THE THERMOANALYSIS OF METAL SINGLE CRYSTALS AND A NEW THERMOELECTRIC EFFECT OF BISMUTH CRYSTALS GROWN IN MAGNETIC FIELDS

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Abstract

Part I. The Thermoanalysis of Bi Single Crystals

Production of crystals.—Crystals of Bi of any desired orientation were grown by the method of Goetz, one half of each normally, the other half within a transversal magnetic field. The orientations, predetermined by a seed crystal, were not affected by this process. Two methods of growth—the continuous and the discontinuous—were used.

The thermoanalysis of a crystal.—A method and its experimental realization—the thermoanalyzer—were developed to measure and to localize any changes of the thermoelectric properties along the lengths of crystals without applying mechanical stresses to them, by progressive local heating of the specimens. Thus very small distortions and imperfections were detectable due to their thermoelectric asymmetry.

Types of thermoanalytic diagrams.—The types of diagrams to be expected in the cases of a perfect single crystal, a double-, and a triple-crystal are discussed and a method is developed to analyze simple diagrams by means of the theory of heat-conduction.

Part II. Experimental Results Obtained for Normal and Magnetic Crystals with a Discussion of the Same

The thermoanalysis of normal crystals.—The application of the thermoanalysis to normal single crystals leads to the discovery of very small (0.1 mm^2) regions within a crystal which are distorted due to very slight variations of the cooling conditions during the growth of the crystal. It is however possible to avoid these faults and to produce comparatively perfect specimens. Hence it was possible to test the results of different methods of crystal production and thus to refine the method used as well as to measure quantitatively the influence of a magnetic field applied to the crystal during the time of its formation.

The thermoanalysis of "magnetic" crystals.—It was found that the normal half of a crystal has a thermoelectric e.m.f. against the "magnetic" half. The sign and size of this e.m.f. depend on many circumstances, though mainly on the orientation the growing crystal has with regard to the direction of the field lines.

The effect as a function of the orientation.—The effect is a maximum if the principal axis of the crystal grows normal to the lines of force and it is very small (probably zero) if the axis grows parallel. It depends furthermore on the orientation of the crystal with regard to the direction of the thermoelectric current, since the two orientations in which the principal axis is normal to the field show different effects: a small one if the axis is normal to the current, and a very large one if it is parallel. —The thermal e.m.f. obtained for the latter case is 4.3 microvolts/degree which would correspond to a change in orientation of ca. 21° though no actual change could be observed.

The effect as a function of the method of growth.—The thermal e.m.f. depends largely upon the method of growth, i.e., whether the crystal is grown by the continuous or the discontinuous method.

The effect as a function of impurities.—The thermal e.m.f. for one and the same method of growth depends also on the amount of chemical impurities. Four kinds of purest Bi of different provenience were used in which the total amount of other substances was less than 0.2%. The metals were spectroscopically examined and it appeared that the purest (electrolytic) metal showed the smallest effect. It was *ca.* 40 times smaller than the effect of another metal. Traces of Ag and Pb seem to affect the "magnetic" sensibility of Bi most whereas Sb is rather ineffectual.

The effect as function of the field strength.—The effect is influenced by the strength of the applied field through this problem is not yet settled quantitatively. The influence of a small field (10^2 Gauss) is comparatively large, whereas fields of more than 13000 Gauss seem to decrease the effect. The maximum seems to depend largely on the kind of the impurity.

The effect as a function of temperature.—The Peltier-effect (extrapolated from the $E-f(\theta)$ curve) shows a sharp discontinuity between 75° and 90°C, indicating a different relation with regard to the transformation of Bi in this region. No indication could be found that annealing above this point (16 hours) and aging (1 month) destroys the difference between the normal and the "magnetic" half of a crystal.

Discussion.—The results obtained are brought into relation with the diamagnetic anisotropy of Bi. They are discussed with regard to the investigations of other authors and it appears possible to describe the effect as due to a change in the secondary (mosaic) lattice of the Bi crystal.

Part I. The Thermoanalysis of Bi Single Crystals

Introduction

IN A previous paper,[1] one of the authors (G) described a method of producing Bi-single crystals which permits the application of strong, transverse, 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 at 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 transverse 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

[1] A. Goetz, Phys. Rev. **35**, 193 (1930).

[2] S. Plücker, Pogg. Ann. **76**, 583 (1849).

[3] M. A. Leduc, C. R. **140**, 1022 (1905).

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-e.m.f. was found with regard to different 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 single crystals introducing a minimum of mechanical stresses has already been described[1,5] as well as the way the magnetic field was applied to the growing crystal only a few additional details need be mentioned.

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 processes. 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 recrystallized 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 of the magnet (200–300 gauss) 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

[4] L. Tieri and E. Persico, Linc. Rend. **30,** 464 (1921).
[5] A. Goetz and M. F. Hasler, Proc. Nat. Acad. **15,** 646 (1929).

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 (111) plane is parallel to the lines of force. It seems improbable that this difference was due entirely to the second recrystallisation, as etching off a layer one mm or more thick does not destroy the phenomenon. This effect must indicate a change of the structure of the crystal-faces within the magnitude of the wave-length of visible light and it thus seems possible that it concerns the mosaic lattice as described by Zwicky[7] and Goetz[8]. This possibility will be treated at length in another paper.

The thermoanalysis of a crystal. Concerning a sensitive and effective method for determining possible differences between these two halves of one and the same crystal, it seemed that the measurement of the thermo-electric 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. Several methods had to be tried until it was possible to obtain reliable results and since such methods, allowing one to measure as well as to localize a thermal e.m.f. within a metal rod, are excellent indicators of inhomogeneities undetectable by other means, their applicability is not limited to this special problem. Thus it seems worth while to give a more detailed description of them. (A similar idea has been put into realization independently by Terada and his collaborators.[9,10,11] Their experiments had been started for testing the reality of the Benedix effect and the method used was fundamentally the same as ours, though quite different in its experimental procedure. It is excellent for the detection of the "residual" thermal e.m.f.'s. but its sensitivity and reproducibility does not meet the requirements of the thermoanalysis of single crystals).

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 mercury 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

[6] A. B. Focke, Phys. Rev. **36,** 319 (1930).

[7] F. Zwicky, Proc. Nat. Acad. **15,** 253, 816 (1929); **16,** 211 (1930).

[8] A. Goetz, Proc. Nat. Acad. **16,** 99 (1930).

[9] T. Terada and T. Tsutsui, Proc. Imp. Acad. Tokio. **5,** 132 (1929).

[10] T. Terada, T. Tsutsui and M. Tamano, Sc. Pap. Inst. Res. Tokio, **7,** 201 (1927).

[11] T. Terada, T. Tsutsui and M. Tamano, Proc. Imp. Acad. Tokoi, **3,** 507 (1927).

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 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
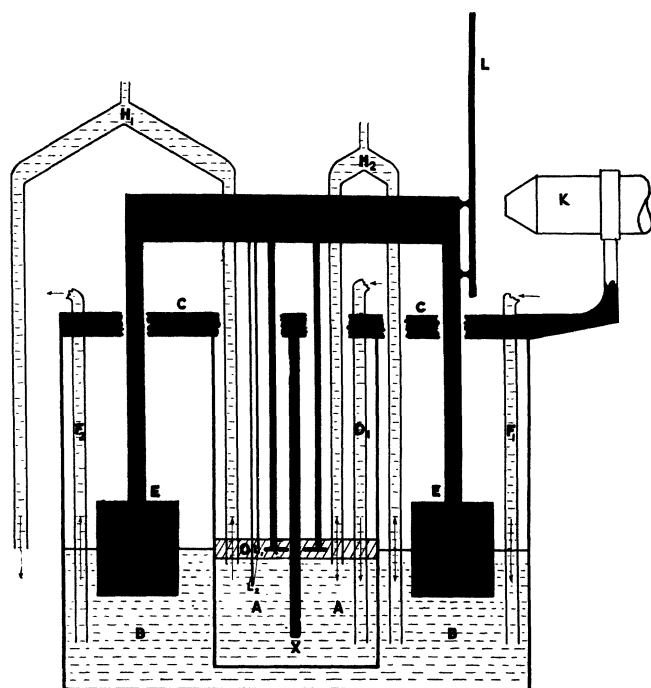

Fig. 1. Diagram of the thermoanalyzer.

