of the thermo-electric properties of single crystal zinc. Since that time papers have appeared by P. W. Bridgman[2] who investigated the thermo-electric properties of Sn, Bi, Cd, Sb, Te, and Zn, from 20 to 100°C for various ranges of orientations, and by Grüneisen and Goens,[3] who made similar measurements on Zn and Cd from -253 to 100°C. The work which is described in this paper is a continuation of that previously reported. It consists of measurements with an improved apparatus of the thermo-electric properties of six Zn crystals, over an increased range of both orientation and temperature.

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[1] E. G. Linder, Phys. Rev. **26**, 486 (1925).

[2] P. W. Bridgman, Nat. Acad. Sci. Proc. **11**, 608 (1925); Proc. Amer. Acad. Sci. **61**, 101 (1926).

[3] Grüneisen and Goens, Zeits. f. Physik. **37**, 378 (1926).

GENERAL METHOD AND APPARATUS

Only in a few details was the general method of investigation different from that usually employed in thermo-electric research. The Zn crystals were prepared by a method similar to that devised by Czochralski,[4] the apparatus shown in Fig. 1 being used. The electric furnace, *F*, contained the crucible of molten Zn from which the crystal was drawn. The square brass bar, *B*, ran vertically through the two guides, *C*, and was raised at the desired rate by a weight motor which wound up a steel wire, *K*, running over a pulley and fastened to the lower end of *B*. Another steel wire, *L*, ran to a counterbalance. The entire mechanism was mounted on a heavy wooden support, *T*. In order to regulate the rate of cooling of the crystal, an air current was directed against it through the tube *R*.

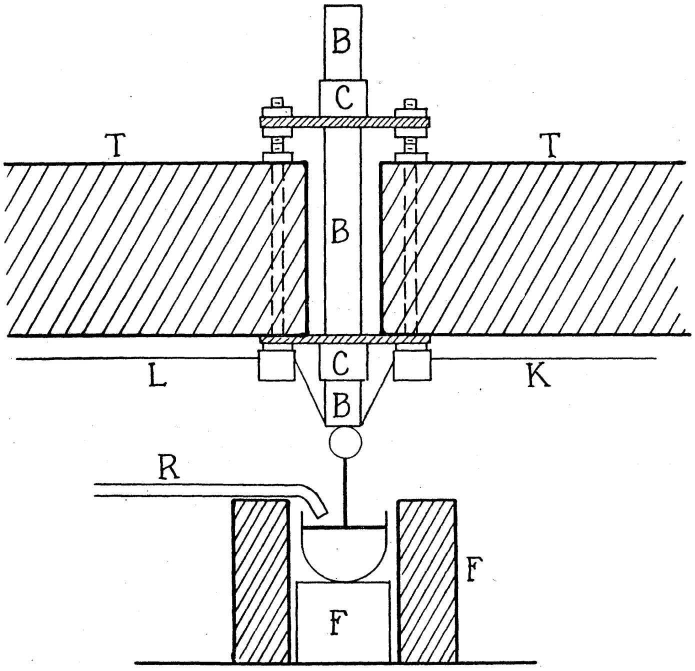

Fig. 1. Apparatus for production of crystals.

The thermal e.m.f. against Cu was measured for various temperature differences by keeping one junction at 0°C and varying the temperature of the other. The essential parts of the apparatus employed for this are shown diagrammatically in Fig. 2. The Zn single crystal, *Z*, was held in a vertical position, its lower end, the hot junction, being at *H*, and the upper end, or cold junction, at *C*. The entire crystal was snugly surrounded by a glass tube, the purpose of which was to protect the crystal and to support it after the temperature at *H* rose above the melting point. *H* was actually a hemispherical Cu block, which closed the lower end of the tube and into

[4] Czochralski, Zeits. f. Phys. Chem. **92**, 219 (1918).

