The Study of the Specific Resistance of Bismuth Crystals and its Change in Strong Magnetic Fields and some Allied Problems.

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[Plates 5–8.]

Introduction.

It is well known that in a magnetic field bismuth shows a greater change of resistance than any other substance, and it is also known that in the case of a crystal this phenomenon varies very much with the orientation of the crystal. A great deal of literature exists on this subject.*

The general view of the phenomenon is that the increase of resistance is largest when the cleavage plane of the crystal is parallel to the magnetic field, and when the current is flowing perpendicular to it. It is also known that the resistance in a magnetic field increases very rapidly with decreasing temperature. A complication in all these phenomena arises through certain time lags. When a current is passed through bismuth placed in a magnetic field, the resistance at the first moment is large, and then gradually decreases to its final value. This time lag accounts for the fact, first discovered by Lenard, that bismuth has a larger resistance for alternating currents than for direct currents. This phenomenon also depends on the crystal state of the bismuth.

In the present experiments both these phenomena in bismuth crystals have been studied, using strong magnetic fields up to 300 kilogauss, obtained by the method recently described.† The magnetic field obtained by this method lasts for only about 1/100 second, so that a special method had to be developed for measuring the changes of resistance occurring in such a short time. As the space available in the coil for the experiment is only 2 c.c., very small samples of bismuth, in the form of rods, must be used. These rods cannot be successfully cut out from a large block of crystal, as it is well known that the surface is disturbed to a considerable depth by such operations. It was therefore decided to develop a method of growing bismuth crystals in the form of small rods, in which the crystal planes have a given orientation. This proved to be

* Graetz, 'Handbook of Electricity,' vol. 3, p. 698, and vol. 4, p. 1026. See also Baedeker, 'Die electrischen erscheinungen in metallischen Leitern,' p. 94.

† Kapitza, 'Roy. Soc. Proc.,' A, vol. 115, p. 658 (1927).

a more difficult task than had been anticipated. Several ways of attack were tried before a satisfactory method was found.

In working out this method of growing rods of bismuth crystal, the author noticed certain phenomena which bear a close relation to those observed in the magnetic field and these will be discussed in some detail. This paper is accordingly divided into three parts, the first dealing with the method of growing bismuth crystals, the second with the methods of measurement, and the third with the magnetic phenomena.

Part I.—*The Growth of Crystal Rods with a Definite Orientation of the Crystal Planes and the Specific Resistance of Bismuth Crystals.*

(1) *Experiments in Growing Bismuth Crystals.*

Bismuth was one of the first metals to be obtained in large crystals, and it is considered to be one of the substances which crystallises most easily. Bismuth crystallises in the hexagonal system, and its crystallising symmetry is that of the rhombohedron, which approaches very closely to a cube. It has a trigonal axis, and perpendicular to it a perfect cleavage plane which is one of the four pseudo-octahedral planes. The other three pseudo-octahedral planes are also cleavage planes, but are not nearly so good as the one perpendicular to the axis. These cleavage planes are easily distinguished from each other. In a good crystal the perfect one has three sets of lines of equal strength intersecting at an angle of 60°. These lines run parallel to the lines of intersection of the three imperfect cleavage planes of the pseudo-octahedron. An imperfect cleavage plane has three sets of lines also, but one set (which is parallel to the perfect cleavage plane) is very strong, and the two sets parallel to the remaining imperfect cleavage planes are weak. The angle between the weak lines is 65° 28′, and between the strong and the weak 57° 16′.

Along the trigonal axis and perpendicular to it practically all the physical properties of bismuth are found to differ. Thus the electrical conductivity along the trigonal axis is smaller than that perpendicular to it. The same is true of the thermal conductivity, while the magnetic properties are also different.

For our experiments we required two sets of crystal rods—one with the perfect cleavage plane perpendicular to the length of the rod, *i.e.*, the axis of the crystal parallel to the axis of the rod; and the second with the crystallographic axis perpendicular to the length of the rod. For the various intermediate positions practically all the phenomena can be generally deduced by the well-known methods of tensor analysis.

The size of rod required for our experiments was about 3 to 5 mm. in length, with a cross section of about 1 square millimetre.

We first tried to obtain such rods by growing them in small glass tubes, of a diameter of 1 mm. filled with fused bismuth, and then slowly cooling them from one end—a method similar to that used by Obreimow and Schubnikow* and Bridgman.† The glass is then dissolved in hydrofluoric acid. In each of these rods the angle between the perfect cleavage plane and the axis of the rod varied from 0° to 60°, but not a single rod had the cleavage plane perpendicular to the axis of the rod. It is worth mentioning here that Bridgman‡ in all his numerous experiments on the growth of bismuth rods never obtained a larger angle than 45°.

We then tried a modification of Czochralski's§ method of growing crystals in which the rod is drawn from a crucible filled with molten bismuth. The rod is cooled and the bismuth is solidified slightly above the level of the molten bismuth in the crucible. The rods obtained in this way are fairly circular but of variable diameter. In order to obtain rods of a given diameter we modified this method, and instead of keeping the molten bismuth in a crucible we used a vertical pyrex tube of 5 mm. cross section and about 5 cm. in length. At the top end the tube was drawn to a nozzle of a diameter slightly larger than the required rod; at the bottom the tube was fitted with a glass piston with asbestos filling. The tube was wound with a few layers of nichrome wire, with asbestos insulation, and a small current through this winding was sufficient to keep the bismuth in a molten state. The crystal was grown from the nozzle by bringing a small piece of bismuth into contact with the meniscus of molten bismuth on the nozzle, and then very uniformly and slowly pulling it vertically up. By means of a simple mechanical device it was arranged that the asbestos piston was moving quite uniformly with the growing crystal rods, but with a reduced velocity, and thus forcing the necessary amount of bismuth through the nozzle. To obtain uniformity of motion, an electric motor with a reduction gear was used.

In this way it was possible to obtain uniform rods of 1 sq. mm. section, but not a single one of these rods had the angle of the perfect cleavage plane closer than 30° to the perpendicular plane of the rod.

* 'Z. f. Physik,' vol. 25, p. 31 (1924).

† 'Proc. Amer. Acad. Arts Sci.,' vol. 60, p. 307 (1925).

‡ *Loc. cit.*, p. 349.

§ 'Z. f. Phys. Chem.,' vol. 92, p. 219 (1917).

Georgieff and Schmid* used the Czochralski method for growing rods of bismuth crystal, but in all their specimens they did not obtain a closer approach of the cleavage plane to the perpendicular than I obtained in these experiments.

Further attempts were made to force the rods to grow with the cleavage plane perpendicular to the length by growing them from a definite plane. This was done in the following way. On the cleavage plane of a large crystal, grown in a crucible and broken along the cleavage plane, was placed vertically a small 1 mm. bore glass tube filled with bismuth. The glass tube was surrounded by a short platinum spiral of a slightly larger diameter, which could be heated by a current, and by means of clockwork, moved, without touching the tube, along its length. The spiral was first placed on the bottom of the rod, and the current was passed until the bismuth melted, and the rod sank slightly into the big crystal. The bismuth could not flow out of the glass tube as it was held back by the barometric pressure. Clockwork was then set in motion and the spiral was gradually lifted, melting the bismuth higher up in the tube and letting it solidify at the bottom. In this way it was expected that a large crystal would grow in the glass tube with the required orientation.

The other method of drawing the crystal rod from the nozzle was used for the same experiment. In this case the small bismuth rod from which the crystal starts to grow was cut out of a big piece of crystal with its cleavage plane perpendicular to the length.

In neither case was a positive result obtained. What actually happened was that in the rod grown in this way a cleavage plane was perpendicular to the rod; this was not the perfect cleavage plane, but one of the remaining three planes of the pseudo-octahedron. This was easily established by looking at the plane under the microscope and also from the specific resistance measured along the rod.

From this experiment it is evident that there was a quite definite cause preventing the crystal from growing along its trigonal axis. Later we shall give what is probably the true explanation of these interesting results, but at first we attempted to explain them in the following way.

It is known that bismuth crystals should grow best in a direction along the perfect cleavage plane, as in this direction the crystal has the maximum heat conductivity and a closer packing of the atoms. As in the two methods of growing the crystals the thermal gradient was along the rod, and as the rod is growing along the gradient, the above-mentioned properties of the bismuth

* 'Z. f. Physik,' vol. 36, p. 759 (1926).

crystal could conceivably account for the failure to grow rods with the perfect cleavage plane perpendicular to the length. An attempt was therefore made to set up a temperature gradient more or less perpendicular to the axis of the rod. This was done in our first method by placing the platinum spiral on one side of the glass rod and a small copper plate on the other side. In the second method the perpendicular gradient was also established by means of a platinum spiral and a copper plate placed on opposite sides of the nozzle. In both cases, however, after making a great number of attempts, we were unable to obtain bismuth rods having a perfect cleavage plane perpendicular to the axis of the rod.

The results were exactly similar to the previous ones; if a rod was started from a perfect cleavage plane of a given crystal, the perfect cleavage plane would change in the grown rod to an imperfect one, and the angle between the perpendicular plane of the rod and the perfect cleavage plane would never be less than 30°. It was therefore clear that another factor was preventing the growth of the crystal with the perfect cleavage plane perpendicular to the axis, and the only possible assumption was that this factor was the strain set up in the crystal during its solidification. In the first method with the glass tube, the strain may be due to the fact that during its solidification bismuth increases in volume by about 3 per cent. This can easily be noted by the fact that in cases where the glass tube had thin walls it cracked during the process of the solidification of bismuth. In the second method, as the bismuth solidified only 3 to 4 mm. from the edges of the nozzle, the strain was longitudinal, due to the weight of the liquid part of the rod.

It was therefore decided to use a method by which no strain is set up during the process of the growth of the crystal. This was accomplished in the following manner. A copper plate *a* (fig. 1), about 25 cm. long, 1 cm. thick and 5 cm. broad, had one end fastened to a stand *b*, and on the other end was wound, for about 5 cm., a heater *c* of nichrome wire insulated with asbestos. When the current was sent through the wire the plate was fairly uniformly heated, having a small gradient of temperature from the heated end towards the supported end. A bismuth rod *d*, with a diameter of 1 to 2 mm., was placed on a glass or quartz plate in the middle part of the copper plate *a*. In order to prevent the cooling of the rod by accidental air currents, it was protected by glass plates which were placed at the sides and on the top of the rod, as is shown in cross section on the small drawing (A). A steady current of 2·5 amperes at 60 volts, from accumulators, was sent through the winding of the heater and the plate was heated to a temperature at which the bismuth began to melt, this requiring about 30 to 45 minutes. When liquid, as a result of surface tension and a small layer of oxide, the rod kept its circular shape very well and was scarcely deformed at all. When the rod was melted the cooler end was pulled out by touching

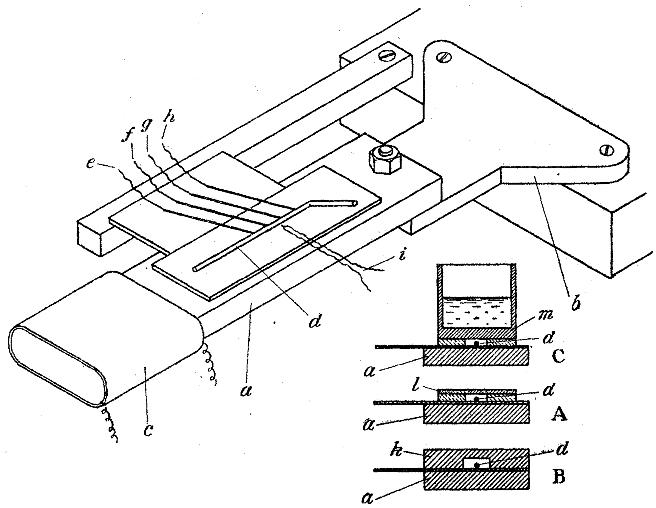

FIG. 1.

it with a small glass rod so as to make a small sharp appendix. (This appendix is necessary for the same reason as in Obreimow's method of growing crystals in glass tubes, where the end of the glass tube was drawn to a capillary, this making it much more certain that the crystal will commence growing in one spot and will produce a monocrystalline rod.) After this the current was very slowly diminished and the rod commenced to solidify from the sharp end of the appendix, crystal rods being obtained in this way. After a few experiments it was found that in such a way it was possible to obtain rods with the cleavage plane orientated at any angle relative to the axis of the rod. In order to make certain that the rod is monocrystalline the solidification time has to be not less than half an hour for a rod 7 to 10 cm. long.

To obtain the desired orientation of the cleavage plane in the crystal, the following method was adopted. A piece of rod, about 2 or 3 cm. in length (obtained by the method described above), was broken off from a long rod along the cleavage plane. A second bismuth rod was then melted on to the first rod in such a way that the cleavage plane formed the desired angle with the axis of the new rod. This was done in the following way. The first rod was fixed on to a glass plate by means of clamps and the second rod was then approached at the required angle, which was drawn on a paper placed under the glass plate. Then a small gas flame, about 3 mm. long, obtained from the end of a capillary glass tube, was brought to the point of contact between these two rods. The bismuth commenced to melt and the rods were slightly pressed to each other. This melting process was slightly tricky, as sometimes a layer of oxide may come in between the joint and spoil the experiment. In order to avoid this it is necessary to melt the rods with the middle part of the flame only, where there is an excess of gas, as this prevents oxidisation. The two rods, melted together in this way, were placed as before, on the glass plate on top of the copper plate, in such a manner that the already crystalline part of the rod was on the cooled end of the plate *a* as shown on fig. 1. The rods were protected from any air currents, except that the outside half of the already crystalline rod was uncovered. This increased the gradient of temperature in this part of the rod when the plate was heated.

The process of growing the crystal is very similar to the previous one. The copper plate is heated up and the bismuth is melted, but in this case it is done in such a way that only half of the already crystalline rod is melted.

It is worthy of mention that the heating of the rod must be done very carefully, as the gradient of temperature is very small, and it is very easy to melt the whole of the rod, including the part from which the crystal is growing. This difficulty can be avoided by fixing a thermo-couple near the rod and recording the temperature accurately, or by placing small pieces of bismuth on various parts of the copper plate near the rod, and touching them with glass rods to see when they have melted. Otherwise it is very difficult to see when the rod begins to liquefy. When the rod was slowly cooled it grew in a crystal in which the cleavage plane was orientated towards the axis of the rod at the necessary angle. In this way, crystals of any given orientation of the cleavage plane towards the axis of the rod could be obtained without difficulty, with an accuracy of 1° to 2°.

The bismuth used for our experiments must be of high chemical purity. We used bismuth obtained from Kahlbaum and from Hartmann and Braun. The latter firm supplied bismuth already drawn in wires of the required diameter of 1 mm. From Kahlbaum's bismuth, supplied in lump form, rods of the necessary diameter can easily be made. This can be done by pressing bismuth, in a warm condition, through a hole, or by filling a small thin walled glass tube with molten bismuth and dissolving the glass in hydrofluoric acid after solidification. From experiments in magnetic fields it was seen that Hartmann and Braun's bismuth has a higher degree of purity than that of Kahlbaum and is therefore more suitable for our experiments.

(2) *Specific Resistance of Bismuth Crystals perpendicular to the Cleavage Plane.*

It is well known that the specific resistance of bismuth crystals is greater perpendicular to the perfect cleavage plane than parallel to it, but the actual values of the specific resistance in either direction obtained by various authors differ considerably. This is particularly noticeable in the data for the specific resistance perpendicular to the cleavage plane. We find that the values range between $1 \cdot 6$ and $2 \cdot 06 \,.\, 10^{-4}$ (Matteucci, Everdingen, Voigt, Lownds, Borelius and Lindh). In this paragraph we shall describe the results of our measurement of the specific resistance in this direction, and we propose to give an explanation of the discrepancies observed in previous investigations.

The measurement of the specific resistance of crystal rods, grown by our method with a definite orientation of the axis, was carried out by measuring the resistance of a rod 2 or 3 cm. long by a potentiometer method. Two readings were taken with the current in opposite directions through the rod so as to exclude the thermo-electric effect, and the mean value taken. The cross section was determined from the weight and the length of the rod by taking the specific gravity of bismuth to be 9·80.* In our measurements we did not aim at an accuracy greater than 1 per cent.

To our surprise we found that the specific resistance perpendicular to the cleavage plane varied with different specimens of crystal rods. The lowest obtained was $1 \cdot 39 \,.\, 10^{-4}$ and the highest $1 \cdot 6 \,.\, 10^{-4}$. The fact that crystal rods grown in approximately the same way, and from the same material, should show such a difference in specific resistance was remarkable.

We found some hints as to the explanation of this phenomenon in the work of Borelius and Lindh.† These authors observed that a specimen of bismuth crystal, cut out from a large crystal, perpendicular to the cleavage plane, diminished its resistance when placed in the holder of their apparatus, where the compression was mainly axial.

We therefore decided to take different samples of our crystals and study the change of the specific resistance when compressed. The arrangement used is shown on fig. 2.

The bismuth rod *a*, which is grown with its cleavage plane perpendicular to its length, is placed vertically and rests on a support *b* which is fixed to a vertical ebonite plate *c*. This plate is fastened to the table. The bottom end of the

* We took this value from our tables and also verified it by direct measurement.

† 'Ann. der Physik,' vol. 51, p. 613 (1916).

bismuth rod *a* rests on a platform *d*. This platform, when lifted, will compress the crystal. To ensure a parallel motion of the platform it has a guide, made of

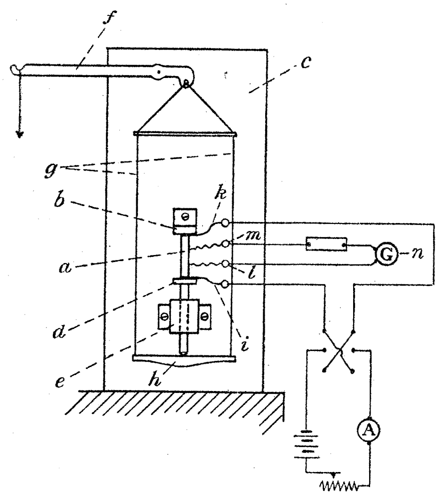

Fig. 2.

a small rod, which slides through a cylindrical hole in the brass piece *e*, fixed to the plate *c*. The compression is transmitted to the crystal by means of an arrangement shown on the same figure, and which consists of a lever *f*, two strings *g* and a small horizontal plate *h*. When the lever is loaded the crystal is compressed. This little apparatus has to be rather carefully made, and the rod accurately adjusted, as it is very easy to bend the crystal during the compression and then the experiment is spoilt. It is also necessary for the diameter of the bismuth specimen to be correctly proportioned to its length. We find that ratio of the diameter to the length should be about 1 : 6, to prevent it from bending.

The resistance was obtained from the potential drop in the rod when a current was passed. The current leads consisted of two fine copper strips, *i* and *k*, soldered by means of a soft solder (Wood's metal or Newton's metal) to the ends of the bismuth rod *a*. The two potential leads, *l* and *m*, are of fine silver wire ($d = 0 \cdot 1$ mm.), and are welded to the rod by means of a spark from a condenser. This is done by a well-known method. The bismuth rod is connected to one end of a condenser (50 microfarads) through a small resistance, and the silver wire to the other end. The condenser is charged to 20 to 30 volts, and it is then sufficient to touch the bismuth rod at the place where we wish to make the joint with the end of the wire. A small spark occurs and the wire is well joined. A good point joint is obtained in this way without spoiling the crystal. The potential drop was measured by a high resistance (about 500 ohms) galvanometer *n*. To exclude the influence of the thermal e.m.fs. two readings are necessary with opposite directions of the power current.

On fig. 3 the experimental results are shown for several rods which have different initial resistances. The abscissæ represent the load in grams per

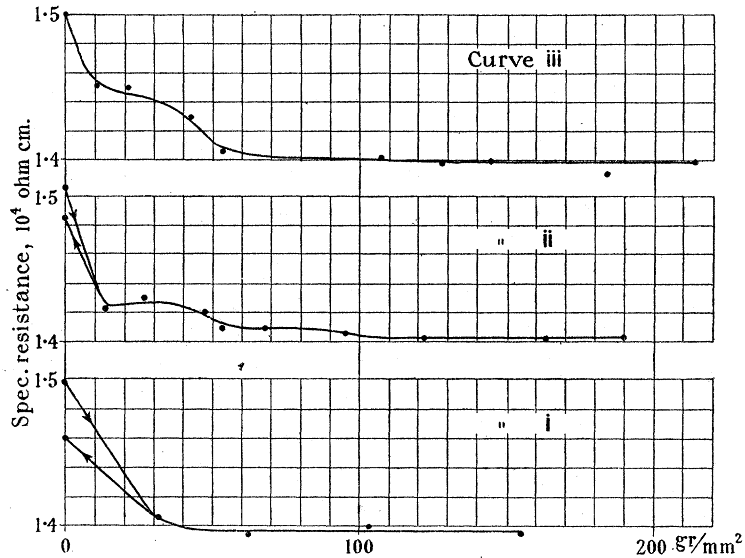

FIG. 3.

square millimetre, and the ordinates the specific resistance. For clearness the three curves are shown one above the other. The bottom curve (i) relates to a compression of a rod made from Hartmann and Braun bismuth and grown in the way described in the previous paragraph. The rod of curve (ii) is made in a similar way, but of bismuth from Kahlbaum. Curve (iii) refers to a rod made from Kahlbaum bismuth, but cut out of a large crystal grown in a crucible.

It is seen that the resistance of various rods in a compressed state approaches $1 \cdot 39$ to $1 \cdot 4 . 10^{-4}$, within the limits of experimental error. After the compression reached the value of about 50 grams per square millimetre the resistance of the rods did not change appreciably.

These experiments suggest that bismuth rods have " cracks " of appreciable resistance along their cleavage plane, and that by means of the compression these cracks close and thus diminish the resistance. The limiting value of the specific resistance, $1 \cdot 39 . 10^{-4}$, is reached when all the cracks have closed. This view is strongly supported by the general character of the change of the resistance of bismuth as it approaches the limiting value under compression. The diminution of the resistance for different specimens occurs in various ways and sometimes occurs in jumps, as is seen on fig. 3. When the load is taken off the resistance increases again, but there is generally a tendency for the crystal to retain the smaller resistance, and the final resistance of bismuth, after unloading, is smaller than the initial one (see curves 1 and 2). A slight pull on the crystal brings the resistance to the initial value, and sometimes makes it higher.

From this experiment we came to the conclusion that the true specific resistance of the bismuth crystal perpendicular to the cleavage plane is $1 \cdot 39 . 10^{-4}$, and the higher value observed in different specimens, both by myself and other authors, is due to the cracks which develop in bismuth, not only during the process of cutting out the rod, but during the growth of the crystal. This development of cracks during the formation of a crystal is a very interesting phenomenon indeed, and we shall discuss the question later in more detail.

At this stage, mention should be made of the recent work of Bridgman,* involving a very careful determination of the specific resistance of a large number of monocrystalline bismuth rods grown in glass tubes. As already mentioned, by this method of growing crystals, Bridgman could only obtain rods having angles ranging from 90° to 45° between the trigonal axis and the axis of the rod. He found that the specific resistance varied for the same orientation of the cleavage plane in the rod. He chose three rods having the smallest resistance, with the perfect cleavage planes inclined to the axis of the rod at angles of 43°, 27° and 4°, and by extrapolation found the specific resistance for a rod in which the cleavage plane is perpendicular to the axis of the rod, obtaining the value of $1 \cdot 38 . 10^{-4}$ which, taking into account the manner in which it was obtained, agrees very well with that found in our experiments.

(3) *The Specific Resistance of Bismuth Crystals parallel to the Perfect Cleavage Plane.*

The results obtained by different authors for the specific resistance of bismuth crystals parallel to the perfect cleavage plane vary to a much less extent than in the case of the specific resistance perpendicular to the cleavage plane. At room temperature the values given range between $1 \cdot 09 . 10^{-4}$ and $1 \cdot 14 . 10^{-4}$

* 'Proc. Amer. Acad. Arts Sci.,' vol. 60, p. 350 (1925).

For our crystals the measurements for a crystal grown on the copper plate (shown in the apparatus given in fig. 1) gave values ranging between 1·07 and $1 \cdot 14 . 10^{-4}$, this being even a larger variation than that obtained in the results of previous investigators. In this case it is hardly possible to attribute the variation to cracks. No compression experiments are possible with bismuth rods grown in this direction, as they are too soft and bend very easily. The reason for this variation of the specific resistance is probably to be found, as will be seen from later experiments, in the fact that the trigonal axis changes its direction in certain very small parts of the bismuth crystal. This explanation leads us to believe that the lower value is the correct one, and this also does not differ greatly from the value given by Bridgman* ($1 \cdot 09 . 10^{-4}$).

(4) *The Influence of Impurities and of the Temperature Gradient on the Formation of Bismuth Crystals.*

The variation in the specific resistance in different directions of the bismuth crystal, discussed in sections 2 and 3, is ascribed to the imperfection of the crystal, which is due to cracks formed along the perfect cleavage plane or to local variations of the crystallographic axis. Since in our method of growing the crystal all outside strains are eliminated and the specific resistance is measured without any strains being produced by the process of cutting it from a large lump of crystal, or removing it from a glass tube, as in previous investigations, we must conclude that this imperfection occurs during the process of the formation of the crystal.

In this case the imperfection may be due to two sources; first, the way in which the crystal is cooled, and secondly, the chemical purity of the bismuth. The study of these two factors will be described at length in this section, and it will be seen that in this way some light is thrown on the problem of the source of the cracks. In the first place the effect of the influence of the temperature gradient on the growth of the crystal is discussed.

In order to vary the temperature gradient perpendicular to the axis of the bismuth rod, we used the arrangements shown on fig. 1 by the small drawings A, B and C. These drawings represent different arrangements used for covering the bismuth rod *d* which is resting on the copper plate *a*. In the arrangement shown on fig. 1 B, the rod is covered by means of a solid copper plate with a channel. It is clear that here the temperature gradient perpendicular to the rod is very small. If a glass plate *l*, fig. 1 A, is used, instead of a copper plate, the temperature gradient is increased, since the rod is cooled more rapidly from

* *Loc. cit.*

the top. Finally, if in the place of a glass plate we have a small copper vessel containing water *m*, fig. 1 C, the temperature gradient is still more increased.

