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SOME ELECTRICAL PROPERTIES OF SPECTROSCOPICALLY PURE ZINC CRYSTALS

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Abstract

With single crystal specimens of *spectroscopically pure* zinc (99.9999 percent zinc), the Thomson coefficient at 49.5°C has been measured as a function of orientation. A very accurate confirmation of the Voigt-Thomson symmetry relation is obtained, the principal values of the Thomson coefficient being: $\sigma_{\perp}=0.86\times10^{-6}$cal./coul./deg., and $\sigma_{\parallel}=0.34\times10^{-6}$ cal./coul./deg. The thermal e.m.f. of these same specimens against copper has been determined as a function of orientation throughout the temperature range $-180°$ to 200°C. From these data, the values of the Peltier coefficient, the Thomson coefficient, and the difference in principal Thomson coefficients have been computed as functions of temperature by means of the relations given by the Kelvin thermodynamical theory of thermoelectricity. The values of the Peltier coefficient of $\mathrm{Zn}_{\perp}$ against $\mathrm{Zn}_{\parallel}$ thus obtained are: $\pi=658$ microvolts at 49.5°C and $\pi=1080$ micro-volts at 125°C. For the difference in the principal Thomson coefficients, the values are: $\sigma_{\perp}-\sigma_{\parallel}=0.58\times10^{-6}$ cal./coul./deg. at 49.5°C and $\sigma_{\perp}-\sigma_{\parallel}=1.20\times10^{-6}$ cal./coul./deg. at 125°C. The predictions of the Kelvin theory regarding $\sigma_{\perp}-\sigma_{\parallel}$ are thus found to be in agreement with the direct determinations by Ware and the writer. The Voigt-Thomson law is found to hold also in the case of thermoelectric power and the other thermoelectric properties to which it should apply. The dependence of resistivity on temperature has been investigated for the temperature range $-170°$ to 25°C. The average value of the temperature coefficient of resistivity obtained is: $\alpha=4.058\times10^{-3}$. For comparison purposes, a direct determination of the Thomson coefficients of single cyrstal specimens of *Kahlbaum's best* zinc at 49.5°C has also been made, as well as a study of the dependence of their resistivities on temperature. For this less pure zinc, the principal values of the Thomson coefficient are: $\sigma_{\perp}=0.91\times10^{-6}$ cal./coul./deg. and $\sigma_{\parallel}=0.38\times10^{-6}$ cal./coul./deg. For the temperature coefficient of resistivity, the average value is: $\alpha=4.009\times10^{-3}$. A variation in the values of α for specimens of the same grade of zinc is observed which is considerably greater than can be attributed to experimental error.

Introduction

THAT the presence of even slight amounts of impurity may have a very pronounced influence on some of the properties of metals is well known. Consequently, in trying to ascertain the properties truly characteristic of a metallic element, it is obviously of great importance that the specimens studied be as free from foreign substances as possible. If at the same time simplicity and uniformity characterize the spatial arrangement of the atoms throughout the specimen, such as is the case in single crystals, it is evident that the characteristics obtained ought to be even more closely associated with the true properties of the element itself. Several investigations dealing with the electrical properties of zinc single crystals have been reported, none, however, for zinc of exceedingly high purity. Linder,[1] Bridgman,[2] and

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[1] E. G. Linder, Phys. Rev. **26**, 486 (1925), **29**, 554 (1927).

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

Grüneisen and Goens[3] have measured the thermal e.m.f. of zinc against copper, and from the thermoelectric power thus obtained have computed by means of the customary thermodynamical relations the Peltier coefficients of the zinc crystals (against copper) and the difference in the Thomson coefficients of the two principal orientations as functions of temperature. Specific resistance and the temperature coefficient of resistivity have been measured by Grüneisen and Goens,[4] Bridgman,[2] and Ware.[5] Direct determinations of the Thomson coefficient have been made by Ware[5] and by Veleger.[6] None of these investigators give the exact analysis of the zinc used except to state that it was Kahlbaum's, Kahlbaum's best, or Merck's brand of zinc. Hence it is reasonable to assume that the specimens varied considerably in purity and that all contained not less than 0.01 percent impurity, the percentage of impurity usually present in chemically pure zinc. The zinc used in the present investigation was obtained through the courtesy of the New Jersey Zinc Company and is known as *spectroscopically pure* zinc. Its analysis is given as 99.9999 percent pure.[7] On single crystal specimens made from this S. P. zinc, a direct determination was made of the Thomson coefficient, together with measurements of thermal e.m.f. against copper, of specific resistance,[8] and of the temperature coefficient of resistivity. From the thermal e.m.f. data, the Peltier coefficient against copper and the difference in the principal Thomson coefficients, $(\sigma_\perp - \sigma_\parallel)$, were computed as functions of temperature. Thus, in view of the fact that the thermal e.m.f. and the Thomson coefficient measurements were obtained for the same crystal specimens, it is possible to make a better comparison between the predictions of thermodynamical theory and the results of direct measurement than would have been possible in using only the results of previous investigators for comparison purposes. In addition, in order that the comparison between the results for the S. P. zinc and less pure grades of zinc might be more trustworthy, the Thomson coefficient, specific resistance,[8] and temperature coefficient of resistivity were also determined for a set of single crystal specimens made from Kahlbaum's best zinc.