which were fused three wires leading to the binding posts A, B and C. No solder was used to make the hot junction, the crystal being fused directly to the copper by pressing it against H while H was heated and a zinc chloride flux applied. It was found that the crystal structure was not thus destroyed, but maintained up to the surface of contact with the copper. Obviously solder would contaminate the junction, especially above its melting point, and further, this contamination would cause serious errors since the temperature gradient at H was usually very steep. This entire junction was surrounded by fire clay held in a crucible and heated by a bunsen burner. For temperatures lower than that of the room the crucible was removed and the junction immersed in, or placed at suitable heights above, the surface of liquid oxygen. The wire leading to A was of Cu, and constituted the second element of the thermo-electric circuit, AG_1CZH. G_1, a sensitive galvanometer in series with a high resistance, was calibrated in microvolts. The wires leading to B and C constituted elements of the Cu-Advance, temperature-measuring circuit, BTG_2CH. The asbestos board, X, served both as a support for H and as a shield between the flame and the ice container L. The crystal in its glass tube, passing into L through a second, larger tube in a rubber stopper, S, was soft soldered to the copper wire at C, and this junction, together with the ends of the two glass tubes surrounded with a wad of sealing wax.

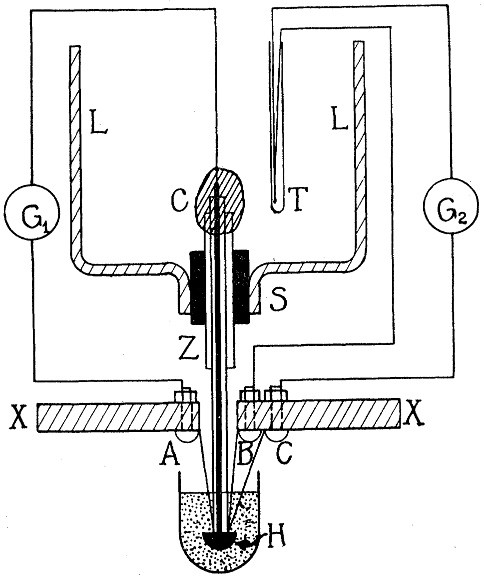

Fig. 2. Apparatus for measuring thermo-electric e.m.f.

This apparatus is different from that employed in the previous work, modifications being necessary in order to measure the e.m.f. above the melting point, and also because it was thought that possibly the previous method of sealing in the crystal had introduced some error.

RESULTS

I. *Thermo-electromotive force, thermo-electric power and Peltier heat as functions of crystal orientation.* The observed values of the thermal e.m.f. against Cu for each of the six single crystals are given in Table I, the e.m.f. being considered positive when it is directed from the hot to the cold junction through the Zn. The data are partially represented in the graphs of Fig. 3 orientations 70° and 74° being omitted since their curves are very nearly coincident with that for 72°. The curves of Fig. 3 may be well represented between 0°C and the melting point by empirical equations of the type: $E = At + Bt^2 + Ct^3$, where E is the thermal e.m.f., t the temperature difference of the junctions, and A, B, C, constants characteristic of the individual curves. Bridgman[2] found that second degree equations represented his results for zinc, but this may be due to his more limited temperature range. Over the same range the writer's results can also be represented by second degree equations. Differentiation of such an equation with respect to t yields the thermo-electric power e.