In order to alter the gradient along the crystal rod we varied the cross section of the copper plate *a*. It was found, however, that such a method did not give a sufficient increase of the temperature gradient along the rod, and therefore an arrangement, shown on fig. 4, was used, whereby it was possible

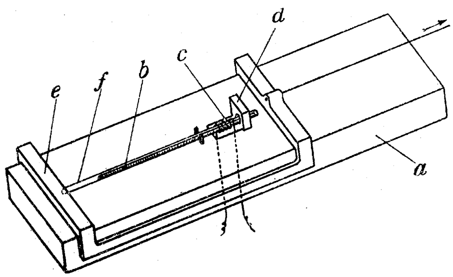

FIG. 4.

to obtain a very large temperature gradient along the rod. This apparatus consisted of a solid copper plate *a* having a square opening in the middle. Above this opening was placed a small spiral *c* made of platinum wire. Through this spiral a pyrex or quartz tube *f* can be moved by means of a frame *e* which is sliding on the copper plate *a*. The tube *f* is resting on the copper plate *a*, and is directed in its motion by passing through a hole made in a small copper appendix *d* which is fixed to the copper plate *a*. The bismuth rod *b* is resting quite freely in the tube *f*. The crystal is grown in this apparatus in the following way.

A current is passed through the spiral, which heats up the bismuth rod locally to a temperature which is sufficient to melt the bismuth. By means of clockwork the tube is pulled very slowly and uniformly through the platinum spiral and fresh portions of the bismuth rod enter the spiral and are melted. On the other hand the bismuth which is already melted is cooled and it then enters the hole in the copper appendix *d*. In this way the whole rod is gradually turned into a crystal. It is obvious that by adjusting the distance between the copper appendix *d* and the spiral *c* any very large temperature gradient may be obtained along the rod. By means of an arrangement (not shown in fig. 4) the spiral and the heated part of the tube were protected from air currents.

To obtain rods with a given orientation of the cleavage plane from crystals grown with this apparatus, the following method was adopted. A short rod with the required orientation of the cleavage plane was prepared on the copper plate of the old apparatus shown on fig. 1, in the way already described in section 2. This rod was then placed in the tube in such a way that the join was slightly to the left of the spiral, and the already crystalline portion passed through the hole in the copper appendix *d* in the cool region. It is therefore evident that in this way all the rod will be turned into a crystal having the same orientation of the crystal axis as in the appendix.

Finally, in order to have a very small temperature gradient in all directions, the simple arrangement in fig. 5 was used. This consists of a solid copper block, in the form of a cylinder *a*, with a small central bore *f*. This cylinder was warmed by means of an electric heater *b*. In order to have the cylinder at a very even temperature it was wrapped up in asbestos. The bismuth rod *d* was freely placed in the glass tube *c* and inserted in the hole *f* of the cylinder, as shown on fig. 5. In all this apparatus it was found that the current had to be supplied by accumulators in order to obtain the requisite steadiness.

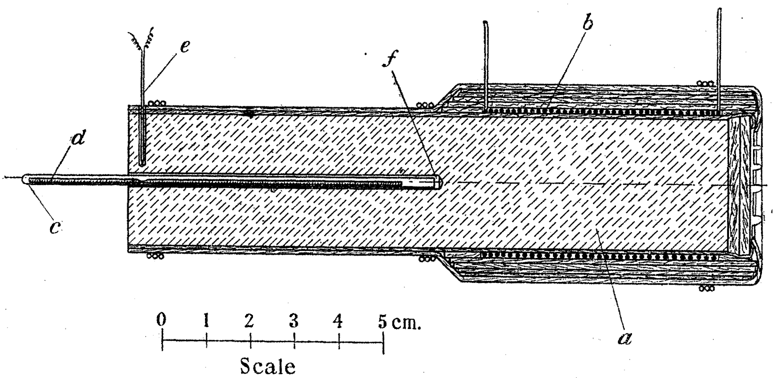

FIG. 5.

To obtain the required orientation of the cleavage plane, the bismuth rod was prepared in exactly the same way as in the previous case. The method of growing the crystal was very simple. The cylinder *a* was heated up to a temperature such that the bismuth rod was melted a little farther from the place where it was joined to the crystalline rod and was then very slowly cooled down by reducing the current of the heater. The moment at which the temperature was sufficient to melt the bismuth was recorded by the thermocouple *e*, which was placed just above the point where the two rods joined. It is worth mentioning that in this method, as in the previous ones, for obtaining good crystals, it is advisable to make one or two reductions in section on the rod (*see* fig. 5). The rod is then certain to be monocrystalline.

In growing the various bismuth crystals by these three methods, and in varying the orientation of the perfect cleavage plane relative to the tempera ture gradient, the following phenomena were observed.

It is known that* the flexibility of monocrystalline bismuth rods varies with the orientation of the perfect cleavage plane relative to the axis of the rod. When the perfect cleavage plane is parallel to the axis of the rod, the rod is fairly flexible, but the flexibility diminishes very rapidly as the cleavage plane approaches a perpendicular orientation to the axis of the rod. Rods in which the cleavage plane is perpendicular to the axis are stated to be very brittle, but in our methods of growing crystals we observed that the flexibility of rods with the same inclination of the cleavage plane, grown with a different temperature gradient, varies greatly. In some instances it was possible to obtain very flexible bismuth rods in which the perfect cleavage plane was only a few degrees from being perpendicular to the axis of the rods. For example, one rod with its perfect cleavage plane only 15° out of the perpendicular position could be bent in a radius of curvature of 3 mm. as easily as a rod made of tin. Another, with the same orientation of the cleavage plane, was so brittle that, when falling on to a table from a height of a few centimetres, it broke into many small pieces along its cleavage plane. The difference between the flexible and the brittle bismuth can also be seen from the following facts. During bending, the less flexible rods, if held close to the ear, emitted cracking sounds, whereas others, being more flexible, did not. It was easily established that the more flexible the rod the less cracking sounds were produced on bending.

It was observed that there is a close relation between the flexibility of the rod and its specific resistance. All the flexible rods gave the same specific resistance, and this resistance corresponded to the two lowest values given for the crystal. It was a curious fact that even after a flexible rod had been considerably bent if no cracking sound was heard the specific resistance increased but slightly. If, however, cracking sounds were heard the resistance increased very rapidly. This suggests that these sounds are probably caused by the development of the cracks and imperfections already existing in the lattice of the bismuth crystals. As regards cleaving the rod with a knife, the softer specimens at room temperature would not cleave at all. The knife would cut almost through it before it broke. The brittle specimens were somewhat better, but frequently a small piece of the rod would be cut through without showing a cleavage plane at all.

We shall discuss later the origin of this difference in flexibility of bismuth rods, but will first describe the effect of the temperature gradient and impurities

* See Georgieff & Schmidt, *loc. cit.*

on the flexibility of bismuth rods. This was at first difficult to trace, but after a large number of experiments we came to the following conclusion.

To obtain the most flexible bismuth rod during the formation of the crystal, a very sharp temperature gradient perpendicular to the perfect cleavage plane is required. We will first consider the case in which the growing crystal has its cleavage plane perpendicular to the axis of the rod. If we grow such crystals in the apparatus shown on fig. 4, with the platinum spiral, we obtain fairly flexible crystals, and it is evident that in this case the gradient will be along the rod and perpendicular to the cleavage plane. The specific resistance of these crystals was always the same and was equal to $1 \cdot 38$ to $1 \cdot 39 . 10^{-4}$. This resistance corresponded exactly to the one observed in the rods when they were compressed in the way described in section 2. This means that the rod has no cracks. The very flexible crystals which, as mentioned previously, could be bent to a radius of 3 mm., were obtained by this method, but only occasionally. In none of these flexible rods was the cleavage plane exactly perpendicular to the axis of the rod, but in the case just mentioned we obtained a crystal in which it was only 15° from perpendicularity. The most probable reason for this is that in order to obtain the most flexible crystals it is necessary to have the temperature gradient very closely perpendicular to the perfect cleavage plane. In the apparatus shown on fig. 4 this condition was only approximately fulfilled, as the cooling round the rod was not quite symmetrical, and it was only in particularly "lucky" experiments that the condition of perpendicularity was fulfilled.

When crystals were grown with this orientation on a copper plate (fig. 1) with a transverse temperature gradient, they were always brittle and their specific resistance varied and was always higher than $1 \cdot 43 . 10^{-4}$. When compressed, this resistance was reduced to the normal value of $1 \cdot 38 . 10^{-4}$, as was mentioned in section 2.

In growing crystals under the most uniform temperature conditions, as produced with the copper cylinder, in the apparatus shown on fig. 5, we obtained the most brittle variety with its cleavage plane perpendicular to its length. Some specimens were accidentally dropped on to the table from a height of a few centimetres and they broke into many small pieces, which were only 2 or 3 mm. long. These small pieces were not very brittle and it was even possible to bend some of them slightly. The specific resistance of these crystals, when carefully handled, would give the normal value of $1 \cdot 38 . 10^{-4}$, but a slight strain would at once increase this resistance.

If the crystal was broken by bending, it was observed that the cleavage plane in the hard specimens was very perfect and gave a perfect mirror-like reflection. In flexible specimens the cleavage plane was slightly uneven, but this unevenness of the surface was not due to the crystal itself, but was produced during the breaking up, as it depended very much on the way in which the crystal was handled. For instance, if the crystal was cooled by liquid air, before being broken, the cleaved plane was quite good. (The X-ray analysis described later in the paper also confirms the statement that a change of the cleavage plane is produced by bending the crystal, as the lattice of the flexible crystal shows no traces of being bent.)

When growing crystals with the cleavage plane parallel to the axis of the rod, we were able to obtain soft flexible rods only when they were grown on a plate (fig. 1) with a rather strong vertical gradient, and when the cleavage plane was almost parallel to the copper plate. The flexible crystals had the normal resistance of 1·07 to 1·08, and in some cases these were so flexible that if one end of the rod was raised it began to bend under its own weight. They could be bent considerably without the least cracking noise being heard. It was found, however, that it was impossible to obtain an entirely flexible rod with its cleavage plane parallel to the length, just as previously we could not obtain one with its plane perpendicular to the length. In the best flexible specimens the angle was 20° out of parallelism with the axis of the rod. The explanation is probably similar to that given for the previous case.

When in the same apparatus the crystal was grown with its cleavage plane perpendicular to the copper plate, the rod was never flexible and the specific resistance lay between $1\cdot10$ and $1\cdot14 \,.\, 10^{-4}$. Similarly, in growing this type of rod in the apparatus with the platinum spiral, shown on fig. 4, it was found that it was never flexible, and the resistance varied in different cases from 1·10 to $1\cdot12 \,.\, 10^{-4}$.

Finally, when the rod was grown in the apparatus, shown in fig. 5, with the most uniform temperature, it always had the smallest resistance, 1·07 to $1\cdot08 \,.\, 10^{-4}$, but was invariably not flexible.

The speed of growth of the crystals in all these cases appears to affect the crystalline character of the rod very little, provided that it does not exceed a certain limiting value. It was also noticed that the speed with which these crystals are grown, with the perpendicular orientation of the perfect cleavage plane, must be less than for the rod with the perfect cleavage plane parallel to its axis. In the apparatus of fig. 4, for the cleavage plane with perpendicular orientation, this speed must be no more than 1 mm. per minute. For the other orientations of the cleavage plane, it may be 7 mm. per minute or even greater.

If the speed is higher, the perfect cleavage plane changes its orientation, or the rod is not monocrystalline. In growing crystals on the copper plate of the apparatus of fig. 1, the speed can be much higher, as in this case the crystal is now growing along the rod, but in a transverse direction. The surface on which the atoms arrange themselves in a lattice is larger and consequently they arrange themselves much more quickly.

The second question we studied was the influence of the impurities on the growth of the crystal. In the first instance we made certain that the variation in the flexibility of the crystal was not caused by the slight variation in the amount of impurity which probably existed in different specimens, by taking a bismuth crystal rod which was flexible, and regrowing half of it at a different temperature gradient. It was then possible to have the first half of the rod flexible and the newly grown part brittle.

In general, we found that more flexible rods were produced with greater ease from the less pure bismuth. We judge the purity of the bismuth from the specific resistance and from some data on the measurements of the change of resistance in a magnetic field, which will be described later.

We also experimented in order to determine the influence of the gases which are always found in the metals. For this purpose we took a rod of bismuth and placed it in an evacuated quartz tube which was made red hot. We kept the bismuth at this temperature for about 1 hour, and pumped the gas out of the tube during the whole of this time. During this process, precautions were taken to prevent the bismuth rod from being broken into drops, by placing round it properly shaped quartz rods. After cooling, the bismuth rod was placed in the apparatus, fig. 4, with the platinum spiral, modifications being made in the apparatus by which it was possible to keep the tube with the rod immobile, and move the spiral. This allowed us to keep the tube evacuated while the crystal was grown in vacuum. No appreciable difference in the flexibility and specific resistance was observed between rods grown in this way and those grown by the usual method. This suggests that the dissolved gases have no great influence on the development of the cracks. From all these experiments we conclude that the imperfections in the lattice are primarily due to the direction of the temperature gradient relative to the orientation of the crystal lattice in the place where the crystal is growing.

(5) *The Origin of the Cracks.*

It seemed important to trace the moment at which the cracks appear during the growth of the crystal, as this would indicate their origin. We expected to find the moment at which the cracks appeared indicated by a sudden change in the resistance of the bismuth during the process of growth. For this purpose we measured the resistance of the crystal during the process of its growth, using the arrangement shown on fig. 1. Four leads, *e*, *f*, *g* and *h*, were soldered to the bismuth rod. The two middle ones, *f* and *g*, were the potential leads, and were placed 10 mm. apart. The two end ones, *e* and *h*, were the power leads. The experiment consisted of melting and solidifying the rod by the method described in section 1, and growing the crystals with a definite orientation of the cleavage plane. The resistance of the bismuth rod during crystallisation was measured by the same method as that used in the compression experiment, described in section 2, only in this case large thermal e.m.fs. occurred and three successive readings were necessary for each given point with three successively changed directions of the current, the mean value being taken in the appropriate way. These experiments looked very simple, but for a long time they were quite unsuccessful, as it was very difficult to find material to form the leads to the rod. We tried to use silver and platinum wire, but these formed an alloy with the bismuth, and during the process of solidification they broke off. The problem was solved by making the leads of fine bismuth wire, manufactured by Hartmann and Braun, of 0·2 mm. in diameter, and welding them by a small flame to the rod. The wires were welded at an acute angle to the bismuth rod (as shown on fig. 1) in such a way that they could not solidify before the place at which they joined with the rod. In order to measure the temperature a constantan-iron thermo-couple *a*, fig. 1, made of fine wires, was placed between the potential leads at a distance of ½ mm. from the bismuth rod. The e.m.f. of the thermo-couple was measured by means of a potentiometer.

Curve i obtained in this experiment, and shown on fig. 6, relates to a bismuth rod which is solidified, and has its cleavage plane perpendicular to its length. The ordinates represent the resistance of the bismuth relative to the resistance in the melted state, and the abscissæ the temperature in arbitrary units. We see from this curve that bismuth at the point about 13·7, where it begins to solidify, increases its resistance practically at once by 2·64 times. The resistance then gradually commences to diminish and reaches at 16° a value of 1·05 times the resistance in the liquid state.

We took such curves, cooling the bismuth with various temperature gradients across the rods by the different arrangements, as already described and shown on fig. 1, by A, B and C, but in each case we obtained practically the same shaped smooth curve without any sharp bends. There was only a very slight difference in the shape of the maximum which was sometimes flat or sharp, but this was easily accounted for by the fact that the bismuth between the

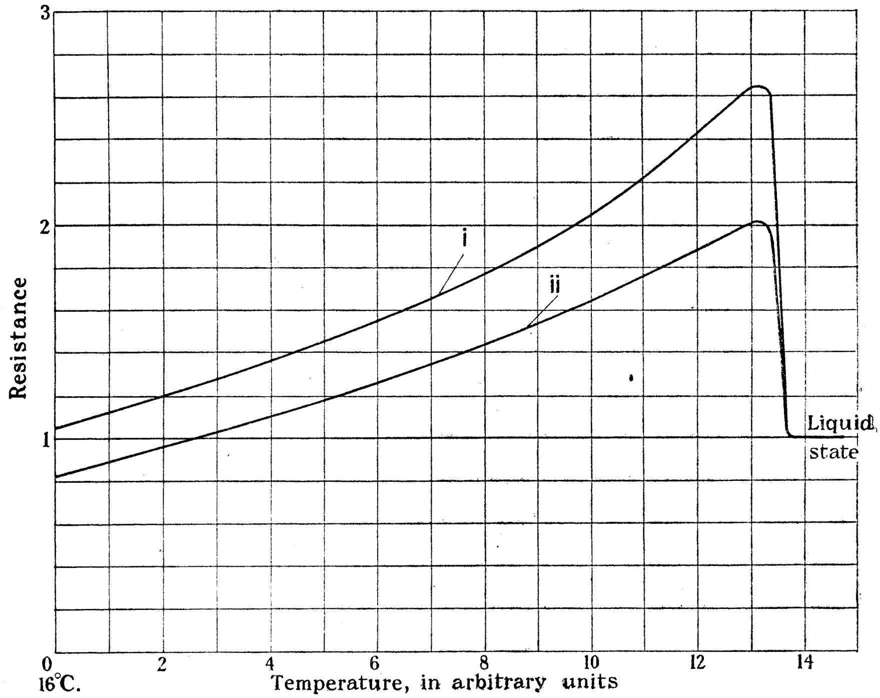

FIG. 6.

potential contacts does not solidify at once. The final resistance of bismuth crystals relative to that of the liquid state varied from 1·04 to 1·08, differing amongst themselves by about 4 per cent. In each experiment a piece of the rod was cut off from the end after the potential contact g and examined for flexibility and specific resistance.*

The crystal rod of curve i had a specific resistance of $1{\cdot}45 . 10^{-4}$ and the cleavage plane was inclined at 84° to the axis of the rod.

For other rods the specific resistance was found to vary between 1·43 and $1{\cdot}51 . 10^{-4}$, This variation is larger than was to be expected from the measurements during the solidification, where, as already stated, the variation was only 4 per cent. This is probably due to the fact that in handling the rod during measurement, some of the cracks widen.

* In order not to destroy the rather fragile contacts of the bismuth rod with the small wires, the cutting up was done by melting the bismuth rod at one point with a small flame.

In the case of the crystal grown with its cleavage plane parallel to the axis, we obtained curves which were also very smooth. One of these, curve ii, is shown in fig. 6. The maximum resistance in this case was $2 \cdot 01$ times that of the liquid state, and the final resistance at room temperature (16°) was $0 \cdot 825$. The specific resistance of the sample cut off was $1 \cdot 14 . 10^{-4}$ and the cleavage plane made an angle of 1° with the axis of the rod.

The smoothness of the curves and the absence of any sharp bends, together with the fact that the resistance increases with decreasing temperature, only at the moment when the crystal is solidified, indicates that the development of the cracks probably occurs almost at the moment when the bismuth passes from the liquid to the solid state.

It is interesting to note that if we take the specific resistance of liquid bismuth to be $1 \cdot 28 . 10^{-4}$, the resistance of the bismuth perpendicular to its cleavage plane would be, from these curves $1 \cdot 28 \times 1 \cdot 05 = 1 \cdot 34 . 10^{-4}$, and the specific resistance for rods with the cleavage plane parallel to the axis of the rod would be $1 \cdot 28 . 10^{-4}\, 0 \cdot 825 = 1 \cdot 055$. In both cases the values thus obtained are smaller than those afterwards measured in the samples cut off. This can be partly explained by the fact that the volume of the rod changes when the rod is cooled, but the difference seems to be rather too large to be explained entirely in this way. It is possibly due to an error in the determination of the specific resistance of liquid bismuth. This datum was taken from tables and represents the results of only one experiment made many years ago.

(6) *The Character of the Imperfection of the Bismuth Crystals.*

From the previous discussion it is seen that the bismuth crystals which we have grown were not perfect, and that the imperfection in the lattice is probably characterised either by cracks which develop along the perfect cleavage plane or by local changing of the direction of the axis in the crystal. It is important to obtain a more definite idea as to the character of these imperfections and the source from which they arise since, as will be seen from the latter part of this paper, crystals obtained by various methods of growth and which differ in flexibility and specific resistance, change their resistance differently in a magnetic field.

We first of all gave our attention to the character of the "cracks," the word being used simply in connection with the fact that the crystal breaks very easily along the cleavage plane ; by the word crack we do not necessarily mean that a slot exists in the crystal. Probably the most correct picture of a crack is that in some layers in the crystal lattice parallel to the perfect cleavage plane the atoms are disturbed from their symmetrical positions and the cohesive forces between two successive layers are reduced to a small value. When the crystal is strained these layers easily break and then real slots are formed. This view is justified by the fact that if real cracks exist in the crystal, then if the crystal is compressed perpendicular to the cleavage plane and the compressibility is measured, we ought to be able to observe a larger compressibility just before the crack closes.

I am indebted to Dr. Webster for making some experiments in this line, but he was unable to trace any larger compressibility of our crystal at the moment when it begins to be loaded.

Evidence for the existence of cracks may, as pointed out to me by Prof. G. I. Taylor, be derived from the observation of W. Spring,* that cast bismuth has a smaller density than drawn bismuth. This can be accounted for if we suppose that during solidification the multitude of individual crystals formed, having different coefficients of expansion along different axes, set up strains on cooling and open the cracks. When, however, the bismuth is drawn into a wire the strong compression force closes the cracks again. Further, cast bismuth, when placed in an electrolyte against drawn bismuth, becomes an anode. This indicates that cast bismuth has a larger energy than drawn bismuth. Prof. Taylor suggested to me that this may be due to the fact that in cast bismuth where many cracks exist there is a larger surface energy, which accounts for this excess of energy relative to drawn bismuth.

More direct evidence of the nature of the lattice imperfections was obtained by X-ray analysis.

My thanks are due to Dr. Alexander Muller, of the Davy Faraday Laboratory, for being kind enough to take X-ray photographs of various specimens of bismuth rods which had been grown by different methods, and the result of his investigation has thrown much light upon the character of the imperfections of the lattice.

First of all it was found that the crystals grown by our method are coated with a surface layer of very small crystals which are distributed at random. After etching the rod, however, and removing in all 0·1 mm. of its diameter, these small crystals disappeared and no trouble was experienced in the study of the crystal lattice. All the data given relate to such etched crystals.

Bismuth rods grown in a uniform temperature condition, as obtained in the apparatus shown on fig. 5, give very good X-ray reflections. This indicates

* 'Bull Acad. R. Belg.,' p. 1066 (1903): see also Desch, "Metallography," p. 287 (1922).

that each rod consists of a quite good crystal with a perfect lattice, so far as can be judged from an X-ray photograph. Since we know that these rods are brittle and that cracks exist, we have to conclude that these cracks are rather widely spaced in the crystal and that the crystals between two successive cracks are perfect and have the same orientation. This view is also confirmed by the fact, already mentioned, that after breaking the crystal into small pieces, the separate pieces do not appear to be very brittle. On the other hand crystals grown with their cleavage planes perpendicular to the axis of the rod (made with the apparatus with the spiral, shown on fig. 4) and which we found to be the most flexible, showed on the X-ray photographs not only well-defined spots of reflection from the main planes, but also faint rings which have to be attributed to very small crystals differently orientated and more or less scattered in between the main lattice.

Thus the difference between a flexible crystal and a very brittle one is due to the fact that in a brittle crystal the imperfections of the lattice are placed in successive layers parallel to the perfect cleavage plane, with sometimes a quite considerable distance between them, whereas in the most flexible crystals the imperfection of the lattice occurs in localised points scattered all over the crystal. This accounts for their flexibility as they have no preferable direction for cleavage. While both crystals are imperfect, in the case of the brittle crystal the imperfections are more regularly distributed and are of a rather macroscopic character.

From this we may conclude that an ideal crystal would be perfectly flexible and would have no well-defined cleavage plane.

With crystals grown on the copper plate (fig. 1) with the transverse temperature gradient and the perfect cleavage plane perpendicular to the axis of the rod, we have an intermediate case. The X-ray photograph shows rings and the crystal, as already stated, is brittle. Comparing crystals grown by our method with a crystal grown in a glass tube in the ordinary way, we find from X-ray photographs that these crystals have also enclosures with crystals distributed at random which make a definite ring on the X-ray photograph. As these rings are broken into small definite spots, we can infer that the enclosed imperfections are larger than in crystals grown by our method, indicating that our method of growing crystals with no outside strains gives a more perfect crystal lattice.

Finally, the X-ray analysis of a crystal made of impure bismuth and grown on a plate, as in apparatus 1, differs from that for a similar crystal of pure bismuth in having a more perfect lattice and showing very few traces of irregular enclosures. This confirms our observation that impure bismuth easily forms flexible crystals.

(7) *Discussion on the Source of the Cracks.*

From these experiments we may draw some conclusions as to the probable origin of the cracks.

First, since X-ray data, as well as the observations on flexibility, indicate that impure bismuth forms crystals with a good lattice more easily, we have to conclude that the imperfections in the lattice of bismuth crystals are not due to the presence of foreign atoms during the crystallisation. On the other hand we saw that the formation of the imperfections in the crystal lattice is very closely connected with the way in which the crystal is cooled and from the experiment, described in section 5, on the change of resistance during solidification, we have seen that the cracks probably occur at the moment when the crystal is solidified. We therefore have to conclude that the spoiling of the lattice is closely related to peculiarities in the crystallisation of bismuth.

I think it would be difficult to find an explanation which accords so well with the facts as the following.

We suppose that when solidified below the melting point bismuth at first forms a crystal having one crystalline modification, which, at a very slightly lower temperature, is transformed into a second crystalline modification, which we know to be the usual modification for bismuth. Since this transformation takes place when the bismuth is in a solid state and must be accompanied by changes in shape, stresses are set up in the crystal lattice which account for the spoiling of the lattice.

When the crystal is grown in a very uniform temperature (as in apparatus 5), the first modification is changed into the second one in larger sections, and between the successive sections we have an imperfect layer of the lattice which, under strain, may develop into a crack, but in between the two cracks the crystal is perfect, as has been shown already by X-ray analysis and as will be confirmed by later experiments in a magnetic field. The small specific resistance for these crystals indicates that the number of the cracks is not large.

In the case where the crystal is a flexible one and is grown with a very sharp temperature gradient perpendicular to the cleavage plane, the transition from one solid modification to the other takes place in smaller layers and in a somewhat irregular way. There will in consequence be many imperfections of the lattice scattered all over the crystal.

The view that during the solidification of bismuth, strains are set up in the crystal was confirmed by the following observation. A crystal rod was placed on a warm copper plate and a white hot platinum strip, heated by current, was placed just above it. In this way the bismuth was melted perpendicularly to the length of the rod, and then by a slow motion of the spiral along the rod, gradually solidified. In this case the cleavage plane was perpendicular to the axis of the rod. When the crystal commenced to grow it was very interesting to notice that the rod began to bend and the ends started to lift from the plate. This bending can only be accounted for by a strain set up in the crystal during the solidification. The crystal obtained in this way was extremely brittle.

If our hypothesis as to the explanation of the appearance of the cracks is correct, we have to admit a change in the shape of a bismuth crystal when it is changing from one modification to the other. We tried to confirm this by heating a bismuth rod to the melting point and observing whether a sudden change in length occurs near the melting point. Accurate experiments are difficult but indications were obtained that in some of the crystal rods there occurred a very small contraction in the length before the melting point, of the order of 0·06 per cent.

