A NEW THERMOELECTRIC EFFECT OF BISMUTH SINGLE GRYSTALS GROWN IN MAGNETIC FIELDS

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A B S T R A C T

Production of crystals.

Crystals of bismuth of any desired orientation were grown, one half of each normally, the other half in a magnetic field. The orientations predetermined by a seed crystal were not affected by this process.

Thermoanalysis of Crystals.

A method was developed to measure and localize any changes of thermoelectric properties along the lengths of crystals without applying mechanical stresses to them. Distortions or imperfections in normal crystals were detectable. Changes in crystal structure caused by the application or variation of forces, such as magnetic fields, heat gradients, etc., at the zone of crystallization, were likewise detectable.

Magnetic Effect as a Function of the Orientation.

Results obtained on crystals having different orientations indicate that thermal e.m.f's exist between the two halves of crystals, unmagnetic and magnetic when the trigonal axis, the axis of least diamagnetism, is forced to grow normal to the lines of force. The mechanical instability of these orientations due to magnetic forces is discussed.

Effect as a Function of the Method of Growth.

The sign of the magnetic -thermoelectric effect was found to be a function of the growing conditions prevailing at the moment when the field was energized. Continuously grown crystals, those whose growth was not interrupted to apply the field, showed different shaped thermoanalysis curves from discontinuously grown crystals, those remelted half way to apply the field. These

differences are discussed on the basis of instability due to heat gradient forces.

Effect as a Function of the Impurities in the Bismuth Used.

It was found that the magnitude of the effect varied greatly with the amount of impurity present in the bismuth, being large for impure metal and small for pure. A spectroscopic analysis of the four kinds of bismuth used was completed. The total amount of impurity present in the worst sample was less than 0.5% and yet the effect for this bismuth was ten times greater than that for the purest electrolytic metal.

Effect as a Function of the Field-strength.

It was found that a complicated relation exists between the magnetic effect, the field strength and growing conditions. Field strengths up to 21,000 gauss were employed. For one case investigated, the effect increased with increasing field strength up to 15,000 gauss above which, however, it dropped off.

Effect as a Function of the Temperature.

The magnetic-thermoelectric effect, investigated as a function of the temperature, indicates the presence of an allotropic modification of bismuth with a transition at some temperature between 70° and 90°.

Effect as a Function of Annealing.

Annealing crystals above the allotropic-modification transition temperature had no influence on the variation in crystal structure producing the effect, as no diminution of the thermal e.m.f was observable.

A NEW THERMOELECTRIC EFFECT OF BISMUTH SINGLE CRYSTALS GROWN IN A MAGNETIC FIELD.

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PART I. Experimental and Theoretical Considerations concerning Thermoelectric Method developed.

Introduction.

In a previous paper[1], one of the authors described a method of producing Bi-single crystals which permits the application of strong, transversal, magnetic fields at the zone of crystallization. The influence of the field with regard to the orientation of the growing crystal was studied. It was stated that the orientation frequently obtained was such that the trigonal axis of the growing crystal was parallel to the lines of force, in case the crystal formed its first center of crystallization within the field . This result was partly to be expected if one considers the anisotropic nature of the diamagnetic susceptibility in Bi-crystals. Since this susceptibility is at a minimum along the trigonal axis and as a maximum in a direction normal to it, the crystal assumes an orientation which corresponds to a minimum of free energy. This result is in agreement with the early observations of Plücker[2] and Leduc[3]. It was, however, unexpected that the orienting forces of the strongest magnetic fields (ca 22000 Gauss) did not show any effect as soon as the orientation of the growing crystal was already predetermined before entering the field. Yet for several reasons, it seemed to be interesting to investigate whether or not a crystal, one half of which was grown without, the other half within a strong transversal magnetic field showed any differences at all between portions, despite the fact that the orientation remained unchanged.

Such differences were to be expected when, for instance, one considers such observations as those by Tieri[4] concerning the Hall-coefficient of Bi specimens crystallized within a strong magnetic field. A large difference of the Hall-em.f. was found with regard to difference directions of the field lines crossing the solidifying specimen, but no interpretation was possible as these experiments were only of a qualitative kind and made on polycrystals.

Production of Crystals.

Since the method of producing bismuth singel crystals without introducing mechanical stresses has already been described[1)5)] it is only necessary to mention how the magnetic field was applied to the growing crystal.

The orientation of the crystal was as usual predetermined by a seed. Three main orientations were grown, which represent the possible primary relations between trigonal axis, the (111) plane, and the lines of force (see below). Two methods of growth were employed which differ principally both in the forces applied to the growing crystal at the moment when the field was energized and in the results obtained.