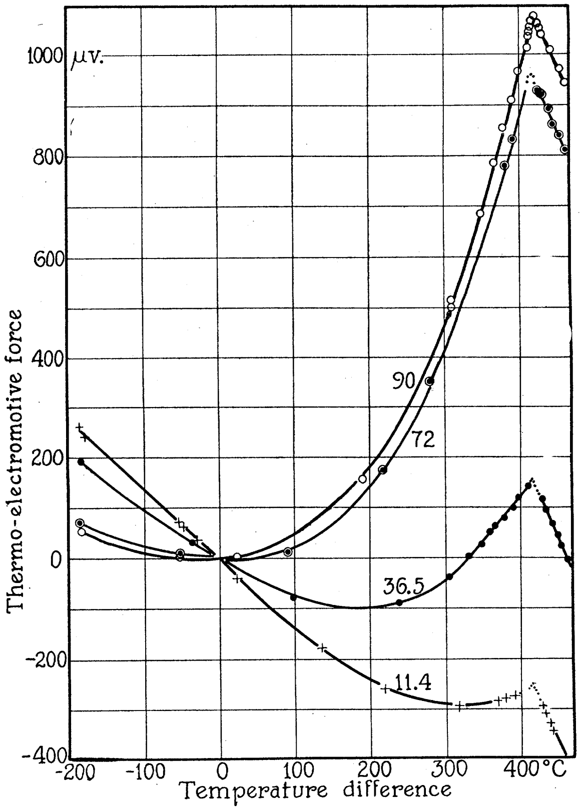

Fig. 3. E.m.f. vs temperature-difference for various orientations. Each curve is labeled with its orientation angle.

TABLE I

Observed thermal e.m.f. of single crystal Zn against Cu.

8, $\theta=11.4°$		10, $\theta=36.5°$		7, $\theta=70°$		11, $\theta=72°$		5, $\theta=74°$		9, $\theta=90°$	
t°C	$E\mu V$	t°C	$E\mu V$	t°C	$E\mu V$	t°C	$E\mu V$	t°C	$E\mu V$	t°C	$E\mu V$
−181	263	−180	192	−182	82	−182	73	−182	75	−181	53
−174	242	−33	34	−179	76	−81	22	−77	20	−52	3
−52	74	99	−76	−68	20	−50	11	20	−1	24	2
−45	64	238	−88	−64	18	90	13	73	9	191	157
−28	39	304	−38	−42	10	217	179	80	12	307	515
25	−34	331	3	−32	7	280	354	191	126	348	686
136	−178	348	27	−26	5	381	780	292	403	307	504
219	−258	358	50	21	−3	389	830	332	565	367	788
317	−292	368	63	56	−1	411	939	361	700	378	856
368	−284	378	79	103	16	413	950	392	925	389	910
378	−278	389	96	194	120	415	956	394	930	398	965
389	−274	398	118	262	287	417	960	413	1060	409	1015
398	−267	409	140	317	480	419	954	418	1020	411	1035
409	−257	411	144	368	720	422	945	419	1020	413	1045
411	−255	413	148	378	725	425	930	422	1025	415	1055
413	−253	415	149	389	808	428	925	425	1013	417	1070
415	−257	417	148	409	910	430	920	428	1013	419	1075
417	−264	419	140	411	920	437	890	431	993	422	1070
419	−270	422	132	413	930	444	860			423	1065
422	−280	423	125	415	944	452	840			425	1055
423	−284	428	114	417	955	459	810			430	1045
425	−294	433	94	419	965	465	800			441	1010
430	−308	441	67	423	982	470	775			452	970
435	−327	448	44	425	990	474	760			459	945
441	−343	455	21	430	972					470	910
455	−400	465	−5	432	970					474	890
465	−436	474	−39	441	935						
470	−455			452	885						
474	−461			465	845						
				474	808						

The only theory so far proposed to explain the thermo-electric properties of crystals is the thermodynamical one of Voigt[5] and Thomson,[6] according to which

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

where θ is the angle between the hexagonal axis and the axis of the wire, $e_{\parallel}$ and $e_{\perp}$ are the thermo-electric powers parallel and perpendicular to the hexagonal axis, respectively.