Apparatus and Experimental Procedure

1. Production of the single crystals

The Czochralski-Gomperz method, described in considerable detail in a recent paper by the writer and E.P.T. Tyndall,[9] was used with a few slight modifications in growing the single crystal specimens. Due to the fact that the quantity of zinc available was comparatively small, approximately 250

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[3] E. Grüneisen and E. Goens, Zeits. f. Physik **37** 278, (1926).

[4] E. Grüneisen and E. Goens, Zeits. f. Physik **26**, 250 (1924).

[5] L. A. Ware, Phys. Rev. **35**, 989 (1930).

[6] H. Veleger, Ann. d. Physik **9**, 366 (1931).

[7] The writer is very grateful to the New Jersey Zinc Company for providing him with a quantity of this exceedingly pure material. For a description of its properties and the method of production, see H. M. Cyr, Tran. Amer. Electrochem. Soc. **52**, 349 (1927).

[8] E. P. T. Tyndall and A. G. Hoyem, Phys. Rev. **37**, 101 (1931).

[9] A. G. Hoyem and E. P. T. Tyndall, Phys. Rev. **33**, 81 (1929).

grams, and the fact that the greater the purity of the metal the more readily it oxidizes when it is in the molten state, it was very necessary to minimize the two chief sources of waste, namely, loss of specimens due to imperfections caused by occasional unsteadiness of the crystal growing apparatus, and loss of material due to oxidation. To overcome the former difficulty, a new drawing mechanism was constructed, the square brass rod and the slides used in the former apparatus being replaced by a hexagonal brass rod which was guided by two sets of three ball-bearings. Oxidation was eliminated by having the entire growth process take place inside of a Pyrex glass tube, 5 cm in diameter and 25 cm tall, which contained a mixture of hydrogen and nitrogen. In order to avoid the possiblities of contamination, the crucible, as well as the tools used for handling the zinc, were also made of Pyrex.

The crystals were all grown in the "region of successful growth" designated in the earlier paper.[9,10] These S. P. crystals are extremely ductile and as a consequence are very difficult to handle without bending. Though the near zero degree orientations are the most brittle, they are not nearly as much so as the corresponding orientations of crystals made from Kahlbaum or other grades of zinc. Twenty-six crystals in all were grown ranging from fifteen to twenty centimeters in length and having a mean diameter of from two to three millimeters. Prior to the growing of these crystals, numerous K zinc crystals were grown under practically the same conditions with the double purpose of establishing the technique of crystal growth in the new apparatus and to provide material for the comparison between the S. P. zinc and a grade of zinc more nearly like that used by previous investigators.

2. The Thomson coefficient

The Thomson coefficient was measured by means of the Nettleton[11] method described by Ware[5] with further slight modifications.[12] In brief, the essential features of the method are as follows: The two ends of a single crystal specimen of zinc are maintained at different, but constant, temperatures. The Thomson effect, which is positive for zinc, will then cause an e.m.f. to be set up within the crystal, directed from the colder to the hotter portion. If an electric current is now set up in the crystal so that it flows down the temperature gradient, there will be a generation of heat in the crystal, a portion of which will be caused by the resistance of the crystal, the remainder being caused by the fact that the current is flowing in opposition to the Thomson

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[10] Some recent work by Mr. H. K. Schilling performed in this laboratory seems to indicate that this region is successful growth may be considerably extended provided exceeding care be taken to minimize vibration and temperature fluctuation during the growth process. This raises the question as to whether the apparatus and procedure described here were not sufficiently improved over the first set-up so that crystals might also have been grown outside of the "region of successful growth." The only positive evidence of this is that attempts to grow Kahlbaum crystals of nearly 0° orientation at too high or at too low temperatures were definite failures. Aside from this the growth of crystals was purposely confined to what was believed to be the only suitable conditions.

[11] H. R. Nettleton, Proc. Phys. Soc. Lond. **34**, 77 (1921) ; **29**, 59 (1916).

[12] For diagrams of the apparatus and the electrical circuits involved see the article by Ware, Figs. 1, 2, and 3.

e.m.f. If the same current through the specimen is reversed, the Joulean heat will be of the same magnitude as before, but the Thomson effect will now produce an absorption of heat, hence the temperature of the specimen will be different in the two cases. On reversal, however, the current may be automatically increased to such a value that the temperature of the specimen remains constant. When such a state is reached that the temperature of the specimen does not change when the current is reversed, it has been shown by Nettleton[11] that if certain conditions are met, the Thomson coefficient, σ, will be equal to i_0R/JU calories per coulomb per degree, where i_0 is the above mentioned difference in currents corresponding to no temperature change, R is the resistance of the crystal, J is the mechanical equivalent of heat in joules per calorie, and U is the difference in temperature between the two ends. The two end temperatures used were 99° and 0°, respectively.