The first, entitled the discontinuous method, consisted of two distinct processds. A crystal was first grown completely without any magnetic field present (the residual field of the magnet was eliminated by removing the pole pieces). It was then removed from the growing trough, etched and carefully examined with regard to irregularities. In case none could be detected, the crystal was put back into the trough, which in turn was put back into the furnace so far that only one half of the crystal melted again, the temperature of the furnace being regulated so as to bring the border between solid and liquid crystal exactly in the middle of

the pole-pieces of the magnet. This process had to be done very carefully in order to avoid irregularities along the molten part of the crystal. As soon as thermal equilibrium was reached, which condition could easily be recognized since the progress of the molten region into the space between the pole-pieces stopped as soon as the heat distribution along the crystal became stable, then the magnetic field was excited and the driving mechanism of the crystal apparatus started, thus the second half of the crystal re-crystallized within a magnetic field.

The second, entitled the continuous method, allowed the growth of the unmagnetic and magnetic portion of the crystal in one operation. This was done by growing the crystals in the usual manner but with the pole-pieces in position, a precaution that was essential as pole-piece moving with its attendent jarring was prohibitive during crystal growth. This method had the advantage over the other process in that the growing forces remained undisturbed when the magnetic field was applied. In the early work, however, it had the disadvantage in that the residual field (200-300 gauss) of the magnet was present while the first portion of the crystal, the so-called unmagnetic half, was growing. Later this was eliminated by providing a magnetic by-pass of soft iron across the pole-pieces and above the trough, which was removed just before the magnet was energized. All these crystals were grown in an atmosphere of CO_2 to prevent oxidation so that in this respect they also differ from those grown by the discontinuous method.

The first observation which was made on crystals produced by the discontinuous method with fairly high fields was the difference in reflectivity of light between the two halves. This was most noticeable in the P_1 orientation, i.e. where the (111) plane is parallel to the lines of force. It seems improbable that this difference was due entirely to the

second recrystallization, as etching off of a one mm layer does not destroy the phenomenon. Nevertheless, no distinct change could be observed under the microscope.

Methods of Thermo-analysis, Apparatus Details, Etc.

Concerning a sensitive and effective means for determining possible differences between these two halves of one and the same crystal, it seemed that the measurement of the thermoelectric effect fulfilled the requirements the most easily. Nevertheless, it was experimentally rather difficult to perform, since it was not only necessary to measure the thermal e.m.f, but also, to localize it as exactly as possible. Thus the crystal had to be heated at a point the position of which was moved gradually along the crystal's length. Furthermore, this had to be done without applying any mechanical stress to the crystal since such a stress results immediately in a thermal e.m.f of its own.

A simple method first tried was as follows: The crystal was first protected by a coat of Duco paint. Leads from the ends were connected to a galvanometer, the contacts with the crystal being kept at constant temperature. The crystal held horizontally, had a small portion heated locally by the touch of a merfury meniscus which topped a column of that metal heated by an electric furnace. If the meniscus was moved slowly along the crystal and the deflections of the galvanometer were observed with relation to the position of the heated point on the crystal, then a thermoelectric analysis of each increment of length could be made. As soon as the heated region came near the border between the "magnetic" and the normal part of the crystal, an e.m.f was indicated, but its size could not be measured accurately enough inasmuch as it depended on the contact conditions of the meniscus which could not be made reproducible. This method was therefore soon abandoned.

The next method that was tried was to heat the crystal locally by focusing the radiation of a powerful incandescant lamp upon it. This method had the advantage over the previous one in that it was not necessary to protect the surface of the crystal against amalgamation, with a covering that was necessarily a poor heat conductor. A large number of observations were made with this apparatus, but due to certain inherent difficulties of the method, it was abandoned. These difficulties were, for instance, providing air cooling of the crystal as a whole while preventing local convection currents at the point of heating, measuring the temperature at the heated point and preventing surface irregularities of the crystal from nulifying results.

The final arrangement which avoided the above difficulties and made possible quantitative measurements is sketched in principle in Fig. 1. A cylindrical glass-container A, 18 cm long and 9 cm wide is held in the

center of a large glass-container B, 24 cm wide, 22 cm long, by means of the bridge C. The glass tube D_1 is fixed in A and brings water at a definite temperature and under constant pressure into A. The vessel B is also filled partially with water, the level of which determines the position of a ring-shaped float E. Two tubes F_1 and F_2 fixed in B permit the raising or lowering of the water level of B, which in turn changes the position of the float E. Fixed to this float E is a frame arrangement which carries several devices among which are syphons H_1 and H_2. Both have one end in A just underneath the water level, the other end of H_1 going outside of B, the corresponding end of H_2 ending beneath the water level in B. The horizontal part of both syphons is shaped to separate air bubbles from the flowing water, while adjustments for bringing the tubes into correct positions with regard to the water levels are provided. Beside the syphons, the float carries an electric heater consisting of a horseshoe-shaped thin mica sheet around which chromel wire is coiled. Other mica sheets above and below insulate this heater from two thin copper plates which bind the whole, making for equal heat-distribution and rigidity. This whole heater is only 1 mm thick. Its position with regard to the frame is so adjusted that it is slightly above the water level in A when the ends of H_1 and H_2 are just beneath that level. On top of the water in A, an oil layer of 5 - 10 mm thickness is put in order to surround the heater completely.