The treatment of Voigt leads specifically to Eq. (1) above. Bridgman[7] considers that Voigt's and Thomson's analyses have taken no account of either the internal or surface Peltier heat and that therefore Eq. (1), as derived by Voigt, cannot be expected to apply to an actual thermocouple. leaving aside the theoretical considerations underlying the derivation of the equation it is interesting to test it experimentally, considering it, for the moment, as purely empirical. Bridgman has made such a test for zinc and other metal crystals and arrives at the conclusion that the equation is not generally valid for the representation of the experimental facts. The

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[5] Voigt, Lehrbuch der Kristallphysik.

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

[7] Reference 2, p. 128.

chief deviation is found in the case of the Peltier heat. This conclusion is based on the non-linear relation between specific resistance and a constant a', which is shown to be proportional to the Peltier heat at 0°C.

The writer's own results have been applied to test the validity of Eq. (1) in a somewhat different fashion. It is evident from the equation that e plotted against $\cos^2 \theta$ should give a straight line. Such curves for various temperature differences are given in Fig. 4, (points plotted as circles) and, as is evident, the law appears to hold for the lower temperatures, but there seems to be a deviation for the 300° and 400° curves. That is deviation actually exists and is not due to experimental error is further indicated by the fact that the author's previous data[1] show the same type of variation. (e was not calculated in the previous paper but may be obtained from the curves there given.) Neither can this be due to the variation of θ with the temperature since a simple calculation based on thermal expansion coefficients found by Grüneisen and Goens[8] shows this to be considerably too small.

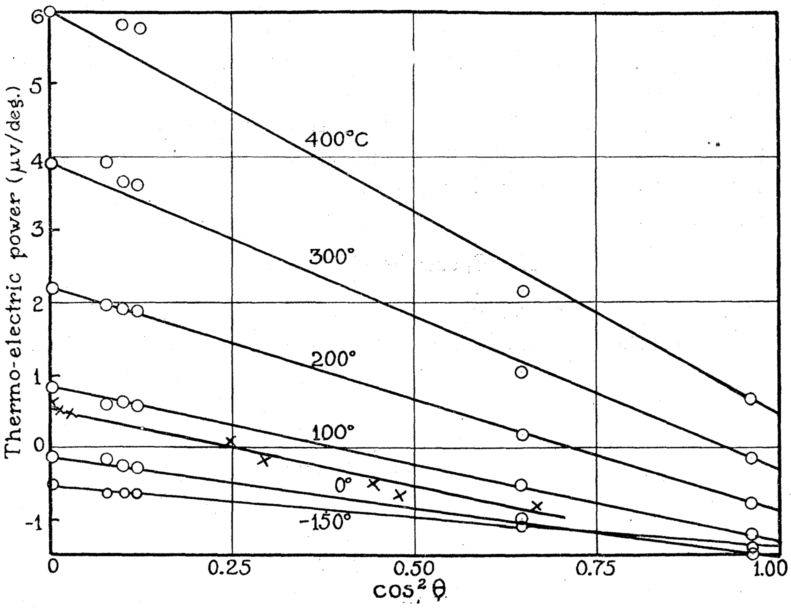

Fig. 4. Thermo-electric power against copper vs $\cos^2 \theta$ for various temperature differences. Linder, O; Bridgman, X.

It should further be pointed out that if the usual thermodynamical relation for the Peltier heat, $\Pi = T\, dE/dt$, is assumed, then the curves of Fig. 4 also show how far Eq. (1) is valid to express the nature of the variation of Peltier heat with the orientation angle. Returning now to Bridgman's data, they may be reduced in a similar fashion. dE/dt is, in his notation, given by $a' + 2bt$, and expressions are given for calculating a' and b from the

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[8] Grüneisen and Goens, Zeits. f. Physik. **29**, 141 (1924).

