THOMSON EFFECT IN ZINC CRYSTALS

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ABSTRACT

The *Thomson coefficient,* σ, is directly determined for a group of zinc crystal rods with orientations distributed fairly uniformly over the entire possible range. At 49.5°C and at 125°C the values of σ seem to obey the Voigt-Thomson symmetry relation, although not as good a check is obtained at the higher temperature on account of increased experimental error. The principal values obtained are:

At 49.5°C, $\sigma_\perp = \mathbf{0.98} \times 10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$
$\sigma_\parallel = \mathbf{0.38} \times 10^{-6}$ " " "
At 125°C, $\sigma_\perp = \mathbf{2.09} \times 10^{-6}$ " " "
$\sigma_\parallel = \mathbf{1.08} \times 10^{-6}$ " " "

The values at 49.5°C are found to compare favorably with values for polycrystalline zinc calculated from Sommerfeld's theory of conduction, ($\mathbf{0.32} \times 10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$), and found by Borelius experimentally, ($\mathbf{0.88} \times 10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$). The increase of σ with increased temperature is greater than has been previously reported for polycrystalline zinc but is in approximate agreement with some earlier determinations by the writer. In addition, *specific resistivity* and *temperature coefficient of resistivity* are determined.

INTRODUCTION

ABOUT two years ago the writer determined directly values of the Thomson coefficient for a few zinc single crystals[1] of orientations[2] near 0° and 90°. The main emphasis in this earlier work was placed on the variation of σ, the Thomson coefficient, with temperature, although it was possible to make some comparison with values of $(\sigma_\perp - \sigma_\parallel)$ computed from the previously published thermal e.m.f. determinations of Linder,[3] Bridgman,[4] and Grüneisen and Goens.[5] Following the work just mentioned, some determinations of σ were made at a single temperature, (about 50°C), on a group of crystals covering a wider range of orientations, particularly with a view to checking the Voigt-Thomson symmetry relation for the Thomson coefficient. These crystals were a by-product of the investigations of Tyndall[6] and of Hoyem and Tyndall[7] and were therefore grown under somewhat different conditions and

[1] M. S. Thesis. University of Iowa, 1927; not published.

[2] Orientation, for a hexagonal crystal, is defined as the angle between the main crystallographic axis and the length of the specimen.

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

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

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

[6] E. P. T. Tyndall, Phys. Rev. **31,** 313 (1928).

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

throughout a rather long period of time. It is certain also that the zinc came from several lots (although of the same kind of zinc). In view of other work done recently in this laboratory, it is not now surprising that such a miscellaneous series of crystals failed to give very consistent results. In particular σ was not determined as a definite function of the orientation. A third series covering a good range of orientations was therefore prepared by Mr. Hoyem. The crystals were made consecutively, were grown at the same rate, were of very nearly the same diameter, and the zinc came from only one original container. The material was Kahlbanm's best zinc. The work reported herein consists mainly of a direct determination of the Thomson coefficient at two temperatures (49.5°C and 125°C) for each crystal of this last series. From these data it is possible to check the usual thermodynamic theory of thermoelectricity and to test the Voigt-Thomson symmetry relation directly for σ.

In addition the specific resistance at 20°C and the temperature coefficient of resistivity were measured, mainly as tests for purity of the zinc, freedom of the crystals from strain, etc.

Apparatus and Experimental Procedure

The Thomson coefficient was measured in the fashion described by Nettleton[8] with some slight modifications which are described below. In this method the two ends of the specimen, which is a short wire or rod, are kept at constant, but different temperatures. At the same time a current, I_1, is passed in such a direction through the specimen that the Thomson effect causes a generation of heat. If this current is reversed the temperature at the center of the specimen will decrease slightly, as the Thomson heat is now being subtracted. If, however, on reversal, a suitable increase in the current, to I_2, is made an extra generation of Joulean heat compensates for the previous loss and the temperature remains unchanged. The apparatus is designed to measure directly the difference between I_2 and $I_1(=i_0)$ and to detect, with a bolometer coil and a Wheatstone bridge, any change in temperature at the center of the crystal, so that the state of zero-change may be found. Let R represent the resistance of the crystals, U, the difference in temperature between the two ends, and J, the constant 4.18 joules per calorie. Then, as Nettleton has shown, the Thomson coefficient, σ, will be given by the equation, $\sigma = i_0R/JU$ cal.$\cdot$coul.$^{-1}\cdot$deg.$^{-1}$ provided certain conditions are satisfied. It is believed that all these are satisfied in the present work except that the crystals were made longer than Nettleton considered because of their very low resistance. The heat insulation was improved greatly, however, over previous methods and it seems certain that the equation is satisfactory for the lengths and diameters used.