The arrangement works as follows: A constant flow of water is sent into A filling it up to a certain point, any surplus being syphoned off. The water level in A is therefore determined by the position of the syphons H_1 and H_2 or what amount to the same thing, by the position of the float E in B. Thus a permanent circulation of the water underneath the heated oil layer results and consequently a constant temperature. If a

certain amount of water is added through F_1, the water in B rises and with it the float E holding the syphons and the heater. The oil layer in turn maintains its relative position with regard to the heater since its supporting water column rises as the syphons rise. It follows that the water has to be added into B at a rate sufficiently slow to permit hydrostatic equilibrium in A. Therefore, the cross sections of H_1 and H_2 are large compared with the cross sections of F_1, F_2 and D. As an indicator of this equilibrium, a differential thermo-couple is also attached to the frame of E. It consists of two copper wires l_1 and l_2 the ends of which, ending one in the middle of the oil-layer, the other within the water flow, are connected by a very thin constantin wire. This arrangement is extremely sensitive because the smallest displacement of the heater with respect to the oil and water level changes the temperature of the l_1 - junction and thus produces a change in the thermal e.m.f.

The reason why the syphon H_2 is used besides H_1 is first, to tie the water systems of B and A together so that no appreciable differences in levels can result, though when everything is properly adjusted this link is largely static, and second to minimize the irregularities of the flow in H_1 caused by small differences in the surface tension of the water at the outside opening of H_1, since H_2 allows the large volume of B to be used as a "shock-absorber".

Thus an arrangement is obtained which permits the production of a constant gradient of temperature which can progress regularly along a crystal (X) hung perpendicularly into the vessel A as indicated in Fig. 1. To complete the ensemble, it is only necessary to mount the crystal in a holder which keeps it in a fixed position with regard to A, to provide connections at both ends with a galvanometer and to keep the upper contact at a constant temperature, a temperature as nearly as possible equal to that of the water

in A. All this was conveniently done with the so-called "crystal holder".

The bakelite tube J in Fig. 2 carries at one end the adjustable fork K while close to the other, the clamp L. Through J sealed in, runs a copper wire, the upper end of which is connected directly with the galvanometer. The other end, bent, has a silver wire (o.1 mm) soldered to it. Furthermore, J carries an adjustable clamping device M which permits one, with the aid of a similar one on the bridge C(Fig. 1), to fix the holder into any position desired with respect to A. To cool the upper end of the crystal, a copper cylinder N is used, provided with two small side-tubings N_1 and N_2, N_1 being connected with a water reservoir possessing a constant temperature and a constant hydrostatic pressure. In this way, a water flow is sent into N_1 and leaves by N_2. To fix the upper end of the crystal X in a position within the water flow without applying any fatal strain to it, a thin rubber membrane O with a small central hole burned into it is stretched over one end of N. After a silver wire similar to the one previously mentioned is spark-welded to the crystal, the hole in O is momentarily widened, the crystal is introduced and the membrane released, thus forming a tight sleeve aroung X able to withstand the water pressure in N. The silver wire protruding now from the other side of N is soldered onto the copper wire P which is fixed in the bakelite plate Q. After a contact is thus made between P and X the plate Q is sealed tight onto N, thereby closing the water chamber. N and X are fixed into the clamps L and K respectively and the silver wire at the lower end is also spark-welded onto X. The whole arrangement is then put vertically into A in such a way as to bring X exactly through the central opening of the heater. The wire P is connected through a resistance box (R) to the galvanometer, thus completing the circuit. Fig. 3 shows a photograph of

the apparatus for thermoelectric analysis and Fig. 4 a picture of a crystal in its holder. It is necessary to mention that the task of mounting crystals without distortion is a very difficult one and requires a special apparatus which avoids critical stresses by facilitating manipulation.