The accuracy with which the balancing current, i_0, can be determined hinges essentially on the sensitivity of the device used in detecting temperature changes in the crystal and on the constancy of the end temperatures. In order to increase this accuracy, the following modifications in Ware's procedure were made: The length of the bolometer coils was approximately doubled and better heat insulation provided in the entire bolometer-bridge circuit. The capacity of both the hot and cold reservoirs was increased so as to make it possible to maintain the temperatures at the ends of the crystal very constant throughout longer periods. The constancy of the hot end was further increased by heating the water by means of a different coil than the one which was used in mounting the crystal. This auxiliary coil was wound on the surface of the boiler as far removed from the end of the specimen as possible thus greatly diminishing the variations in temperature caused by occasional fluctuations in the heating current. With these modifications, the uncertainty in the determination of the balancing current, i_0, for most of the crystals was reduced to less than two percent. Two thermocouples, permanently imbedded in the reservoir blocks adjacent to the block-crystal junctions, served in determining the temperatures at the ends of the crystal.

3. Thermal e.m.f.

The thermal e.m.f. of zinc against copper was measured immediately following the determination of the Thomson coefficient of each crystal specimen, that is, while the specimen was still in the Thomson apparatus. A diagram of the circuit is shown in Fig. 1. Determination of the temperature at the ends of the crystal was made by connecting the potentiometer across terminals 1 and 4, and 2 and 3, respectively. These constantan-copper thermocouples are the two couples referred to in the preceding section. Readings across terminals 1 and 3 gave the thermal e.m.f. of the crystal against copper. In obtaning the various temperature differences, the cold end of the Thomson apparatus was maintained at 0°C, while the hot end served as the variable junction. The necessary low temperatures were secured by draining the boiler chamber and then introducing various quantities of liquid air directly into the chamber, the depth of the temperature obtained at the junction naturally depending on the amount of liquid air introduced and on the extent of the heat insulation. To obtain the high temperatures, use was made of the heating element located in the boiler near the end of the crystal, currents ranging from 0.5 to 1.5 amperes being used. At both the high and the low temperatures, the fluctuation encountered while the readings of temperature and the thermal e.m.f. were being taken and checked was usually less than half a degree.

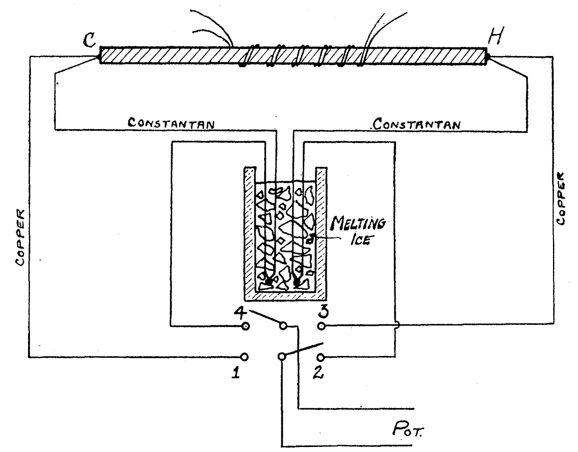

Fig. 1. The thermal e.m.f. circuit.

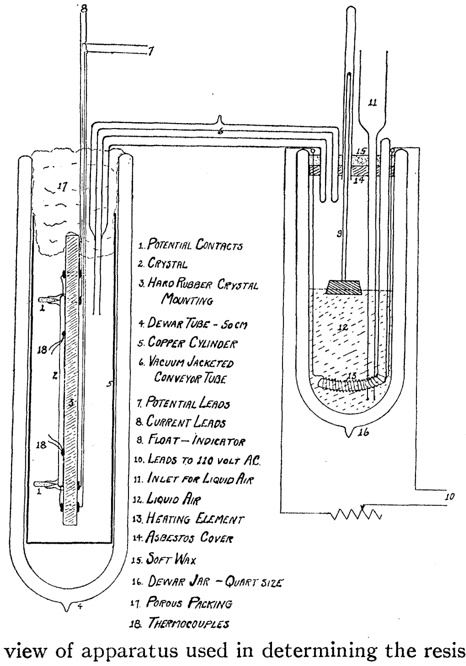

Fig. 2. Cross-sectional view of apparatus used in determining the resistance of the specimens at temperatures ranging from 25° to −170°C.