Our hypothesis is supported by some old experiments of Curie,* which confirm the existence of a second modification of bismuth slightly below the melting point. Studying the diamagnetic properties of bismuth at a temperature very close to the melting point, Curie noticed that bismuth loses its strong diamagnetic properties practically at once at a temperature slightly lower than that of the melting point, when the bismuth is still solid. This suggests that bismuth may exist in a solid state without having its strong diamagnetic properties, and this would correspond to the second modification of bismuth which is necessary for our hypothesis. From the experiments of Curie and the experiments on the change of length of bismuth during solidification, we conclude that the transition from the first modification to the second occurs at a temperature very near to the melting point, and probably only a few degrees below.

The existence of the second modification is also suggested by a phenomenon observed by Bridgman† in his pressure experiments. Usually solid bismuth, unlike other conductors, shows a positive coefficient of change in resistance when submitted to a uniform pressure. Below the freezing point, however, Bridgman observed a negative coefficient. He suggests that this change of sign is produced by strains set up in bismuth, as it is solidified in a small tube,

* 'J. de Physique,' vol. 4, p. 206 (1895), footnote.

† 'Proc. Amer. Acad. Arts Sci.,' vol. 56, p. 115 (1921).

but it is also possible to account for this difference in sign by the existence of the second modification, which is more like other metals.

In this hypothesis the influence of the impurities which help to make the crystal flexible and more perfect may probably be accounted for by the fact that the impurities make the first modification of bismuth more unstable, and the transition takes place more gradually.

The following tentative suggestion may be made to account for the two crystal modifications. It is well known that an element of the rhombohedral bismuth crystal lattice can easily be obtained by a slight deformation of a cubic cell when it is stretched in the direction of one of the four main diagonals. On this view the first modification is a cubic one which is transformed into the second modification by this type of deformation.

The physical differences between these two crystal modifications can be explained by the idea suggested by Ehrenfest* that in the ordinary bismuth modification the strong diamagnetic properties can only be accounted for by taking the orbits of electrons inside the crystal to be of such a size that they include two centres of the lattice. In this case we have to suppose that in the first " cubic " modification the electrons move in rather smaller orbits, including only one nucleus, and that the crystal shows no strong diamagnetism, as indicated by Curie's experiments.† When the electron orbits change so as to include several nuclei, the forces of cohesion alter and the crystal is deformed and takes its rhombohedral shape and the bismuth begins to be strongly diamagnetic. Probably a close investigation of the crystal lattice by X-rays near the melting point will be necessary to give a definite proof, but at present this view is suggested as a useful working hypothesis.

In this way we can also easily explain the curious fact, observed and described in the beginning of this paper, that a slight strain set up in a crystal, when it is grown from a given crystal, will change the orientation of the perfect cleavage plane without changing the general orientation of the lattice. It is easily seen that when the crystal is growing in a " cubic " state, then this cubic modification can be transformed to the rhombohedral modification in four different ways corresponding to pulling out the elementary cubes along the four possible diagonals. The strain set up in the lattice by the cooler part of the rod, which has already transformed itself into the rhombohedral modification, will direct the transformation from the cubic state, but if we have an outside factor, such as the pressure from the walls of a tube, or the extension

* 'Physika,' p. 388 (1925).

† *Loc. cit.*

forces as in the Czochralski method, this factor may play a predominant part in the orientation of the trigonal axis in the rhombohedral modification. It is evident that this explanation accounts for the fact that the general orientation of the crystal is unaltered and only the perfect cleavage plane changes from one plane of the pseudo-octahedron to the other.

From a closer consideration of the strains set up by the methods of growing bismuth crystals in glass tubes, or pulling them out of a crucible, we may see that there is always a tendency for the perfect cleavage plane to be orientated parallel to the main shearing stresses in the rod. The strain set up in the bismuth when it is growing in a glass tube is produced by a pressure of the walls of the tube at the moment when the bismuth is crystallised and changes its volume and shape. In the Czochralski method the strain is produced by a slight pull under the weight of the liquid part of the rod. In both cases the shearing forces are not perpendicular to the rod and probably approach an angle of 45°. This indicates why rods grown by both these methods have this preferable angle for the perfect cleavage plane.

It may also be possible that the local variation in the direction of the axis of the crystal grown with its cleavage plane parallel to its length may be due to local stressing set up in the crystal owing to the non-uniformity of the temperature gradient.

(8) *Discussion of Results.*

From the results of the previously described experiments, leaving aside the hypothesis of the origin of the imperfection of the crystals, we may explain many of the peculiar phenomena observed in bismuth, which make this metal so unlike others.

In one of the previous sections we have already given an explanation of the increase of density in drawn bismuth wires. As an instance of other phenomena it has been stated by several authors* that bismuth has two modifications, called α and β. The temperatures of transformation for these two bismuth modifications has been very much discussed and different authors have given quite different results (75°, 112° and 161° C.). From the results we have obtained we may conclude that no such α and β modifications exist, but only bismuth having more or less imperfections in its crystal structure. When, for instance, a lump of bismuth, consisting of many small crystals, is cooled, the stresses occurring between the individual crystals may open the cracks, and since the small individual crystals are probably regular in size, we

* Jänecke, 'Z. f. Phys. Chem.,' vol. 90, p. 313 (1915); Cohen and Moesveld, *ibid.*, vol. 85, p. 419 (1913).

may expect the cracking to occur at a more or less definite temperature. The energy absorbed in producing the cracks and the increase of volume may give the impression of the existence of two modifications of bismuth, but in another lump of bismuth, having individual crystals of another size, this cracking will take place at a different temperature.

It has also been observed that bismuth has a variable temperature coefficient for its specific resistance. This again can be easily explained by the fact that in changing the temperature of the bismuth the cracks open or close and the resistance varies in a different way for each rod. In our experiments with single bismuth crystals, as shown on fig. 6, no such phenomena occurred.

Finally, we have the fact that after cooling bismuth and bringing it back to the initial temperature, the resistance is not the same. This again may be explained by the opening of cracks which failed to close when the bismuth was cooled down.

While we have mentioned here only a few cases where the existence of cracks in bismuth throws a considerable light on the peculiarities observed in this metal, we think it probable that in many other phenomena (such as observed in the Hall effect) the occurrence of cracks may offer an adequate explanation.

Unfortunately, in our experiments, we were unable to obtain an ideal monocrystalline bismuth rod, except in so far as the small pieces of bismuth rod, which broke off when a rod was obtained in the apparatus on fig. 5, were probably good crystals. From our experiments, however, we may conclude that an ideal bismuth crystal at room temperature is flexible and does not cleave at all.

It will be of interest to see how far the conclusion drawn from this investigation can be applied to other crystals. For example, is a cleavage plane in a crystal always a consequence of an imperfection in the lattice ? Do other similar crystals, such as antimony, develop their brittleness in the same way as bismuth ? Has the strain a directing influence on the orientation of the axis of other growing crystals as it has in bismuth ?

Summary of Part I.

It has been shown that during the process of the growth of bismuth crystals a small strain set up in the material has a great influence on the orientation of the trigonal axis of the crystal lattice. This strain has the effect of changing the perfect cleavage plane from being one of the pseudo-octahedral planes to one of the three remaining planes of the same pseudo-octahedron according to the character of the strain.

In order to obtain crystal rods with the perfect cleavage plane orientated in any desired direction relative to the axis of the rod, no strain must be set up in bismuth during crystallisation, and a method is described by which this is effected.

Further, it has been shown that during the process of the growth of bismuth crystals, cracks and imperfections are developed in the lattice which account for the variation of the specific resistance in bismuth observed in previous researches.

It has been shown that in the case of a perfect crystal the specific resistance along the trigonal axis is $1 \cdot 38 . 10^{-4} \pm 1$ per cent. and perpendicular to the axis $1 \cdot 07 . 10^{-4} \pm 1$ per cent. at a temperature of 16° C.

The origin of the cracks is studied and it is found that they are produced during cooling at a temperature very near to that at which bismuth is solidified. The character of these cracks depends chiefly upon the temperature gradient at the point where the bismuth is crystallised.

It has been shown that a perfect bismuth crystal at room temperature will probably have no well-defined cleavage plane and is very flexible.

The hypothesis put forward to explain the origin of the cracks is that there are two crystalline bismuth modifications ; one of them at present unknown, but which is probably cubic, is transferred to the ordinary rhombohedral modification at a temperature slightly lower than the melting point. This transition is accompanied by a change of shape which accounts for the occurrence of the cracks. On the basis of this hypothesis and the phenomena stated in this paper, several physical properties of bismuth have been explained.

The Study of the Specific Resistance of Bismuth Crystals and its Change in Strong Magnetic Fields and some Allied Problems.

By P. Kapitza.

(Communicated by Sir Ernest Rutherford, P.R.S.—Received April 30, 1928.)

Part II.—*The Method and Apparatus for Observing the Change of Resistance of Bismuth in Strong Magnetic Fields.*

(1) *Introduction.*

It is evident that the change of resistance of a bismuth crystal in a magnetic field, which exists for 1/100 second only and varies during the whole of this time, cannot be measured by standard methods. It is, however, possible to develop a method which gives an accuracy of the same order as that obtained in previous investigations in weaker magnetic fields produced by electro-magnets, in spite of three main difficulties, viz., the briefness of the time of the experiment; the variation of the field during this time which may produce an induced e.m.f. in the crystal, and finally the small value of the resistance of the crystal, this being only a few thousandths of an ohm. The reason is that in our case we have two factors which help us out of the difficulty. The first is that the magnetic field is very strong and this increases the change of resistance making it much easier to measure. Secondly, as any resistance measurement is chiefly reduced to the absolute or relative measurement of the potential drop along the conductor when a current is passed, we made this particular drop very much larger by passing much heavier currents through the crystal than is usually permissible in ordinary experiments. This is possible because the current is sent through the crystal for one or two hundredths of a second only, and the bismuth rod cannot warm up to any great extent during this time. Another advantage of these experiments is that by using very heavy currents and large potential drops we are not troubled by any thermal e.m.fs., which in our case are relatively small, but in the usual resistance measurements with bismuth may prove very awkward. Finally, by making the experiment in one hundredth of a second we can be sure that throughout the whole of the experiment the temperature of the bismuth will remain constant.

(2) *The Method of Measuring the Resistance.*

The method adopted for the measurement of the resistance was to send a known current through the bismuth crystal, and by means of potential leads to observe the difference of potential across the bismuth crystal. Both the current and the potential difference are measured by oscillographs appropriately adjusted for the measurements. By means of these two oscillographs and a third one, which measured the current through the coil producing the magnetic field, three curves were simultaneously taken on the same photographic plate. Thus, at a given moment, the magnetic field can be deduced from the curve of the current through the coil, and the resistance of the bismuth from the two other curves. As the current was kept constant during the experiment, we can take it that the deflection of the potential oscillograph was practically always proportional to the resistance of the bismuth. On fig. 7 the general arrangement of the experiments is shown diagrammatically.

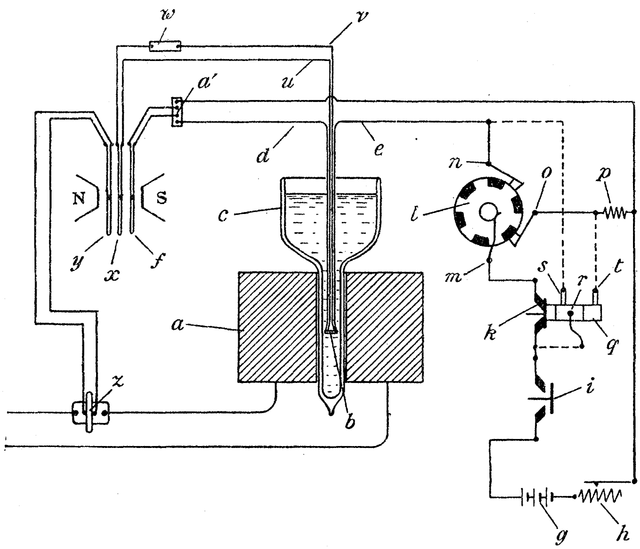

Fig. 7.

In the coil *a*, where the magnetic field is produced, the bismuth crystal rod *b* is placed. In most of the experiments the crystal was surrounded by a Dewar vessel *c*. The current is supplied to the crystal from an accumulator battery *g* through the power leads, *d* and *e*, an oscillograph *f* and a large resistance *h*. We used two alternative arrangements for sending the current through the crystal, one of them being shown by a continuous line and the other by a dotted one.

In the first arrangement, shown by the continuous line, the current was sent through a special automatically timed switch which sends the current through it for the required short time of the experiment. This switch will be described in detail later on, but its general functions are as follows. The brush *i* of this switch closes the circuit from the battery a few thousandths of a second before the magnetic field is produced in the coil. For breaking the current another independent brush *k* is used. In some of the experiments we required to make and break the current through the crystal several times during the time when the field was on. This was carried out by a very simple arrangement shown on the same fig. 7. It consisted of a copper wheel *l* with six sectors cut out and filled with insulation. Three brushes were sliding on this wheel. Brush *m* pressed on the middle of the copper disc and remained permanently in contact. Brushes, *n* and *o*, were sliding on the sectors and were brought alternately into connection with the copper wheel. The crystal and with it the oscillograph *f* were connected to the brush *n* and to one terminal of the battery. Between the other brush *o* and the terminal of the battery was connected a resistance *p* equal to that of the crystal together with the oscillograph. The third brush *m* was connected to the other terminal of the battery through the automatic switches, *i* and *k*. It is evident from this arrangement that when the disc was set in rotation impulses of current were sent through the crystal, and as the disc was worked by a little motor at 2000 r.p.m., the duration of such an impulse was about 1/400 of a second. By using two brushes, *n* and *o*, on the disc, it was possible to adjust the distance between these brushes in such a way that the current from the battery was never interrupted, and with this arrangement it was possible to make very sharp interruptions of the current in the crystal without sparking anywhere on the contacts. For the experiments in which it was not required to have such a frequent interruption of the current, the sector interrupter was left in the connections, but the disc was left stationary, in such a position that only the brush *n*, which is connected to the crystal, made contact with one of the copper segments.

The other scheme of connections, indicated by dotted lines on fig. 7, makes it possible to break the current through the crystal very sharply at any required moment during the current wave in the main coil. As will be shown in Part III, this was necessary for the experiment in which we studied the residual e.m.f. in bismuth. The principle for breaking the current used in this case is similar to that adopted in the sector interrupter just described. To the brush *k* of the automatic switch is attached a small ebonite cylinder *q* which has a copper ring *r* embedded in the middle. On the cylinder rest two brushes, *s* and *t*, made of fine copper strips (details can be seen on fig. 8 of the automatic switch). When the brush *k* of the automatic switch opens, this cylinder moves about 8 mm. along its axis, and by this motion the copper ring is shifted from the small brush *s* to the brush *t*. The brush *s* is connected, as before, to the oscillograph and the crystal, and the other brush *t*, through an equivalent resistance, to one terminal of the accumulator battery. The copper ring is connected by means of a flexible wire to the brush *i* which makes the circuit of the automatic switch. In this arrangement the brush *k* of the switch was not used, as the copper ring arrangement interrupted the current in the crystal. In this case, as in the sector interrupter, the current through the crystal was broken very sharply. It is evident that when this interrupter was used the leads to the brushes of the sector interrupter had to be disconnected and vice versa.

As will be seen from the description of the automatic switch given later, the operation of the brush *k* with the ebonite cylinder and the copper ring can be timed relative to the current wave in the coil. Thus the interruption of the current through the crystal can be adjusted to occur at any given moment in the current wave.

The potential leads, *u* and *v*, are connected through a resistance box *w* to the oscillograph *x*. There is also a third oscillograph *y* which measures the current in the coil by means of a shunt *z* in the manner described in one of the previous publications.* The three loops of the oscillographs, *f*, *x* and *y*, were placed close to each other in the air gap of the same electromagnet, and the oscillograms from them were taken on the same falling plate one above the other. The oscillographs, *y* and *f*, for the coil and for the current in the crystal were both of the same type. They had a natural frequency of about 20,000 and gave a deflection of about 3 cm. for 0·3 ampere. The current through the crystal varied from 6 to 0·5 ampere in the different experiments, and the oscillograph *f* in the crystal circuit was accordingly connected across a small shunt *a'*.

Evidently the potential oscillograph ought to be made of a different type, as only a small fraction of the power current can be used in the potential circuit. This oscillograph was made by using much finer wire for the loop and by having a greater distance between the bridges. The oscillograph actually used has a natural frequency of about 6000 per second and had a ten times greater current sensitivity than the other two elements.

* 'Roy. Soc. Proc.,' A, vol. 105, p. 701 (1924).

(3) *The Switch.*

The purpose of the synchronous automatic switch is clear from the previous paragraphs. It has to make and break the circuit through the power leads of the crystal at given moments relative to the current wave through the coil.

The general arrangement of the synchronous switch which satisfies these requirements is shown on fig. 8. It consists of a fly-wheel *a* which is driven

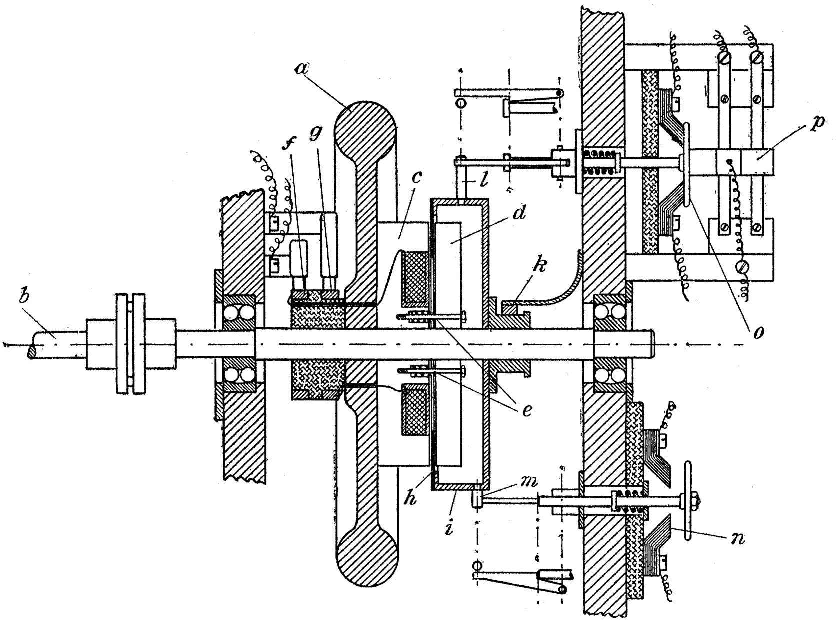

FIG. 8.

by an electrical motor from the shaft *b* at a speed of 1500 revolutions per second. A standard centrifugal regulator with a contact breaker keeps the speed constant. To the fly-wheel *a* a laminated core electromagnet *c* is attached in the way shown on the drawing. This can pull up a laminated iron core *d* which rotates together with the magnet and is pressed away from the electromagnet by two small springs *e* embedded in the core of the electromagnet. By means of two brushes and two sliding rings, *f* and *g*, a current can be sent through the winding of the electromagnet, and the core pressed to the electromagnet with a large force. In the gap between the iron core *d* and the electromagnet *c* a thin iron disc *h* is placed attached to a light aluminium cylinder *i*. When the electromagnet rotates, the disc is kept in a fixed position by means of a small friction produced by the brake *k*. When the current is sent through the electromagnet the core is attracted, and, owing to the large friction, the disc and cylinder begin to rotate practically at once with the same velocity as the motor. The cylinder has two adjustable radial pins, *l* and *m*, screwed in its rim. These pins, when in rotation, strike two triggers of two switches, *n* and *o*, which are released by springs and which open and close the circuits. One of these switches *o* bears the arrangement with the ring *p* described in the previous section.

During the experiment this apparatus functions in the following way. Through one of the brushes fixed to the commutator on the main switch of the big dynamo, which was described in a previous paper,* a current can be sent through the electromagnet which will set the cylinder *i*, with the pins, in rotation exactly at a definite moment before the current wave passes in the coil. By a proper choice of the position of the pins on the cylinder, these moments at which the current is made and broken can be suitably adjusted relative to the current wave. It took some time to develop the construction of this switch in order to ensure it working with sufficient reliability, the main difficulty being in making the magnetic clutch operate sufficiently quickly. By sending a strong current in the electromagnet *c* (which can be done without danger of burning the winding, as the current is sent for a few hundredths of a second only), and by making the disc *h* and the cylinder *i* light, we were finally able to adjust the moment of make and break with an accuracy of 1/5000 second. This was sufficient for these experiments.

(4) *The Fixing of the Crystal in the Coil.*

Great care has to be taken in finding the proper way of fixing the crystal in the space in the middle of the coil where the field is produced. The coil used in all these experiments had an inside diameter of 1 cm. and is described in detail in the writer's previous publication.†

To prevent the crystal from being heated by the coil, and also to make experiments at the temperature of liquid air and solid CO_2, the crystal has to be placed in a Dewar flask. This Dewar flask, shown on fig. 7, had an outside diameter of less than 1 cm. in order to fit the coil, thus leaving an inside diameter of 6 mm. only. Thus the crystal with all the leads and the holder has to be fairly small so as to fit this Dewar flask.

On the other hand, the crystal has to fit tightly in the holder as, during the experiment, electrodynamical forces try to press it sideways. These forces

* 'Roy. Soc. Proc.,' A, vol. 115, p. 671 (1927).

† 'Roy. Soc. Proc.,' A, vol. 115, p. 678 (1927).

are relatively small—for instance, for a rod of 4 mm. length in a field of 300 kilogauss, when a current of 3 amperes is passing (these are the normal data for one of our experiments) the sideways force is only 36 grams. A much larger force due to a different cause, however, appeared in the experiments at low temperatures when the Dewar flask was filled with liquid air. In this case, when the field is on, owing to the strong paramagnetism of the liquid air, it is pulled into the Dewar flask, and the crystal with the holder is forced out. This force, for a field of 300 kg. if the cross section of the holder is 25 sq. mm., has a value lying between 1 and 5 kg., varying with the concentration of oxygen in the liquid air. The larger value of this force may be easily demonstrated by a simple experiment. The Dewar flask is placed in the coil and is filled with liquid air. A glass rod, 3 mm. in diameter and about 10 cm. long, is dropped in the flask. The field is then produced and the force just described is sufficient to throw the glass rod to a height of 7 or 8 metres. Thus it is necessary to make the holder sufficiently strong and to fasten it to a stand to avoid any displacement of the crystal.

Finally, great care has to be taken in arranging the leads to the crystal. Not only a good contact has to be established, but the leads have also to be arranged in such a way that the minimum possible e.m.f. is induced in the potential oscillograph circuit. We have to remember that in our experiments this e.m.f. may be very considerable, as the field during 1/100 of a second rises in general from 0 to 300 kilogauss and then falls again to zero. It is necessary, therefore, that the leads to the crystal shall be run bifilarly as long as possible, and the connection to the crystal arranged in such a way that no circuit is made with its plane perpendicular to the lines of force in the coil. The crystal rods have to be placed in some experiments parallel to the magnetic lines in the coil and in others perpendicular. We will first describe the perpendicular fastening which is the most difficult.

For experiments with the magnetic field transverse to the current, two methods of fastening the crystal have been generally used and both have been found satisfactory. They are shown on fig. 9, drawings A and B. In the first one (drawing A), a crystal rod *a*, about 4 to 5 mm. long and 1 mm. in diameter, is placed in a small Bakelite cylinder *b* of about the same length. This cylinder has at the ends a slightly smaller diameter, in which are made two perpendicular holes. Two silver discs *c* are fixed with shellac to the part of the cylinder with the largest diameter, and two silver wires *d*, which form the potential leads, are soldered to the rod and to the silver discs. The soldering of the silver wires to the bismuth is done by means of a spark from a condenser in the way described in Part I of this paper. As already mentioned, this does not spoil the bismuth and forms a very reliable contact.

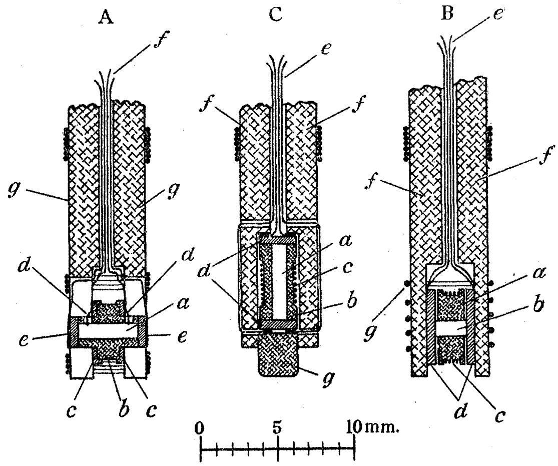

Fig. 9.

To the end of the bismuth rod are soldered two silver discs *e* by means of a low melting point solder. The silver discs form the contacts for the power leads. To make all these connections is difficult, as the dimensions are small, and it is advisable to do most of the work under a binocular low magnification power microscope.

The mounted crystal is placed in a holder. Four fine copper strips *f*, insulated from each other and pressed together between two ebonite strips *g*, which are bound together, form the holder. The end of the holder, which is connected to the crystal, is made like a double fork into which the crystal with its Bakelite fitting can be pushed. The contact between the copper strips and the silver discs is established in the following way. The two middle strips which form the potential leads each have holes at the end into which the thinner parts of the Bakelite cylinder *b* fit. They are pressed on the two silver rings and form the contact. The two remaining copper strips form the power leads and are connected to the silver disc *e* simply by making the end of the copper strips narrow, and by taking them out through the side slots of the holder and pressing them against the discs. The contacts and the steady position of the crystal are secured by a silk thread which is wound round the bottom part of the holder. It should be noticed that in such a fixing arrangement the crystal can be turned about its axis and orientated at any desired angle.

This arrangement for fastening the crystal is very elaborate and takes much time to make. It has also the disadvantage that the crystal cannot be sufficiently tightly fixed in the Bakelite cylinder, since it is only supported by the silver discs at the ends, and very often we find that when placed in the magnetic field, as a result of the electromagnetic forces, the crystal rod bends. The result is that some of the cracks, which were mentioned in the previous part of this paper, open and the resistance of the crystal increases.