To determine the specific resistance, ρ, and the temperature coefficient of resistivity, α, curves were plotted for resistance against temperature between room temperature and 110°C. For a linear relationship between resistance and temperature, α is given by;—

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

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

in which $p = R_1/R_2$; R_1 and R_2 being resistances measured at temperatures t_1 and t_2 respectively. The specific resistance at any temperature is given by:

$$\rho = RM/\delta L^2$$

where R is the resistance at the desired temperature, M is the mass of the crystal, δ is the density, and L is the length. The resistance measurements were made by the usual potentiometer method, the crystal being immersed in a constant temperature oil-bath heated by an electric heating coil. The bath could be adjusted easily for any temperature between room temperature and 125°C. In this case, room temperature to 110°C was used as the range.

Fig. 1 shows the arrangement of apparatus used to measure the Thomson coefficient. The details of the terminals H and C will be considered with Fig. 3. In Fig. 1, H represents the hot end of the crystal and C, the cold. V is

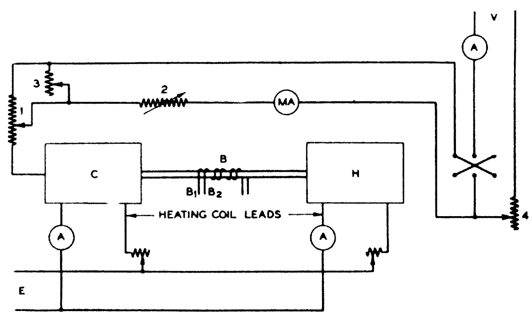

Fig. 1. Apparatus wiring diagram.

a source of 12 volts for which storage batteries were used so that the current would be as uniform as possible. B_1 and B_2 represent the two bolometer coils wound around the middle third of the crystal for the purpose of detecting a change in temperature when the current through the crystal is reversed. Apparently only one coil was used by Nettleton, but the use of two coils in opposite arms of the Wheatstone bridge was adopted on account of the increased sensitivity. The bridge is shown in Fig. 2. Actually the windings of B_1 and B_2 are interspaced as shown in Fig. 1 although shown separated in Fig. 2 to render the electrical connections clearer. In Fig. 1 the resistance 1 is about 10 ohms, 2 is a 500 ohm resistance box adjustable to 0.1 ohm, 3 is a rheostat of 2000 ohms, and 4, which controls the main current, is 47 ohms. The switch S is especially constructed to be very rapid and of very low resistance. E is a source of 110 volts A.C. supplying the heater coils at both ends of the crystal.

Fig. 3 presents the method of producing the constant temperatures at the ends of the crystals. Brass blocks were turned down to make the pieces A and

B, each about one inch in diameter and 1.5 inches long. *A* was threaded into the end of the basin *C* so that the crystal could be directly connected to it. An opening *D* was made in *A* to facilitate the circulation of water. On *A*, a heating coil was wound of No. 24 Karma wire and leads taken out. The heating coil was used to melt the solder for the purpose of either putting the crystal in place or removing it. A screen partition, *E*, was placed as shown to prevent the ice getting into the stirrer. This arrangement maintained the cold end of the crystal very constantly at about one degree above 0°C. At *H*, a double

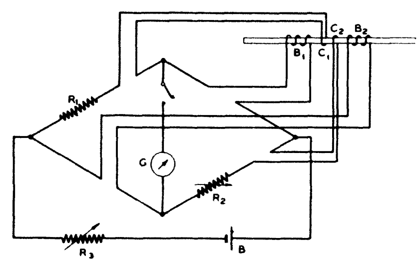

Fig. 2. Wheatstone bridge connection.

cylinder was used with heat insulating powder in the space *F*. The block, *B*, was similar in all respects to *A*, it being threaded into the end of the cylinder, and having a heating coil for the double purpose of mounting the crystal and heating the enclosure to a constant temperature when readings were being made. During an experiment the space, *G*, was filled with water and maintained by the heater at very nearly the boiling point. The thermometer, *T*, was used to read the temperature. By keeping the current about 0.9 ampere, *B* could be maintained at a remarkably uniform temperature for about three hours. Thus was obtained a very satisfactory method of maintaining a tem-

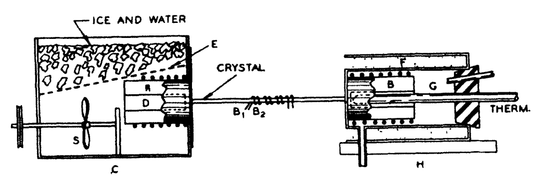

Fig. 3. Details of hot and cold terminals.

perature difference of about 97°C for a considerable length of time and it proved to be a much better method than that used later in obtaining the results for an average temperature of 125°C.