4. Temperature coefficient of resistivity

The apparatus used in the determination of the temperature coefficient of resistivity is shown in Fig. 2. It employs the method for the production of low temperatures described by Cioffi and Taylor[13], namely, the evaporation of liquid air by the use of a heating element and the subjection of the specimens under investigation to the stream of cold dry air thus produced, the degree of cold depending on the rate of evaporation and on the insulation used in the transfer of the cold air. In this apparatus cold dry air, obtained by the forced evaporation of the liquid air in the small Dewar container, was transferred by means of the vacuum-jacketed tube into the large Dewar container, the entire apparatus being entirely enclosed in heat insulating material. Two crystal specimens were investigated simultaneously, being placed in parallel grooves on the hard rubber mounting. Chisel-shaped pieces of zinc, held in contact with the specimens by means of springs, served in obtaining the potential drop across any desired portions. These contacts were devised so as to eliminate the possibility of effects which might be due to contamination by soldered connections or due to irregularities in the crystal structure caused by cutting. The current leads were attached to the ends of the specimens. To insure greater constancy and uniformity of temperature throughout the region containing the specimens, the specimens and the mounting were placed inside of a copper cylinder fitting closely in the large Dewar container. Two thermocouples placed about ten centimeters apart between the two specimens furnished the means of determining the exact temperature as well as to show the absence of any appreciable vertical temperature gradient. The temperature coefficient was computed by using the relationship:

$$\alpha = \frac{1 - p}{t_2 p - t_1}$$

where p is the ratio of R_1 to R_2, R_1 and R_2 being the resistances of the specimen at the temperatures t_1 and t_2, respectively. The resistance measurements were made by the usual potentiometer method, the current used in the crystals being 0.5 ampere.

This low temperature apparatus proved very satisfactory particularly in regard to the constancy with which the temperature could be maintained and the fact that a temperature as low as $-170°$C could be obtained without excessive consumption of liquid air. At this temperature the consumption was approximately three liters per hour, but less, of course, at higher temperatures.

RESULTS

1. Thomson coefficient

The experimental results obtained in the direct determination of the Thomson coefficient are represented graphically in Fig. 3. The values obtained for the S.P. crystals are represented by circles, the values for the K crystals being denoted by dots. Both sets of data are for a mean temperature of 49.5°C.

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[13] P. P. Cioffi and L. S. Taylor, Opt. Soc. Amer. J. **6**, 906 (1922).

In agreement with Ware's findings, both sets of data indicate that the Voigt-Thomson symmetry relationship for the Thomson coefficient holds at this temperature, the linearity being particularly definite in the case of the S.P. zinc. It is only fair to state that the greater regularity in the results for the S.P. zinc is largely due to the greater care taken in this case and that with the possible exception of the two points for the K zinc at $\cos^2\theta = 0$ and at $\cos^2\theta = 0.74$, the deviations are no larger than the probable experimental error.

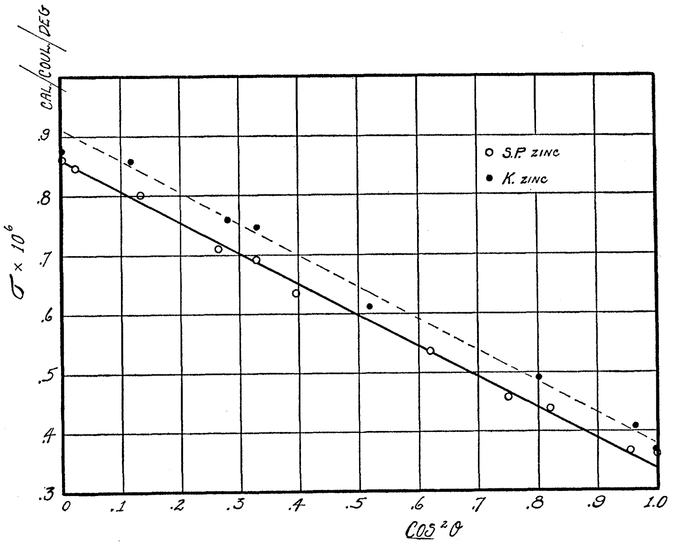

Fig. 3. Directly determined values of the Thomson coefficient plotted against $\cos^2\theta$. The S.P· values are represented by ○————○, and the K zinc values by ●- - - - -●.

The values for $\sigma_\perp$ and $\sigma_\parallel$ for the S.P. zinc, expressed in micro-calories per coulomb per degree, are 0.86 and 0.34, respectively, while for the K zinc the values are 0.91 and 0.38, respectively, in fairly good agreement with Ware's values of 0.98 and 0.38 respectively, for the same grade of zinc. Comparing the results for the S.P. crystals with the writer's K crystals it is evident that the effect of impurity is to cause a practically constant increase in the Thomson coefficient for all orientations, the ratio, $\sigma_\perp/\sigma_\parallel$, and the difference, $\sigma_\perp - \sigma_\parallel$, being almost identical for the two sets of crystals. The effect of impurity on specific resistance is apparently of the same type.[8]

2. Thermal e.m.f.

The observed values of the thermal e.m.f. of zinc against copper are represented graphically in Fig. 4, the e.m.f. being considered positive when it is directed from the hot to the cold junction through the zinc. The four different notations used in plotting these values were used merely for the sake of clarity to aid in associating the various points with the curves to which they belong. The numbers alongside the curves indicate the crystal orientations. Representing these curves by empirical equations of the form: $E = at^3 + bt^2 + ct$, where *a*, *b*, and *c* are constants which are characteristic of the individual curves, and differentiating these equations with respect to *t*, equations giving the value of the thermoelectric power, $e(=dE/dt)$, are obtained. Fig. 5 shows the values of the thermoelectric power, obtained in this manner, plotted against the square of the cosine of the angle of orientation. The ordinate scale indicated applies to the curve for the temperature of −180°. To avoid confusion, the origin for the values corresponding to a temperature of −150° is shifted upward one whole unit, the origin for those corresponding to −100° being shifted upward two whole units, etc. That the Voigt-Thomson symmetry relation holds for this zinc throughout the range of temperature investigated seems quite evident. The slight scattering of points for the tempera-