This led to the development of a simple method of fixing the crystal. In this method we took advantage of the fact that the specific resistance of bismuth in normal conditions is about 75 times that of silver, and, as in our experiments we limit ourselves to an accuracy of 1 per cent., it is not necessary to make proper potential leads. It is sufficient to solder on the end of the bismuth rod two silver discs, $\frac{1}{4}$ mm. thick, and to bring the power and the potential leads from these discs. Owing to the large conductivity of silver the resistance of the disc can be neglected. The arrangement for this method is shown on fig. 9, drawing B. It consists of a Bakelite cylinder *a*, cut in two parts, with a small groove in which the crystal rod *b*, about 3 mm. long, is placed. The two halves of the Bakelite cylinder are pressed together by winding round them a silk thread *c*. This provides a tight fitting of the crystal in the Bakelite, the necessity of which has just been stressed. Two silver discs *d* are soldered by a low melting point solder on to the ends of the bismuth rod, special care being taken to make a good joint with as little solder as possible. The holder consists as before, of four copper strips *e* pressed between two ebonite plates *f*. The end of the holder is made like a simple fork, and the copper strips, to which are soldered silver wire at the ends, are bent in place close to the two inside faces of the fork. When the crystal is pushed into the fork these wires touch the silver discs and form the contact. By means of a silk thread *g* wound round the fork the contacts are made safe and the crystal is kept tight. In this case, as before, the crystal rod can be turned round its axis.

The fastening of the crystal in experiments where the current was flowing longitudinally to the magnetic field is shown in fig. 9, drawing C. The crystal rod *a*, about 5 mm. long, is placed as before in a small Bakelite cylinder *b* which, in this case, is thinner and longer. The Bakelite cylinder is made in two parts and the crystal rod is fixed tightly by fastening these two parts by a thread *c*. Two silver discs *d* are soldered to the ends of the rod. The holder, as before, consists of four copper strips *e* and two ebonite plates *f*. The holder has a fork with a cylindrical opening, where the crystal with its Bakelite cylinder is inserted. To the end of the bare copper strips are soldered wires which touch the silver discs in pairs, in the way shown on the drawing. The contact between the discs and the wires is produced by a screw plug *g* which is screwed into the bottom of the holder.

In all these methods, in cases where the crystal has its cleavage plane perpendicular to the axis of the rod, special care has to be taken to prevent any tensile forces along the rod which may arise from the difference of thermal expansion of the Bakelite and the bismuth. The Bakelite cylinder, expanding more than the bismuth rod, may press the silver disc and strain the rod. This will result in opening the cracks in the bismuth and in changing its resistance. To avoid this strain a clearance has to be left between the silver disc and the Bakelite cylinder. This is easily accomplished by placing a small mica washer between the silver disc and the Bakelite cylinder during the process of soldering and then removing it.

(5) *The Method of Measurement.*

The experiment for measuring the change of resistance of bismuth crystals was performed in the following way. The required bismuth rod was fixed in the holder in the manner described in section 4 and placed in the Dewar flask, which, according to the requirements of the experiment, was either empty or filled with a freezing mixture of ether and solid CO_2 or liquid air. The absolute resistance of the crystal was measured by means of the potentiometer method described in the previous Part of this paper. The Dewar flask was then placed in the coil and the connection made according to one of the methods described in section 2. The current to be sent through the crystal was adjusted by passing it through an equivalent resistance. The resistance in series with the potential oscillograph (*w*, fig. 7) was also adjusted in such a way as to have the deflection of the oscillograph of a suitable amplitude for measurement. During the whole of this experiment the machine was used in the way described in my previous paper.* After the experiment was made an oscillograph with three lines was obtained, as shown on the reproductions. The resistance of the bismuth rod was then measured again. If the bismuth rod was properly fixed no change of resistance was observed.

After the plate was dry it was placed in an enlarging camera, which projected the oscillogram on to a piece of paper enlarged about ten times. By means of pencil the enlarged oscillogram was copied. On the same paper reference lines were traced and the deflections were measured by means of a simple mm. rule. The thickness of the lines of the oscillograms were about 2 to 3 mm.

* 'Roy. Soc. Proc.,' A, vol. 115, p. 181 (1927).

and the measurements were always made from the middle of one line to the middle of the zero line. The accuracy of measurement was about $\frac{1}{4}$ mm. and as the maximum deflection was adjusted to be between 50 to 80 mm., the accuracy of such a simple method of measurement was quite sufficient. From a measured deflection of the oscillogram which measured the current through the main coil, the magnetic field in the coil was determined in the way described in my previous paper.* From the two other curves the resistance of the bismuth rod in this magnetic field can be determined. As the current in the coil had a sine form, the change of the resistance of bismuth can be deduced from a single oscillogram for practically all fields from 0 to the maximum value obtained in the experiment. Actually, in most of the experiments, the potential curve only is used, as the current through the crystal remains constant and has a value adjusted beforehand. Thus the ordinates of the potential oscillograph curve are proportional to the resistance of the bismuth.

The relative change of resistance is obtained by dividing the deflection of the potential oscillograph, measured with the field, by its deflection without the field. This deflection can either be calculated from the measured resistance of the crystal and the constants of the oscillograph and of the circuit, or measured from the oscillogram directly. This, however, can only be done on oscillograms taken in weak fields where the resistance of bismuth does not change more than ten times, as, for instance, in oscillogram No. 5, Plate 6. On this oscillogram the current started before the field was established, and the initial deflection was easily measured. But when the change of resistance is about 100 or more times, and the resistance in series with the potential oscillograph is very large, the initial deflection is so small that it cannot be measured correctly (*see* oscillogram No. 8, Plate 7). It must be mentioned that such a simple calculation for the change of resistance of bismuth can only be used when the change of resistance is small—up to 50 or 100 times, otherwise the increased resistance changes the condition of the circuit appreciably. For instance, if we have an increase of resistance of 1000 times or more, as happens at the temperature of liquid air, the resistance of the crystal rod, which is initially between 0·002 to 0·005 ohm, will increase to a value of 2 to 5 ohms. In this experiment only half an ampere can be safely sent through the crystal in order to avoid heating it, even in 1/100 second. The potential drop across the crystal will be 2 to 5 volts, and if an accumulator battery of 30 volts is

* *Loc. cit.*, p. 679.

used the main current through the crystal will diminish by 6 or 7 per cent., and a correction has accordingly to be introduced.

The potential oscillograph consumed about 15 milliamps. for its full deflection. When a current of 3 amperes was passing through the crystal, the measurement was not affected by more than $\frac{1}{2}$ per cent. But in the cases where the current through the crystal was limited by heating considerations to one ampere or less, the current through the potential oscillograph is already comparable with the current through the crystal, and a correction has to be introduced. The introduction of these corrections is simple and was always made at any moment when it was more than 1 per cent. No special mention of this subject will be made later on in the paper, and in all subsequent discussions it will be assumed that these corrections have been made. When the resistance of bismuth changes more than 2000 times, the correction commences to be rather large and the measurement becomes less reliable. Indeed, with such an increased resistance, bismuth has a specific resistance 200,000 times that of silver and is more like a non-conductor. Special methods of accurately measuring the resistance beyond this point are quite possible but have yet to be worked out.

(6) *The Errors and Stray Effects.*

The sources of error have to be considered rather carefully in our experiments, as in any new method of experimenting. We have already mentioned that we limited the accuracy of the experiments to 1 or 2 per cent., this being quite sufficient in this kind of experiment, as it will be seen that the error which arises from the unknown purity of bismuth may be considerably larger.

From the method of measuring the oscillograms, and by carefully calibrating the oscillograph, we are fairly sure that the quantity measured from the oscillograms represents the actual values well within 1 per cent. All the possible errors occurring in this method of measurement with oscillographs have already been fully discussed in the author's previous papers.*

The next source of error is the e.m.f. in the potential leads, which is induced by the variation of the magnetic field during the experiments. Experiment shows that by the arrangement for fixing the crystal, described in section 4, where all the leads have been arranged bifilarly, the induced e.m.f. is made very small compared with the potential drop along the crystal, and the effect produced in most cases is negligible within the limits of experimental error. This is easily proved by taking an oscillogram with the battery (g, fig. 7) disconnected. The deflection of the potential oscillograph is then entirely

* 'Roy. Soc. Proc.,' A, vol. 105, p. 701 (1924).

due to this effect. On fig. No. 1, Plate 5, such an oscillogram is reproduced. In this case the amplitude of the magnetic field reaches the value of 320 kilogauss, and only by very careful examination can we detect a slight curving in the line traced by the potential oscillograph.

In certain experiments where the crystal was not fastened so successfully, and in cases where the resistance in series with the oscillograph was small, we were able to observe at the beginning and the end of the current wave a slightly larger deflection. In these cases the error can be easily eliminated by taking two oscillograms with the same field, but with the direction of the current through the crystal reversed. Taking the average of the measurements from the two oscillograms, the disturbing e.m.f. will be eliminated. This e.m.f. was also automatically eliminated in all the experiments when we used the sector interrupter, which was described in section 2. With the sector interrupter we obtained oscillograms similar to Nos. 5 to 10 (Plates 6 and 7). The necessity for using the sector interrupter arose in cases where it was necessary to eliminate the e.m.f., which occurs in bismuth crystals in a magnetic field when a current is passing through the crystal. By use of the interrupter this e.m.f., and the induced one are automatically eliminated. In these oscillograms, obtained with the sector interrupter, a new source of error may come in as the potential oscillograph now works under severe conditions. During two-hundredths of a second it has to swing across the plate over ten times from below zero to the full deflection. As the frequency of the potential oscillograph was comparatively low (6000), and comparable with the time of a deflection, the time lag of the deflection is noticeable on all the oscillograms taken. It can also be noticed that the oscillograph was slightly under-damped. As we required to measure the difference of the negative and positive deflections at the moment when the current is broken or started, an extrapolation of the deflection was necessary which naturally made the measurement less accurate. We estimate the error of this extrapolation in the worst cases to be about 3 per cent.

Finally, we have to consider the effect of the heating of the crystal produced by the current. It becomes serious only when we deal with the crystal at the temperature of liquid air and in strong fields. The specific resistance of bismuth is in this case so high that even a small current may heat it up. Let us make a numerical examination. The heat generated in the crystal is

$$Q = 0 \cdot 24 \int_0^T (Is)^2 \, R dt, \qquad (1)$$

where I is the current density in the crystal, s is the cross section and R the resistance. With sufficient approximation (as will be seen from the next Part of this paper) we may take R to be proportional to the magnetic field, and, as the magnetic field changes sinusoidally, we may take

$$R = R_{max.} \sin (\pi t/T), \tag{2}$$

where T is the half period of the current wave. We obtain from (1)

$$Q = 0 \cdot 15 \, R_{max.} \, T \, (Is)^2. \tag{3}$$

It is easy to see that the rise of temperature will be

$$\delta t = 0 \cdot 15 n \sigma I^2 T / kd. \tag{4}$$

In this formula $n = R_{max.}/R_0$ the relative increase of resistance; k and σ are the specific heat and resistance, and d the density. At liquid air temperatures $k = 0 \cdot 028$, $\sigma = 0 \cdot 5 \,.\, 10^{-4}$, $d = 9 \cdot 80$ and in our experiments $T = 1/40$, so that we get

$$\delta t = 0 \cdot 68 \,.\, 10^{-6} \, nI^2.$$

Now in our experiments with a bismuth rod of 1 mm. diameter, if we take the current $i = 0 \cdot 5$ amp., and the increase of resistance is about 2000 times, we get an increase of temperature $\delta t = 5 \cdot 5°$, which is already appreciable.* On the other hand we cannot greatly decrease the current, as then the correction for the potential oscillograph will be too large.

This, however, only happens in liquid air experiments; in other experiments the rise of temperature is never greater than $0 \cdot 5°$.

These are practically all the errors which can be introduced into the experiments by this method of measuring the resistance change in the magnetic field. The other errors which arise from the impurities of bismuth, from the imperfection of orientation of the crystal and similar causes, will be considered later in connection with each individual experiment.

Summary.

A description is given of a method for measuring the change of resistance of a conductor when it is placed in a magnetic field which exists for 1/100 second.

The study of the change of resistance is made possible by the fact that larger current densities are permitted in the conductor, for such a short time, without heating the conductor, and no specially sensitive apparatus is required. The measurements can be made with an oscillograph.

* When the sector interrupter is used the increase of temperature is about half.

A special switch is described which permits the current to be sent through the investigated conductor for a very short time, during the existence of the magnetic field. The make and break of this switch may be adjusted relative to the current wave through the coil, which produced the magnetic field with an accuracy of about 1/5000 second.

The experimental arrangements are described which permit the study of the change of the resistance of bismuth crystals in a magnetic field at different temperatures.

The elimination of errors, due to the induction effects and heating up of the crystal during the process of measurement, are discussed.

The Study of the Specific Resistance of Bismuth Crystals and its Change in Strong Magnetic Fields and some Allied Problems.

By P. Kapitza.

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Part III.—*The Change of Resistance of Bismuth and the Time Lag in Magnetic Fields.*

Introduction.

The study of the change of resistance of bismuth crystals in a magnetic field is an involved problem in which a number of variables have to be taken into account.

In the first place the change of resistance of bismuth crystals depends on the strength of the magnetic field; secondly, on the direction of the current relative to the axis of the crystal; thirdly, on the orientation of the crystal in the magnetic field, and finally, on the temperature. It also depends on the chemical purity of the bismuth, on the state of perfection of the crystal lattice and on the strains which may be set up in the crystal.

In order to study these phenomena a great deal of experimental work is required, the difficulty being increased by the time lag phenomenon. A large amount of generalisation can be achieved, however, if we combine the results with some of the phenomena described in Part I of this paper, especially with the observations on the development of imperfections and cracks in the bismuth crystal.

(1) *The E.M.F. which accounts for the Time Lag and its Elimination in the Resistance Measurement.*

Before commencing the measurement of the change of resistance of bismuth crystals, it was necessary to eliminate the time lag phenomena and to determine the true resistance of bismuth in magnetic fields. The magnitude of the time lag can be very easily seen on oscillogram No. 2, Plate 5, for a crystal where the current is passing perpendicular to the cleavage plane, and where the current is also perpendicular to the lines of force of the magnetic field; for this orientation, the lag phenomenon is most marked. We see from the curve p traced by the potential oscillograph, that during the time from x to y, when the current in the coil is constant and the magnetic field also remains constant, the deflection changes its amplitude quite appreciably, beginning with a high value and then gradually decreasing. As the deflection of the potential oscillograph is proportional to the resistance of the crystal, this decrease means that the resistance of bismuth is diminishing with the time. The cause of this diminution can easily be seen on the same oscillogram. In the second half of the current wave, when the current through the crystal is suddenly broken, the deflection of the potential oscillograph does not drop to zero, but retains a quite definite negative value. This means that along the crystal there exists a residual e.m.f. when there is no current. This residual e.m.f. in the crystal reduces the fall of potential due to the ohmic resistance as it is in the direction "to help" the current to pass through the crystal. The origin of this e.m.f. will be considered later in a special paragraph, but at present it suffices to mention that it has already been traced by Seidler,* and has been studied by several investigators.

We shall now describe the method by which this e.m.f. in the crystal can be eliminated and the actual potential drop along the crystal due to the change in the ohmic resistance obtained. In the first place we see from the fact that the deflection of the potential oscillograph diminishes during the time when the field is constant, that the e.m.f. gradually increases in value with the time. This can be seen in oscillograms (Nos. 2 and 3, Plate 5) for the same crystal, under the same conditions, except that the current was broken, by means of the switch described in Part II, section 3, at two different moments during the flat part of the current wave, in (3) near the beginning,

* 'Ann. d. Physik,' vol. 32, p. 337 (1910).

and in (2) towards the end. It is easily seen from the negative deflections of the potential oscillograph that the e.m.f. is larger when the current is broken later. On these two oscillograms we take the full swing of the potential oscillograph, at the moment when the current through the crystal is broken, to be proportional to the ohmic potential drop along the crystal, since the deflection before the break is diminished by the amount of the residual e.m.f. This assumption is confirmed by direct measurements of these oscillograms (Nos. 2 and 3), which show that the amplitude of swing is independent of the moment at which the current is broken. In this way, therefore, we are able to eliminate the time lag phenomenon from our experiments. As the development of this residual e.m.f. takes some time, it appears that by this method we measure the resistance which would occur in an ideal experiment in which the current is suddenly established in the crystal and in which the e.m.f. has no time to develop. Later on, when we consider the origin of this e.m.f. in section 6, we shall give a more complete justification of this method of measuring the resistance.

The elimination of the e.m.f. for several points along the current wave is obtained by using the sector interrupter, which has been described in Part II, section 2, of the present paper. Oscillogram No. 4, Plate 5, is taken for a crystal without the sector interrupter. If we plot the curve of the relative change of the resistance of the crystal taken from this oscillogram, we obtain a curve in the shape of a loop, as shown on fig. 10, by means of a broken line. It is obvious that this loop results from the asymmetrical form of the deflection of the potential oscillograph, which is due to the e.m.f. developed in the crystal.

To eliminate the e.m.f. in the crystal we take another oscillogram similar to oscillograms Nos. 5, 6, 7 and 8, Plates 6 and 7, in which the sector interrupter is used and take the true ohmic potential drop to be equal to the full swing at the beginning and at the end of each interruption, in the way described for oscillograms Nos. 2 or 3. The curve obtained in this way is shown on fig. 10 by means of a continuous line, and it is seen that the points taken on the side of the increasing fields, marked by circles, and the points taken on the descending part of the current wave, marked by crosses, lie on a practically continuous line within the limits of experimental error. As already mentioned in this method of elimination of the e.m.f. by means of the sector interrupter, the lag in the deflection of the oscillograph begins to be appreciable and the accuracy of the experiment is diminished.

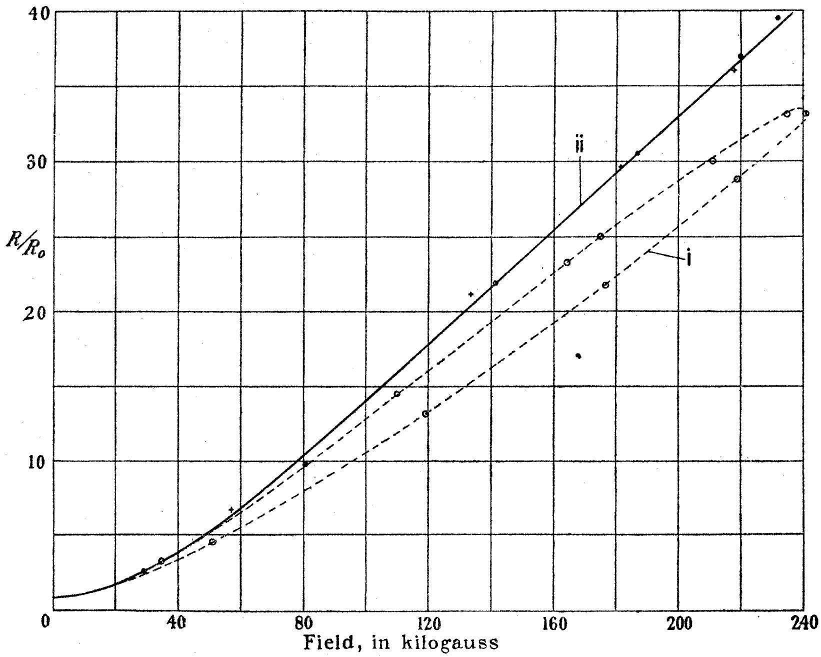

Fig. 10.—Crystal orientated I || Axis and I ⊥ H temperature 17° C. Curve i taken from oscillogram No. 4 without using the sector interrupter and the residual e.m.f. is not eliminated. Curve ii taken with the sector interrupter and the residual e.m.f. is eliminated.

(2) *The Change of Resistance of Bismuth Crystals in a Magnetic Field with the Current perpendicular to the Field.*

Some of the results of our experiments are represented by curves on diagrams, figs. 11 to 16, the ordinates representing the ratio of the resistance R of the crystal in a magnetic field to its resistance R_0 without the field, and the abscissæ the magnetic field in kilogauss. Curves marked by the same letter refer to the same crystal, the suffix indicating the orientation of the crystal relative to the magnetic field.

Most of the curves range from 0 to 320 kilogauss and each was obtained from at least two oscillograms. The first was taken with weaker fields and covered the range from 0 to 100 kilogauss, one or more additional oscillograms covering the remaining part of the range to 320 kilogauss. On some of the curves the measured points are marked to give an idea of the accuracy of the experiments; on others this has not been done for the sake of clearness in the drawing. For illustration some oscillograms are reproduced, the details of which can be learnt from the description.

The experiments for most of the crystals were made at three different temperatures. First at room temperature, secondly at a temperature of about − 80° C., this being obtained by filling the Dewar flask *c* of fig. 7, in which the crystal was placed, with a mixture of solid CO_2 and ether, and finally at a temperature of −182° C. by filling the Dewar flask with liquid air.

We will first describe the change of resistance of bismuth crystals when the current is flowing along the trigonal axis, *i.e.*, perpendicular to the cleavage plane. For abbreviation we call this case I ⊥ H and I ∥ Axis, and the corresponding experimental results are represented in diagrams, figs. 11, 12 and 13.

We first consider the effect of the orientation of the crystal when it is rotated round the trigonal axis, six similar orientations of the crystal relative to the direction of the magnetic field being possible in this case. In the first set one of the lines on the perfect cleavage plane which, as was stated in Part I of this paper, corresponded to the intersection of one of the three remaining pseudo-octahedral planes with the perfect cleavage plane, is perpendicular to the lines of magnetic force, and the other two lines form an angle of 30° with the magnetic field. (This we shall call Line ⊥ H.) In this case we have the maximum change of resistance of bismuth in a magnetic field (given by curve A_1). When the crystal is turned through 30° two of the three lines on the perfect cleavage plane form an angle of 60° with the magnetic field, the remaining line being parallel to the field (Line ∥ H) and the increase of resistance with the strength of the magnetic field is a minimum (curve A_2).

I am indebted to Dr. Webster who studied this phenomenon in weak magnetic fields at room temperature, and who found that in turning a crystal round its axis in a magnetic field, these minima and maxima repeat themselves with a periodicity of 60°, and the variation in the change of resistance in a constant field almost approaches a sine curve. This effect of orientation is illustrated in oscillograms 5 and 6, taken for the same crystal under exactly similar conditions, except that in oscillogram 5 the crystal was in the position to give the maximum change of resistance (Line ⊥ H) whilst in oscillogram 6 the crystal was turned round its axis by 30° (Line ∥ H) and the minimum change of resistance was obtained. On comparing the two oscillograms, the smaller amplitude of the potential oscillograph traced by curve *p* is evident. In curves figs. 11, 12 and 13, where the change of resistance for the three above-mentioned temperatures is represented, the crystals with the orientation which gives the maximum change of resistance are marked by the suffix 1, and correspondingly the crystals in the minimum position bear the suffix 2.

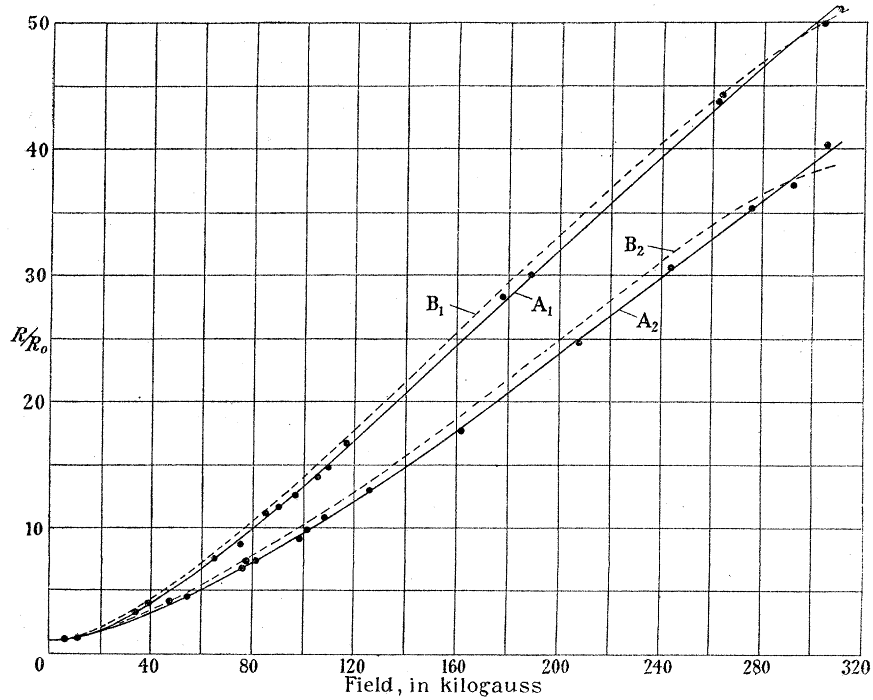

FIG. 11.—Room temperature, orientation I ∥ Axis and I ⊥ H. Curve A_1, Crystal A, Line ⊥ H. Curve A_2, Crystal A, Line ∥ H. Curve B_1, Crystal B, Line ⊥ H. Curve B_2, Crystal B, Line ∥ H.

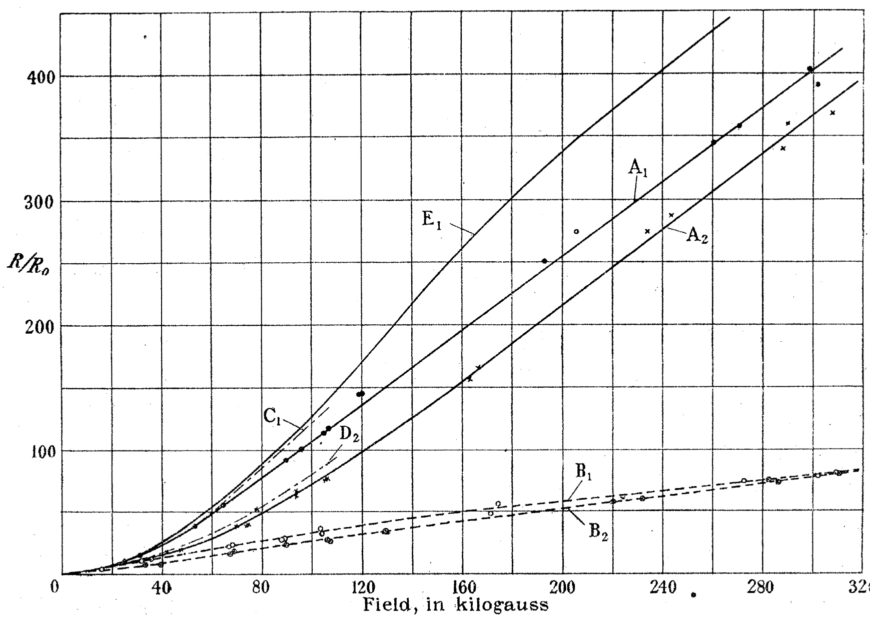

FIG. 12.—Temperature of the mixture of solid CO_2 and Ether, Orientation I ∥ Axis and I ⊥ H. Curves A_1, B_1, C_1, E_1, Line ⊥ H. Curves A_2, B_2, D_2, Line ∥ H.