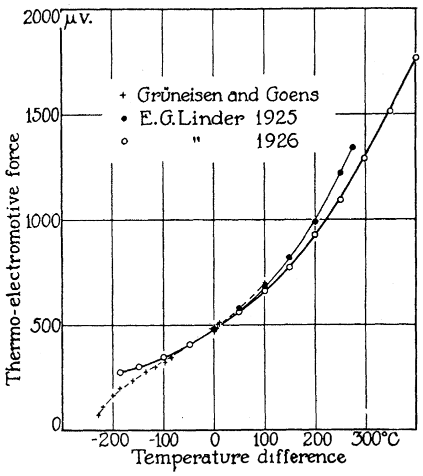
points plotted in his Fig. 4.[9] The thermo-electric power thus computed for $t=60°$ is plotted as crosses (×) in Fig. 4 against $\cos^2\theta$. As is evident, a fairly good straight line results; what deviations exist are not systematic and may well be due to experimental error. In fact Bridgman's 46.5° curve[10] is of doubtful validity since it differs considerably from its neighbors and resembles very much curves which the author has obtained from specimens which were not single crystals but consisted of two or three single crystals together. The same criticism may be made of his 80° or 83° curve. The other curves for the Peltier effect, which Bridgman gives are all nearly straight lines with the exception of the one for tin. Here, however, the experimental points are so scattered that it is uncertain whether the curve is straight. In view of the above it seems that the Voigt-Thomson symmetry relation is obeyed to a much closer degree than was concluded by Bridgman.

II. *Relative Thermo-electric Properties of* $Zn_\perp$ *and* $Zn_\parallel$. Grüneisen and Goens[3] have pointed out the desirability of obtaining the thermo-electric properties of a single metal. To do this they have expressed the various thermo-electric constants of one principal orientation, $\mathrm{Zn}_\perp$(i.e., $\theta=90°$) against the other, $\mathrm{Zn}_\parallel$(i.e., $\theta=0°$). The results described under Section I above may be presented in a similar fashion.

From the Voigt-Thomson law, Eq. (1), we get, by integration,

$$E=E_\parallel\cos^2\theta+E_\perp\sin^2\theta, \tag{2}$$

where E is the e.m.f., providing that θ is independent of the temperature difference, t, of the junctions. As has been mentioned above, this is very



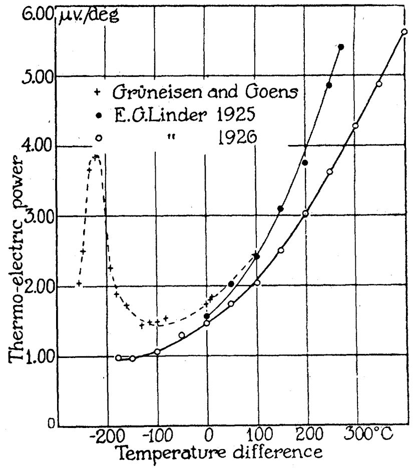


Fig. 5. Thermal e.m.f. for $\mathrm{Zn}_\perp$ against $\mathrm{Zn}_\parallel$.

Fig. 6. Thermo-electric power for $\mathrm{Zn}_\perp$ against $\mathrm{Zn}_\parallel$.

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[9] Reference 2. There is an error in Bridgman's Fig. 4, p. 116, since he has not plotted the angles between the crystal axis and the length of the rod as abscissas but their complements. He also has the sign of his Δ wrong according to its definition on p. 114.

[10] Reference 2, Fig. 3, p. 115.

nearly true and will be assumed so. Hence, by introducing into Eq. (2) the observed values of $E_\perp$ and E for 11.4°, the values of $E_\parallel$ may be calculated. For the purpose of comparison we now introduce the value $E(0°, -253°) = 483.6\mu$v. (i.e., the e.m.f. with one junction at 0° and the other at −253°C) taken from the work of Grüneisen and Goens, and by use of the law of intermediate metals, get

$$E(t, -253°) = E(0°, -253°) + E(t, 0°)$$

where all of the E's are for Zn$_\perp$ against Zn$_\parallel$. The values obtained in this manner together with those of Grüneisen and Goens are represented graphically in Fig. 5, and are tabulated in Table II. In this figure, and also in Figs. 6 and 7, are displayed the writer's earlier results, reduced in the same fashion, together with those of Grüneisen and Goens.