After the crystal, mounted in its holder, is fixes in the vessel A, the different water flows are started and the furnace-plate is heated, in general, to a temperature 18° above the temperature of the running water. After thermal equilibrium is reached measurements are taken, i.e. the deflections of the galvanometer are measured as a function of the position of the oil-layer relative to the crystal. Simultaneously the e.m.f of the differential thermocouple is measured to assure the maintaanance of thermal equilibrium. Schematically, this is shown in Fig. 5 where X is the crystal, W_1 is the water cooling the lower end of the crystal and W_2 that cooling the upper end, G_1 is the galvanometer measuring the thermal e.m.f of the crystal G_2 (one) measuring the difference of temperature betwwen the heated oil layer and the water W_1.

Diagram Types.

First it will be considered what type of curve one would expect to obtain with this kind of an arrangement. The obvious way of plotting the diagrams is to represent the thermal e.m.f indicated by G_1 (Fig. 5) as ordinates and the position of the heated oil layer with respect to the crystal as abscissa. If one considers first , the diagram that would be obtained by the thermoanalysis of a perfectly homogeneous crystal, one realizes immediately that it should not show any thermoelectric potential. However, certain deviations from this purely theoretical concept would be expected due to imperfect cooling conditions and the heat-conductivity of the crystal. Hence, a curve of the type of Fig. 6 should be expected where the dotted line would represent a constant thermal e.m.f due to a slight difference of

temperature between the two different -end cooling systems. While the curve drawn in full with its deviations from linearity would be obtained under normal conditions, where the cooling of the ends of the crystal is not sufficient to prevent a slight heating by conductivity through the metal. To make this "end-effect" as small as possible, the crystal used has to have a small cross section.

The second case to be considered is shown in Fig. 7 a, which represents an unhomogeneous crystal consisting of two halves which have a thermal e.m.f against each other. In this case, a curve as shown in Fig. 7 b would be obtained, where a maximum would permit the exact localization of the junction of the two halves.

Superimposed upon this would be the effects previously mentioned (Fig. 6) though the constant thermal em.f. due to unequal end cooling would have a different value since the thermoelectric power of the two halves against the contact metal would be different than in the case of a single crystal. Also, the end effects due to heat conduction would be slightly assymetrical since the two different halves are involved. The sharpness of the maximum would depend on the gradient of temperature along the crystal and the extension of the heated zone, thus the former should be as large while the latter as small as possible.

The third case in which the crystal consists of three sections, the second of which has the same thermal e.m.f against the first and third (Fig. 8 ab) would result in a curve which is more complicated. With the heated oil layer at the junction of part I and II, there would be a maximum similar to that of Fig. 7 . Furthermore, on reaching the transition from II to III, the same thing would happen but in the opposite direction. Of course, the shape of the whole curve would depend very much on the

relative sizes of the three sections. For a given thermoelectric difference of II, against I and III, and a given difference of temperature in the analyzing apparatus, the maximum and minimum would not change their size as long as II is large enough to contain the whole drop of temperature given by the analyser. If II is smaller, the maxima would decrease and finally there is a size below which no effect whatsoever would be observed. This threshold determines the resolving power of the arrangement and depends on the construction of the analyser and on the cross-section, thermal conductivity and surface conditions of the crystal.

This relation can be illustrated by the following considerations: If one assumes the simple case of a double crystal, infinitely long and very thin; a very thin, heated oil-layer with an infinite gradient on either side at one point of the crystal; and the rest surrounded by a medium at constant temperature, then one can write down the equation

$$\vartheta = T e^{-\sqrt{\frac{K}{r\sigma}}\, x}$$

where r = radius of crystal (1)

σ = specific conductivity

K = constant (depending on surface conditions of the crystal).

x = coordinate measured from the oil layer along the crystal.

ϑ = temperature at point (x).

T = temperature of oil layer.

If the rather valid assumption be made that e, the thermoelectric force is directly proportional to the temperature, then the equation may be written

$$e = E_{max}\, e^{-\sqrt{\frac{K}{r\sigma}}\, x} \qquad (2)$$

where E_{max} represents value of e when heated zone is at the junction. To

construct the thermoelectric curve, it is then only necessary to draw the curve from equation (2) with its maximum at the point of the crystal being analyzed, i.e. the point where the oil layer is (C), Fig. 9.

The intersection of this curve with (G) then gives the value of e that must be obtained at (C). If this is done for each point along the crystal the complete thermoelectric curve may be constructed. The dotted curve in Fig. 9 corresponds to a crystalline portion of lower conductivity which might easily result for a different orientation of the crystal.