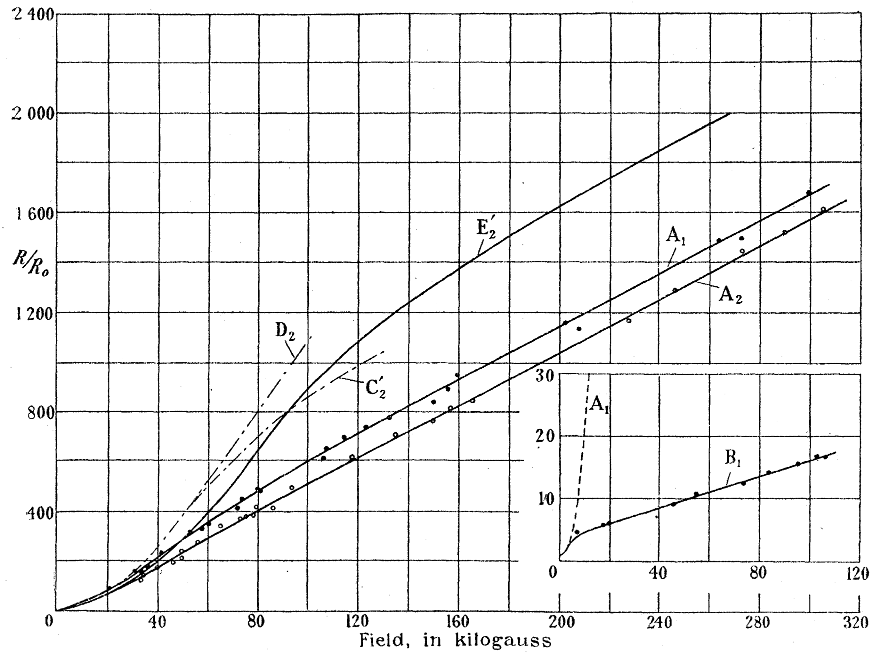

FIG. 13.—Temperature of Liquid Air, Orientation I || Axis and I ⊥ H. Curves A_1, B_1, Line I ⊥ H. Curves A_2, B_2, C'_2, D_2, E'_2, Line || H.

The effect of the orientation has been most completely studied in the case of crystal A. We notice that the difference between the ordinates of the curves A_1 and A_2 increases up to a certain field and then remains practically constant, the curves being very nearly parallel or even showing a slight tendency to coincide at very strong fields. It is also seen that the constant difference is reached at smaller fields when the temperature is lower. It is reached in liquid air at about 70 kilogauss, in solid CO_2 at about 120 kilogauss, and in air the parallelism is not completely attained even at 320 kilogauss.

It is well known that the effect of the temperature on the resistance change is very great; it is illustrated by the three oscillograms 5, 7 and 8, taken for the same crystal A, in the same orientation, but for three different temperatures. Oscillogram 5 was taken from the crystal at room temperature. The crystal had an initial resistance of 0·00325 ohm (12° C.) and the deflection of the potential oscillograph (curve *p*) is very noticeable, even without the field. Oscillogram 7 corresponds to a temperature of —80°. The initial resistance of the crystal was 0·00215 ohm, and the sensitivity of the potential oscillograph was diminished four times (by diminution of the current through the crystal and increasing the resistance, *w*, fig. 7), the initial deflection without the field being scarcely noticeable. Oscillogram 8 is for liquid air. In this experiment the magnetic field was about three times larger than in the two previous cases, and the potential oscillograph was made 36 times less sensitive. The initial deflection of the oscillograph can no longer be traced on curve p.

The general way in which the resistance alters with the magnetic field at different temperatures can be seen from fig. 11, where the results are given for experiments at room temperature, from fig. 12 for a temperature of solid CO_2 and ether, and from fig. 13 for liquid air. We shall discuss these results in detail later, but at present we may remark that all the curves are of a similar character. At the beginning the resistance changes as the square of the magnetic field, and at stronger fields the change is proportional to the field.

We will now consider the influence of chemical impurities in the bismuth. For this purpose we compare two crystals, A and B.

The crystal A, for which the curves A_1 and A_2 corresponding to the two orientations were just described, was grown from a Hartmann and Braun rod on the copper plate (fig. 1), with the cover B, and had, on measurement, a specific resistance of $1 \cdot 51 \, . \, 10^{-4}$. The cleavage plane formed an angle of 89° with the axis of the rod. The crystal was fixed in the holder, fig. 9, B.

The second crystal rod B was grown in a similar way, but was made from ordinary bismuth obtained from Kahlbaum. The crystal was fastened in the holder in the same way as crystal A. The change of resistance in the magnetic field for this crystal is given in figs. 11, 12 and 13, by curves B_1 and B_2. In fig. 11, at room temperature, it is to be noticed that curves B_1 and A_1 and B_2 and A_2 agree well within the limits of experimental error. At a temperature of solid CO_2, however, the curves for the crystal B, made of Kahlbaum bismuth, show quite a different change of resistance from that for crystal A. At first, up to about 15 kilogauss, they practically agree with curves A_1 and A_2, but after this field it is seen that the curves B_1 and B_2 are well below the curves of A_1 and A_2, corresponding to a much smaller change of resistance. We see from fig. 13 that at a temperature of liquid air the Kahlbaum bismuth rod gives a very small change of resistance. The results are shown on the right-hand bottom corner of the same drawing. The change of resistance of crystal B was so small, in comparison with crystal A, that it was necessary for the scale to be considerably increased in order to draw the curve. It is seen that up to a field of 8 kilogauss the Kahlbaum bismuth rod has the same change of resistance as the Hartmann and Braun bismuth rod, which is shown by a dotted line A_1 on this figure. Afterwards there is a sharp bend and the curve then runs in practically a straight line and the increase of resistance is very small.

These experiments confirm the already known fact that impurities have a large effect in diminishing the change of resistance of bismuth in a magnetic field, and we see that this is chiefly noticed in strong fields and at low temperatures. As a practical result in our case we deduced that Hartmann and Braun bismuth was of a higher chemical purity than Kahlbaum bismuth. This fact was made use of in judging the purity of bismuth for our experiments, described in Part I, when we discussed the influence of impurities on the growth of crystals.

We shall now describe one of the most interesting points, namely, that the imperfection of the crystal lattice also has an important effect on the change of resistance. In the First Part of this paper the various imperfections of the lattice were described, and it was shown how these imperfections depend upon the manner in which the crystal is grown. We have now investigated the effect of different methods of crystal growth on the change of resistance.

We first chose two samples of crystals made of Hartmann and Braun bismuth, both grown with a sharp temperature gradient along the rod, as obtained in the apparatus with the platinum spiral (fig. 4). One of these (D) was the most flexible crystal we had ever been able to obtain, having its cleavage plane inclined at 75° to the axis of the rod. The second crystal (C) was less flexible, and had its perfect cleavage plane at an angle of 89° to the axis of the rod. Both these crystals had the normal specific resistance, viz., $1 \cdot 365 . 10^{-4}$ and $1 \cdot 38 . 10^{-4}$.*

At room temperature the change of resistance of these two crystals was exactly similar to that shown by crystal A and represented by curves A_1 and A_2 on fig. 11. We have not drawn these two curves simply because they could not be distinguished from each other. At a lower temperature, however, in solid CO_2 and ether, the change of resistance of the flexible crystals was larger in stronger magnetic fields. The very flexible crystal is shown by curve D_2 and the less flexible one is represented by curve C_1. We see that in both these cases the resistance changes are practically the same as for the crystal A for fields up to 60 kilogauss, but for higher field strengths the crystals C and D give a larger increase of resistance.

At the temperature of liquid air we have even more marked differences between curves for the flexible crystals D and C and the crystal A, as can be seen from fig. 13. Here again, however, the difference appears only for stronger magnetic

* The crystal D had the lower resistance, due to the inclination of the cleavage plane. This variation of resistance is in agreement with the Voigt-Thomson law ($\cos^2 \theta$) which we found to hold very well for our crystals.

fields, and at a field of 100 kilogauss the flexible crystal C (curve C_1) gives a change of resistance which is about twice greater than that obtained for the crystal shown by curve A_1.

This difference in the behaviour of crystals indicated clearly that it was due to variations in the perfection of the crystalline lattice, and this inspired the X-ray investigations of the crystals described in the First Part of this paper. As we have seen in Part I, the result of these investigations was to show that neither the crystal A grown on the plate, nor the flexible crystals C and D, grown in the apparatus of fig. 4 with a platinum spiral, have a perfect crystal lattice. It was also seen that the relatively best crystals were obtained by growth under very uniform temperature conditions as produced in the apparatus of fig. 5. We have chosen one of the best of the crystal rods grown in this apparatus, which had a specific resistance $1 \cdot 38 \,.\, 10^{-4}$, the cleavage plane having an angle of 89° with the axis of the rod, and studied the change of resistance in the magnetic field. We denote the curves for this crystal by E. This crystal was very carefully etched in order to remove the surface layer, which, as had been seen from X-ray examination, might contain small crystals. It was placed in a holder similar to the one given on fig. 9, B, only in this case special care was taken in handling not to produce any strain in the crystal when it was fixed. Furthermore, to avoid any strain from the holder, the two ebonite plates of the holder *f*, which pressed on the sides of the crystal, were removed and the wires were soldered to the silver discs *d*.

No difference in the change of resistance for this crystal E from that of crystals A and B was observed at an ordinary temperature, and we obtained a curve which again coincided with the curve A_2 given on fig. 11. At the temperature of CO_2, the difference between the curves E_1 and A_1 was much more marked. The change of resistance in E is larger and is straight only after 200 kilogauss.

Before describing the results for the change of resistance of crystal E at the temperature of liquid air, mention should be made of certain difficulties in the exact measurement of the ratio of R/R_0, which were met with in all the crystals at such low temperatures. The first of these difficulties is that the very brittle crystals when immersed in liquid air become very fragile and often break by themselves along the cleavage planes. This is a result of the opening of one of the cracks in the rod which is difficult to avoid in this kind of crystal (*see* Part I). As this happened with the crystal E, in order to study it at liquid air temperature we had to take another bit from the same crystal rod, and, before immersing this in liquid air, bound it with a silk thread.

This prevented the crystal from cracking. In order to distinguish this new piece we called it E′. Another difficulty is the breaking of the solder by which the silver discs were fastened to the rod. This was probably due to the strains set up between the bismuth and the silver due to a difference of expansion coefficient, and to the fact that at the temperature of liquid air the solder is very fragile. In some cases the disc did not break completely away, but the resistance of the crystal after being submitted to low temperatures increased by 10 or 20 per cent. This was probably due to cracks developed in the solder, as after resoldering the crystal the resistance generally returned to the initial value. In some cases, when the crystal was imperfect, the resistance of the rod retained its larger value, this being due to the imperfections developed in the crystal. Before each experiment and after, we measured the resistance of the crystal after bringing it to room temperature. If a variation of more than 5 per cent. was noticed, the experiment was not taken into account.

Finally, as will be seen from the next paragraph, for a given magnetic field the resistance changes approximately as the fourth power of the temperature, and at liquid air temperature a difference of 1 degree will result in a change of about 5 per cent. in the absolute value of the increase of resistance. We may easily admit that between individual experiments a difference of 1 or 2 degrees occurred from the variations in the temperature of the liquid air, which result from a difference in the concentration of oxygen.

All these sources of error probably reduce the accuracy of the absolute value of R/R_0 taken at liquid air temperature for different samples of crystals. The error in some cases may reach a value of 15 to 20 per cent. The general shape of the curve, however, is not affected by this error, which is too small to account for the large differences which were observed between the crystals A, C and D, as shown by the curves on fig. 13.

The same considerations apply to the curve E'_2 in the same diagram for the crystal E taken at the temperature of liquid air. We see that the change of resistance is again about twice as large as for crystal A, and the curve has a different shape, becoming a straight line only at the higher field of about 140 kilogauss.

The reason why we did not wish to place the crystal E in an ordinary holder, where it would be slightly compressed by the ebonite fork, was that we observed that a strain set up by the longitudinal pressure in a crystal influences the change of resistance of bismuth in magnetic fields. This phenomenon, which only happens at the temperature of liquid air, was accidentally traced from the observation that if a crystal is carelessly soldered to the silver discs, without a mica washer, as described in the Second Part of this paper, a different change of resistance is obtained. In order to prove the existence of this effect we soldered a bismuth crystal between two silver plates and measured the change of resistance in liquid air. Then, by means of a silk thread, we bound the crystal as strongly as was possible without spoiling it, and again measured the change of resistance. We found then that in strong fields the crystal gives a change of resistance which is about 10 per cent. less than that obtained for crystal which is not so bound. At the temperature of solid CO_2, or room temperature, this effect was not observed. This indicates that a pressure set up in a crystal has a similar effect to imperfections of the lattice in diminishing the change of resistance in magnetic fields.

We shall now describe the results for other orientations of the crystal, taking the case when the cleavage plane is parallel to the axis of the rod and the current is passing perpendicular to the magnetic field. We will call I $\perp$ H and I $\perp$ axis. In this case we have to consider the effect of the orientation of the cleavage plane relative to the field and study two main cases—first where the cleavage plane is parallel to the lines of magnetic force and the second when it is perpendicular. These two cases we will call respectively axis $\perp$ H and axis $\parallel$ H. Two further cases ought to have been considered, depending upon the position of the lines on the cleavage plane relative to the direction of the current, but as it is impossible to alter the direction of the current relative to these lines by a mere rotation of the crystal, it would be necessary to regrow the crystal with a different orientation of the lines. We should then be faced with a possible difference in the perfection of the two crystals which at present we cannot estimate in an independent way and which might completely vitiate the comparison. We shall not therefore consider these two cases.

For the crystals with the cleavage plane parallel to the axis of the rod, we have not made that systematic study of the effect of impurities and imperfections of the crystal lattice on the change of resistance which was attempted for the perpendicular orientation. We simply took a crystal, which we call **X** grown from Hartmann and Braun bismuth, under the most uniform temperature conditions in the apparatus of fig. 5, this crystal having a specific resistance of $1{\cdot}07 \,.\, 10^{-4}$ at 14° C., which is the smallest we have observed. From the low value of the specific resistance, we assumed that this was the most perfect crystal which we were able to obtain. It happened that in this crystal two of the lines on the perfect cleavage plane, resulting from the intersection of the three remaining planes of the pseudo-octahedron, formed an angle of nearly 60° with the direction of the rod. For a piece cut from this crystal for each of the three temperatures which we had been using, we took two curves of change of resistance, having the crystal orientated with the axis parallel and perpendicular to the magnetic field. These two orientations are obtained by turning the crystal rod round its axis in the holder A or B on fig. 9. In the first position (axis ⊥ H) the change of resistance in the magnetic field is larger and is given on figs. 14, 15 and 16

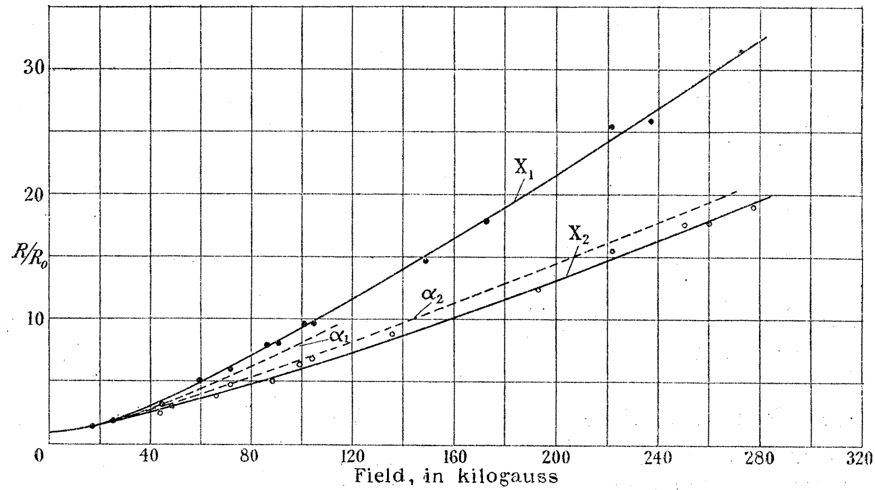

Fig. 14.—Room temperature, Orientation I ⊥ Axis and I ⊥ H. Curve X_1, Crystal X, Axis ∥ H. Curve X_2, Crystal X, Axis ⊥ H. Curve α_1 and α_2 for bismuth condensed from vapour in vacuum.

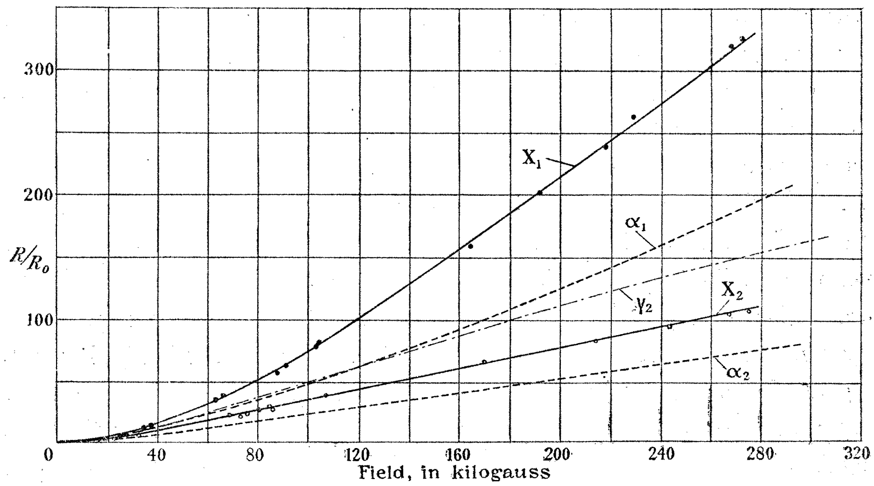

Fig. 15.—Temperature of the mixture of solid CO_2 and Ether, Orientation I ⊥ Axis and I ⊥ H. Curve X_1, Axis ∥ H. Curve X_2, Axis ⊥ H. Curve Y_2, Crystal Y, Axis ⊥ H. Curve α_1 and α_2 for condensed bismuth.

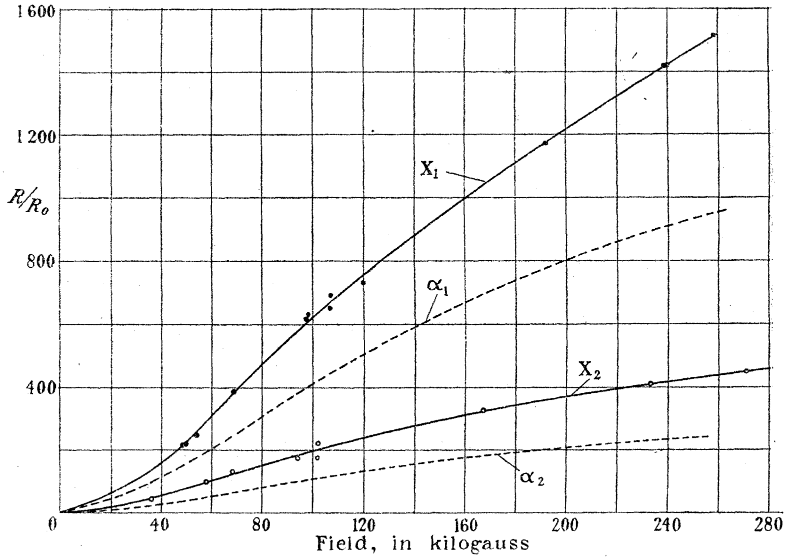

FIG. 16.—Temperature of Liquid Air, Orientation I ⊥ Axis and I ⊥ H. Curve X_1, Axis ‖ H. Curve X_2, Axis ⊥ H. Curves α_1 and α_2 for condensed bismuth.

by curve X_1; in the second position (axis ‖ H) the experimental results are represented on the same diagram by curve X_2.

The diagram of fig. 14 shows the results for the change of resistance at room temperature (15°). The crystal rod had the resistance of 0·00423 ohm. The change of resistance in this case is of the same magnitude and, in fact, is practically the same as curve A_2 on diagram fig. 11, where the current was perpendicular to the cleavage plane. Curve X_2 is for the same crystal rod when it is turned through an angle of 90° round its axis. The change of resistance is smaller, but the general character of both curves is the same. We have a curvature in the beginning which tends to a straight line at stronger fields.

Curves X_1 and X_2 in fig. 15 relate to the case where the crystal was placed in a mixture of solid CO_2 and ether. The resistance of the crystal was 0·00285 ohm. The curves are of an exactly similar character as at room temperature—they commence with a curvature and then straighten out. Finally, in fig. 16, we give the curve for liquid air temperature. Here the resistance of the crystal was 0·00155 ohm. We see that the general character of the curve is again the same. From a comparison of the results for the three temperatures we see that the difference between curve X_1, relating to the case where the cleavage plane was perpendicular to the magnetic field, and curve X_2, referring to the case where it was parallel, gets larger, as the temperature is lower. The magnitude of change of resistance for the position X_1 is of the same order as the one observed for the crystal A with the axis perpendicular to the cleavage plane (figs. 11, 12 and 13).

To see how the imperfection of the lattice affects the change of resistance for this orientation, we took a crystal which we had grown on a copper plate and which was probably far from being perfect, since its specific resistance was $1 \cdot 14 . 10^{-4}$. For this crystal, which we call Y, at room temperature we obtained the same change of resistance as given by the curves shown in fig. 14 (X_1 and X_2), but at the temperature of solid CO_2, where we made only one measurement in which the cleavage plane was parallel to the magnetic field, we obtained a larger change of resistance than for the crystal X, this being shown by curve Y_2 on fig. 15. This is probably due to the fact that in this case we had in the crystal Y, as suggested in Part I, local changes in the direction of the trigonal axis in the crystal lattice. This would account for both the large specific resistance and the departure of the curve Y_2 from X_2 since in the local imperfections, the cleavage plane will be more nearly perpendicular to the current and the resistance is thereby increased.

(3) *Discussion of the Results for the Experiments on the Change of Resistance when the Current is perpendicular to the Magnetic Field.*

From the results described it is easily seen that when the current is flowing perpendicular to the magnetic field there is *a great similarity in the change of resistance in the field for crystals differently orientated.* All the curves of figs. 11, 12, 13, 14, 15 and 16 are curved at the beginning, when the field is weak, and then at stronger fields straighten out. On closer examination we find that the initial part of each curve can be expressed by a quadratic law, viz.,

$$\Delta R/R_0 = \alpha H^2. \tag{1}$$

For the straight part of the curve we have

$$\Delta R/R_0 = \beta H. \tag{2}$$

It is convenient to describe each curve by the constant α and β, and also by the strength of the magnetic field at which the curve ceases to follow the square law (1) and changes to the linear law (2). This critical field strength, which we shall call H_K, can be given only very approximately, as in most curves no definite bends exist.

If we consider the influence of orientation of the crystal on these three constants, we see that for a definite *temperature the orientation of the crystal axis* *relative to the magnetic field chiefly affects the constant* α *of the square law, but the constant* β *of the linear law is the same for all orientations but one.* Thus the crystal A (fig. 12) at the temperature of solid CO_2 has the same slope of the linear part ($\beta = 1\cdot48 \cdot 10^{-3}$) on both the curves, but in the orientation A_1 line $\perp$ H $\alpha = 1\cdot36 \cdot 10^{-8}$ and in the orientation (line || H) curve A_2, $\alpha = 0\cdot8 \cdot 10^{-8}$. At liquid air temperature the curves A_1 and A_2 (fig. 13) again have the same slope ($\beta = 5\cdot44 \cdot 10^{-3}$). At room temperature (fig. 11) the slopes are different, but as is indicated by the slight curvature, it is very probable that at stronger fields (beyond 320 kilogauss) they will come to parallelism. In this case we have for the curve A_1, $\alpha = 1\cdot28 \cdot 10^{-9}$ and $\beta = 1\cdot27 \cdot 10^{-4}$, and for the curve A_2, $\alpha = 1\cdot4 \cdot 10^{-9}$ and $\beta = 1\cdot53 \cdot 10^{-4}$. For the crystal X with its cleavage plane along the axis of the rod, we have for the orientation (axis || H), curve X_1, exactly the same values for β as for the crystal A at the corresponding temperatures, but the α for the three temperatures under investigation has smaller values than for crystal A, viz., for room temperature $\alpha = 1\cdot24 \cdot 10^{-9}$, for solid CO_2 $1\cdot0 \cdot 10^{-8}$, and for liquid air $0\cdot88 \cdot 10^{-7}$. The only exception is for the orientation (axis $\perp$ H) curve X_2. Here the part of the curve which obeys the square law is very short and the values for α and β are smaller than for the curves A_1, A_2 and X_1.

The effect of the temperature is primarily to produce a very rapid increase in α and β with the lowering of the temperature. From experiments at only three temperatures no definite law of change of α and β can be deduced, but we estimate from our measurements that α and β change inversely as the fourth or fifth power of the absolute temperature.

The effect of the chemical impurities of the crystal on the change of resistance may be described as only affecting H_K and β, making them smaller. From a comparison of the curves for the pure crystals made from Hartmann and Braun bismuth with the crystal B made of the less pure bismuth of Kahlbaum, we saw that the curves have the same initial change of resistance at all temperatures. This means that α is the same. But for the temperature of liquid air (*see* the corner of fig. 13) already at a field of $H_K = 8$ kilogauss, the curve B changes sharply to a straight line with a very small β ($1\cdot35 \cdot 10^{-4}$). At the temperature of CO_2, this change point is not very well seen from fig. 12, as the scale of the diagram is too large, but actually it is given approximately by $H_K = 18$ kilogauss and the curve then follows a straight line with $\beta = 2\cdot8 \cdot 10^{-4}$. At room temperature this change occurs only at a field of 260 kilogauss (fig. 11).

If now we consider *the influence of the perfection of the lattice, we see that it* *only affects the value of the critical field H_K*, the values of α and β being independent of the state of perfection of the lattice. This we see from a study of the curves for the crystals A, C, D and E, which were made from the same purest bismuth of Hartmann and Braun, but grown in different ways. It is seen from fig. 12 that at the temperature of solid CO_2, the temperature at which we were able to trace the influence of the imperfection of the lattice, all the different crystals having the same orientation have the same value for α within the limits of experimental error. This means that in the beginning they follow the same square law, but with the difference that the crystals which we take to be most perfect, such as the crystal E, follow this square law to higher fields, that is H_K is larger.

After the change to the linear law of increase of resistance, however, we have the same slope, or β is the same. For instance, the crystal E, at a temperature of solid CO_2, follows the square law fairly well to a field strength of 100 kilogauss, and the crystal which is less perfect only to 60 kilogauss. Similarly, we observe on the curves of fig. 13 taken at liquid air temperature, that the breakdown from the square law for the crystal E does not occur until 120 kilogauss, but for the crystal A_2 at a field strength of about 40 kilogauss.

To sum up all these results in a general way, we may think of the influence of the temperature, impurities and other factors, on the change of the resistance of bismuth in the magnetic field in the following way.