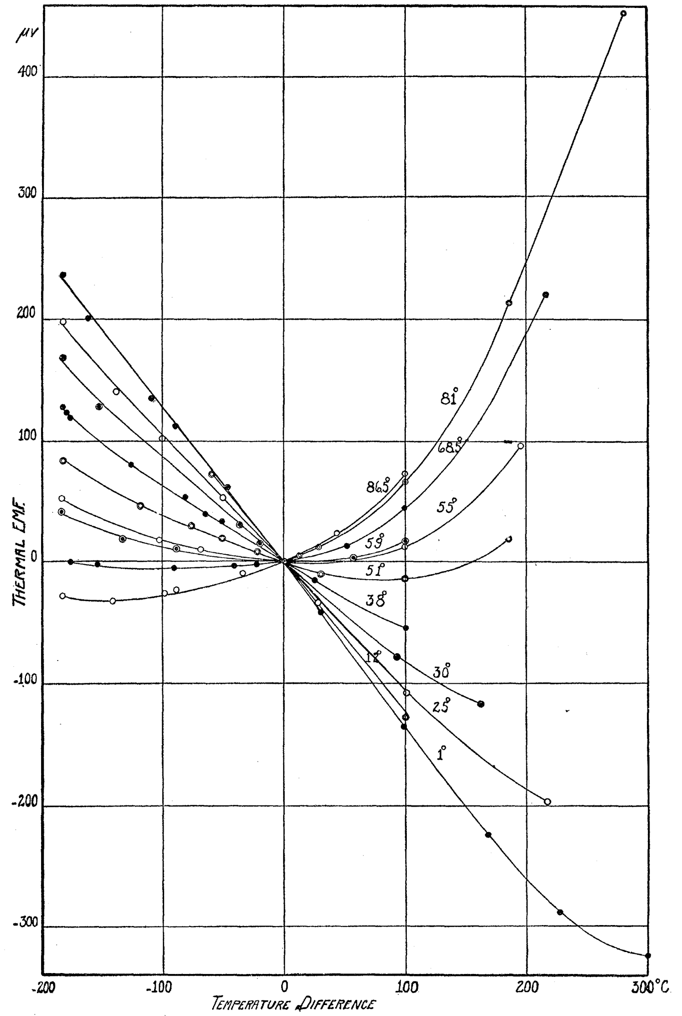

Fig. 4. Thermal e.m.f. of S.P. zinc against copper represented as a function of temperature difference. The crystal orientations are indicated on the curves.

ture of 180° is believed to be due to the fact that the probable error in the determination of e is greatest here, since this region is for some of the crystals very near the upper limit for the thermal e.m.f. measurements and is also a region for which e changes quite rapidly.

The thermoelectric properties of single crystals may be obtained without reference to any other metal by expressing the characteristic values for the one principal orientation ($\theta=90°$), against those for the other principal orientation ($\theta=0°$). These values for thermal e.m.f. were obtained by using the empirical equations for E and plotting values of E against $\cos^2\theta$ in the same manner as e is represented in Fig. 5. Definite straight line relations were obtained from which the values of $E_\perp$ and $E_\parallel$ were observed and their difference plotted against the corresponding temperature. The results are represented in Fig. 6 by the circles and the solid, heavy curve. The results obtained by Linder[1] and by Grüneisen and Goens[3] are also shown, being represented by the double circles and the dots, respectively. In order to make this comparison, the writer's results had to be reduced by the use of the law of intermediate temperatures, whereby

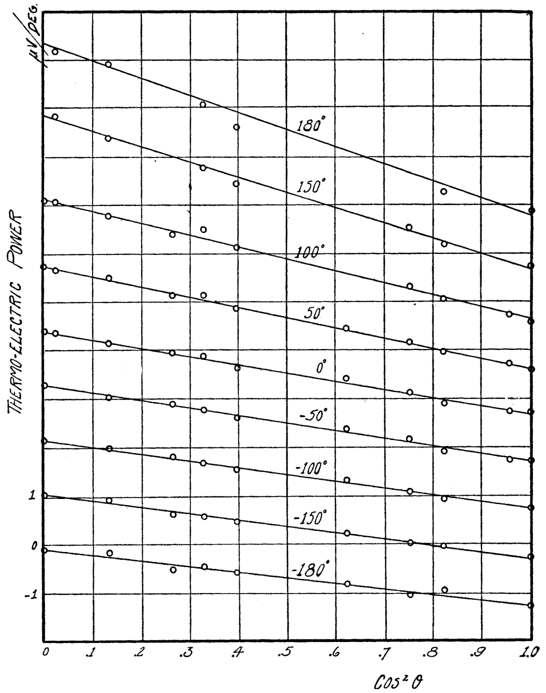

Fig. 5. Thermoelectric power at various temperatures represented as a function of $\cos^2\theta$.