The details of the bridge circuit are shown in Fig. 2. Here, R_1 is a fixed resistance of about 6 ohms which, with as much of the wiring as possible,was inclosed in a heat insulated box. R_2 is a resistance made up of shunts across a coil, similar to R_1, and in series with a slide wire resistance of 0.1 ohm capable of adjustment to about 0.01 ohm. The function of the two coils, B_1 and B_2, has been described already. The compensating coils, C_1 and C_2, are used to decrease the drift of the galvanometer due to the change of resistance of the leads to B_1 and B_2. B_1, B_2, and R_2 as well as R_1 are all about 6 ohms resistance. The bolometer coils and compensators were constructed of No. 40 copper wire silk insulated. The Wheatstone bridge thus arranged proved to be much more sensitive than the arrangement used in the previous work, which contained only one bolometer coil and no compensating coils.

For the purpose of determining σ at the average temperature of 125°C it was necessary to make a few minor changes in the arrangement shown in Figs. 1 and 3. In Fig. 1 the source, V, was reversed as well as all the meters contained in the circuit. A little inspection will demonstrate that this allows the measurement of positive σ* if H and C are also interchanged. In this case the method of heating H was unchanged, it being, as before, maintained near the boiling point of water. However, the ice water in C was removed and polarine oil was substituted. The heating coil on A was brought into use and the temperature of the oil maintained at about 150°C. Here it was rather difficult to maintain the temperature sufficiently constant, a condition which slowed the procedure somewhat. The temperature at the hot end of the crystal was measured by a sensitive thermometer placed in the opening, D. The readings of the thermometers at both ends of the crystal were checked by means of thermocouples connected to the face of A and B near the ends of the crystal. It was found that the temperature gradient determined from the readings of the thermometers differed from the actual gradient by about 2 percent. In computing the results, a suitable correction was, of course, made.

Measurements on the crystals were taken as follows. First a crystal is carefully cut to about 9 cm length, weighed, and to each end is soldered, by a very small amount of solder, a small copper wire, at about the middle of the wire, so that its two ends can serve as current and potential leads, respectively, for the resistance measurements. The crystal is then suspended in the oil bath, the heater in the oil bath is adjusted for the desired temperature, and the assembly is allowed to stand until the temperature, as indicated on a calibrated thermometer, is steady. A current of 0.3 ampere is then sent through the crystal and the P.D. read on the potentiometer. The current is reversed and readings made again. The average of four readings, (two in each direction), gives sufficient data to determine the resistance at this particular temperature. This is repeated for six or seven different temperatures and a curve plotted from which ρ and α can be determined.

After these data have been obtained the crystal is taken from the oil bath, the leads unsoldered, and two bolometer coils wound on at the center as indicated above. The heaters A and B of Fig. 3 are then started and when sufficiently hot the crystal is soldered closely against the face of A and B as there indicated. It is necessary in this procedure to be very careful not to strain the crystal. When the crystal has been fastened in place and the bolometer and compensating coils have been connected to the bridge, kieselguhr is

* σ is positive if heat is generated for current flow down the temperature gradient.

packed into the space between A and B and around the crystal to a radius of about 5 cm. Over this is packed a considerable amount of cotton and the apparatus is ready for the establishment of a temperature gradient. The space, G, is filled with water, and with the thermometer in place the current is established through the heater, B. It is given a high value at first and as the temperature approaches 98° or 99°C it is reduced to 0.9 ampere, where it is left. In the meantime, with the current shut off in A, the container is filled with water, the screen put in place, and the space above the screen filled with cracked ice. The stirrer is then started and the whole assembly is allowed to attain a steady state. As it begins to approach such a state the currents through the Wheatstone bridge and through the crystal are established. A determination of the balancing current, i_0, is made as follows: Referring to Fig. 1, it is seen that with the switch, S, to the left the main current divides, part going through the crystal and part through the milliammeter, M.A. When S is thrown to the right all the line current goes through the crystal. Thus the current through the crystal has been increased on reversal and if the rheostats 1 and 3 are correctly adjusted, the milliammeter, for any particular setting of resistance 2 and the main current, will read the same for either position of the switch, S. In this case the reading of the milliammeter is the i_0 required in the working equation. Thus it is necessary first to adjust resistances, 1 and 3, (Fig. 1), so that the milliammeter reads the same for both positions of S, then, if the system is otherwise balanced, some value of i is tried and the bridge, (Fig. 2), is adjusted for left position of S. Switch S is then thrown to the right and if the bridge indicates a decrease of temperature at the center of the crystal, i is increased, and the procedure repeated until it is just determinable that the current, i, is too low. A similar process is gone through with i being successively reduced from a value initially too high. The balancing current, i_0, is the mean of these two limiting values of i. The difference between these two values is generally less than 10 percent of i_0.