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 nullifying 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 carried several devices among which are the syphons H_1 and H_2 and the scale L. The latter serves to measure the position of the float (incl. oil-layer, furnace, etc). with regard to the crystal by means of the reading microscope K attached to the frame C. The syphons H_1 and H_2 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 amounts 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_1. As an indicator of this equilibrium, a differential thermocouple 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 constantan 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 the syphon H_2 is used in addition to 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 in the vessel A as indicated in Fig. 1. To com-

plete 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 (0.1 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
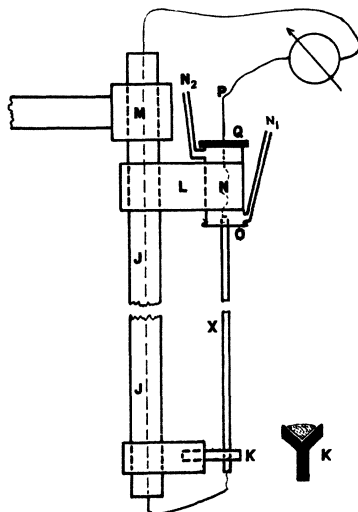

Fig. 2. Diagram of the crystal-holder of the thermoanalyzer.

connected with a water reservoir of constant temperature and 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 (toy balloon), 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 around 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 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.

Fig. 3. Photographic view of the thermoanalyzer.

After the crystal, mounted in its holder, is fixed 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 maintenance 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, and G_2 one

measuring the difference of temperature between the heated oil layer O and the water W_1.

Types of thermoanalytic diagrams. 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 X of the heated oil layer with respect to the crystal as abscissas. 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 thermo-
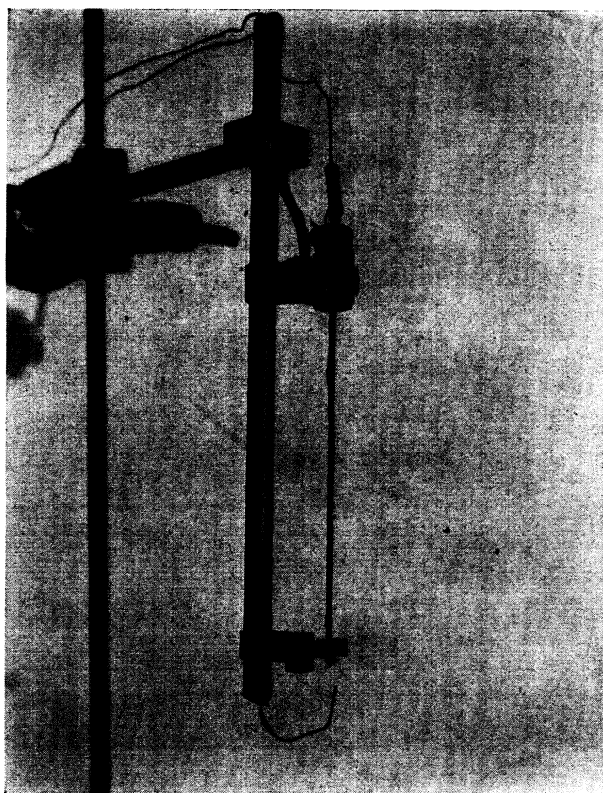
Fig. 4. Photographic view of the crystal-holder.

electric potential (Magnus' Law). However, certain deviations from this purely theoretical concept would be expected as a result of imperfect cooling conditions and the heat-conductivity of the crystal. Hence, a curve of the type (Fig. 6a) should be expected where the dotted line would represent a constant thermal e.m.f. (τ) 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. 6b, which represents an unhomogeneous crystal consisting of two halves (I and II) which have a thermal e.m.f. against each other. In this case, a curve as shown would be obtained, where a maximum would permit the exact localization of the junc-
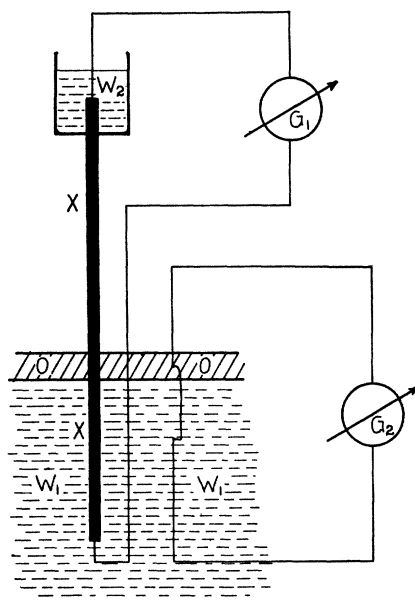

Fig. 5. The electrical connections of the thermoanalyzer.

tion of the two halves. Superimposed upon this would be the effects previously mentioned (Fig. 6a) though the constant thermal e.m.f. due to unequal end cooling would have a different value since the thermoelectric
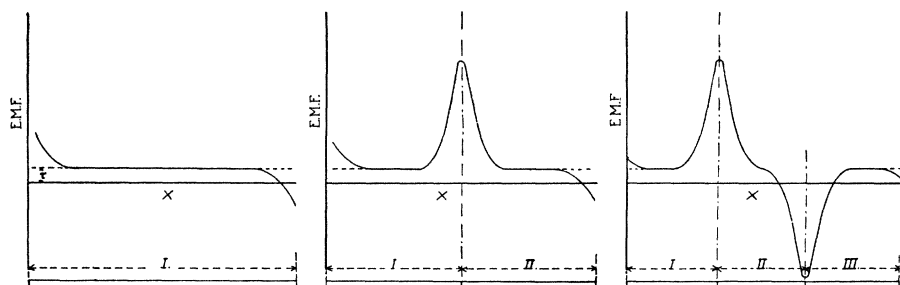

Fig. 6. a. b. c. Ideal thermoanalytic diagrams of a perfect single-crystal (a), a perfect double-crystal (b), and a perfect triple-crystal (c).

power of the two halves against the contact metal would be different from that in the case of a single crystal. Also, the end effects due to heat conduction would be slightly asymmetrical 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 (I: III, Fig. 6c) 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. 6b. 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 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 the cross-section, thermal conductivity, etc., of the crystal as follows: The thermal conditions along the crystal within the thermo-analyser are easily treated by the general equation of the temporal and local distribution of temperature in a linear conductor:[12]

$$\frac{\partial \theta}{\partial t} = \frac{\sigma}{\rho\,c}\,\frac{\partial^2 \theta}{\partial x^2} - \frac{h}{\rho\,c}\,\frac{U}{S}\,\theta \qquad (1)$$

where: θ is the temperature for (x) and (t); r the radius of the crystal; U the circumference of a cross-section of the crystal; S the cross-section of the crystal; x the length-coordinate of the crystal; h, the thermal emissivity of the crystal surface; c the specific heat; ρ the density; and σ the specific heat-conductivity.

Since the movement of the oil-layer along the crystal within the thermoanalyser is very slow we assume stationary condition, i.e. $\partial\theta/\partial t = 0$. Thus Eq. (1) becomes:

$$\frac{\partial^2 \theta}{\partial x^2} = \frac{U}{S}\,\frac{h}{\sigma}\,\theta = \frac{2}{r}\,\frac{h}{\sigma}\,\theta \qquad (2)$$

and:

$$\theta = A \exp\left[-\,(2h/r\sigma)^{1/2}x\right] + B \exp\left[(2h/r\sigma)^{1/2}x\right]. \qquad (3)$$

For the assumption of $x = \infty$, i.e. in case the crystal cools down so fast that the gradient is zero before the end of the crystal (which fact is indicated by the absence of the end-effects mentioned above), B and therewith the second term of Eq. (3) equals zero; hence we obtain:

$$\theta = A \exp\left[-\,(2h/r\sigma)^{1/2}x\right] \qquad (4)$$

where A equals θ_{max}, the temperature of the oil layer, if one assumes the absence of any gradient across the crystal as was already done for the entire crystal implicitly in Eq. (1).

[12] Enzyklopädie d. Math. Wiss. 5, I, 181.