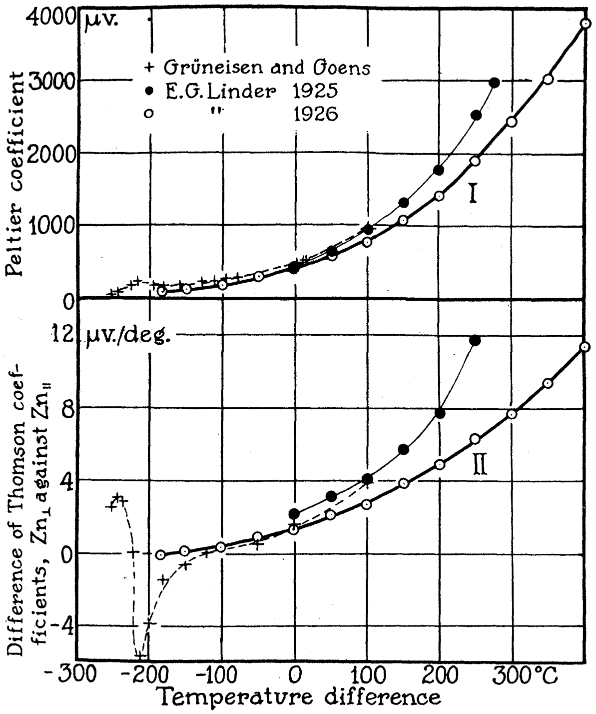

Fig. 7. I Peltier coefficient for Zn$_\perp$ against Zn$_\parallel$. II differences of the Thomson coefficients for Zn$_\perp$ against Zn$_\parallel$.

The thermo-electric power, $e = dE/dt$, can be obtained by measuring the slope of the tangents to the curve of Fig. 5. It is to be noted that dE/dt is independent of the additive constant, $E(0°, -253°)$. The values of the thermo-electric power thus obtained are listed in Table II and graphed in Fig. 6.

According to Kelvin's thermodynamical theory, the Peltier coefficient is given by

$$\Pi = Te,$$

where T is the absolute temperature of the junction. The values calculated according to this formula are given in Table II and curve I, of Fig. 7.

The difference of the Thomson coefficients, which, from the same theory, is given by

$$\sigma_\perp - \sigma_\parallel = T(de/dt),$$

TABLE II

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

T	$E(t, -253°)$	e	Π	$\sigma_\perp - \sigma_\parallel$
−182°C	275 μv	.99 μv/deg.	90 μv	−.11μv/deg.
−150	304	.96	118	.10
−100	355	1.07	185	.37
− 50	414	1.32	295	.92
0	484	1.47	402	1.39
50	564	1.77	572	2.18
100	661	2.05	765	2.69
150	771	2.53	1075	3.87
200	921	3.00	1420	4.87
250	1087	3.63	1900	6.33
300	1285	4.28	2450	7.67
350	1511	4.85	3025	9.45
400	1770	5.65	3800	11.40

can also be calculated by using values of de/dt obtained by measuring the slope of the tangents to the curve of Fig. 5. The data so obtained are given in Table II and curve II of Fig. 7.

III. *Behavior at the melting point.* Observers disagree as to whether there is a break in the thermo-electric power curve at the melting point. For zinc Darling and Grace[11] and also H. Pélabon[12] write that they observed no change, while, on the other hand, J. Koenigsberger[13] observed one, and gives the experimental value $e_e - e_s = -10\mu$v./degree, where e_e is the thermoelectric power of liquid Zn and e_s that of solid Zn. He also gives the theoretical values, -5.6μv./deg. from Bernoulli's formula[13] and -6.0μv./deg. from Lorentz's formula.[13] As may be seen from Fig. 3, the author found a distinct break at the melting point. The crystal structure—at least insofar as it determines the thermo-electromotive force—breaks down suddenly and not gradually as the temperature passes that point. Further, those parts of the curves above 419°C are approximately parallel, which is precisely what we should expect, for after the Zn crystal has melted we have the situation depicted in Fig. 8. The junction A, between the solid Cu and liquid

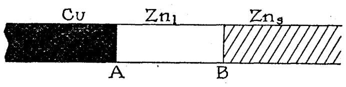

Fig. 8. Diagram of zinc crystal—copper junction above the melting point of zinc.