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

The value of $E(0°, -253°) = 483.6\mu v$, taken from the work of Grüneisen and Goens, was used in carrying out the reduction. It is to be noted that the writer's results are in closest agreement with those of Grüneisen and Goens.

By noting the values of $e_\perp$ and $e_\parallel$, in Fig. 5, and plotting their difference against temperature, the variation of thermoelectric power for $\mathrm{Zn}_\perp$ against $\mathrm{Zn}_\parallel$ is obtained. This is represented in Fig. 7.

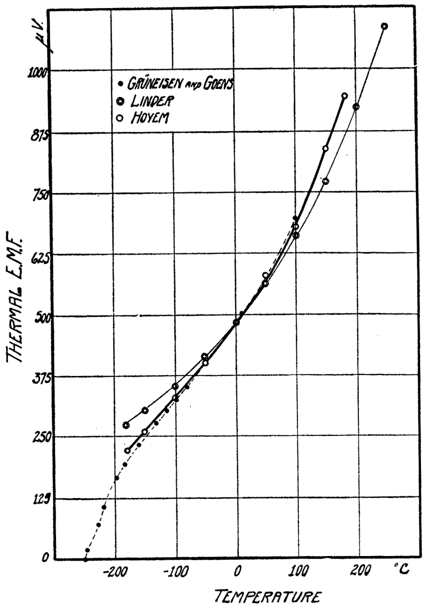

Fig. 6. Thermal e.m.f. of $\mathrm{Zn}_\perp$ against $\mathrm{Zn}_\parallel$.

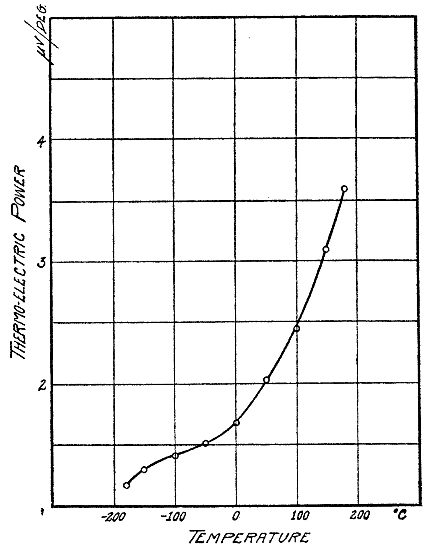

Fig. 7. Thermoelectric power of $\mathrm{Zn}_\perp$ against $\mathrm{Zn}_\parallel$.

The Peltier coefficient, π, for $\mathrm{Zn}_\perp$ against $\mathrm{Zn}_\parallel$ and the difference in the principal Thomson coefficients, $\sigma_\perp - \sigma_\parallel$, are, according to the Kelvin thermodynamical theory, given by Te and $T(de/dt)$, respectively, where T is the absolute temperature and e is the thermoelectric power for $Zn_{\perp}$ against $Zn_{\parallel}$. The Peltier coefficient, π, obtained in this manner, is represented in Fig. 8 as a function of temperature. Similar results obtained by Linder[1] and by Grüneisen and Goens[3] have been included on the graph for comparison. The values obtained by the writer throughout the greater part of the range are seen to be in very close agreement with those obtained by Grüneisen and

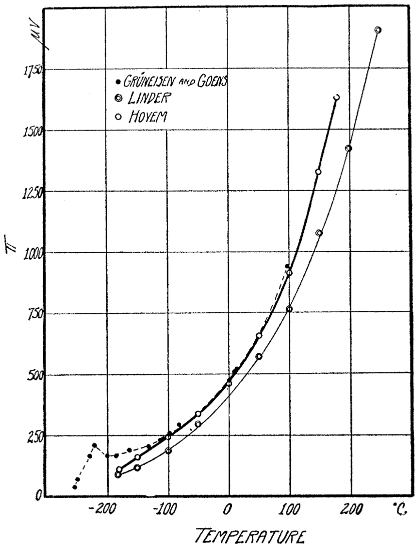

Fig. 8. The Peltier coefficient of $Zn_{\perp}$ against $Zn_{\parallel}$.

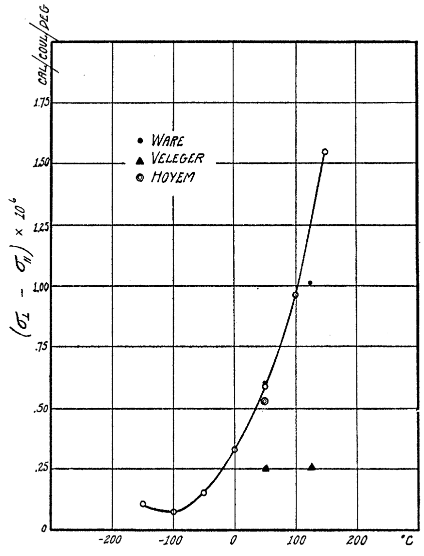

Fig. 9. The difference in the principal Thomson coefficients represented as a function of temperature.