In the case of a triple-crystal, the process is the same but the curve is more complicated as shown in Fig. 10 a. In constructing this diagram, it is only necessary to subtract the intersections of the conductivity lines crossing one transition from those crossing the other since the sign of the e.m.f. is negative in one case. Fig. 10 b shows a diagram in which the section II is smaller, but the conductivity the same as in Fig. 10 a. The last figure illustrates thus the resolving limit of a given arrangement, as in this case, the two maxima almost disappear. It is apparent that the length of the strange section II is related to the indicated e.m.f in the limit by the relation

$$de = -E_{max} \sqrt{\frac{k}{r\sigma}}\, e^{-\sqrt{\frac{k}{r\sigma}}\, x}\, dx$$

which, if the oil layer is at section II reduces to

$$de = -E_{max} \sqrt{\frac{k}{r\sigma}}\, dx$$

The limit of resolution is then given by a value dx which cannot produce a measurable de.

In the described apparatus, conditions are more complicated due to the finite dimensions of both the crystal and the oil layer gradient. The latter can be found quite readily, however, by putting a very thin thermocouple into the thermoanalyser instead of the Crystal. Fig. 11 shows such a curve.

PART II. Experimental Results obtained for Normal and Magnetic Crystals with a Discussion of the Same.

The Thermo Analysis of Normal Crystals.

It is obvious that the described method of thermo analysis can serve the purpose of detecting and locating imperfections within ~~one~~ a crystal only as soon as the size of these imperfections is above the resolving power of the analyser. Furthermore, it is only possible to detect imperfections which cause a thermoelectric force, though it seems very probable that any imperfection due to a distortion or change in the orientation within the crystal causes one, the detection of which depends only on the sensitivity of the galvanometer used. Thus this method is an excellent one to detect and locate heterogeneous inclosures and local plastic deformations. The latter became particularly evident in the case of bismuth since they result in the production of twin lamellae, a phenomenon treated at length in another paper.[16]

Because of the effectiveness of this method, the different means used for the production of single-crystals were examined as to their results, and the development of a method of crystal growth, ~~crystals~~ a method to be used in the final experiments (i.e.) was guided step by step by this kind of an analysis. First crystals grown in glass tubes by the ordinary method were analysed. The deviations of the thermoanalysis curves from linearity were to be expected, especially as the taking off of the glass cover caused many twin lamellae. Fig. 12 shows a diagram of such a crystal.

The dotted curve in Fig. 13 shows a crystal with one maximum due to a magnetic effect (see later). After the analysis had been taken, the crystal was plastically deformed just enough to produce two small sets of twin lamellae visible under the magnifying glass. The diagram taken afterwards is shown as the lined curve where now two new maxima occur, the position of which coindided exactly with the location of the twin-sets.

Fig. 14 shows the diagram of a crystal of the same orientation (P_3) as Fig. 13 as homogeneous as it could be produced.

Among the large number of diagrams which have been taken, it occurred very often that an apparently perfect crystal (as far as its examination after etching was concerned) showed one or more distinct maxima. If the crystal then was cleaved at the point where a maximum had occurred, a microscopic investigation led always to a detection of the inclusion of a crystal of different orientation which orientation was preferably that of a twin. Fig. 15 shows a microphotograph of an inclosure of that kind which shows distinctly the twinned region characterized by a regular penetration of the (111) plane through the ($11\bar{1}$) plane. The cause of these imperfections was, in general, a disturbance (vibration shock, etc) happening at the time when this section of crystal was forming.

THE Thermoanalysis of "Magnetic"Crystals.

The described method of thermoanalysis was applied to crystals, one half of which was grown without, the other half within a magnetic field, which was the purpose for which the method was originally designed. It was found that the border between the magnetic and the normal half of the same crystal was the origin of a thermoelectric force. Furthermore, the thermoanalysis gave the evidence that the origin of this force is exactly at the point where the magnetic field was applied.

Nevertheless, it proved to be very difficult to measure this force quantitatively and not even the sign of the force could at first be reproduced although ~~all~~ each curve showed a maximum if it was not fogged by other maxima due to distortions of the kind mentioned in the previous chapter.

To obtain a higher degree of reproducibility, certain definite

conditions were imposed, both on the growth and on the analysis of the crystals. In the case of the former, four factors were considered in detail; oriantation, method of growth, impurities in the metal,and field strength. For the latter two were considered: temperature of the analyser, and annealing.

The actual results obtained indicate that at least for the first group of factors the thermoelectric effect is a very complicated function. Despite this complexity, however, duplication of results, for any given set of conditions, with less than ten percent deviation was always possible which indicates that all the principle variants were being controlled.

In presenting the results, the effect of each of the factors on the thermoelectric e.m.f will be considered separately, the stationary values of the other factors being given in each case. Up to date, no attempt has been made to systematically evaluate the effect for a large number of values of each of the factors involved, thus the results given can be considered as merely illustrating the type of variation to be expected.

For all the curves to be presented unless specifically stated, the temperature difference in the analyzer was 18° measured above tap water.temperature of 19° to 21° Centigrade.