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[11] Darling and Grace, Proc. Lond. Phys. Soc. **30,** 14 (1917).

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

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

(homogeneous) Zn may vary in temperature from 419°C up, and the e.m.f., E_A, due to it, is the same for all crystals; on the other hand, the junction B, between liquid Zn and crystalline Zn, is always at the same temperature, i.e., 419°C, but the e.m.f. due to it, E_B, is different for crystals having different orientations. Thus E_B acts as an additive constant, and the total e.m.f., $E = E_A + E_B$, represents a family of parallel lines. The values of $e_l - e_s$ for different orientations, and values for two specimens of polycrystalline Zn are arranged in Table III. The average value, -7.98 μv./deg., which the author obtained for $\mathrm{Zn}_{\mathrm{poly}}$, is in better agreement with the theoretical values than those of Koenigsberger mentioned above.

TABLE III

Thermo-electric power of solid and liquid zinc at the melting point.

θ	e_s μv/deg.	e_l μv/deg.	$e_l - e_s$ μv/deg.
11.4	1.13	−3.61	−4.75
36.5	2.00	−3.20	−5.20
72	4.87	−3.58	−8.45
90	5.30	−3.23	−8.55
P.C. 1	4.25	−3.64	−7.89
P.C. 2	4.88	−3.18	−8.06

The principal sources of error in the measurements presented in the above three sections probably are: (1) the determination of the orientation[1]; (2) the measurement of the temperature of the hot junction (a different copper-advance thermocouple and block, H, Fig. 2, were used in order to prevent contamination of the block due to diffusion into it by the liquid Zn, each being made, however, with wires from the same spools and in an identical manner); (3) impurity of the zinc. Merck "highly pure" zinc was employed.

IV. *Effect in polycrystalline substances.* As is well known, many so-called isotropic substances are, in reality, quasi-isotropic, i.e., random aggregates of small crystal particles. Since this is the case, it should be possible to express the properties of the aggregate in terms of the properties of its component single crystal parts. An attempt to do this in the case of the thermo-electric properties of polycrystalline metals has met with a fair degree of success.

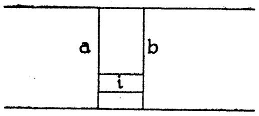

Fig. 9.

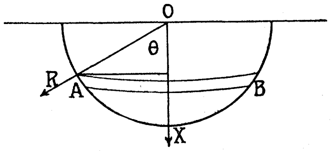

Fig. 10.

Consider an arbitrary, cross-sectional element, ab, Fig. 9, of a polycrystalline conductor constituting one of the elements of a thermo-electric circuit. The two plane boundaries of ab, we shall assume to be equipotential surfaces. Let V be the potential difference between them. Let I_i, r_i and E_i be the current, resistance and thermal e.m.f. of any one crystal in this element Then, assuming that each crystal extends from a to b, we have, from Kirchoff's second law

$$V=I_i r_i+E_i.$$

Further, the total current I is given by

$$I=\sum_i p_i I_i=\sum_i p_i\ V-E_i)/r_i, \tag{3}$$

where p_i is the concentration of crystals having the orientation θ_i. This may be found as follows: In Fig. 10 let OX represent the axis of the Zn wire, and OR the hexagonal axis of any crystal. It is evident that the probability of the hexagonal axis making an angle between θ_i and $\theta_i+d\theta$ with the wire axis is (area of strip $AB_i)/2\pi r^2$ or $p_i=\sin\theta_i d\theta$. Now Eq. (3) holds for any value of I, hence put $I=0$, then,

$$V\sum_i p_i/\sigma_i=\sum_i p_i E_i/\sigma_i,$$

where σ_i is the specific resistance of any Zn crystal of orientation θ_i, and is given by

$$\sigma_i=\sigma_\parallel\cos^2\theta_i+\sigma_\perp\sin^2\theta_i.$$ [5]