Goens. The writer's measurements did not extend below the temperature of liquid air, consequently all that can be said about the slight maximum in the Peltier coefficient at low temperatures obtained by these earlier investigators is that there is no definite indication of such an increase in the present results.

In Fig. 9 the difference in the principal Thomson coefficients,[14] $\sigma_\perp - \sigma_\parallel = (T/J)(de/dt)$, is represented also as a function of temperature. The value of de/dt used in the above computations was obtained by differentiation of a series of second degree equations which represented overlapping sections of the thermoelectric power versus temperature curve shown in Fig. 7. These equations were of the form: $e = at^2 + bt + c$, where a, b, and c were constants characteristic of the various sections of the curve. This method for determing de/dt was chosen primarily because of its simplicity and because of its superiority to the graphical method of measuring the slopes of tangents drawn to the curve. The graph indicates that for temperatures above -100°C there should be a very definite increase in the difference in Thomson coefficients with temperature. On this graph are also indicated the values of $\sigma_\perp - \sigma_\parallel$ taken from the direct determinations of Ware,[5] Veleger,[6] and the writer. The writer's values for the S.P. zinc and for the K zinc are represented by the one double circle at $t = 49$°C, the two values being practically identical. The results of Ware and Veleger are represented by dots and by triangles, respectively. Very good agreement is seen to exist between the predictions of the thermodynamical theory, as exemplified by the curve in the figure, and the directly determined results of Ware and the writer. Veleger's results, on the other hand, show considerable disagreement both as to magnitude and as to variation with temperature. In view of the fact that all other "indirectly determined" values of the difference in the principal Thomson coefficients, such as those by Linder,[1] Bridgman,[2] and Grüneisen and Goens,[3] are in much better agreement with the writer's results than with those of Veleger, it seems very improbable that the discrepancy in the latter's results can denote any failure on the part of the thermodynamical theory.[15] It should be borne in mind here that the writer's "indirectly determined" values, given by the curve in the figure, were obtained from the same set of S.P. specimens as were used in the direct determination for the S.P. zinc.

It is possible also to obtain from the thermal e.m.f. curves (Fig. 4) the Thomson coefficient of any specimen as a function of temperature, the procedure being as follows: Differentiating the empirical equations for E twice with respect to t and multiplying by the absolute temperature, T, one obtains $T(d^2E/dt^2) = \sigma_{\mathrm{ZN}} - \sigma_{\mathrm{CU}}$. By adding the Thomson coefficient of copper at the given temperature, the coefficient for the zinc specimen results. This has been done for crystals representing the extreme orientations, using a 1° crystal to get $\sigma_\parallel$ and two crystals, 81° and 86.5°, for $\sigma_\perp$. The 81° crystal was used since the thermal e.m.f. curve for the highest orientation (86.5°) did not extend above 100°C. From 0° to 100°C the range common to both, the crystals yield

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[14] Expressed in calories per coulomb per degree, the units previously used for the Thomson coefficient.

[15] See for instance Table 6 in Veleger's article.

practically identical values. The results of this computation are shown in Fig. 10. The values of the Thomson coefficient for copper at various temperatures were taken from the work of Berg[16] and Borelius and Gunneson,[17] a mean value being adopted. Since the writer, of course, used a different specimen of copper, the results shown in Fig. 10 cannot be expected to represent absolute values. The variation with temperature, to obtain which the computations were especially made, is considered somewhat more reliable. In this connection it is to be noted that this variation of σ with temperature is very different from that recently obtained by Veleger, but in good agreement with Ware's results, as may be seen in the figure.

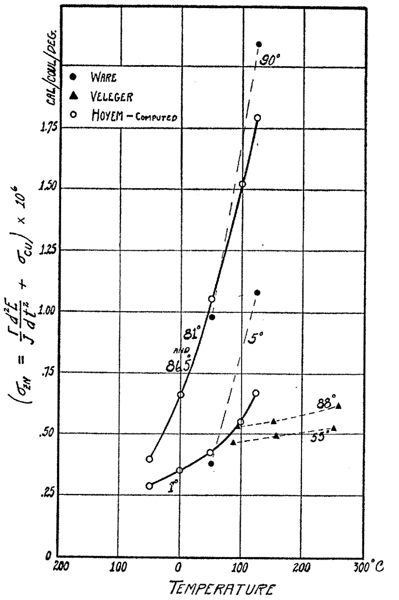

Fig. 10. The Thomson coefficients of the specimens having orientations 86.5°, 81°, and 1°, represented as functions of temperature. Veleger's directly determined values are indicated by ▲------ ▲-, Ware's by ●-------●.