The ordinate scale for the curves unless designated otherwise is 7.8×10^{-6} volts per numbered division. It indicates positive volts for increasing values.

The solid line, mid-way along the abscissa scale on the curves, indicates the position where the furnace was at the intersection between magnetic and unmagnetic portions of the crystal. The dotted lines indicate the extent of the oil layer to each side of the furnace.

THE Effect as a Function of the Orientation.

As stated already in a previous paper[1], there are three different orientations, the crystal can have with regard to the rod, or to the direction of the lines of force, which are principally different from each other. Fig. 16 shows the trough G dotted, and the crystal white, the latter cut parallel to its main cleavage plane. These three oriantations are:

TABLE I.

Name	Trigonal Axis ~~to~~			(111) plane ~~to~~		
	rod	field	vector	rod	field	vector.
P_1	⊥	⊥	⊥	∥	∥	∥
P_2	⊥	∥	⊥	∥	⊥	∥
P_3	∥	⊥	∥	⊥	∥	⊥

(The third column entitled "vector" shows the direction of the heat flow and the electric current during the thermo analysis.)

Fig. 17 shows analysis curves for crystals of these three orientations. The method of growth employed was the discontinuous (see Part I), the metal of purity "B" (see later), and the field-strength 21,000 gauss.

The Effect as a Function of the Method of Growth.

Methods of growth employed have been described in detail in Part I of this paper. They were the so-called continuous and discontinuous methods. Fig. 18 shows curves obtained from crystals produced in these different manners. "Q_1" represents the former, "Q_2" the latter. In both these cases, no appreciable residual field was present over the so-called unmagnetic portion of the crystal. "Q_3" , on the other hand, represents a continuous method result with the residual field present during the growth of the first portion of the crystal.

For this series, the orientation was "P_3", the metal of purity "B" (see later) and the field-strength 13,800 gauss.

The Effect as a Function of the Impurities.

Four kinds of bismuth, obtained from different sources, were used to make crystals. Table III shows the designations adopted for this work.

TABLE III.

Designation	Characterization	Source
"A"	Bismuth C.P.	Brown Corp., Philadelphia, Pa.
"B"	Bismuth purissimum	Hartmann & Braun, Frankfurt a,
"C"	Electrolytic bismuth	" "
"D"	Bismuth "Kahlbaum"	Kahlbaum A.G., Adlershof.

Fig. 19 a illustrates diagrams for crystals made from "A", "B", "C" and "D" bismuth. The orientation was P_3, the method of growth discontinuous and the field-strength 21,000 gauss.

Fig. 19 b represents curves for crystals made from "A", "B" and "D" bismuth. The orientation was P_3, the method of growth discontinuous (with no residual field) and the field strength 13,800 gauss.

Since from this work as well from papers of Bridgeman and Kapitza it was well-known how large the influence of small impurities on the electric effects of Bi can be, an accurate chemical analysis of the different kinds of bismuth was made. The results obtained showed that a very small trace of silver was present in "A" and "B" though the amount was too small to measure accurately. Since this indicated that the impurities involved were only present in extremely small amounts, a spectral analysis seemed necessary. Dr. R.M. Badger was kind enough to perform this type of analysis on our different metals. The amount of any impurity was measured by comparing the intensities of its different lines as observed for the specimen, with the intensity of the lines obtained from these metals by themselves in a spark. The Bismuth electrodes were prepared by putting the metal into Pyrex tubes after it had been ascertained that the glass did not contain any of the metals involved in the analysis. The results are given in the following table, where the numbers give the approximate relative intesisties of the indicated lines of the different impurities.

TABLE IV

In general, it can be said that the amount of impurity is probably on the whole, smaller than 0.5 percent in the worst case which is "B". It is smaller for "A" which contains less Pb. "D" differs from "B" in its smaller content of Pb, though in its Ag content, it compares badly, whereas "C" is by far the purest metal.

The Effect as A Function of the Field-Strength.

The field-strength was capable of variation both by changing the

current through the magnet and the distance between pole-pieces.

Unfortunately the latter caused a change in the distribution of the field, so that results obtained with the same field-strength but different pole-pieces distances were not directly comparable.

Fig. 20 shows the variation with field-strength (polepiece distance constant) in the single-valued effect obtained for crystals grown with the P_3 orientation, by the discontinuous method, of metal "B". (See Fig. 17, P_3, for typical curve.)

For the continuous method of growth, for instance, this function was very complex indicating that no simple relation holds in this case, either, as a rule, despite the curve presented.

The Effect as a Function of the Temperature.