The procedure for the determination of σ at the higher temperature, 125°C, is similar to that at 49.5°C. However, in this case it should be pointed out that it was not so easy to maintain a constant temperature at the hot end. This introduced a certain amount of unsteadiness, and a corresponding decrease in the reliability of the results.

Results

The experimental results are exhibited graphically in Figs. 4 and 5. The specific resistance will be considered first. It is plotted in Fig. 4 against the square of the cosine of the orientation. This plot should yield a straight line since the validity of the Voigt-Thomson law for specific resistance of zinc crystals has been established, particularly by Bridgman.* The solid straight line shown is that for data recently obtained by Bridgman.[9] It is actually drawn by him through the lowest of his points, in spite of the fact that the

* The Voigt-Thomson symmetry relation states that the thermo-electric effects in crystals plotted against the square of the cosine of the angle of orientation should yield a straight line.

[9] P. W. Bridgman, Proc. Am. Acad. Arts and Sc. **63**, 351 (1929).

scattering of his observations is about half as great as that shown in Fig. 4. This procedure is justified by his discovery that any very slight strain raises the resistance of a zinc crystal. Five of the writer's crystals were therefore rechecked with the purpose of determining what effect resulted from intentional slight strains. The points so obtained are indicated by triangles. In two cases the resistivity changed and it increased. Of the three crystals which

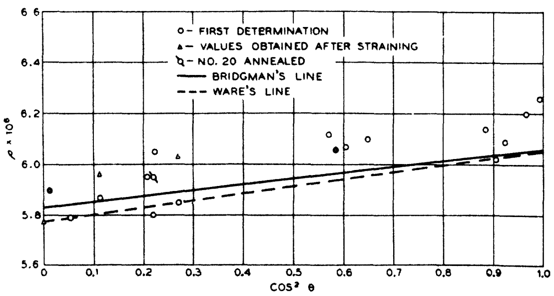

Fig. 4. Specific resistivity in ohms per cm^3 plotted against $\cos^2\theta$.

did not change in resistivity, two already had high values and the other probably was not very much strained as it was a 90° crystal and therefore stiff. The greatest increase was about 3 percent. It will be noted also that the value for crystal No. 20, ($\rho = 5.8 \times 10^{-6}$, $\cos^2\theta = 0.22$) has increased due to annealing. However, this crystal has shown very inconsistent results in other respects. Following the idea of Bridgman that the lowest values are more probably correct, the dashed straight line has been drawn through four low

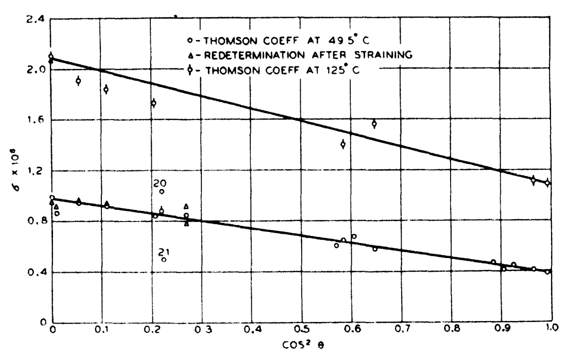

Fig. 5. The Thomson coefficient in cal. coul.$^{-1}\cdot$deg.$^{-1}$ as a function of $\cos^2\theta$.

points neglecting the point for crystal No. 20. The values of ρ obtained from this line for $\cos^2\theta = 0$ and $\cos^2\theta = 1$ are: $\rho_\perp = \mathbf{5.78} \times 10^{-6}$, $\rho_\parallel = \mathbf{6.05} \times 10^{-6}$. These given for $(\rho_\parallel - \rho_\perp)$, **0.27** whereas Bridgman obtains **0.23**. Bridgman's ratio $\rho_\parallel/\rho_\perp$ is **1.04** while the values above yield **1.05**. Grüneisen and Goens obtain **1.08**. The agreement with Bridgman in the matter of specific resistance and the effect of strains is quite satisfactory.