The graphical interpretation of the records of the thermoanalyzer is more convenient if Eq. (4) is transformed into a logarithmic system:

$$\ln \theta = \ln A - (\alpha h)^{1/2} x \qquad (5)$$

where $\alpha = 2/r\sigma$. If $\ln \theta$ is chosen as ordinate and $(h^{\frac{1}{2}}x)^{-1}$ as abscissa, the cooling curve becomes a straight line as shown in Fig. 7a, its inclination $(tg \ \phi)$
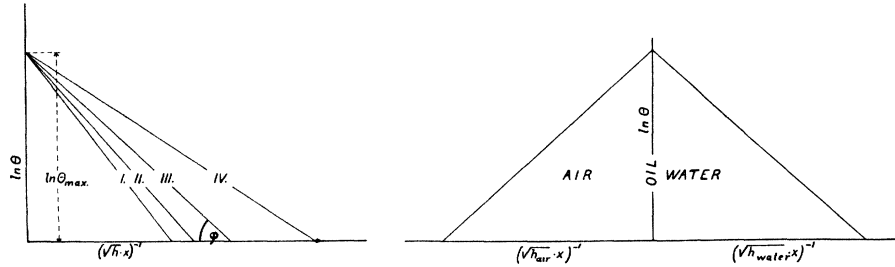

Fig. 7. a. b. Ideal logarithmical diagrams of a perfect double-crystal. The difference between the thermal "emissivity" for water (h_{water}) and air (h_{air}) of the crystal surface is compensated to obtain a symmetrical diagram. (Read $+1$ for -1 as abscissa-exponent!)

is for the same crystal directly proportional to $\ln\theta_{\text{max}}$ and $h^{-\frac{1}{2}}$, since r as well as σ is constant for a perfect single crystal over its whole length. However h differs with the surrounding medium, for instance is $h_{\text{air}} < h_{\text{water}}$. Hence the diagram is simplified if the abscissa indicates $\xi = (h^{\frac{1}{2}}x)$ instead of x, since in this case $tg \ \phi$ is the same for the cooling curve above and below the oil layer (Fig. 7b).
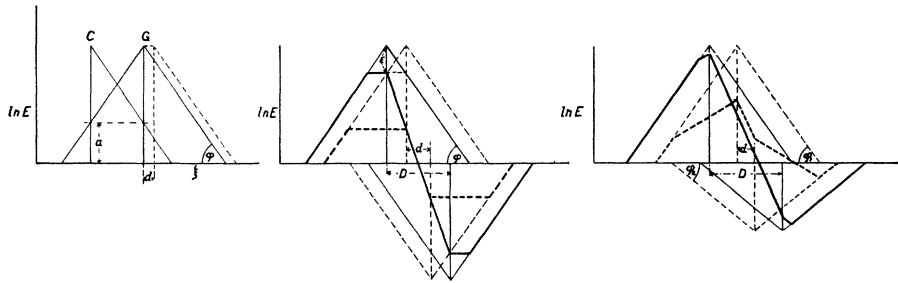

Fig. 8. a. b. c. The geometric construction of an ideal thermoanalytic diagram of a double crystal (a), a symmetrical triple-crystal (b), and an asymmetrical triple-crystal (c). 8b and 8c show each two different cases, the diagram of a large intersection $(D;$ full-drawn lines) and of a narrow one $(d;$ dotted lines).

If the rather valid assumption be made that E, the thermoelectric force is directly proportional to the (small) difference of temperature between oil and water (resp. air), then equation (5) may be written:

$$\ln E + \ln E_{\text{max}} - \alpha^{1/2}\xi \qquad (6)$$

where E_{max} represents the value of E for $\theta = \theta_{\text{max}}$.

The e.m.f. produced at the ends of a double crystal (Fig. 6b) in a certain position (G) of the oil layer (C) (Fig. 8a) is given by the intersection with

the ln E- ξ line (a). Hence it is evident that the thermoanalytic curve $E =$ $f(x)$ will follow that line in the coordination used if one moves the intersection gradually through the oil layer; i.e. the diagram (Fig. 8a) thus obtained is identical with the measured curve to be expected from an ideal double crystal if one considers (according to the medium surrounding the intersection) the two different values of h which are easy to find empirically.

It goes without saying that the assumption of a two-dimensional oil layer is not justified by the actual conditions, since the oil layer is of considerable thickness (d), its temperature is not uniform, and $d\theta/dx$ has a definite value as well as being a function of x_{oil}.
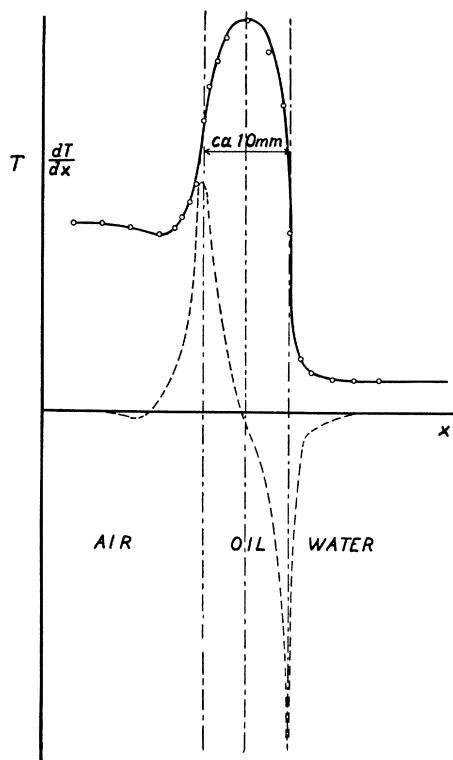

Fig. 9. The temperature diagram of the thermoanalyzer. The full drawn curve shows $T=f(x)$, the dotted lines show $dT/dx=f(x)$.

However the real curves are not fundamentally different from the constructed ones as soon as the oil layer is comparatively thin and the thermal conductivity of the crystal is large. If those conditions are fullfilled one can account for the oil layer by moving the starting point of the second half of the diagram the distance d (dotted in Fig. 8a). This also is only a first approximation on account of the neglection of $\partial^2\theta/\partial x^2 \neq$ const.

Fig. 9 shows the measured temperature-curve within the thermoanalyzer (full line). The latter can be found readily by putting a very thin thermocouple into the thermoanalyzer instead of the crystal. The dotted line in Fig. 9.

indicates the temperature gradient obtained by graphical differentiation of the first curve. It shows that very large gradients could be obtained at the boundary layer of oil and water and furthermore that the theoretical assumptions are not very far from the facts.

In the case of a triple-crystal (Fig. 6c) the construction of the curve is more complicated though fundamentally the same. Here it is necessary to subtract the intersections of the $\ln E$-ξ lines crossing one transition from those crossing the other. The diagram obtained thus has ordinates $(\ln E_1 - \ln E_2)$, while what is actually desired is $\ln (E_1 - E_2)$. Since the latter, however, give curves it was considered advisable from the view-point of a convenient graphical synthesis of the analytic curves to plot the former, which give the correct position of the maxima though not the correct amplitudes. The ordinates of the two elementary curves have to be plotted into the opposite direction since the sign of the e.m.f. is negative in one case. Fig. 8b. shows the diagrams of two different triple-crystals, one with a large II-section (full lines) (distance D) the other with a small section (dotted lines) (distance d). The thermal e.m.f. between I and II, and II and III is the same in both cases.

It is apparent that the size of the maxima depends on the length of the heterogeneous section II as soon as $d < x_0$; (x_0 means the distance from the heated intersection to where θ is so small that the thermal e.m.f. cannot be measured anymore).

The decrease of $E_{\max}$ is then simply given by:

$$\ln \epsilon = (\xi_0 - d) \ tg\phi \text{ for } d < (h^{1/2} \cdot x_0) = \xi_0. \tag{7}$$

Moreover it is evident that the width of the maxima increases with the decrease of their sharpness.

Fig. 8c. shows another case of a triple crystal, for different lengths of section II. Hence where all three sections are thermoelectrically different, one obtains asymmetrical curves as well as an asymmetrical decrease of the maxima with the length of section II.