If in Fig. 10 the difference in the ordinates of the two curves corresponding to a given temperature be noted, the difference should obviously be very nearly equal to $\sigma_{\perp} - \sigma_{\parallel}$. Values so obtained are found to be in very good agreement with the $\sigma_{\perp} - \sigma_{\parallel}$ values given in Fig. 9. It should be mentioned here that while the first method of computing $\sigma_{\perp} - \sigma_{\parallel}$ makes use only of first derivatives of empirical equations, the second uses second derivatives. The agreement between the two methods thus serves as a double check on the reduction of the results. It need hardly be said that the values obtained by the first method are more reliable, depending as they do on data for all the crystals, whereas data for only two crystals are used in the second method. The second method can obviously be extended to include all the crystals, but it is not considered worthwhile to do so.

[16] O. Berg, Ann. d. Physik **32**, 477 (1910).

[17] G. Borelius and F. Gunneson, Ann. d. Physik **65**, 520 (1921).

3. Temperature coefficient of resistivity

The observed values of the temperature coefficient of resistivity are listed in Table I. These results were obtained by plotting the resistance of the various specimens against temperature on millimeter cross-section paper, the dimensions of the graph being approximately one by one and a half meters. On this immense scale nine-tenths of the points fall within one millimeter of the lines as drawn, the remaining points having deviations which would lead to errors in α not to exceed three-tenths of one percent. Hence the relationship between resistance and temperature throughout the entire ranged used, ($-170°$ to $25°$C), is considered to be accurately linear. With this degree of accuracy it is evident that the difference in the values of α for the individual crystals must be thought of as real. The distinct difference which exists between the average value of α for the K specimens and the average value for the S.P. specimens, α in general being higher for the S.P. group, is in accord with what would be expected in view of the higher purity of the S.P. zinc. It might be argued that the variation of α within a group (such as the S.P.) should also be used as an indication of difference in purity, with the idea that either contamination occurred during the growth of the crystals or that some purifying process took place, the residue of zinc in the crucible getting more impure with time. In either case there should be a correlation between the order of growing a crystal and its value of α. No such correlation exists. Moreover it may be pointed out that if α is taken as an indicator of relative purity within a group, there should be a corresponding well-marked effect in the specific resistance. This, however, is not true. In spite of the over-lapping of

TABLE I.

S.P. crystals		K crystals	
θ	α	θ	α
1	4.043×10^{-3}	26.5	3.994×10^{-3}
12	4.086	34	3.960
16	4.039	40	3.986
22.5	4.019	44	4.019
25	4.049	66	3.963
28.5	4.059	90	4.069
30	4.042	90	4.069
33	4.043		
37	4.064		
39	4.046		
42	4.051		
44	4.004		
52	4.072		
53	4.049		
55	4.051		
59	4.067		
61.5	4.080		
65	4.055		
68.5	4.071		
71	4.058		
81	4.086		
81	4.096		
86.5	4.081		
Average value	4.058×10^{-3}		4.009×10^{-3}

the α-values in the two groups, S.P. and K crystals, the resistivities of the S.P. crystals are almost without exception lower than those of the K crystals, comparing, of course, corresponding orientations. It may be further remarked that other properties, such as the Thomson effect, the unusual mechanical properties of the very pure zinc crystals, etc., should also give some clue to any possible purity difference of individual crystals in the same group. No such effects are found. Hence the difference in α amongst crystals made from the same grade of zinc must be attributed to some other factor than purity. There is an indication that α may increase with orientation, but the presence of several anomalous cases, high values for low orientations and vice versa, makes it difficult to consider α as purely a function of orientation. This variation of α amongst specimens made from the same grade of zinc is therefore a rather open question.

Ware in his determination obtained an average value of 0.00425 for the temperature coefficient in the temperature range, 20° to 110°C. In this connection, the writer wishes to point out that prior to the measurements of the temperature coefficient of resistivity just mentioned, an oil bath arrangement similar to that described by Ware was employed using a temperature range, 20° to 110°C. The average value of α obtained with that apparatus for K specimens was in very close agreement with Ware's results. It was, however, observed that with the writer's set-up, the resistance-temperature relationship was not linear in all cases, the departure from linearity being greater the longer the specimens had been immersed in the oil bath and always of such a type as to make the curves concave upward. This apparent increase in the resistance of the specimens, when the readings are taken starting with low temperatures, tends to give α a high value. An investigation proved that the zinc was being dissolved in the oil, the increased resistance of the specimens being exactly accounted for by the loss in weight. The effect was first noted with the same grade of oil that was used by Ware and the dissolution was more pronounced the longer the oil had been in use. At this time the oil was heated in a tin container with the heating element and its asbestos board form directly immersed in the oil. Removing the heating element from contact with the oil, using a Pyrex container, and a different grade of oil did not eliminate the effect. Since there is no indication of any departure from linearity in the upper range of the low temperature determinations and in view of the effect of the oil bath, it seems very unlikely that there is any departure of the resistance-temperature curves from linearity in the temperature range 20° to 100°C. Hence only the values obtained from the low temperature determinations have been listed in the table and in all probability these will apply to the higher temperature range as well.

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