A crystal lattice can be distorted, first by the temperature, due to the vibration of the atoms, secondly by impurities, thirdly by the imperfections of the lattice, of the type described in the First Part of this paper, and finally by a strain set up in the crystal. At room temperature the disturbance of the lattice due to the thermal motion of the atoms plays a predominant part and the other factors have no marked influence. This explains why, for all our crystals at room temperature, we had similar curves to those given by A_1 and A_2 on fig. 11.

At the temperature of CO_2 the disturbances due to the impurities in the lattice, as in the case of the Kahlbaum bismuth crystal B, begin to be comparable with the disturbances due to the temperature motion of the separate atoms in the lattice, and we have the difference between pure and impure bismuth as seen from the curves on fig. 12. The lattice imperfections produced during the growth of the crystal are also comparable with the disturbance due to the temperature, and on fig. 12 we see the difference in the curves A, E, C and D.

Finally, at a temperature of liquid air the disturbances of the lattice, produced by the temperature motion, are so small in comparison with those due to the disturbances due to the imperfection of the lattice, that the latter factors are even more appreciable and may make a still greater difference in the curve for the change of the resistance, as seen on fig. 13. In this case, for example, it is even possible to trace the very small disturbances produced in the lattice by small strains set up through binding the holder with a silk thread, as was described in the last paragraph.

As the results obtained in our experiments depend upon the chemical impurities and upon the imperfections of the crystal lattice, it is important to discuss the question of how perfect our crystals were from a chemical and physical point of view, and how closely the change of resistance in a magnetic field, which, we observed, approaches that of an ideally perfect crystal. It is very difficult to answer these questions. As regards the chemical purity of the bismuth which we used, that of Hartmann and Braun is by reputation the purest, and it is possible that the purity was sufficiently high to make the results independent of the influence of chemical impurities. To settle this question systematic analysis and further purification of bismuth are necessary. It is unfortunately much more difficult to find out how perfect was the crystalline lattice of our best crystals. The difficulty lies in the fact that we possess at present only one independent means of judging the perfection of the crystal lattice, viz., X-ray analysis, but in our case it appears not to be sufficiently certain. We saw from the first part of this paper that the X-ray analysis shows us that a crystal such as E, which was grown in the uniform temperature condition (*see* fig. 5), is, as far as can be determined by the X-ray reflections, a perfect crystal, but the X-ray analysis fails to trace the existence of a few cracks which we know still exist in the crystal.

It is very probable that these cracks, if they are not very numerous, have no influence on the change of resistance in the case when the current is perpendicular to the perfect cleavage plane (I || axis). As, however, we are not sure of the number of cracks, the question of the perfection of the crystal lattice must be left open. The question is made more difficult by the fact that even if we admit that the crystal is nearly perfect after growth, it is very difficult to be sure that after cutting a piece 3 or 5 mm. long from the rod, and fixing it in the holder, the lattice is not disturbed. It was noticed that if the crystal was carelessly handled, *e.g.*, by over-heating when it is soldered between the silver discs *d*, fig. 9, or by pressing it too hard when the crystal is introduced in the ebonite holder *f*, fig. 9, the crystal was very often spoiled. This could sometimes be traced by an examination of the crystal under a microscope. The crystal appeared bent and had lines on the surface, which indicate that slipping occurred between the cleavage planes. We also noticed that such damaged crystals behaved, in a magnetic field, like crystals with an imperfect lattice. In the latest experiments we took the greatest care to handle the crystals carefully, but even then it was impossible to be sure that strains set up from the holder, due to the difference of thermal expansion between the ebonite and bismuth, do not spoil the lattice. It is very difficult to avoid all these disturbances produced in fixing the crystal, when such small pieces of the crystal are used. To avoid all these difficulties the experiments would have to be repeated with a coil of larger diameter, where a more satisfactory method of fixing the crystal would be possible. We think, however, that in cases where special attention was given to fixing the crystal (as in the case of crystal E), the distortion was not very great and the error introduced was of the same order as the general precision of our measurements.

In the following paragraph, where the change of the resistance of bismuth with the current parallel to the magnetic field is described, we shall again discuss the perfection of the lattice of our crystal, as in this case the imperfections of the lattice have an even larger influence on the change of resistance. It will be shown that it is even possible that all the effect is to be ascribed to the imperfections. If this be the case, these experiments afford another method of finding the perfection of the crystal.

Leaving aside the question of the absolute perfection of the crystals which we were using, we may still, from a comparison of the results from different crystals, obtain information as to how an ideally perfect bismuth crystal will change its resistance in a magnetic field.

First of all it is evident that even an ideal crystal in all orientations within the range of temperature which we investigated will first change its resistance with the square of the magnetic field and after the critical field linearly. Secondly, taking into account the influence of the impurities and imperfections of the lattice, it is evident that an ideal bismuth crystal in the region of weak fields, when the change of resistance follows the square law, will have the same coefficient α as our crystals in corresponding orientations and at corresponding temperatures. The difference between our crystal and a crystal made of ideally pure bismuth will be that the latter may have a larger value for the coefficient β for the fields where the increase of resistance follows the linear law, and a crystal which has a more perfect lattice than ours may have a larger value for the critical field H_K, which separates the region of the square and linear laws. This difference between an ideal crystal and our crystal may, however, be apparent only at lower temperatures, and we may be sure that for ordinary temperatures the two curves A_1 and A_2, fig. 11, and curves X_1 and X_2, fig. 14, will be practically identical with that of an ideal crystal, as the influence of the imperfection of the crystal is in this case small compared with the disturbances produced by the heat motions of the atoms.

For the experiments at a temperature of solid CO_2, we find that the impurities and the imperfections of the crystal lattice have already a marked influence, and all that we can say is that for our most perfect crystal E, H_K is about 100 kilogauss (whilst for the less perfect crystal A, $H_K = 60$ kilogauss), so that it is impossible from our data to fix the value of H_K for an ideal crystal, but it will certainly not be less than 100 kilogauss. The same argument applies to the linear part of the curve, the slope of which gives the coefficient β, and also to the experiments at the temperature of liquid air.

We shall now discuss one of the most interesting phenomena—the existence of what we have called the critical field H_K in the change of resistance of bismuth. This critical field is not well defined, but it may have an important theoretical significance. Below the critical field the crystal follows a square law of change of resistance, the coefficient α of which depends very much on the orientation of the crystal, but after the critical field we have a linear law which, for all orientations of the crystal [except one in the orientation for the curve (X_2)] is the same for any crystal made of the same bismuth and observed at the same temperature. This suggests that in the region of the linear change of resistance after the critical field, the condition for the motion of the conducting electrons is similar in all crystals for all orientations. It would appear, therefore, that above the critical field the influence of the neighbouring atoms on the conducting electrons, which depends on the symmetry of the crystalline lattice, is lost. This change or "reconstruction," as we may call it, produced by the field, whatever it may be, probably takes place during the increase of the magnetic field from O to H_K during the square law part of the curve. The ease with which the reconstruction takes place depends not only on the initial orientation of the crystal relative to the field, but also on the perfection of the crystal. We may say that impurities and imperfection in the crystal which disturb the lattice makes the reconstruction easier and reduces the value of H_K.

It will be interesting to see whether any other physical phenomena, such as diamagnetism, also change after the critical field is reached. If such a change be observed it will throw light on the character of the reconstruction, about which we can speak only vaguely at present.

As we may expect this reconstruction to be noticeable in the most favourable cases only at fields higher than 50 kilogauss, it is evident that it could not have been observed in the weak fields used by previous investigators.

Finally, we have to remark that it is difficult to compare the results just described with old ones. First, because in previous experiments the residual e.m.f. was never eliminated, and this, even in weak fields, as has been shown by Geipel,* reaches a value of 7 to 8 per cent. of the potential drop along the crystal. Secondly, because the crystals were not so perfect as those prepared by our methods, and we have seen how markedly the measurements are affected by the imperfection of the crystal lattice, and thirdly, because observations were confined to weak magnetic fields which were not covered in our investigations.

(4) *The Study of the Change of Resistance of Bismuth Crystals when the Current is parallel to the Magnetic Field.*

For the experiments described in this paragraph, we have been using a holder for the crystal given on fig. 9c. The results of the observation are given by curves in the same way as before, the scale for the ordinates being in this case much greater as the change of resistance is here very small. The letters by which the curves are marked refer to the same crystal as studied in the transverse phenomenon, but the suffixes in this case refer not to the orientation of the crystal but to the temperature. We use the suffix $_1$ for room temperature, $_2$ for solid CO_2, and $_3$ for the temperature of liquid air. We will first consider the set of observations relating to the curve when the current was perpendicular to the cleavage plane. We call this case $I \parallel H$ and $I \parallel$ axis.

In the first place we studied a piece of the same rod from which the crystal A was cut. The results are given on curves A_1, A_2 and A_3, fig. 17. Here we are at once struck by the fact that the resistance change is not only very small but quite definitely reaches a limiting value. For instance, at room temperature, curve A_1, fig. 17, shows that the resistance increases very little after reaching a field of 120 kilogauss. At a temperature of CO_2, the curve A_2 shows a slightly larger change of resistance, but the saturation phenomenon is even more marked and it is reached at a smaller field—about 80 kilogauss. The oscillogram, No. 10, taken for this curve, illustrates this saturation phenomenon. It can be seen very clearly that the deflection of the potential oscillograph reaches a limiting value and remains constant, although the current through the main coil is increased.

* 'Ann. d. Physik,' vol. 38, p. 149 (1912).

The most curious curve was obtained for liquid temperature (curve A_3). This shows not only this saturation phenomenon, but in addition the resistance,

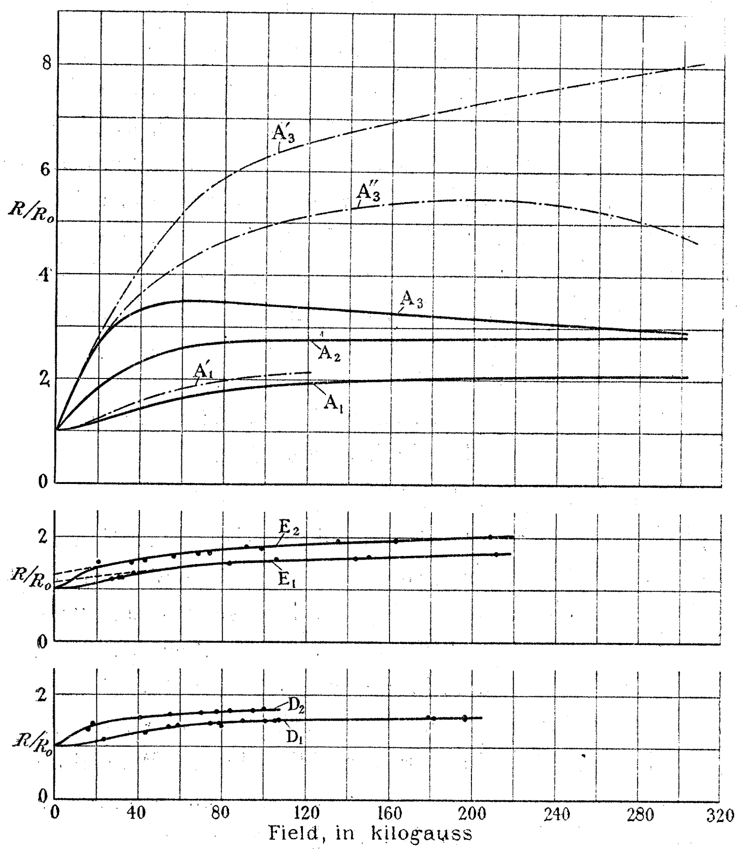

FIG. 17.—Orientation I || Axis and I || H. Curves A_1, A'_1, D_1, E_1 room temperature. Curves A_2, D_2, E_2, temperature of solid CO_2 and Ether. Curves A_3, A'_3, A''_3, temperature of Liquid Air.

after reaching a maximum, at about 60 kilogauss, gradually began to drop. The phenomenon was so curious that we decided to repeat the experiment. It happened that the first experiment was made towards the end of the week, when the liquid air used had been stored for a week. The experiment was repeated at the beginning of the next week with fresh liquid air. Unfortunately the contacts in the crystal were spoiled before this experiment, and to re-establish them the screw g on fig. 9 C was pressed down, thereby changing the stress conditions in the crystal. First of all we found the change of resistance in this experiment to be larger than before, as is seen from curve A'_3, but no drop of resistance was observed. Repeating the experiment with the old liquid air we obtained curve A''_3 and here again a drop of resistance is seen. The explanation of this phenomenon is very simple. When we used old liquid air most of the nitrogen had evaporated and we had a larger concentration of oxygen in the liquid air than in a fresh sample. It was mentioned in Part II of this paper that, owing to the larger paramagnetism of liquid oxygen, the pressure in the Dewar flask in very strong fields may be very considerable. For instance, if we had pure oxygen only, the pressure corresponding to a field of 300 kilogauss will be about 15 kilograms per cm.^{2}. With fresh liquid air this pressure will be only about 3 kilograms per cm.^{2}. Now it is evident that the fall in the resistance, curves A_3 and A_3'' can easily be accounted for by this pressure, if we assume that the cracks in the crystal close under the pressure produced by the liquid air, thereby diminishing the resistance. With the increased concentration of oxygen in old liquid air the pressure is larger and the closing of the cracks is more effective.

After the experiment with liquid air the curve was again taken for room temperature, and we obtained the curve A'_1. We see that the change of resistance is somewhat larger than for curve A_1 before the screw *g* was tightened up. When the crystal was taken out and examined under a microscope we found that the crystal rod was considerably bent, and the deformation of the crystal was quite evident. Apparently this deformation was produced when the screw *g* was screwed down.

For the next experiment we took a piece of the very flexible crystal and made a special holder; the leads (*e*), fig. 9 C, were arranged so that they were pressed to the silver discs from the sides, and practically no longitudinal pressure on the crystal was possible. With this flexible crystal we obtained curves D_1 and D_2. We see that the change of resistance is about one-half of that for the crystal A for the two corresponding temperatures. Using a piece of the rod from which the crystal E was made, grown, as stated, in the apparatus, fig. 5, and believed to be the best crystal, we again obtained a smaller change of resistance than for the crystal A at room temperature (curve E_1) and also at the temperature of CO_2 (curve E_2).

We were unable to perform the experiments for the crystals E and D at the temperature of liquid air for the reason that in the new holder, in which there was no axial pressure on the crystal, the soldering broke in the case of the crystal D when placed in liquid air, and in the case of crystal E the crystal itself broke. It has already been mentioned that it is very difficult to use these brittle crystals in liquid air, as most of them crack along the cleavage plane, if no pressure is applied to the crystal along its axis.

We shall now describe experiments with the other possible orientations of the crystal with its cleavage plane parallel to the axis of the rod (case I || H and H ⊥ axis). The crystal was placed in the same holder, fig. 9 C, and the results of the experiments are given by the curves in fig. 18. A piece of the

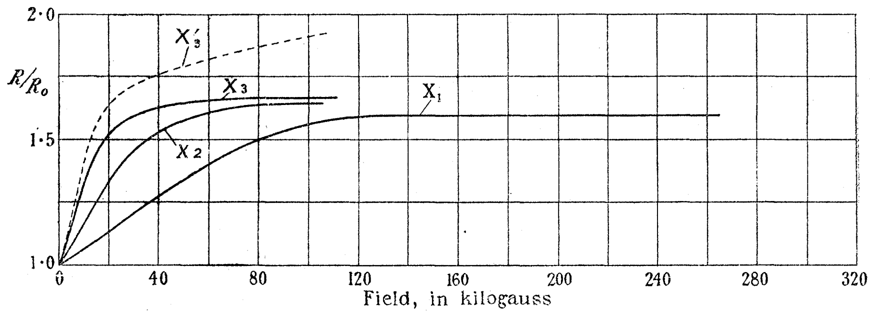

Fig. 18.—Orientation I ⊥, Axis and I || H. Curve X_1, room temperature. Curve X_2, temperature of solid CO_2 and Ether. Curve X_3, X'_3, temperature of Liquid Air.

same crystal rod was used as in the experiments with the current perpendicular to the field, and which we called crystal X. The curve marked by X_1 refers to room temperature, by X_2 to solid CO_2 and ether, and X_3 to the temperature of liquid air. The results from the point of view of magnitude and general character are exactly similar to those obtained in the case previously treated, except that the pressure effect of liquid air does not now appear. This we ought to expect as the possible cracks are parallel to the current, and their closing or opening will not influence the resistance of the crystal rod.

From all these experiments we see that in this case we have an exactly opposite phenomenon to that observed in the experiments when the current was flowing perpendicular to the magnetic field. The change of resistance is much larger for the imperfect crystals than for the perfect ones, and in the case (I || axis) it is very easily influenced by the pressure. This all suggests a simple explanation of these phenomena. If we imagine that there is a crack, as in crystal A, or an imperfection, as in crystal X, which produces a large local increase in the resistance of the crystal, then the current in these places will not flow parallel to the axis of the rod, but will simply choose the way of the minimum resistance and may conceivably have local components which are perpendicular to the axis of the rod. Now when the crystal is placed in a magnetic field which is parallel to the axis of the rod, these perpendicular components of the current will flow perpendicular to the magnetic field, and the resistance, in the perpendicular direction, will be very much increased, as has been seen from the previous section. Finally, the current will be compelled to flow parallel to the rod, taking the paths which had a larger resistance, in the absence of the field. When this parallelism in the lines of flow of current is reached no further increase of the resistance of the bismuth rod is possible, and we have the saturation phenomenon as shown by the curves on figs. 17 and 18. If we have a crack in the crystal, which offers at a certain place a very large resistance, the current will flow round this crack, but when the crack is closed by means of pressure, as may happen in the case of liquid air, the current may flow through the broken part again, and it is evident that the resistance of the rod will diminish. It is highly probable that all the effect of the change of resistance, which we have observed in the case where the current is parallel to the magnetic field, is due to the imperfection of the crystal. This point of view, which reduces all the phenomena to a secondary effect, simply due to the imperfection of the crystals, is also confirmed by the fact that all the changes of resistance for the three different temperatures are of the same order. This fact alone makes it almost impossible to suppose that the phenomena have the same origin as in the case where the current is perpendicular to the magnetic field. On the other hand the observation that the saturation value is reached at a lower temperature with a smaller field, exactly supports our view, as at low temperatures, owing to the very rapid increase of the resistance for the small perpendicular components of the current with increasing magnetic field, the straightening out of the current parallel to the rod will happen more quickly. Our view is also strongly supported by the fact that at all the three temperatures the same relative change of resistance is observed. This is seen most clearly on fig. 18, where the curves X_1, X_2 and X_3 have the same saturation value. This is exactly what we should expect from our explanation. The path of the current without the magnetic field, as well as the changed path with the field, will be the same if the imperfections of the crystal do not alter for different temperatures, and this will evidently result in the same relative change of resistance.

If this explanation of the phenomenon is correct, we may use it for judging the perfection of the crystals. In our most perfect crystals, such as crystal E, we are still left with some increase of resistance. This is not necessarily due to the imperfection of the crystal, but may be produced by some imperfection of experimental arrangement. For example, at the point where the bismuth rod is soldered to the silver disc, the contact may not be equally good over the whole surface and this will result in the current being brought out of parallelism producing exactly the same result as the imperfection of the crystal. This was confirmed in some experiments in which after resoldering the crystal the limiting value for the change of resistance sometimes increased or diminished. The breaking of the contacts in liquid air, described in the previous paragraph, has also a very large effect on the increase of resistance.

In addition, part of the effect is no doubt due to the fact that it is impossible to cut out a piece of rod without damaging the crystal near the place of section. This effect is probably more marked in the crystal with the cleavage plane parallel to the rod, like crystal X, where more strain is put upon the crystal when it is cut, than in a crystal where the cutting is made along the cleavage plane.

The small rise in resistance after the saturation value is reached may be attributed to the fact that the crystal was not perfectly aligned with the magnetic field and the magnetic field was not perfectly uniform in that part of the coil where the crystal was placed. It is evident that if this is the case the current flowing in the crystal will tend to flow along the lines of force of the magnetic field, for if it flows perpendicular to the lines of force it will meet a very large resistance. With increasing field, the lines of flow of the current will gradually shift, and the resistance of the crystal will increase. On fig. 18 we have an illustration of this phenomenon. Crystal X was turned in the holder to make a small angle with the magnetic field, and instead of having the curve X_3 the curve X'_3 was obtained which has the same saturation value, but after which a steady increase of resistance is still well marked.

In our experiments, as we were working with small pieces of bismuth, a perfect alignment of the axis of the rod with the magnetic field was not obtainable. But we may roughly separate the increase of resistance due to this error in setting the crystal, from the other, if we extrapolate the flatter part of the curve as shown by dotted lines for the crystal E on fig. 17. Then the ordinate at which this curve intersects the axis of co-ordinates will give us the saturation value of the change of resistance which will occur in the same crystal when it is properly aligned with the field.

We see that the increase of resistance for the most perfect crystal E in this case will be only 15 per cent. at room temperature. At the temperature solid CO_2 and ether it will be about double. This is probably due to the strains set up in the crystal at lower temperatures owing to the difference of temperature expansion in the crystal which may open the cracks and affect the contacts between the silver disc and the bismuth rod. The change of resistance in crystal E is very small and it is quite possible that it may be fully accounted for by the imperfection of the experimental arrangement, as already described. It is very probable that by further refinement of the experimental arrangements we may be able still further to reduce the small change of resistance observed. It is important to mention that the change of resistance which we have observed is already considerably smaller than in previous observations.* A precise comparison is unfortunately difficult as these results all relate to weak fields (about 2 to 4 kilogauss) in the region where we can only extrapolate our data with an accuracy of 20 to 30 per cent. Even in this case, however, the values obtained in our experiment showed that the increase of resistance was several times (in no case less than three times) smaller than previously obtained, showing that our crystals, grown in the way described in the First Part of this paper, were much more perfect This is also confirmed by some other facts, for it is known that imperfect crystals give a smaller decrease of resistance when the temperature is diminished. In the table below we give the ratio of the resistance at the temperature of solid CO_2 (193° K.) and at the temperature of liquid air (91° K.) to that at room temperature (290° K.) for the two directions along and perpendicular to the crystal axis for our best crystals and compare them with the results for crystals which were grown in crucibles and studied by Borelius and Lindh in a magnetic field A.†

	I ∥ Axis.		I ⊥ Axis.	
	$\frac{R_{290}}{R_{193}}$	$\frac{R_{290}}{R_{91}}$	$\frac{R_{290}}{R_{193}}$	$\frac{R_{290}}{R_{91}}$
Our crystals	1·84	3·00	1·54	2·73
B. and L.	1·33	1·88	1·46	2·46

From this table it is evident that our crystals were more perfect than those obtained previously.

If our suggestion for the explanation of the phenomenon of change of resistance is correct, we see that our best crystal is crystal E, as we assumed in the previous section and as was confirmed by X-ray analysis.

* Borelius and Lindh, 'Ann. d. Physik,' vol. 53, p. 104 (1917); Schneider, 'Phys. Rev.,' vol. 31, p. 251 (1928).

† Borelius and Lindh, 'Ann. d. Physik,' vol. 51, p. 613 (1916).

(5) *The Change of the Resistance of Bismuth condensed from Vapour in Vacuum.*

As has been seen from the previous experiments at low temperatures, the influence of the imperfection of the crystal lattice plays an important part in the phenomenon of the change of resistance in magnetic fields.

Since we were unable to produce what we may call an ideally perfect crystal by the methods described in Part I, an attempt was made to produce perfect bismuth crystals by growing them by means of direct deposition of bismuth vapour on a plate. The general idea of this experiment was that if the bismuth atoms from the vapour were directly deposited on the crystal they would at once place themselves on a rhombohedral lattice, and all possible strains, due to the transformation from one modification to another, as described in Part I, would be avoided. These experiments were not successful, but some results obtained may be of interest.

The apparatus used in these experiments consisted of a quartz tube, 30 cm. long and about 1 cm. in diameter, having a bulb about 3 cm. from the bottom end, this end being sealed. Beneath the bulb the quartz tube was drawn to a neck of 3 or 4 mm. inside cross section. During the experiment the tube was evacuated to the highest possible vacuum by means of charcoal and liquid air. Some pure Hartmann and Braun bismuth was placed in the bottom of the tube. About 1 cm. above the neck, in the middle of the bulb, a quartz plate, 8 mm. in diameter, was placed on a solid copper holder. The holder was fixed to a glass tube inserted in the quartz tube from the open end in such a way that the disc with the holder did not touch the quartz tube. When the bismuth in the bottom of the tube was heated a molecular beam was formed which struck the quartz plate and formed a deposit. Arrangements were provided to warm up the copper holder by means of an electrical heater, or to cool it with water or liquid air. A thermo-couple, touching the quartz disc, recorded the temperature.

When the deposit was obtained the following curious phenomenon was observed. If the temperature of the quartz plate was low—at the temperature of liquid air, or even at room temperature—the bismuth deposit had no apparent crystalline structure. If the bismuth deposit was $\frac{1}{2}$ mm. thick, it formed a grey mass which was very brittle and in no way resembled ordinary bismuth. The specific resistance of this bismuth was very high, and the temperature coefficient was negative.

It appears from these experiments that at low temperatures the atoms stick to the plate without forming a crystal and most probably form an amorphous mass. We noticed that on the surface of the quartz bulb, which kept fairly warm during the experiment, the layer deposited was of a different character, and was much more like ordinary bismuth. This suggested heating the quartz plate to a higher temperature by means of the electric heater. In this way we were really able to obtain layers which were of a quite definite crystalline character. When we kept the plate at 200° C. the bismuth deposit obtained no longer had a negative temperature coefficient, and its specific resistance was about $1 \cdot 7 . 10^{-4}$. Depositing bismuth throughout the day at such a temperature we obtained a deposit of about 3 to 4 mm. thick which looked very like a little mountain made of needles stuck perpendicular to the quartz plate. These needles slightly adhered to one another, and it could be seen under the microscope how these needles broke away when pressed by the point of a sewing needle. Each individual needle apparently consisted of other needles, which, by the slight pressure of a pin, could be separated. It was clear that the structure of the deposit was crystalline, consisting of many very small needles having only one general orientation in the direction of the incident beam of molecules.

The following attempts were made to obtain single crystals instead of a bunch of needles. In the first place, instead of the quartz plate, a large bismuth crystal was used with its freshly broken cleavage plane perpendicular to the beam, but the deposit grew on it in an exactly similar way as on the quartz plate. This might be due to impurities absorbed on the surface layer of the bismuth crystal. The following experiment was then made to obtain a clean surface. After a small layer of bismuth had been deposited on a quartz plate it was heated above the melting point of bismuth. The surface layer then broke up into small drops which remained stuck to the plate, and when cooled each drop turned to a single crystal providing a centre of crystallisation for the condensing bismuth atoms. As the whole procedure took place in a high vacuum, the possibility of having a contaminated surface layer was less likely. The bismuth deposit was then made on the drops, as before, at a temperature of 200°, but on examination it was seen that the cleavage plane of these drops had no relevance to the small needles which stuck to them, and that there were about 50 or 60 needles growing from one drop. This means that the orientation effect on the crystalline axis, produced by the direction of the falling molecules, is much more important in the growth of the deposit than the plane of the crystal on which it is deposited.