The dependence of the size of the maxima indicated by the thermoanalyzer on the length of the straight section II determines the resolving power of the analyser in each case since it is related to the indicated e.m.f. in the limit by the relation:

$$de = -E_{\max} \left(\frac{2h}{r \ \sigma}\right)^{1/2} \exp\left[- (2h/r\sigma)^{1/2}x\right]dx \tag{8}$$

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

$$de = -E_{\max} \left(\frac{2h}{r \ \sigma}\right)^{1/2} dx. \tag{8a}$$

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

The above considerations show that the analyzer, since it does not necessitate the slightest stress to the specimen, is a very useful instrument

for the detection of all kinds of invisible imperfections and inhomogenities in a metal rod, especially in a delicate single crystal. The size of the smallest imperfection still resolved distinctively was *ca*. 0.1 mm. It is evident that thin rodes (2 mm diameter in the present case) give better results than those of large diameter since the method integrates necessarily over the whole cross-section.

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 thermoanalysis can serve the purpose of detecting and locating imperfections within a crystal only when the size of these imperfections is above the resolving power of the analyzer. Furthermore, it is only possible to detect imperfections which cause a thermoelectric force, though it seems
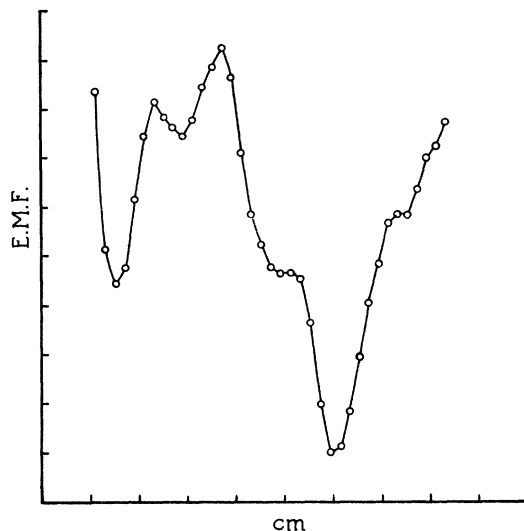

Fig. 10. The thermoanalytic curve of a Bi crystal grown in a glass tube.

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 other papers.[1,8]

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—a method to be used in the final experiments—was guided step by step by this kind of an analysis. First crystals grown in glass tubes by the ordinary method (Tammann, Bridgman) 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. 10 shows a diagram of such a crystal.

The lower curve in Fig. 11 shows a crystal with one maximum (M) 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
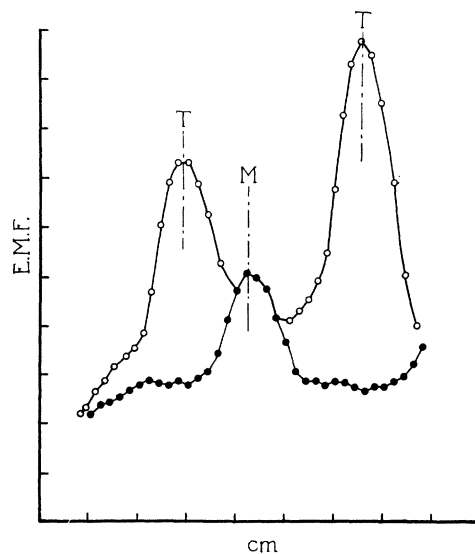

Fig. 11. The thermoanalytic curve of a crystal before (black points) and after artificial deformations at the points $T-T$ (white points). M is the starting point of the magnetic field.

is shown as the upper curve where now two new maxima (T, T) occur, the position of which coincided exactly with the location of the twin-sets.

Fig. 12 shows the diagram of a crystal of the same orientation (P_3) as Fig. 11 as homogenous as it could be produced by means of the graphite
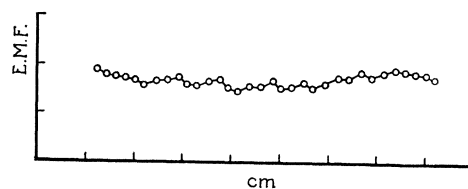

Fig. 12. Thermoanalytic diagram of a "perfect" Bi cyrstal grown after the method of Goetz. Orientation: P_3; Kind "B."

trough, protecting atmosphere, etc., as previously described.[1] Since the scale of this diagram is the same as that of the previous ones it is quite evident that the method used for the production of the crystals gave quite uniform results.

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 the detection of the inclusion of a crystal of different orientation, which orientation was usually that of a twin. Fig. 13 is a microphotograph of an inclosure of that kind which shows distinctly a twinned region within a normal (111) plane characterized by an alternating penetration of (11$\bar{1}$) planes through the original (111) plane bordered by (110) planes. The cause of these imperfections was, in general, a disturbance

Fig. 13.   Microphotograph of an etched (111) plane (ca. 120X), illuminated by polarized light, showing the inclosure of a region of periodical twinning.

(vibration, shock, etc.) happening at the time when this section of the 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. *It was found that the border between the magnetic and the normal half of the same crystal was the origin of a thermo-electric force.* Furthermore, the thermoanalysis gave 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 quantita-

tively and not even the sign of the force could at first be reproduced although 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; orientation, 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 principal variants were being controlled.

In presenting the results, the effect of each of the factors on the thermo-electric e.m.f. will be considered separately, the stationary values of the
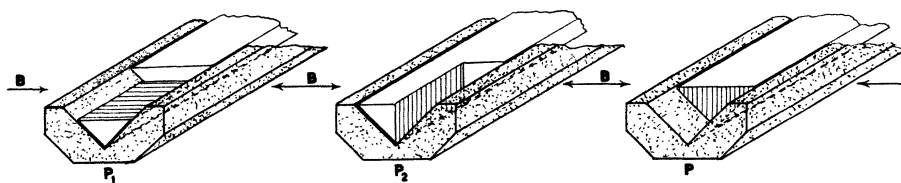

Fig. 14. Scheme of the three principal orientations used. The hatched plane indicates (111), the arrow shows the direction of the field lines.

other factors being given in each case. Up to date, no attempt has been made systematically to 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°C measured above tap water temperature of 19° to 21°C.

TABLE I. *The three orientations of the crystal.* The third column entitled "vector" shows the direction of the heat flow and the electric current during the thermoanalysis.

| Name | Trigonal axis to | | | (111) plane to | | |
	rod	field	vector	rod	field	vector
P_1	⊥	⊥	⊥	‖	‖	‖
P_2	⊥	‖	⊥	‖	⊥	‖
P_3	‖	⊥	‖	⊥	‖	⊥

The ordinate scale for the curves unless designated otherwise is 7.8×10^{-6} volts per division. It indicates positive volts for increasing values. The units of the abscissa (length of the crystal) are centimeters.

The solid line, mid-way along the abscissa scale on the curves, indicates the position of the furnace at the intersection between magnetic and normal

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 essentially different from each other.** Fig. 14 shows the trough G dotted, and the crystal white, the latter cut parallel to its main cleavage plane. These three orientations are given in Table I.
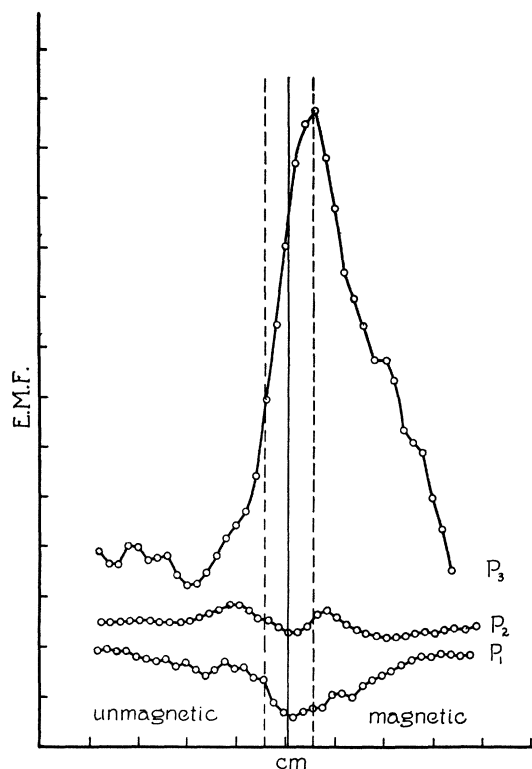

Fig. 15. The thermoanalytic curves of three principal orientations of crystals (kind "B") grown discontinuously. Field: 21,000 Gauss.