Introducing the similar expression for E, Eq. (2), we have

$$V=\frac{\displaystyle\int_0^{\pi/2}\frac{E_\parallel\cos^2\theta+E_\perp\sin^2\theta}{\sigma_\parallel\cos^2\theta+\sigma_\perp\sin^2\theta}\sin\theta d\theta}{\displaystyle\int_0^{\pi/2}\frac{\sin\theta}{\sigma_\parallel\cos^2\theta+\sigma_\perp\sin^2\theta}d\theta}$$

$$=E_\perp+(E_\parallel-E_\perp)/(4-r)$$

where $r=\sigma_\parallel/\sigma_\perp$. Assuming that $r=1$, we have

$$V=\overline{E}=E_\perp+(1/3)(E_\parallel-E_\perp) \tag{4}$$

and by comparison with Eq. (2) it follows that $\cos^2\theta=1/3$; whence $\bar{\theta}=54.5°$. In other words, a polycrystalline wire should give the same thermal e.m.f. as a single crystal wire having an orientation of 54.5°. The author found the experimental value of 65 − 70° for Zn. The agreement is not good, but in view of the assumptions we could not expect it to be better.

Unfortunately, as far as the author is aware, there are no other data suitable for checking this result. The variation among the different available measurements on polycrystalline metals is so great that it appears that a reliable check can be obtained only when the polycrystalline and single crystal measurements are made by *identical* methods and on the *same* samples of metal. For this reason it seems that Bridgman's conclusion, based on experimental data, that the thermo-electric properties of the aggregate cannot be found by averaging the properties of the single crystals, is scarcely justified.

By differentiating Eq. (4) with respect to t, and rearranging, we have,

$$\bar{e} = (1/3)(2e_{\perp} + e_{\parallel}),$$

and this is identical with a type of formula which has been found to give the thermo-electric properties of alloys of mechanically mixed crystals of different metals,[14] therefore it appears as if polycrystalline metal, might be considered as an alloy of three components having properties corresponding to the three crystallographic axes, respectively, (two parts $\mathrm{Zn}_{\perp}$ and one part $\mathrm{Zn}_{\parallel}$ in the present case).

It should be pointed out that we obtain the same result, if, instead of taking a cross-sectional element, we consider a long strip parallel to the axis of the wire. In this case, instead of assuming the electrical conductivities equal, we assume the thermal conductivities so, and hence the temperature difference across each crystal will, on the average, be the same, so that we get,

$$\bar{E} = \sum_{i} p_i E_i,$$

which leads to Eq. (4).

It may also be worthwhile to mention that expressions for the thermal and electrical conductivities of polycrystalline metals can be obtained by similar methods and that these formulas are identical with those which have been found to hold for alloys of mechanically mixed crystals.[15]

CONCLUSION

Obviously the present electron theories of thermo-electricity are inadequate for the explanation of this effect in crystals, since electron gas pressure or electron concentration, as ordinarily understood, are not vector quantities, i.e., their magnitude is not a function of direction in the crystal. If, however, we take into consideration the fact that the spacing of the atoms in the lattice is different for different directions, and that, therefore, the mean free path of the free electrons would vary with direction and in consequence the electron gas pressure, we have a possible explanation.

The author wishes to express his thanks to Professor E. P. T. Tyndall for his valuable suggestions and criticism.

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November, 1926.

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