However, a plate about 1 mm. thick and 3 mm. wide was cut out from the

3 mm. thick deposit made of needles, and was placed in the holder in order to investigate its change of resistance in a magnetic field. The results obtained are shown by curves α_1 and α_2 in fig. 14 for room temperature, in fig. 15 for a temperature of solid CO_2, and in fig. 16 for the temperature of liquid air. These curves all relate to the case when the current is perpendicular to the magnetic field. In the case described by curve α_1 the current passed through the plate under examination, parallel to the direction of the needles. In the case of α_2 the current passed perpendicularly to the needles. The same plate was used for obtaining both these curves, only it was soldered in the holder in different ways. We see that the change of resistance in this case, especially at low temperatures, is smaller than for the bismuth crystal in our experiments. The reason for this is probably that the boundary layers between the individual needles, which are probably quite good crystals, play the rôle of imperfections in the crystal lattice. This point of view is confirmed by the fact that curve α_1 is always above curve α_2, because in the former case the current is passing along the needles, so that it has fewer boundaries to cross.

The phenomenon here observed bears a close relation to the observation made by Patterson* and afterwards studied by Holliveque† and studied in more detail by Hecker and Curtis.‡ They found that a very thin bismuth layer, deposited by cathodic sputtering on a cooled plate, does not change its resistance in a magnetic field. The deposited layer commences to show a change of resistance in magnetic fields only after it has been heated to a higher temperature. This phenomenon is apparently not connected with the thinness of the layer, but is simply due to the fact that bismuth deposited by cathodic sputtering on a cold surface probably forms an amorphous mass in the same way as by vapour deposition, which may be described as a crystal spoiled to its limit, and in this amorphous state bismuth has no change of resistance in a magnetic field. As soon as it is heated, the layer crystallises itself and the normal bismuth properties appear. This is confirmed by some of our observations in which much smaller changes of resistance in magnetic fields were found for layers about $\frac{1}{2}$ mm. thick, when these layers were deposited on a cooled plate.

(6) *The Residual E.M.F. occurring in Bismuth in the Magnetic Field.*

The residual e.m.f. developed in bismuth in a magnetic field, when a current is passed, reached a very considerable value in our experiments as is easily

* 'Phil. Mag.,' vol. 64, p. 562 (1902).

† 'Phil. Mag.,' vol. 64, p. 135 (1902).

‡ 'Phys. Rev.,' vol. 15, pp. 65 and 457 (1920).

seen from oscillograms 2 and 3. Our experimental method was not suited to a study of this phenomenon with great accuracy, since, as is seen from the oscillogram, the inverse e.m.f. does not reach its limiting value in 1/100 second. We therefore made only a general study of the magnitude of this phenomenon in different field strengths, for different orientations of the crystal and for varying temperatures. The magnitude of the residual e.m.f. was estimated in the following way. We used the field with the flat top, as shown on oscillograms Nos. 2 and 3, Plate 5, and broke the current in the crystal in a quite definite place towards the end of the flat part of the current wave in the coil by means of the special switch described in Part II. Then from the oscillograms we measured the ratio of the negative deflection of the potential oscillograph, which is due to the residual e.m.f., to the full amplitude, at the moment of break of the current through the crystal. This ratio, which we call n, is evidently given by

$$n = \frac{E}{IR}, \tag{3}$$

where E is the residual e.m.f., R the resistance of the crystal in a magnetic field, and I the current through the crystal. From the value of n and R we were able to judge the absolute magnitude of E. It was at once noticed that this e.m.f. occurs only in the cases where the current was flowing perpendicularly to the magnetic field. The maximum e.m.f. for crystals is observed in an orientation when the current is perpendicular to the perfect cleavage plane, the phenomenon being several times smaller, when the current is parallel to the cleavage plane. This result is in agreement with the previous observations made by Geipel.* In this research we limited our study to the case where the current is perpendicular to the cleavage plane, as only in this case could we expect a reasonable accuracy from our method of measurement of the e.m.f.

In the first instance we verified that n is independent of the current sent through the crystal. This was easily done by taking an oscillogram, as shown on oscillogram 2, then doubling the current through the crystal and taking another oscillogram with the same magnetic field in the coil, but halving the sensitivity of the potential oscillograph. When the two oscillograms were superposed the complete coincidence of the lines traced by the potential oscillograph proved that the ratio n does not depend on the current density, and that E is proportional to I. We also proved that n does not depend on the length of the crystal rod. Using a holder for the crystal, shown in fig. 9, A, we first

* 'Ann. d. Physik,' vol. 51, p. 503 (1916).

measured n for a given field between the potential leads and afterwards between the silver discs, in this way doubling the length of the crystal. The value of n obtained for these two experiments was the same. These results are in agreement with those of Seidler* and Geipel,† for smaller current densities and for weaker fields.

The first result which we will consider is the change in the e.m.f. produced by changing the orientation of the crystal when it is turned round its axis by 30°. We took a crystal in the two orientations described in para. 2 (line $\|$ H and line $\perp$ H), and it was easily noticed that the ratio n is larger in the case when the crystal is placed relative to the magnetic field in such a way that one of the lines on the perfect cleavage plane was perpendicular to the lines of magnetic force (line $\perp$ H), for which the crystal has also its maximum change of resistance. For instance, for one of the crystals, which we call K, at room temperature, at a field of about 190 kilogauss, in the orientation (line $\perp$ H), the ratio $n = 0{\cdot}18$, and for the same magnetic field, but after being turned by 30° to the position (line $\|$ H), the ratio $n = 0{\cdot}10$. These two cases are illustrated in oscillograms 11 and 12, both taken under similar conditions, oscillogram 11 being for the position (line $\perp$ H) and oscillogram 12 for (line $\|$ H). It can easily be seen that n is greater in oscillogram 11. This influence of the orientation for a given crystal remains unaltered for all strengths of the magnetic field and for different temperatures.

The influence of temperature and the field strength on the e.m.f. depends very much on the perfection of the crystal, the chemical and crystalline perfection of the crystal influencing the e.m.f. even at room temperature. We observed that the most perfect crystals, which at low temperatures give the largest increase of resistance, also have the largest values for the ratio n. We shall first consider the influence of the field and temperature on the value of n for one of the best crystals K. The value of n at each temperature was measured for two or three field strengths, and we found that at room temperature, for the orientation (line $\perp$ H), and a field H = 95 kg., $n = 0{\cdot}175$; for H = 191 kg., $n = 0{\cdot}18$. For the orientation (line $\|$ H), H = 95 kg., $n = 0{\cdot}09$, and for H = 194 kg., $n = 0{\cdot}10$. At the temperature of solid CO_2 for the orientation (line $\perp$ H) we had for H = 97 kg., $n = 0{\cdot}22$, and for H = 194 kg., $n = 0{\cdot}19$ (oscillogram 2). At liquid air temperature different specimens of a good crystal gave the following values for n: at H = 95 kg., $n = 0{\cdot}06$; H = 156 kg., $n = 0{\cdot}075$, and H = 247 kg., $n = 0{\cdot}04$. From

* *Loc. cit.*

† *Loc. cit.*

these data we see first of all that n increases slightly at the temperature of solid CO_2 and drops to a small value at liquid air temperatures. For each of these three temperatures the value of n does not seem to depend much on the field strength. The small drop in n, which is observed with increasing strength of the field, may be accounted for by the fact that in strong fields the time to develop the full e.m.f. may be longer. The experimental error is also considerable in these experiments as the negative deflection due to the e.m.f. is small. In most cases the estimated error in the absolute value of n is $\pm 0 \cdot 01$.

From the expression (3) for n, we see that if n is constant, E will be proportional to R. This means that the residual e.m.f. will change with the magnetic field in the same way as the resistance, as shown in the curves, figs. 11, 12 and 13. Thus in weak fields the e.m.f. will be proportional to the square of the magnetic field and will afterwards increase linearly with the field strength.

The imperfections of the lattice are found to exert a great effect on the absolute value of n, but as in the case just described, n changes but little with the magnitude of the magnetic field, even for a relatively imperfect crystal. If we compare the oscillogram No. 9, Plate 7, which was taken for one of our best crystals E, with the oscillogram No. 7, Plate 6, taken at the same temperature, but for a less perfect crystal, we see that the negative deflection of the potential oscillograph is nearly twice as large for the crystal E as for A. This shows that the most perfect crystal from the point of imperfections of the lattice showed the largest e.m.f. For instance, at room temperature, when the crystal was placed in the maximum position (line $\perp$ H), different specimens of bismuth crystal, grown in different ways from the same Hartmann and Braun bismuth, gave values of n ranging between $n = 0 \cdot 13$ and $n = 0 \cdot 19$ (for the crystal A, $n = 0 \cdot 14$); at a temperature of solid CO_2 and ether n ranged from $0 \cdot 22$ to $0 \cdot 14$ (for the crystal A, $n = 0 \cdot 15$).

The chemical impurities prove to have an enormous effect on the e.m.f. The less pure crystal B, already described in para. 2, which was made from Kahlbaum bismuth, gave at room temperature the following values for n. For the maximum position (line $\perp$ H), where $H = 95$ kg., $n = 0 \cdot 14$; where $H = 194$ kg., $n = 0 \cdot 17$ (oscillogram No. 13, Plate 8); in the position (line $\parallel$ H) where $H = 93$ kg., $n = 0 \cdot 07$, and where $H = 195$ kg., $n = 0 \cdot 10$, these values being only slightly on the small side. For the temperature of solid CO_2, however, we have the following data. In the maximum position B (line $\perp$ H), where $H =$ 195 kg., $n = 0$—no noticeable e.m.f. In the minimum position B_2 (line $\parallel$ H) where H = 95 kg., $n = 0 \cdot 03$ (oscillogram No. 14, Plate 8), and where H = 195, $n = 0$—again no e.m.f. This suggests, if we examine the curves B_1 and B_2 on figs. 11 and 12, that as long as the change of resistance of the impure crystal B follows the curves of the pure crystals A, C and D, the e.m.f. has a more or less normal value, but as soon as the field reaches such values that the curve of B no longer follows the curve A, the e.m.f. not only ceases to increase, but gradually drops to zero.

As previously stated, the e.m.f. has already been studied by Seidler and Geipel,* and a theoretical explanation of this effect has been given by Heurlinger.† Their experiment was carried out by means of a ballistic galvanometer which was switched on to the bismuth wire after the main current had been broken. If we compare their results with ours, we find that the maximum value of n which they observed, if expressed in our way, was $n = 0 \cdot 08$, which is about three times smaller than our maximum value. This is probably due to the greater imperfections in the lattice of their crystals. Our results for the change of the e.m.f. with the temperature, when expressed in the same way as those of Seidler or Geipel, do not quite agree with theirs. These investigators state that the maximum e.m.f. is observed about the temperature of solid CO_2 and ether. In our case this was only true for imperfect crystals, the best crystals showing a continuous increase in e.m.f. with decreasing temperature. For instance, if we take the crystal K, taking the e.m.f. to be unity at room temperature, in a field of 95 kilogauss at the temperature of solid CO_2 E = 13, and for the temperature of liquid air E = 50. The crystals with a bad lattice do not show any appreciable e.m.f. at the temperature of liquid air, and this is probably why Geipel observed his maxima for the e.m.f.

We very roughly studied the decrease of the e.m.f. with the time from oscillograms like oscillogram 3, where the current was switched off at the beginning of the flat part of the current wave. The value obtained was of the same order as observed by Seidler and Geipel, and as would be expected from the theory.

The explanation of the origin of the residual e.m.f. as given by Heurlinger‡ can be described in the following way. It is known that if a current is passing through a conductor in a magnetic field a difference of temperature occurs across the conductor in a manner very similar to the Hall effect. This phenomenon was discovered by Ettinghausen and is called after his name. As a result

* *Loc. cit.*

† 'Phys. Z.,' vol. 17, p. 221 (1916).

‡ *Loc. cit.*

of this transverse temperature gradient, a thermal current is set up perpendicular to the bismuth rod. On the other hand, Nernst has discovered that perpendicular to a thermal current in a magnetic field a difference of potential will occur. In our experiments with bismuth we have the two phenomena occurring at once. The difference of temperature produced perpendicular to the rod, due to the Ettinghausen phenomenon, results in a thermal current which produces the longitudinal e.m.f.

As it appears from the study of the Ettinghausen phenomenon that it takes some time to establish the temperature gradient, this accounts for the time lag phenomenon. From the data given by Zahn* for the Nernst and Ettinghausen phenomenon, Heurlinger obtains the correct value and sign for the resulting e.m.f. in bismuth. A verification of this theory is impossible in our case as the magnitude of the Nernst and Ettinghausen phenomenon is not known for the field strengths with which we are working. As, however, the general theory of the phenomenon is no doubt the same, we find from this theory a full justification for the elimination of the e.m.f. in the way stated in section 1 of this paper. It is evident that this e.m.f. is only a secondary phenomenon, which unfortunately reaches very large values for good crystals in strong magnetic fields. (For instance, in the case of measurements made in liquid air in a field of about 155 kilogauss, when a current of $\frac{1}{2}$ ampere was sent through the crystal, the e.m.f. reached the value of 0·16 volt in the length of 3 mm.)

As already stated, our experiments were of an approximate character only, but as the residual e.m.f. is only a secondary phenomenon, depending on the separate effects of Ettinghausen and Nernst, it was not thought worth while to refine our experiments. We hope later to make a separate study of these two effects in strong fields, but even from our present experiments it is quite evident that the Ettinghausen and Nernst effects in bismuth depend not only on the orientation of the crystal but also markedly on the state of perfection of the crystal. Further, from the constancy of n for a definite crystal in a variable magnetic field which makes the change of resistance proportional to the residual e.m.f., we must also admit a close physical connection between the phenomena of Nernst and Ettinghausen and the change of resistance of bismuth in magnetic fields.

If the difference of temperature due to the Ettinghausen phenomenon, at a given temperature, in a crystal of given orientation, is

$$\Delta T = f(H)\, I \qquad (4)$$

* See note *, p. 436.

where I is the current and f (H) a function depending in this case only on the field H, then in the same bismuth crystal, at the same temperature, the longitudinal e.m.f. due to the Nernst effect will be equal to

$$E = \Delta T . F(H) \tag{5}$$

where F is another function characterising the Nernst phenomenon. We get from (3), (4) and (5) $F(H) f(H)/R = n =$ constant for a given crystal at given temperature.

From measurements of Zahn* for weak fields we know that $f(H) \propto H$ and $F(H) \propto H$. Thus we get $R \propto H^2$ as we actually observe in weaker magnetic fields. Since for stronger fields $R \propto H$ we must have

$$F(H) . f(H) \propto H.$$

This shows that in strong fields the Ettinghausen and Nernst phenomena cannot both be proportional to the magnetic field as is usually assumed, and as is true for weak fields.

(7) *Comparison with Theory.*

The theory of the change of resistance of conductors in a magnetic field was first given by J. J. Thomson,† then by Ganz‡ and recently by Sommerfeld,§ but it is very difficult to account by means of any of these theories for the large change of resistance which takes place in such a peculiar substance as bismuth.

In Sommerfeld's theories of electrical conductivity it is assumed that free electrons exist in the metal, but, as a result of the strong interaction between the electrons, they have not the classical distribution of velocities, but a different one given by the modern quantum and wave mechanical theory. The law of distribution of velocity derived from the quantum theory, as given by the Fermi-Dirac statistics, makes the velocity of the electrons much higher than on the classical theory, and also shows that the velocity distribution in a metal under ordinary conditions is practically independent of the temperature. This is the main difference between the new and the older theories. The picture of a current passing through a metal remains the same, namely, that when a difference of potential is applied to a conductor the free electrons get an excess of momenta in the electric field which is absorbed by the nuclei of the heavy

* 'Jahr. d. Rad.,' vol. 5, p. 166 (1908).
† 'Rapports, Congrès internat. Phys.,' vol. 3, p. 138 (1900).
‡ 'Ann. d. Physik,' vol. 20, p. 293 (1906).
§ 'Z. d. Physik,' vol. 47, p. 43 (1928).

atoms which form the lattice of the crystal. The specific resistance of the conductor depends on the efficiency of the mechanism of transmission of the excess of momenta from the electrons to the lattice. The effect of the magnetic field on a conductor after the theory of Ganz and Sommerfeld, consists in the fact that the electrons, due to the deflection of their paths by the magnetic field, accumulate less momenta between two collisions from the applied electric field, and the result is an increase of resistance of the conductor. The magnitude of the change of resistance in a magnetic field, calculated on the basis of this picture, is very small, and even for a substance like silver, which changes its resistance very little in a magnetic field, is, as was pointed out by Sommerfeld,* about ten thousand times less than the experimentally observed value. For bismuth, the discrepancy between the theory and experiments is even larger. If, for instance, from the formula 77A, given by Sommerfeld, we approximately calculate the free path of an electron necessary to account for the change of resistance in magnetic fields, taking the values for the coefficient of change of resistance (1), at liquid air temperature of $\alpha = 2 \cdot 76 . 10^{-7}$ (Sommerfeld's B), we find that the value l of the free path is above 1 cm., which seems impossibly large.

Further discrepancies between the theory and experiment lie in the fact that the theory gives the change of resistance to be proportional to the square of the field. For bismuth this is only true for weaker fields (1), but for higher fields we have the linear relation (2). We shall shortly publish some results for the change in resistance of other substances, and here again we find that the change of resistance in strong fields follows more closely the linear law. For instance, copper at liquid air temperature, in a field of 300 kilogauss, increases its resistance by approximately 35 per cent., and this increase follows very closely the linear law.

This difference, not only in magnitude of the effect, but also in the way in which it depends on the field, shows the difficulty of accounting for the change of resistance of a conductor in magnetic fields by deviation of electrons moving freely between two collisions. A more likely picture for the change of resistance in magnetic fields can be obtained if we assume that the magnetic field has a direct influence on the mechanism of collision between the electron and the atoms. It is quite evident that the picture given at the beginning of the paragraph, for the mechanism which accounts for the resistance of a conductor, is only a very crude one and is usually adopted only as an illustration. We see from the value of the free path of an electron of a conductor, as obtained

* *Loc. cit.*, p. 56.

from Sommerfeld's theory* that an electron passes a few hundred atoms before making a collision in which all the excess of energy and momentum is given up to the atom. Probably what actually happens is that the electron is continually transferring small amounts of its excess energy and momentum to the atoms, and the effect of all these small collisions will, at a distance which is called the free path, be equivalent to a complete collision.

Our suggestion is that the disturbance produced by the magnetic field in the atoms of the conductor will increase the efficiency of these " small collisions," and this will increase the resistance. This hypothesis will not affect all the important advantages of Sommerfeld's theory, and, from a formal point of view, the effect of a magnetic field may be regarded as a decrease in the length of the free path of the electron.

The elaboration of this suggestion is difficult, as the mechanism of a collision between an electron and an atom is at present unknown in detail, but from the attempts already made† we may expect‡ to have this question solved on the basis of the wave mechanics. At present all that we may attempt to do is to compare the collision between an electron and an atom in a conductor with that which we observe in gases. Here we have the well-known Ramsauer phenomenon. This effect, so far as it has been studied, has two definite factors. First, that the interchange of energy, between an electron and an atom may be much smaller than may be expected from a collision theory; and secondly, that the efficiency of the collision depends to a great extent upon the structure of the atom. The most symmetrical atoms, like those of the inert gases, absorb very little momentum and energy from the electron in a collision, and for them we have the most complete Ramsauer effect.

To develop our suggestion further, we shall also assume that the free electrons in the metal make the most efficient collisions with the atoms of the crystalline lattice when they have an unsymmetrical structure.

By means of this hypothesis we may obtain an explanation of several phenomena observed in conductors. First of all we can explain why the specific resistance of bismuth is high and is so sensitive to the magnetic field. From our hypothesis we should expect that those elements, which have the most symmetrical configuration of the core when the free electron is removed, will make the least effective collisions with the electrons and will have the highest conductivity per atom. In the first column of the periodic system we

* *Loc. cit.*, p. 24.

† L. Mensing, 'Z. f. Physik,' vol. 45, p. 603 (1927).

‡ Ehrenfest and Rutyers, 'Naturwiss.,' vol. 11, p. 184 (1928).

may expect to have the most symmetrical atomic-cores, as they are similar to the inert gases, and we actually observe the highest conductivity per atom.* In bismuth the state of affairs is very different. It has been suggested by Ehrenfest,† from a consideration of the diamagnetism of bismuth, that the electrons move round several nuclei forming large orbits. These orbits will make the crystal lattice behave as though it were made up of molecules having a very unsymmetrical structure, which will be very unlike the structure of inert gases, and we have to expect a very small "Ramsauer effect," and this will account for the high specific resistance of bismuth.

From our point of view we regard the effect of the magnetic field in increasing the resistance of a metal, as originating from its disturbing effect on an atom in changing the velocity of the electrons and orientating the orbits, making it thereby less symmetrical, and thus increasing its efficiency of collisions with electrons. Owing to the large size of the electronic orbits in bismuth the magnetic field will be much more efficient in spoiling the symmetry of the molecules, and in this way may very easily account for the exceptionally large increase of resistance. The experimentally observed influence of the orientation of the crystal lattice relative to the magnetic field on the change of resistance in bismuth may be explained by the fact that these large electronic orbits must have a definite orientation in the crystal, as the diamagnetic susceptibility of bismuth is different in different directions relative to the crystal axis. They are therefore differently affected by the magnetic field when it is applied at a different angle, and the efficiency of collision is changed leading to a different increase in the resistance.

The existence of a critical field (section 3) which separates the region of weak fields, where the change of the resistance is quadratic from the fields where it is linear may probably be explained by the fact that above H_K the critical value for the orientation effect of the magnetic field on the orbits is stronger than that of the inter-molecular forces arising from the symmetrical distribution of the atoms in the lattice, and the orbits reach a steady orientation. In this state the orbits are probably less affected by the field and have a smaller (linear) change of resistance. This is also strongly supported by the observed fact that the change of resistance after the critical field is reached in most cases does not depend on the initial orientation of the crystal.

The temperature effect may be described as follows. The atoms in a metal conductor, or, in the particular case of bismuth, the molecules, suffer a thermal

* *See* Bridgman, 'Reports Solway Conference,' p. 70 (1927).

† *Loc. cit.*, Part I.

oscillation in the lattice and disturb each other. This disturbance is evidently equivalent to making the atom less symmetrical and this increases the efficiency of the collision with the free electrons, the disturbances evidently being larger at higher temperatures. This will account for the decrease of resistance at low temperatures. As the amplitude of vibration is directly connected with the absolute temperature, we may expect that the decrease of resistance will also be a function of the absolute temperature. The combined effect of the magnetic field and the temperature is more difficult to picture, but it is conceivable that the two phenomena produce disturbances of a different character in the atoms which are not additive. At room temperature in bismuth the disturbances due to the temperature motion of the atoms prevail, and we have a smaller influence of the magnetic field. The lower the temperature the more prominent are the disturbances produced by the field.

Impurities and imperfections of the lattice also have a similar effect on the conductivity. A foreign atom introduced in the lattice will disturb the symmetry of the lattice and each atom will be less symmetrically surrounded by others and the symmetry of the atom itself will be diminished. Since one foreign atom may disturb quite a large portion of the lattice, we can see why the value of the specific resistance is so sensitive to traces of certain impurities. A genuine imperfection of the lattice will act in a similar way. It is evident that at high temperatures the asymmetry produced by this imperfection will be small compared with that produced by the temperature motion of the atoms and will have less effect on the specific resistance and the change of resistance in magnetic fields (*see* section 2).

We have seen that all the conductivity phenomena of bismuth are more sensitive to impurities and imperfections of the lattice than those of any other metal. This can be explained by the fact that any imperfection not only affects the symmetry of the molecules, but may also break the large orbits into small ones. These have different properties and are less affected by the magnetic field, as is seen from experiments with the amorphous deposits. Here the large Ehrenfest orbits probably no longer exist, and no marked change of resistance in magnetic fields occurs. (It would be interesting to test the magnetic properties of the amorphous bismuth ; on our assumptions it must be much less diamagnetic than in crystals.)

In sketching out these suggestions, we have always spoken about electrons in collision with atoms. We took this picture as it is more familiar. No doubt, however, any quantitative development of these ideas, if possible, can only be attempted on the basis of wave mechanics. In this case we have to replace the word electron by the word wave, and write, instead of the "efficiency of collision," the "scattering power of an atom," and so on. The chief assumption, however, upon which all this speculation depends will be in the wave mechanics that the scattering power of an atom in a metal is increased by the disturbance produced in the atom by a magnetic or any other kind of field, as, for example, that of neighbouring atoms.

Summary of Part III.

A method is described by which it is possible to eliminate the time lag phenomenon in the measurement of the change of resistance of bismuth in a magnetic field.

Experimental results are given for the change of the resistance of bismuth crystals when the current is perpendicular to the magnetic field, for different orientations of the axis of the bismuth crystal relative to the magnetic field.

The measurements have been made at 290°, 193° and 91° absolute.

It has been shown that the impurities and imperfections in the crystal lattice greatly influence the change of the resistance of bismuth. This is specially noticeable at low temperatures and in strong magnetic fields.

The change of resistance in a magnetic field of an ideal perfect crystal is discussed. It has been shown that in weak fields the change of resistance follows a square law and in strong fields it follows a linear law. The linear law of the change of resistance is practically independent of the orientation of the crystal relative to the magnetic field.

The case when the current is parallel to the lines of force of the magnetic field was also investigated for different orientations of the crystal axis relative to the magnetic field and a "saturation effect" was found. The change of resistance in this case is very small, is not much affected by the temperature, and its magnitude is strongly affected by the imperfection of the crystal. It is suggested that this small change of resistance is due to the imperfection of the crystals and to the defective aligning of the current in the crystal with the direction of the lines of the magnetic field.

Experiments are described in which it was attempted to make perfect bismuth crystals by direct deposition of bismuth vapour in vacuum on cooled plates. The experiments for obtaining single crystals were unsuccessful, but by studying the change of resistance in a strong magnetic field of the deposits obtained, it was possible to clear up certain phenomena previously observed in thin bismuth layers.

A rough investigation was made of the residual e.m.f. which occurs in bismuth in a magnetic field when a current is passing and which accounts for the time lag phenomenon. It is shown that the ratio of the residual e.m.f. to the resistance is independent of the strength of the magnetic field in the region of investigation, but is strongly affected by the orientation and by the perfection of the crystal.

A general discussion is given on the failure of the present theory of metallic conductivity to account for the phenomenon of the change of resistance in a magnetic field and in this connection some suggestions are made.

All the work produced in the three parts of this paper has been done with the continuous assistance of Mr. E. Laurmann, to whom I would like to express my personal thanks.