Fig. 15 shows analysis curves typical 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 thickness of the center line is misleading in so far as the furnace plate was 1 mm thick and since it was impossible to measure exactly its location within the oil layer.

** The possibilities of azimuthal variation were neglected in these experiments. There are:

two for P_1 with regard to field and vector;

two for P_2 with regard to vector;

two for P_3 with regard to field;

which differ essentially from each other.

The diagram shows that the thermal e.m.f. depends very much on the orientation of the principal axis of the crystal to the field lines. The effect is very large for P_3 and very small for P_2; it is even very probable that the latter effect does not exist at all, and that the deviations of the P_2-diagram are due to inaccuracies in orientation.

The thermal e.m.f. is positive for P_3 and negative for P_1.[***] Furthermore it is apparent from Fig. 15 that the thermal e.m.f. is different from what should be expected, (see Part I) since the maximum of the P_3-curve is not at the intersection with the center line, i.e. within the region where θ is largest (see Fig. 9), but at the border between oil and water, where $d\theta/dx$ is a maximum, a fact which seems to be of fundamental importance.

The size of the thermal e.m.f. of the P_3 curve seems remarkable (7.8×10^{-5} volt or 4.33×10^{-6} volt. degree^{-1}), if one calculates the change in orientation of the crystal necessary to produce this e.m.f. due to the thermoelectric anisotropy of the Bi crystal. Taking the data from Bridgman's last paper[13] one finds that change would have to be $21°$[****] though it is certain that there is no larger change of orientation at the intersection than $0.5°$, which fact makes it quite impossible that the thermal e.m.f. is just caused by a change of orientation at the intersection.

The Effect as a Function of the method of growth. The 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. 16 shows curves obtained from crystals of P_3 orientation produced in these different ways. "1" represents the former, "3" the latter; in both these cases, no appreciable residual field was present over the so-called unmagnetic portion of the crystal. "2" on the other hand, represents a crystal of continuous growth with the residual field present during the growth of the first portion of the crystal.

It was entirely unexpected to find that the thermal e.m.f. depended on the method of growth to such an extent as shown in Fig. 16. The fundamental difference between "3" and "1" is that there exists only one maximum in the former (the small second maximum at "b" has a different cause and will be discussed later) and a maximum and a minimum in the latter. The sign of these maxima is opposite in "1" and "3" but their positions coincide again with the extreme values of $d\theta/dx$ in the thermoanalyzer, for "1" the thermoanalytic curve is even an exact repetition of the $d\theta/dx$ curve in Fig. 9. The case of "2" shows the large effect of a small field strength which seems to suppress entirely the first maximum.

[***] The thermal e.m.f. is called positive, if the end of the "magnetic" part of the crystal had a potential positive with regard to the end of the normal half, if the temperature of the intersection was higher than the temperature of the ends.

[****] This diagram (Fig. 16, page 384) shows the thermal e.m.f. as a function of $\cos^2 \phi$ (angle of orientation). The units of the ordinate are 3.10×10^{-4} volt for a difference of temperature of $68°$. Since the curve is no straight line it is necessary to measure at an orientation corresponding to P_3, i.e., starting from $\cos^2 \phi = 1.0$. Since the e.m.f. unit in that diagram equals $3.10 \times 10^{-4}/68° = 4.56 \times 10^{-6}$ volt. degree^{-1} our e.m.f. corresponds to $4.33/4.56 = .95$ units. For the P_3-orientation ($\cos \phi = 1$) .95 ordinate-units correspond to 1.3 units of the abscissa, i.e. $\cos \phi = (0.87)^{1/2}$, $\phi - 21°$.

The effect as a function of the impurities. It became evident that the magnitude of the effect depended on the purity of metal used to a very large extent. The crystals were therefore prepared from four kinds of Bi, obtained
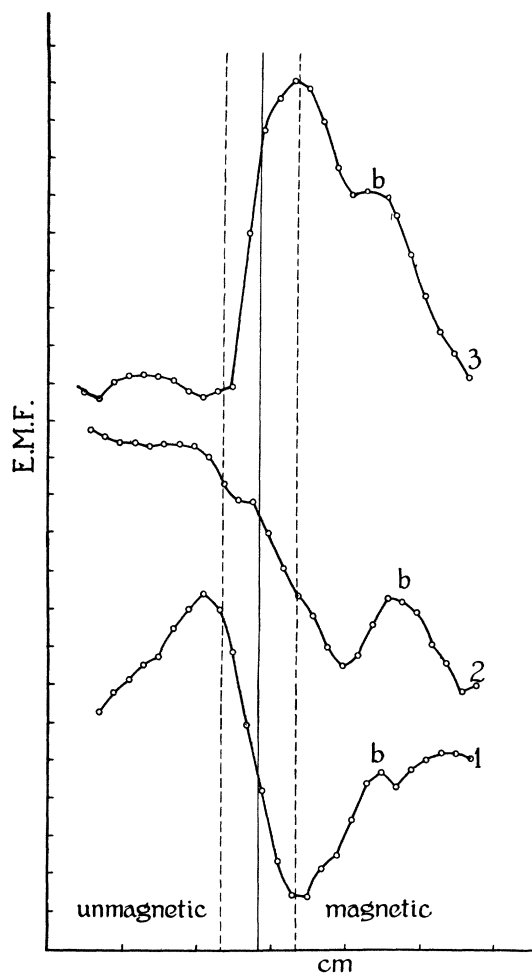

Fig. 16. The thermoanalytic curves of three different types of growth:

1. represents the continuous method without residual field. Field: 13,800 Gauss; kind "B;" orientation: P_3.

2. represents the continuous method with residual field.

3. represents the discontinuous method.

from different sources which were designated as "A", "B", "C", and "D" as shown in the following table:

TABLE III.   *Sources of the bismuth used.*

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

Fig. 17 shows curves of the P_3 orientation made from these four different kinds of Bi by the discontinuous method, whereas Fig. 18 represents the corresponding crystals of continuous growth.

Since from this work as well from papers of Bridgman[13] and Kapitza[14] 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
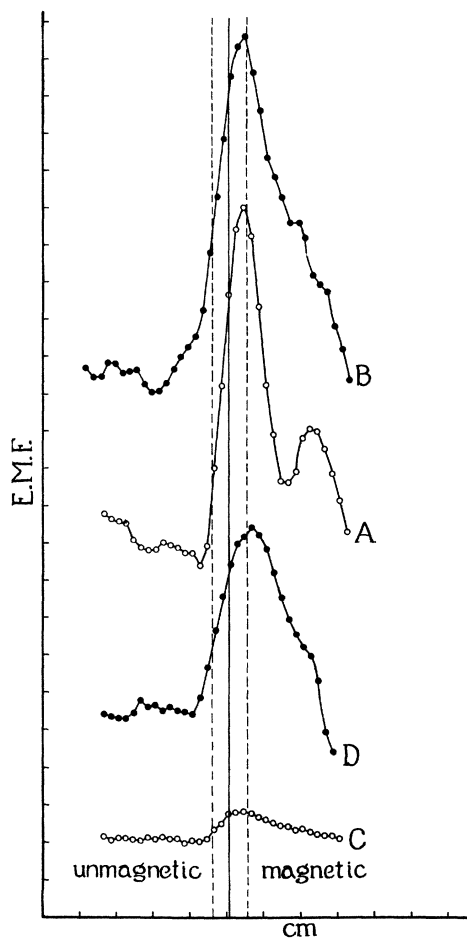

Fig. 17. The thermoanalytic curves for P_3 crystals of four different degrees of chemical purity, grown discontinuously; field: 21,000 Gauss.