Fig. 21 shows the thermoelectric effect between the magnetic and the normal half of a crystal as a function of the temperature of the analyzer. The curve was taken by first finding the exact position of the maximum e.m.f with regard to the crystal (crystal of Fig. 17, P_3 type), and then keeping the oil layer in this position while its temperature was gradually increased.

This temperature function seems independent of the type of crystal involved at least with regard to the discontinuity and general shape. The former seems to be directly related to the allotropic transformation known to take place, at some temperature between 75°and 90°. [Cohen and Moesveld[7], Wurschmidt[8], Cohen[9].]

It must be mentioned that the temperature scale of the curve presented cannot be very accurate in its absolute magnitude as the temperatures existing within the crystals may have been appreciably different from those measured in the oil.

The Effect as a Function of Annealing.

In order to decide whether a transition occurs from "magnetic" to

normal crystal at an appreciable rate as might be expected if the effect were due to strains, such as magnetostriction, for instance, specimens showing large effects were reinvestigated after being annealed. The temperature of annealing was chosen sufficiently high, above 90°, to see whether the transition would occur any faster for the allotropic modification existing above that temperature than for that existing at room temperature.

Fig. 22 shows a diagram of a crystal analyzed the day it was produced (curve 1) and again, one month later, after it had been annealed for 16 hours at 100° (curve 2). No change of any kind could be detected, which indicates that any change that may have occurred could certainly not have been greater than the experimental error in making the analysis.

The crystal used was of the P_3 orientation, grown by the continuous method (residual field present), of metal "B", and with a field-strength of 13,800 gauss.

Discussion.

In analyzing the experiments performed, several interesting facts appear. In the first place, it becomes quite apparent that the forces acting at the moment of crystallization effect the physical properties of the final crystal materially.

If the well-known anisotropy of bismuth be considered, the experimental results obtained can at least be explained qualitatively. In the first place, it is known that the diamagnetic susceptibility of bismuth is greater normal to the trigonal axis (in the (111) plane) than parallel to it; secondly, that both thermal and electrical conductivity are better in the 111 plane than along the trigonal axis; and thirdly, that the anisotropic properties of bismuth are functions of the impurities present in the metal, seeming to increase with increasing amounts of the impurities

in general. The first statement has been checked at this laboratory where experiments that will be soon published indicate that this anisotropy is considerable. The second and third statements follow from work by Bridgeman [10] who finds that the ratio of the resistance along the trigonal axis to that in the lll plane is always greater than one, and that this ratio which is 1.27 for the purest bismuth may have values up to 1.6 for impure bismuth.

The experiments concerning the effect as a function of the orientation show, as indicated in the curves of Fig. 17 as well as by all other experience, that the P_3 orientation is the most sensitive to the effect, that the P_1, is next, and that the P_2 is the least. If this sensitivity is interpreted as an instability of the growing crystal system in the presence of the summation of the forces acting, then certain correlations follow at once. The P_3 and P_1 orientations both have the trigonal axis perpendicular to the field. Magnetically, however, the stable position is with this axis parallel to the field, P_2 case. Thus it is evident that if the crystal always prefers a configuration with a minimum of free energy the magnetic portions of the P_3 and P_1 orientation should have different properties than the normal crystal. This difference would presumably cause a thermoelectric effect, as that observed. To account for the differences in magnitude of the e.m.f in the P_3 and P_1 case, the thermal conductivity must be considered. In the method of crystad growth employed most of the heat was conducted along the crystal. Since the heat conductivity is better in the lll plane than along the trigonal axis, the P_1 and P_2 orientations are the stable ones thermally, while the P_3 orientation is unstable in this respect. These facts have been born out by a number of observations such as that P_1 and P_2 crystals are much more easily grown perfect, than P_3 crystals, and that the thermo-analysis for normal crystals

of these three orientations always gives very smooth lines for the P_1 and P_2 type, while those for the P_3 type are quite irregular. Thus the difference in magnitude between the P_3 and P_1 case probably arises from the fact that P_3 is unstable thermally as well as magnetically, while P_1 is unstable only magnetically. By this sort of reasoning, no effect at all should be encountered in the P_2 case. The small amount that actually seems to occur may perhaps be attributed to the fact that the orientations of the crystals employed were probably not exactly P_2.

Concerning the experiments treating the effect as a function of the method of growth the same sort of reasoning can be applied. The results show (Fig. 18) that depending on the method of growth employed the sign of the thermoelectric effect (indicated by the upbending (+), or down bending (-), of the curve at the intersection) may be practically reversed for crystals of the P_3 orientation. This fact may be considered from the standpoint of heat conduction anisotropy. In the continuous method, the heat gradient is a constant, in both magnitude and direction throughout the crystal's growth, including the moment when the field is applied; while in the discontinuous method, the heat gradient is changing its magnitude and direction at the moment when the crystal-growing mechanism is started, which is just when the field is applied. It is certainly conceivable that the cooperation of the two influences, magnetic field and heat gradient, may produce effects of practically different sign when the latter is changed, since it is just this latter which determines the rate of crystallization, - an extremely important factor. For the P_1 case, experience seems to indicate that no large change occurs when the different methods of growth are used as the type of curve depicted in Fig. 17 is always obtained.