The variation of resistance with temperature, between 20°C and 110°C is for all but four of the crystals accurately linear. These four show only a very slight deviation. The temperature coefficient, α, was therefore computed in the manner explained above. The values of α lie between 0.00413 and 0.00437 and show no very certain variation with orientation. The average value is **0.00425**, a value about 2 percent higher than that obtained by Bridgman.

The values of the Thomson coefficient for both 49.5°C and 125°C are presented in Fig. 5. If the best straight line is drawn through the points for 49.5°C it will be found that the deviation from the line is, in all except two cases, within the experimental error. These two cases are those of crystals No. 20 and No. 21, ($\theta=62°$). No. 20 has already been mentioned in the case of resistivity as being anomalous and here it is seen that even at 125°C the value of σ is lower than for 49.5°C. Also, No. 20 was annealed, as mentioned before, and the same value for σ was again obtained at 49.5°C. There was no visible evidence of No. 20 or No. 21 being different from the other crystals and the explanation of their deviation is not readily apparent.

Although a straight line has been drawn through the points for 125°C, the writer does not claim that the data afford a test of the Voigt-Thomson symmetry relation at this temperature. The deviations from the line as drawn are no greater, however, than the experimental error at this temperature. Moreover the value of $(\sigma_\perp-\sigma_\parallel)$, obtained from this line and stated just below agrees as well with indirectly determined values as is the case at 49.5°C.

The values of $\sigma_\perp$ and $\sigma_\parallel$ at 49.5°C are $\mathbf{0.98}\times10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$ and $\mathbf{0.38}\times10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$ respectively. Thus a value of $(\sigma_\perp-\sigma_\parallel)$, $\mathbf{0.60}\times10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$ results. From the relation, $(\sigma_\perp-\sigma_\parallel)=T\ d^2E/dT^2$, Bridgman[9] obtains $\mathbf{0.661}\times10^{-6}$, Grüneisen and Goens,[5] $\mathbf{0.622}\times10^{-6}$, and Linder,[3] $\mathbf{0.521}\times10^{-6}$ cal. coul.$^{-1}$·deg.$^{-1}$ At 125°C the writer obtains the value $\mathbf{1.01}\times10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$ as compared with Bridgman's[9] $\mathbf{0.813}\times10^{-6}$, Grüneisen and Goens' $\mathbf{1.12}\times10^{-6}$, and Linder's $\mathbf{0.795}\times10^{-6}$ cal.·coul^{-1}·deg.$^{-1}$ Borelius and Gunneson[10] have made measurements on several polycrystalline metals and obtain for zinc at 49.5°C, $\mathbf{0.885}\times10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$ Taking $\sigma_{54.5}$ as representative of σ in polycrystalline zinc, the writer obtains $\mathbf{0.78}\times10^{-6}$ cal.·coul.$^{-1}$·deg.$^{-1}$ The difference in purity of the material used by the various investigators may well account for the rather wide range of values obtained.

In general it can be said that the observation of Bridgman concerning resistivity is substantiated. The average value of α obtained is slightly higher than that given by Bridgman and there appears to be a somewhat greater difference between $\alpha_\perp$ and $\alpha_\parallel$ than that which Bridgman finds. The values of $(\sigma_\perp-\sigma_\parallel)$ for 49.5°C agree with those calculated by the thermodynamic formula from the previously observed thermal e.m.f. vs. temperature curve. The Voigt-Thomson relation is supported within the limits of error by the data on $\sigma_{49.5}$. The data on σ_{125} are presented for what they may be worth.

Sommerfeld,[11] by an extension of his theory of electrical conduction, has

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

[11] A. Sommerfeld, Zeits. f. Physik **47,** 143 (1928).

developed an equation for the Thomson coefficient which to the first approximation is:

$$\sigma = \frac{2\pi^2}{3}\frac{mk^2T}{eh^2}\left[\frac{8\pi}{3n}\right]^{2/3}$$

which is seen to be dependent on T, the absolute temperature, and n, the number of atoms per cc, only as variables. This, calculated for zinc, gives, at 49.5°C, 0.32×10^{-6} cal. coul.$^{-1}\cdot$deg.$^{-1}$, a value agreeing, in order of magnitude with existing data.

No theory has been developed for the Thomson effect in single crystals, although Houston[12] has extended his work in this direction.

The writer wishes to express his thanks to Dr. E. P. T. Tyndall, under whose direction this work was undertaken, for his help and encouragement at all times. He wishes also to thank Mr. Hoyem for so kindly consenting to grow the crystals used in this work. Thanks are also extended to members of the department for their advice and suggestions.

[12] W. V. Houston, Zeits. f. Physik **48**, 449 (1928)