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

[13] P. W. Bridgman, Proc. Am. Acad. 63, 351 (1929).
[14] P. Kapitza, Proc. Roy. Soc. A119, 358 (1929).

on our different metals. The amount of any impurity was measured by com-
paring 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 Pryex tubes
after it had been ascertained that the glass did not contain any of the metals
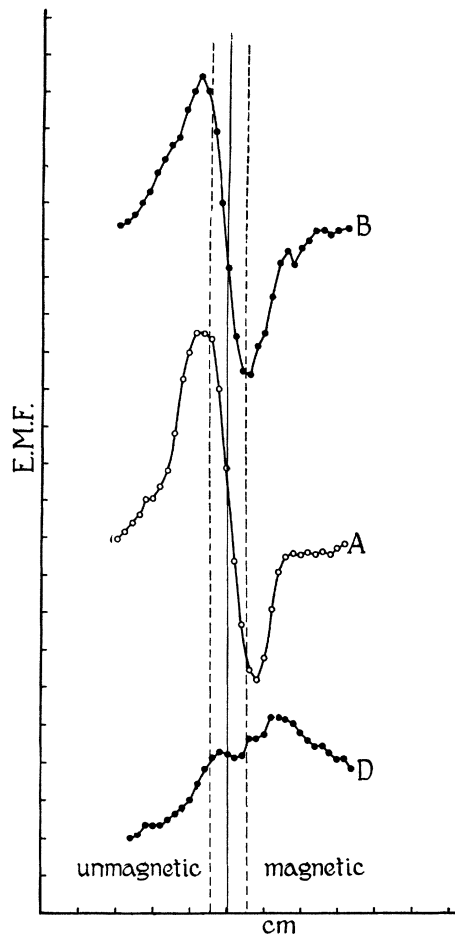

Fig. 18. The thermoanalytic curves for P_3 crystals of three different degrees
chemical purity, grown continuously; field: 13,800 Gauss.

involved in the analysis. The results are given in the following table, where
the numbers give the approximate relative intensities of the indicated lines
of the different impurities.

In general, it can be said that the amount of impurity is probably on the
whole, smaller than 0.2 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.

TABLE IV. *Spectroscopic analysis of Bi samples.*

Sample	Ag		Cu		Sn		Pb						Zn			Sb			
	3281	3383	3247	3274	3262	2863	4058	3683	3639	3275	2802	2613	4810	4722	3345	3267	3232	2598	2528.5
A	4	1	1			?	5	1		?									?
B₁	5	2	1			?	10	4	3										
B₂	5	2	1			?	10	4	2										
C₁	1		5	3		?	1						?						?
C₂	1		5	3			1	?					?						?
D₁	7	3	1–0		1		6	1											
D₂	7	4			1		5												?

Thus it is apparent from the diagrams that the purest metal shows the smallest effect and also that the shape of the curve is but little affected. However the secondary maximum ("b" in Fig. 16) depends apparently on certain impurities, since it is very large for "A" (Fig. 17) and extremly small for "C". The method of continuous growth shows very little difference between "A" and "B" and a large one for "D". It is however doubtful whether the latter measurement is a correct one, since it is based only on a few crystals.
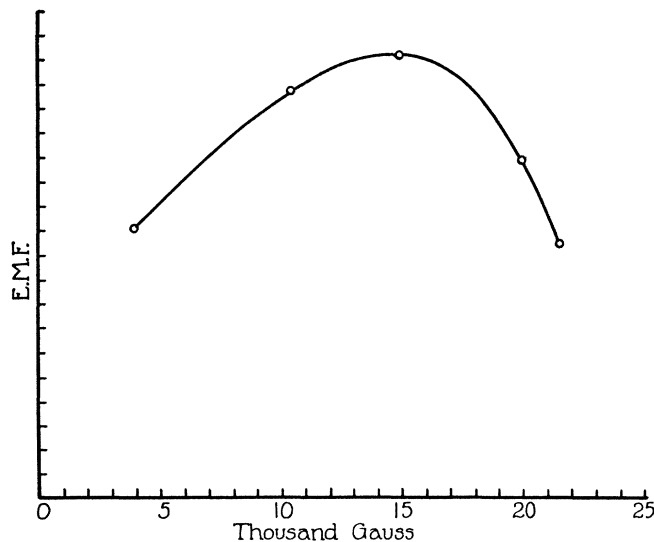

Fig. 19. The size of the maximum thermal e.m.f. as a function of the field strength for P_3 crystals, kind "B," grown discontinuously.

The effect as function of the field strength. Although it is very important to investigate what influence the strength of the applied field has upon the thermoelectric effect, it appeared very difficult to obtain reliable results, since the effect does not depend merely on the orientation of the crystal but also on the method of growth, the degree of impurity, etc. Thus

it has not yet been possible to obtain results of sufficient generality in spite of a great number of experiments. It seems however quite safe to state that there exists a large influence of the field strength upon the effect for crystals of the P_3-orientation. (Other orientations have not yet been investigated.) The influence of weak fields is very large whereas strong fields (20,000 Gauss) decrease the effect considerably in the case of the discontinuous method of growth.

Fig. 19 shows the variation with field strength obtained for crystals grown with the P_3 orientation, composed from a series of curves of the type of Fig. 15.

The field which produces the maximum thermoelectric effect seems to depend on the degree of impurity.
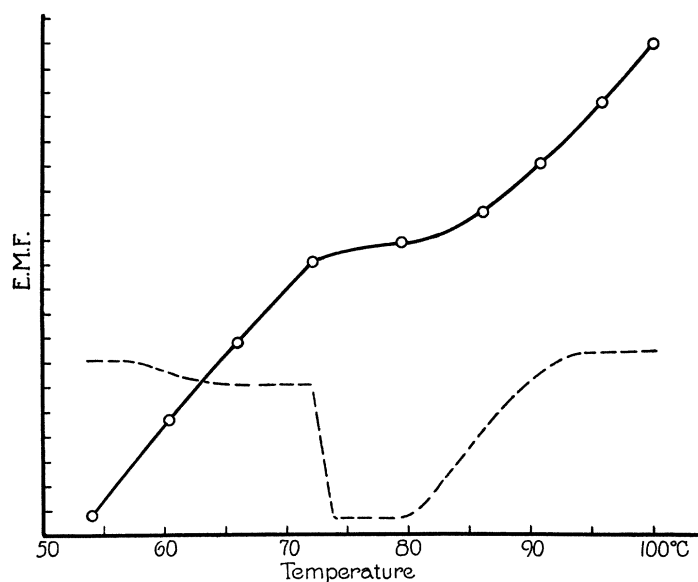

Fig. 20. The size of the maximum thermal e.m.f. as a function of the temperature (The hypothetical transformation of α into β-bismuth.) P_3-crystal, grown discontinuously, kind "B," field: 21,000 Gauss. The dotted curve gives $dE/dT=f(T)$.

The effect as a function of the temperature. Fig. 20 shows the thermo-electric effect between the magnetic and the normal half of a crystal as a function of the temperature of the analyzer and its differential curve (dotted). The curve was taken by first finding the exact position of the maximum e.m.f. with regard to the crystal (crystal of the type shown in Fig. 15) and then keeping the oil layer in this position while its temperature was gradually increased.

This experiment performed on many crystals of different types showed that the temperature function is independent of the impurity as far as the general shape of the curve is concerned. It seems quite interesting that the differential curve $dE/d\theta$ shows a large discontinuity between 75° and 90°C.

Since it is well known that this type of curve is obtained in case of an allotropic transformation (as for instance typically represented by the thermoelectric effects of pure iron[15]) the shape of the curve obtained indicates that the discontinuity in that region of temperature affects the magnetic half of the crystal in a different way than the normal.*

In order to decide whether or not the magnetic state is just a more or less unstable allotropic state caused by 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°C, to see whether the transition into the normal state would occur at all. Since this annealing temperature lies above the point of the mentioned "allotropic" transformation, it is probable that the instability of the magnetic state should increase, or the transformation speed into the normal state should be larger.

Hence a crystal (P_3 of "B") was analyzed the day it had been grown, it was then annealed for 16 hours at 100°C and analyzed again a month later. No change of any kind could be detected which indicates that the magnetic state is either perfectly stable or that it has an extremly slow speed of transformation. It is certainly not affected by passing the critical temperature of normal Bi. (75°–90°C)

This experiment shows also that the effect of "aging" Bi crystals does not occur in specimens of good crystallographic perfection, either for normal or for magnetic crystals.