The same reason as previously mentioned thermal stability, may account for this fact also. In a number of curves, there may be noted a secondary effect which occurs along the magnetic half of the crystal. This seems to be related to the position of the edge of the furnace at the moment when the field was applied. If, as one of the authors has indicated in another paper [1], a block phase should exist in the molten metal the probable boundary for it would be at this furnace edge where the temperature suddenly increases.

The effect as a function of the impurities shows striking variations as was to be expected from a consideration of the fact previously mentioned; namely, the dependence of the anisotropy of properties on the impurities present. Two sets of curves are presented for this case, Figs. 19a and 19b to show that this dependence on impurities is real and presists under markedly different conditions of growth. "A" and "B" curves depicting relatively impure metals (See spectroscopic analysis) show large effect while "D" and "C", "C" in particular representing a very pure metal, show small effects. It is interesting to note that the ratio of specific resistances parallel to the trigonal axis and normal to it $R_{\parallel} / R_{\perp}$ as determined in this laboratory are for "B", 1.42; for "A", 1.38; for "D", 1.30 ; and for "C", 1.23. The decreasing values follow the same sequence as the decreasing thermal e.m.f's depicted in 19a. The second group of curves illustrates another point worth mentioning; namely, the dependence on impurities of the shape of the analysis curve (sign of the effect - compare "D" with "A" and "B"), A comparison of the magnitude of the effects "D" in 19a with "D" in 19b shows how sensitive the thermal e.m.f can be for a change of conditions of growth when certain impurities are present.

The results for the other factors of which the thermoelectric effect is a function hardly require discussion as they are wholly consis-

tent with the line of reasoning employed throughout.

Before closing, some comparisons with Kapitza's work[14] can be made. Concerning his observations of the change of the resistance of bismuth crystals in a magnetic field, it is rather unexpected to find that the bismuth which produced an extremely small effect (Kapitza's crystal "B" in his Fig. 13, p. 407, l. c) produces in our case, one of medium magnitude, since his metal corresponds to our "D", whereas his crystal "A" which produced large effects was of metal of the same source as our "C" giving, for our work, the smallest values. With regard to the orientation effects, a few comparisons can also be made. Being limited to only one direction of both the field to the rod, and the thermoelectric current to the rod, only one kind of Kapitza's experiments can be considered for comparison, i.e. where the field is normal to the current. Neglecting the azimuthal effects which seem in our case small, at best, comparison shows that the largest value obtained of the ratio R / R_o is for our so-called P_3 orientation, while the value obtained for P_1 was only a fractional part of that for P_3, both facts being analogous to our results. In the case of P_2 however, a larger value of R / R_o than the P_1 case was obtained, which might be interpreted as a disagreement, since our effect seems rather uncertain for this orientation.

Conclusion.

Although these experiments were begun several years ago during which time a large number of measurements have been taken, it is not yet possible to come to any definite conclusion concerning the actual mechanics of the "magnetic" effect.

Numerous measurements concerning the electrical conductivity,

the density, and the magnetic susceptibility were performed and are still going on, as well as a thorough X-ray analysis of these crystals. Papers concerning these subjects will be published as soon as reliable results have been obtained.

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- REFERENCES. -

1) A. Goetz, Phys. Rev., 35, 193, (1930).
2) S. Plucker, Pogg. Ann. 76, 583, (1849).
3) M. A. Leduc C. R. 140, 1022 (1905).
4) L. Tieri, & E. Persico, Tincei Rend. 30, 464 (1921).
5) A. Goetz & M. F. Hasler, Proc. Nat. Acad. 15, 646 (1929).
6) A. Goetz, Proc. Nat. Acad., 16, 99 (1930).
7) Cohen and Moesveld, Zs. f. Phys., Chem., 85, 420 (1913).
8) J. Wurschmidt, Verh. d. D. Phys. Ges., 16, 799 (1914).
9) Cohen, Verls. Acad. Amsterdam, 23, 1224 (1914-15).
~~J. J. Berzelius & A. E. Lindh, Ann. d. Phys., 51, 607 (1917).~~
10) P. W. Bridgeman, Proc. Am. Acad. 63, 351 (1929).
11) P. Kapitza, Proc. Roy. Soc., A 119, 358 (1929).

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April 1930.