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* The question of the existence of an allotropic state of Bi is still unsettled; Cohen[16] and Cohen and Moesveld[17] concluded from their pyknometric and dilatometric measurements the existence of an α and a β modification, of which the α-state is stable below 75°C having a larger density than the β-state. However those authors found other transformations at 81° and 90° where the volume of the metal changed suddenly according to its thermal history. Würschmidt[18] found also the transformation point at 75° indicated by a large contraction, whereas the temperature coefficient of the conductivity of Bi as investigated by Bridgman[19] and Holborn[20] does not indicate such transformation at all.—Furthermore the thermoelectric effects as a function of temperature of Bi single crystals were investigated by Boydston;[21] his $E=f(\theta)$ curves show a slight indication of an irregularity in this region of temperature which becomes much more evident in the case of the Peltier effect curve: $\Pi = T\ dE/d\theta = f(\theta)$. A recent investigation of the Peltier and Thomson effect by Fagan and Collins[22] would have cleared this question, if the authors had extended their measurements into this region of temperature. The exact coincidence of the critical temperatures in our measurements with the transformation-point of Cohen, Moesveld, and Würschmidt seem to render the existence more probable. It may be however another example of "pseudo-allotropy" due to traces of impurities as shown recently in the case of extremely pure Zn by Guertler and Anastasiadis.[23]

[15] A. Goetz, Phys. Zeits. **25**, 562 (1924); **26**, 260 (1925).
[16] E. Cohen, Akad. Amsterdam Verls. **23**, 1224 (1914/15).
[17] E. Cohen and A. L. Th. Moesveld, Zeits. f. Phys. Chem. **85**, 420 (1913).
[18] J. Würschmidt, Verh. d. Dt. Phys. Ges. **16**, 799 (1914).
[19] P. W. Bridgman, Proc. Am. Acad. **52**, 636 (1916/17).
[20] L. Holborn, Ann. d. Physik (4) **59**, 152 (1919).
[21] R. W. Boydston, Phys. Rev. **30**, 911 (1927).
[22] H. D. Fagan and T. R. D. Collins, Phys. Rev. **35**, 421 (1930).
[23] W. Guertler and L. Anastasiadis, Zeits. f. Metallkd. **21**, 338 (1929).

DISCUSSION

Generally speaking the above results are far from sufficient to start an explanation of the effect on a theoretical basis. However the results seem to us complete enough to describe the phenomenology of the new effect approximately.

In the first place, it becomes quite apparent that the forces acting at the moment of crystallization affect the physical properties of the final crystal, though neither orientation nor any other macroscopic quality of the crystal is changed.

The effect as a function of the orientation of the crystal with regard to the field seems the most obvious of all the different variations of the experimental conditions. Here we obtain the largest thermal e.m.f. if the principal axis is normal to the field lines and parallel to the heat flow, i.e. the direction of the thermoelectric current (P_3); whereas the effect is extremly small if the axis is parallel to the lines of force and normal to the flow (P_2).

If one considers the anisotropy of the diamagnetic susceptibility of Bi crystals as measured recently by Focke[6] a relation between the two effects is quite evident, since in case of P_3 the crystal is in a position where the direction of the largest diamagnetism is parallel to the lines of force, and in the case of P_2 the most "paramagnetic" direction is parallel to the field. Hence there is a difference between the content of free energy in these cases, for the stability of the latter orientation is larger than of the former. If thus a crystal is grown first under normal conditions and then in a field the stability does not change in case of P_2 but is does considerably in case of P_3. One knows from other observations that a crystal prefers the P_2 orientation when forming its first center of crystallization in a transverse field and also that the field does not even change the opposite orientation if the latter is enforced on it by inoculation with a seed crystal. The fact that the point where the field (i.e. the instability) started is indicated by a thermal e.m.f. shows that the crystal undergoes a change in spite of the constancy of the orientation. Thus the question about the nature of this change becomes quite interesting.

Regarding the shape of the thermoanalytic curves it seems as if the curves of discontinuous growth (Fig. 15) were due to a double-crystal, and the curves of continuous growth (Fig. 18) represent a triple crystal, as has been discussed in Part I of this paper. The interpretation however of the latter diagram as being produced by a triple-crystal seems to be inadequate in view of the fact that the length of sandwiched section (d in Fig. 8b and 8c) would have to coincide with the thickness of the oil layer to produce the maxima and minima at the borders of the layer, which coincidence would seem highly improbable; i.e. the maxima and minima of the diagrams are too close together to be sufficiently resolved if caused by a section smaller than the thickness of the oil layer. Furthermore those points are not situated at the hottest part of the oil layer of the thermoanalyzer (Fig. 9), which means that the e.m.f. does not reach its maximum if the intersection of the crystal passes θ_{max}. This concerns also the simpler curves of discontinuously grown crystals.

It is very remarkable that the maximum of the thermoanalytic curves of P_3 crystals of that kind does not coincide with the position of the maximum of temperature, it does however with the maximum of the $d\theta/dx$ curve (Fig. 9), i.e. at the border of water and oil. *The only simple interpretation is thus that the thermal e.m.f. must depend on the temperature gradient or the density of the heat flow crossing the intersection between the normal and the magnetic half of the crystal.*

It is apparent that such effect cannot be caused simply by a double or a triple crystal, since the normal thermoelectric effect between two different metals or orientations of a crystal depends on the difference of the temperature and is quite independent of the gradient.

Although the assumption of such a type of a thermoelectric effect seems to be quite uncertain in view of the fact that the passing of the opposite gradient (air-oil, see Fig. 9) is much less expressed by the thermoanalytic curves of discontinuously grown crystals, such interpretation gains some probability in the case of continuously grown crystals (Fig. 18). Here we have curves which are the exact duplicates of the $d\theta/dx$-curve in Fig. 9. The sign of the effect is opposite in these two cases as follows: If the heat flow passes the intersection *from* the magnetic *to* the unmagnetic half of the crystal, the magnetic half is *positive* for *continuous* growth and *negative* for discontinuous growth, it is opposite if the heat flows the other way. In case of the discontinuous kind of growth the flow in the latter direction seems to be quite uneffective.

It is apparent that the influence of the impurities makes the effect very complex since the amount as well as the kind of impurity affects the thermal e.m.f. considerably as is to be expected from a consideration of the dependence of the anisotropy of the electric qualities of the crystal on the impurities present. Hence the mentioned instability of a growing crystal for certain orientations to the field should increase with an increasing anisotropy due to impurities and one should expect a kind of proportionality of the thermal e.m.f. with the impurity. This however is misleading, since it seems highly probable from the behavior of the metal "C" that an ideally pure Bi would not show any effect at all though the electric anisotropy still exists. Thus one is forced to assume that the whole effect is due to disturbances of the odd atoms in the Bi lattice, which disturbance is the more distinct the better the crystal is grown. The disturbance for a given amount and kind of odd atoms depends apparently on their arrangement and is easily affected by external influences during the act of crystallization.

Very little can be said as yet about the actual nature of the disturbance though the fact that an extremely small amount of impurities has such a large influence seems to indicate a surface effect, i.e. an effect due to a formation of mono- or bimolecular layers of odd atoms sandwiched between perfect sections of the crystal. Such arrangement similar to the "II-planes" of the mosaic structure of Zwicky[7,24] would require an extremely small amount of impurity to affect the electronic relations inside the lattice. In case of such an interpretation one has to assume that the arrangement of the odd atoms is changed under the influence of the magnetic field. It is quite plausible that such a

change differs with different crystallographic planes as well as that its effect works differently upon an electric current, which might explain the difference between the thermoanalytic curves of P_1 and P_3. (As has been mentioned already, these two orientations do not differ with regard to the field though they do with regard to the direction of the thermoelectric current and the heat flow.)

The arrangement of the odd atoms within the crystal must depend furthermore on the growth of the crystal, since any disturbance during the formation will affect the structure of the impurity layers to a certain extent and therewith the final influence of the magnetic field. This would explain the difference between the thermoanalytic curves of continuous and discontinuous growth. The highly metastable state of the configuration of the odd atoms within the II-planes during the formation of the mosaic structure is probably the cause of the extreme experimental difficulties in obtaining reproducable results.

Before closing, some comparisons with Kapitza's work[14] may be made. Concerning his observations of the change of the resistance of Bi crystals in a strong magnetic field, it is to be expected from the above hypothesis that the Bi which produced an extremly small effect (K.'s crystal "B" in his Fig. 13, p. 407, l.c.) would produce 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. Since the influence of an external field upon the change of the resistance depends on the size of the disturbances within the lattice, our experience with "D" and "C" compares very well with Kapitza's result, his effect being fogged by impurities and ours depending apparently wholly on their presence.

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 values obtained of the ratio R/R_0 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_0 than the P_1 case was obtained which might be interpreted as suggested above, because our effect shows no appreciable influence of the odd atoms upon this orientation.

CONCLUSION

Although these experiments were begun several years ago during which time a very large number of measurements have been taken, it is not yet possible to give more than a rather vague hypothetical explanation as outlined above. Since the experimental difficulties proved to be very large the

[24] F. Zwicky, Helv. Phys. Acta **3**, 269 (1930).

actual progress has been slow and the present paper cannot be more than a first report about the new effect.

Systematic measurements concerning the electrical conductivity, the specific gravity, and the magnetic susceptibility were performed and are still going on, as well as a detailed x-ray analysis of the "magnetic" crystals. Papers concerning these subjects will be published in near future.

In conclusion, the authors wish to express their great obligation to Dr. R. A. Millikan for the interest he has taken in the work, to Dr. R. M. Badger to whom they owe the spectroscopical analysis of the bismuths, to Mr. J. Pearson for his helpful technical advice and to Mr. A. Focke for his general assistance.
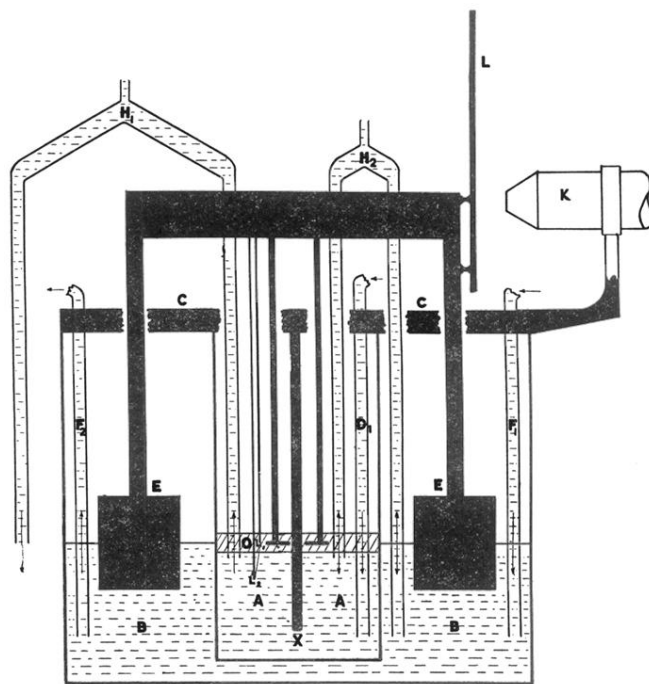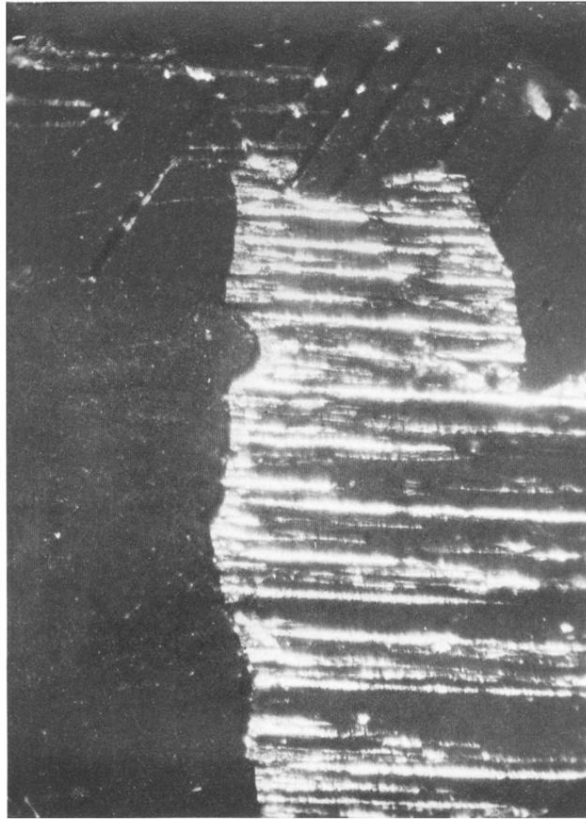
Fig. 1. Diagram of the thermoanalyzer.

Fig. 13. Microphotograph of an etched (111) plane (ca. 120×), illuminated by polarized light, showing the inclosure of a region of periodical twinning.
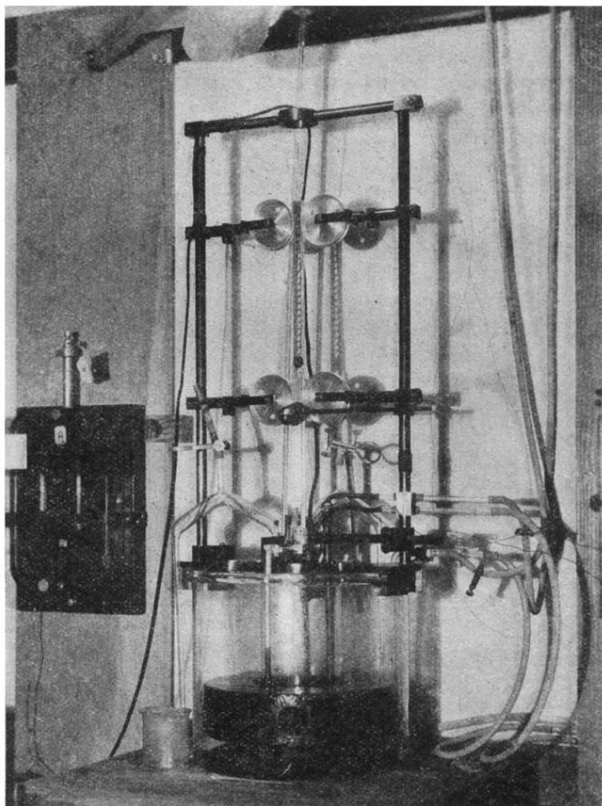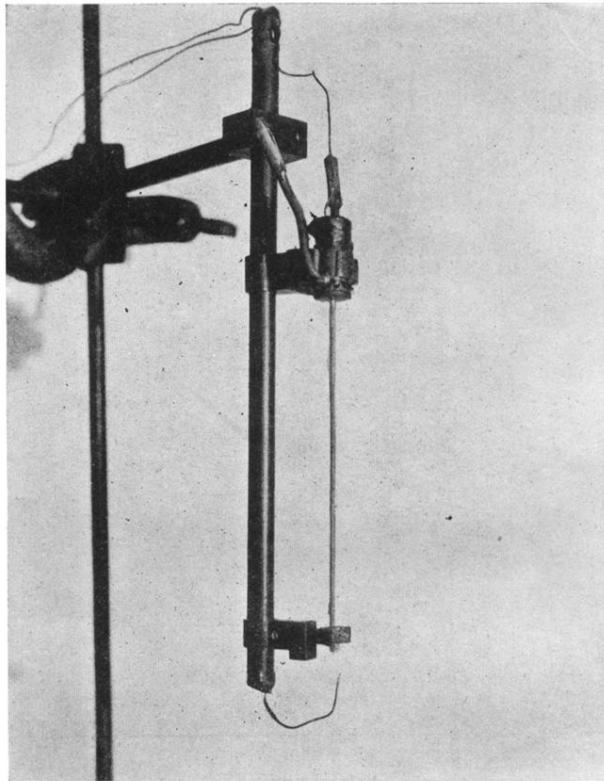
Fig. 3. Photographic view of the thermoanalyzer.

Fig. 4. Photographic view of the crystal-holder.