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The work was all carried out in the Magnetic Laboratory with the support of the Department of Scientific and Industrial Research.

EXPLANATION OF PLATES 5 TO 8.

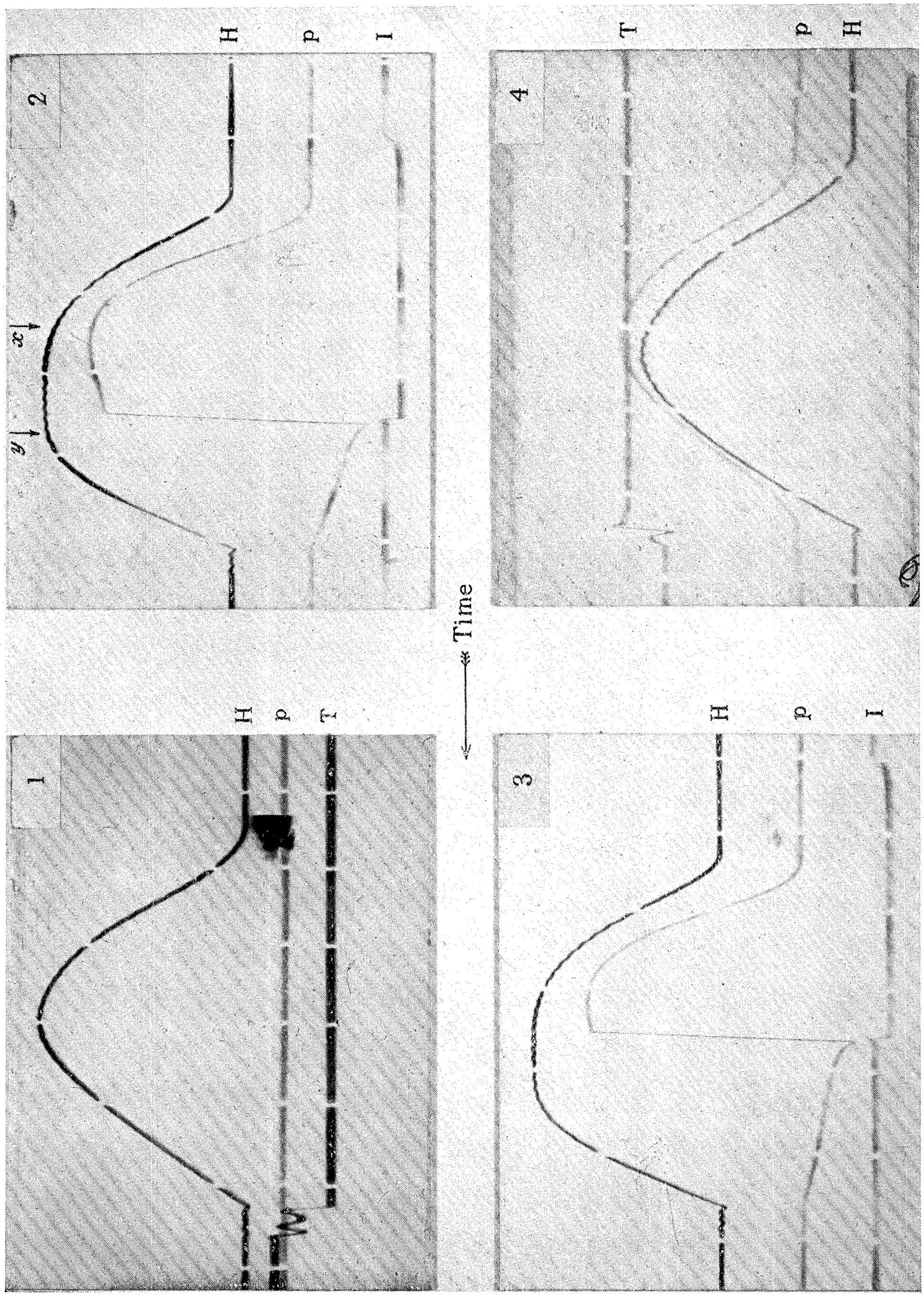
(Description of the Oscillograms.)

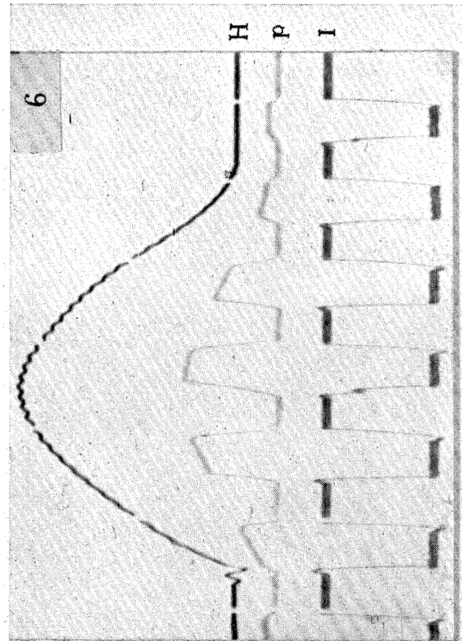
In all the oscillograms the time scale is from the right to the left. The interruption in the lines seen on some of the oscillograms are caused by interruption of the beam of light falling on a mirror of the three oscillographs by a little shutter operated by a synchronous motor. The interval of time between two interruptions is 1/180 of a second. One of the objects of the interruption is to mark corresponding points on the different curves.

Curve H is traced by the oscillograph which records the current through the coil where the magnetic field is obtained. Curve I is traced by the oscillograph which records the current through the crystal. Curve p is traced by the oscillograph connected to the potential leads of the crystal. In some experiments it was found necessary to measure the tension across the break of the main current through the coil, this curve is marked by T.

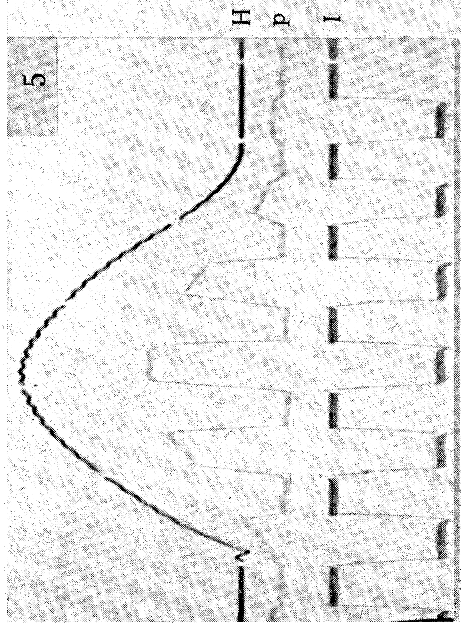
OSCILLOGRAM No. 1.—This oscillogram was taken to illustrate the induction in the circuit of the potential oscillograph due to the variation of the magnetic field. For this purpose no current was sent through the crystal and the traces of a deflection of the potential oscillograph were due to the induction. Holder fig. 9 B with the crystal B was used. Temperature 22·5° C. The field on the top of the current wave $H_{max.} = 320$ kilogauss.

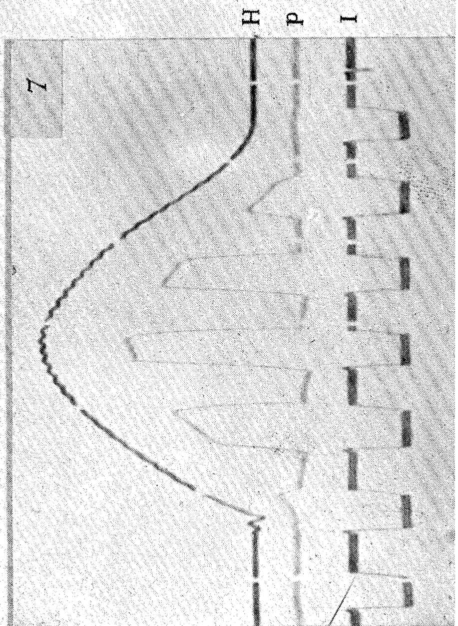
OSCILLOGRAM No. 2.—($I \perp H$) and ($I \parallel$ Axis), crystal K. Holder fig. 9 B. (Line $\perp$ H). Resistance of the crystal $R_0 = 0{\cdot}00331\ \Omega$. Temperature $T = 193°$ K. (solid CO_2 and ether). $H_{max.} = 194$ kilogauss. Current through the crystal $I = 1$ amp. Resistance w (fig. 7) of the potential oscillograph $r = 20{\cdot}5\ \Omega$. Ratio between the residual e.m.f. and the potential drop due to the change of resistance $n = 0{\cdot}19$.

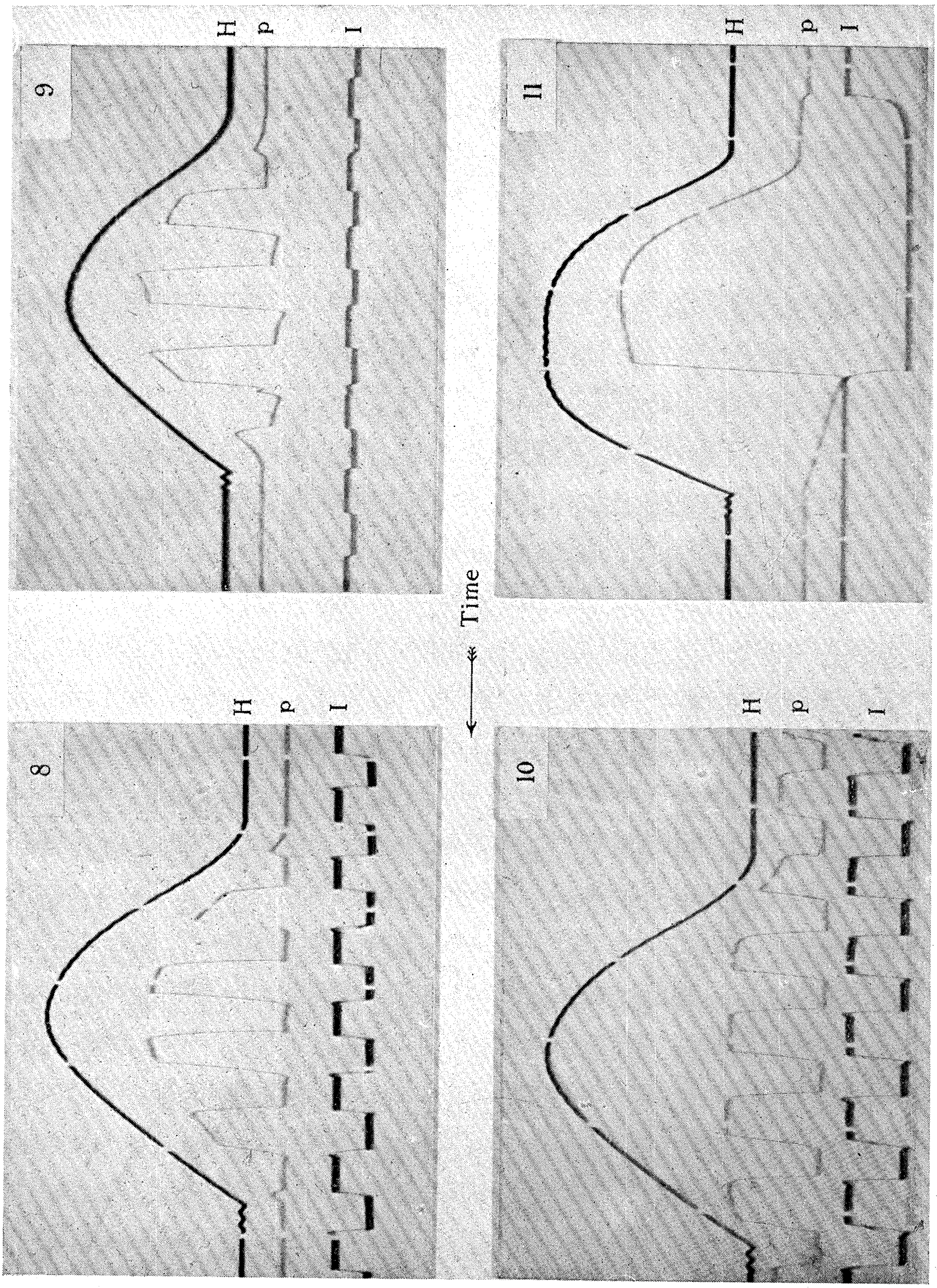

1
H
p
T
2
H
p
I
x
y
3
H
p
I
4
T
p
H
Time

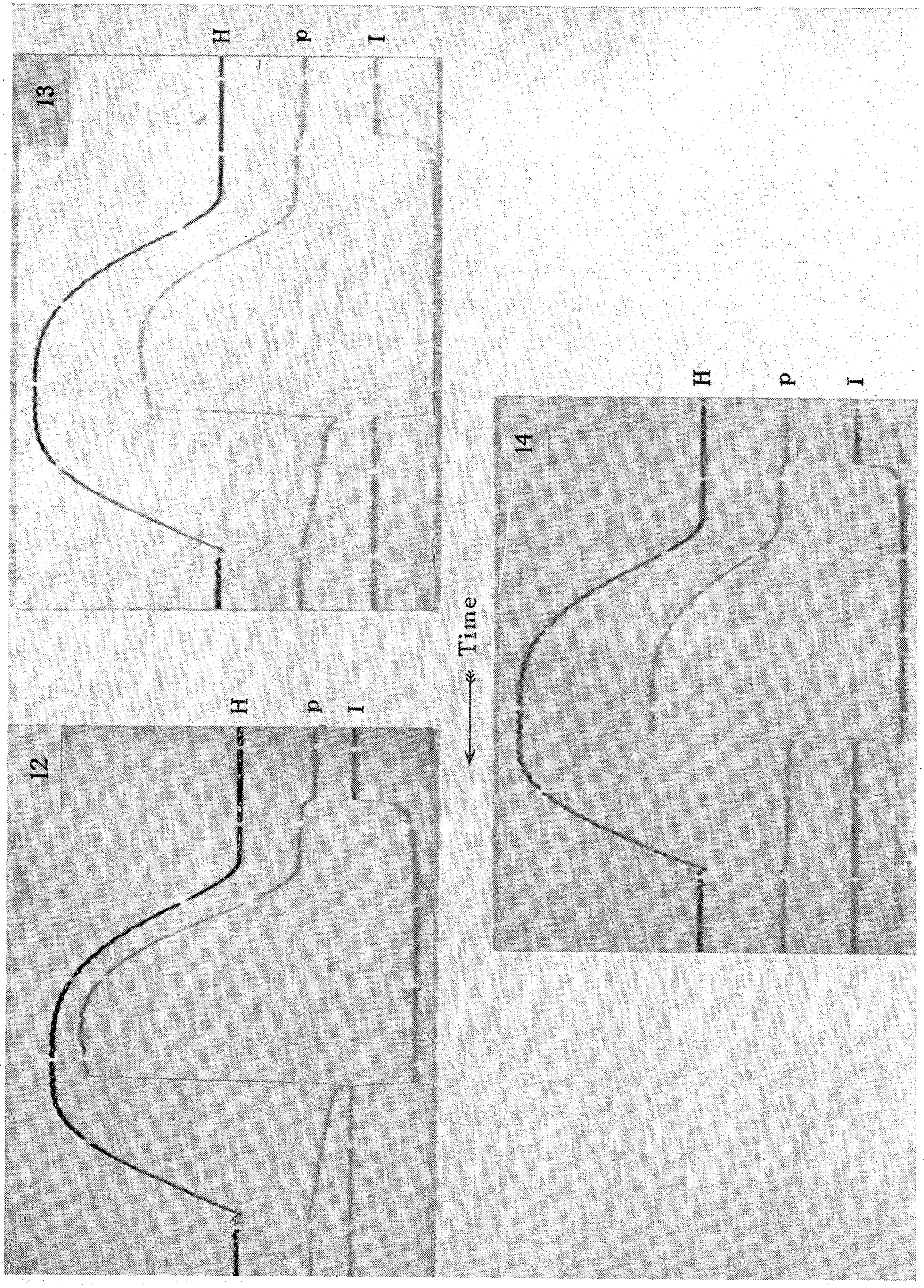


Time






9
H
p
I
11
H
p
I
8
H
p
I
10
H
p
I
Time


13
H
p
I
12
H
p
I
14
H
p
I
Time

OSCILLOGRAM No. 3.—The same conditions as oscillogram No. 2, with the exception that in this case the current through the crystal is broken earlier, $n = 0\cdot16$.

OSCILLOGRAM No. 4.—From this oscillogram the loop curve on fig. 10 is taken. (I $\perp$ H) and (I || Axis). The crystal was cut from a bismuth plate grown like the rods in the apparatus on fig. 1. Holder fig. 9 A. $R_0 = 0\cdot0075\ \Omega$. Temperature 22° C. $H_{max.} = 242$ kilogauss. I = 3 amp.

OSCILLOGRAM No. 5.—(I $\perp$ H) and (I || Axis). Curve A_1, fig. 11 (Line $\perp$ H). Holder fig. 9 B. $R_0 = 0\cdot00325\ \Omega$. Temperature = 17° C. $H_{max.} = 109\cdot5$ kilogauss. I = 3 amp. $r = 5\cdot05\ \Omega$.

OSCILLOGRAM No. 6.—All conditions similar to those in oscillogram No. 5 with the exception that the crystal is turned by 30°. Curve A_2, fig. 11. (Line || H), $H_{max.} = 108$ kilogauss.

OSCILLOGRAM No. 7.—Crystal A in the same position as on oscillogram No. 5 (I $\perp$ H) and (I || Axis). Curve A_1, fig. 12 (Line $\perp$ H). Holder 9 B. $R_0 = 0\cdot00205\ \Omega$. Temperature = 193° absolute. $H_{max.} = 107$ kilogauss. $I = 1\cdot5$ amp. $r = 10\cdot05\ \Omega$.

OSCILLOGRAM No. 8.—Crystal A in the same position as in No. 5 (I $\perp$ H) and (I || Axis) Curve A_1, fig. 13. (Line $\perp$ H), holder fig. 9 B. $R_0 = 0\cdot00112\ \Omega$. Temperature = 91° absolute (liquid air). $H_{max.} = 300$ kilogauss. $I = 1\cdot0$ amp. $r = 60\cdot05\ \Omega$.

OSCILLOGRAM No. 9.—Crystal E. (I $\perp$ H) and (I || Axis). Curve E_1, fig. 12. (Line $\perp$ H). Holder fig. 9 B. $R_0 = 0\cdot00805\ \Omega$. Temperature = 193° absolute. $H_{max.} = 280$ kilogauss. $I = 0\cdot5$ amp. $r = 60\cdot32\ \Omega$.

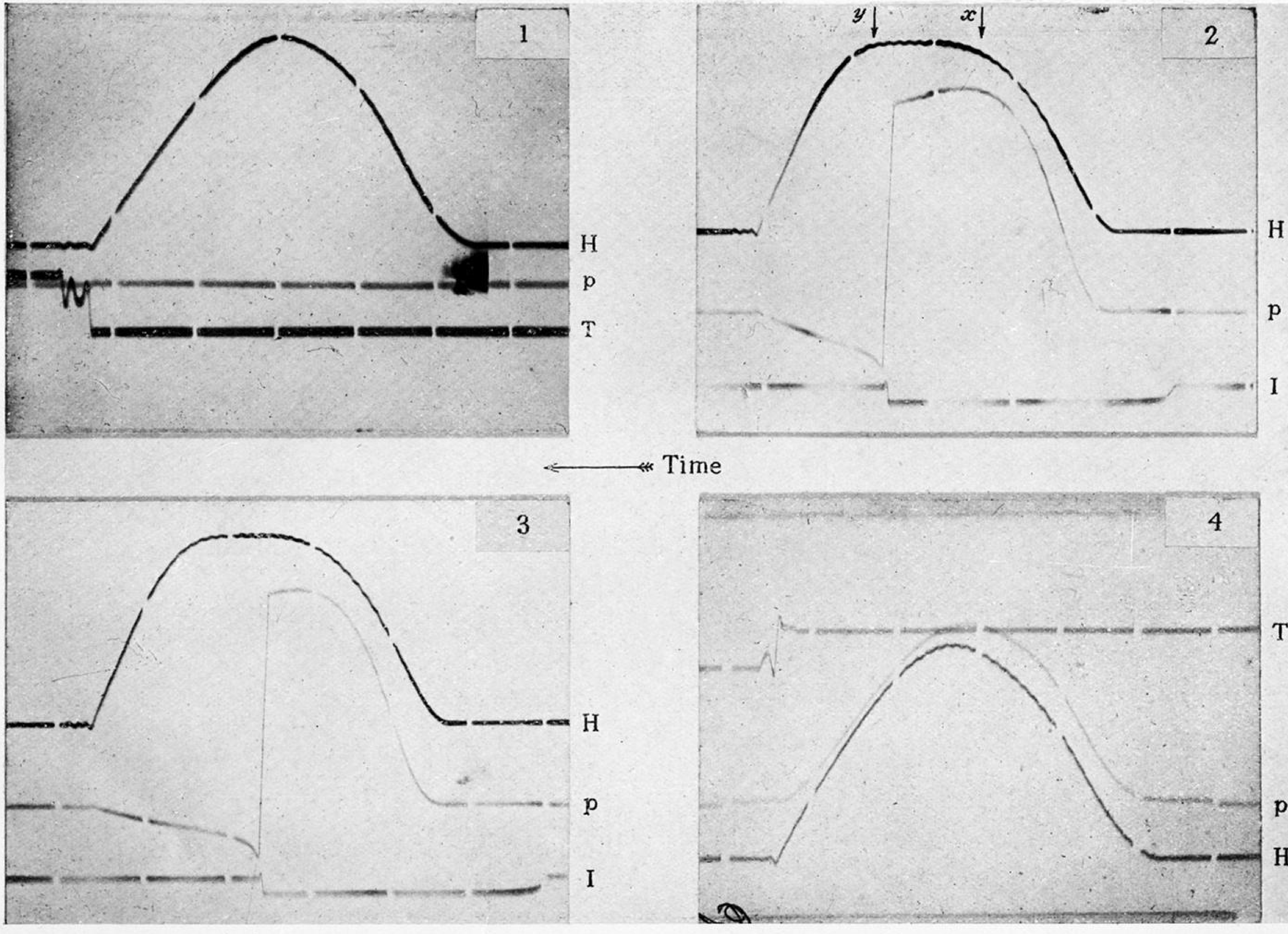
OSCILLOGRAM No. 10.—Crystal A. (I $\perp$ H) and (I || Axis). Curve A_1, fig. 17. Holder fig. 9 C. $R_0 = 0\cdot001055\ \Omega$. Temperature = 22·5° C. $H_{max.} = 300$ kilogauss. I = 3 amps. $r = 4\cdot05\ \Omega$.

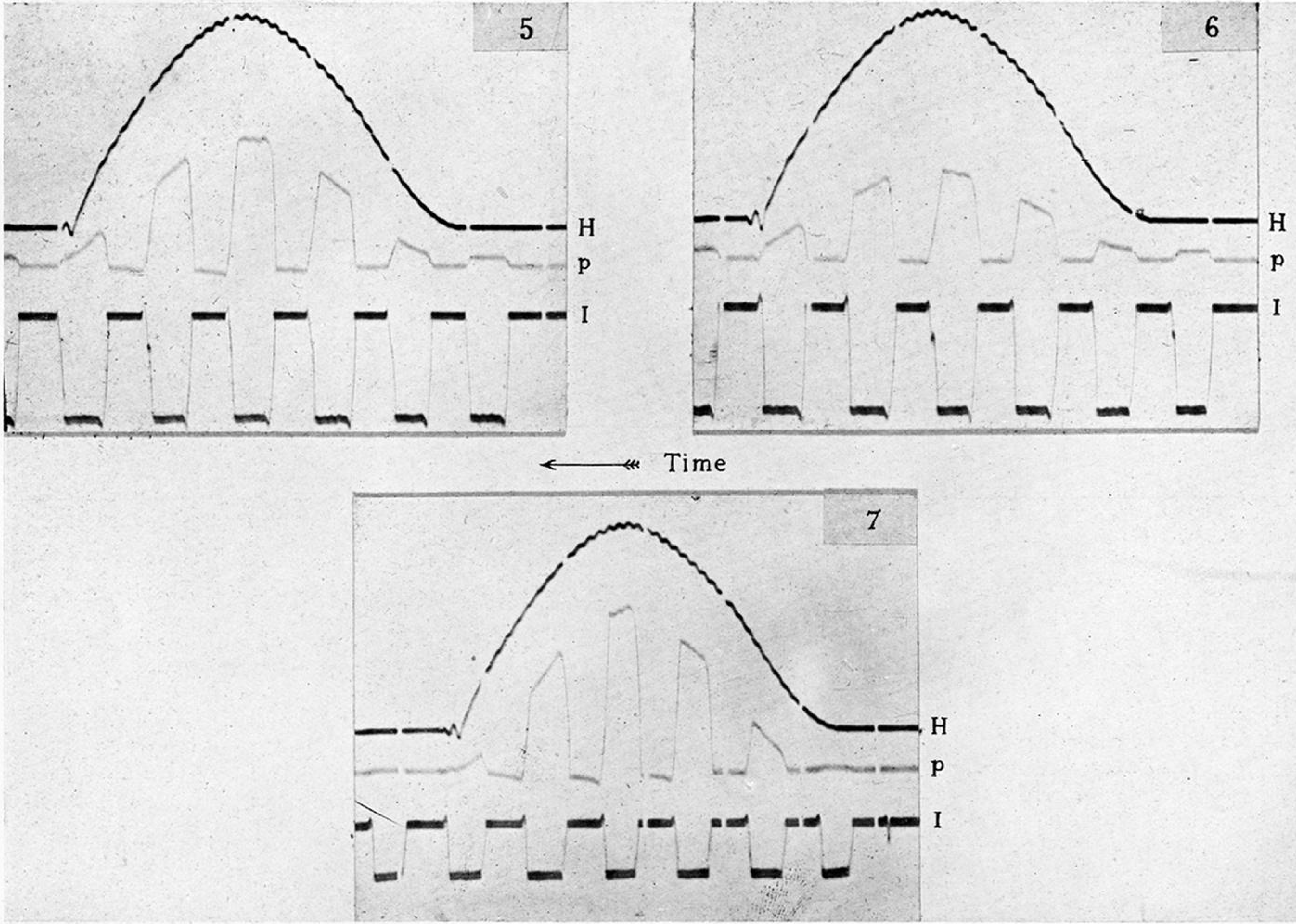
OSCILLOGRAM No. 11.—Crystal K. (I $\perp$ H) and (I || Axis), the crystal in this case being turned by 30° (Line $\perp$ H). $R_0 = 0\cdot0053\ \Omega$. Temperature = 23·5° C. $H_{max.} = 191$ kilogauss. I = 3 amps. $r = 10\cdot05\ \Omega$. $n = 0\cdot183$.

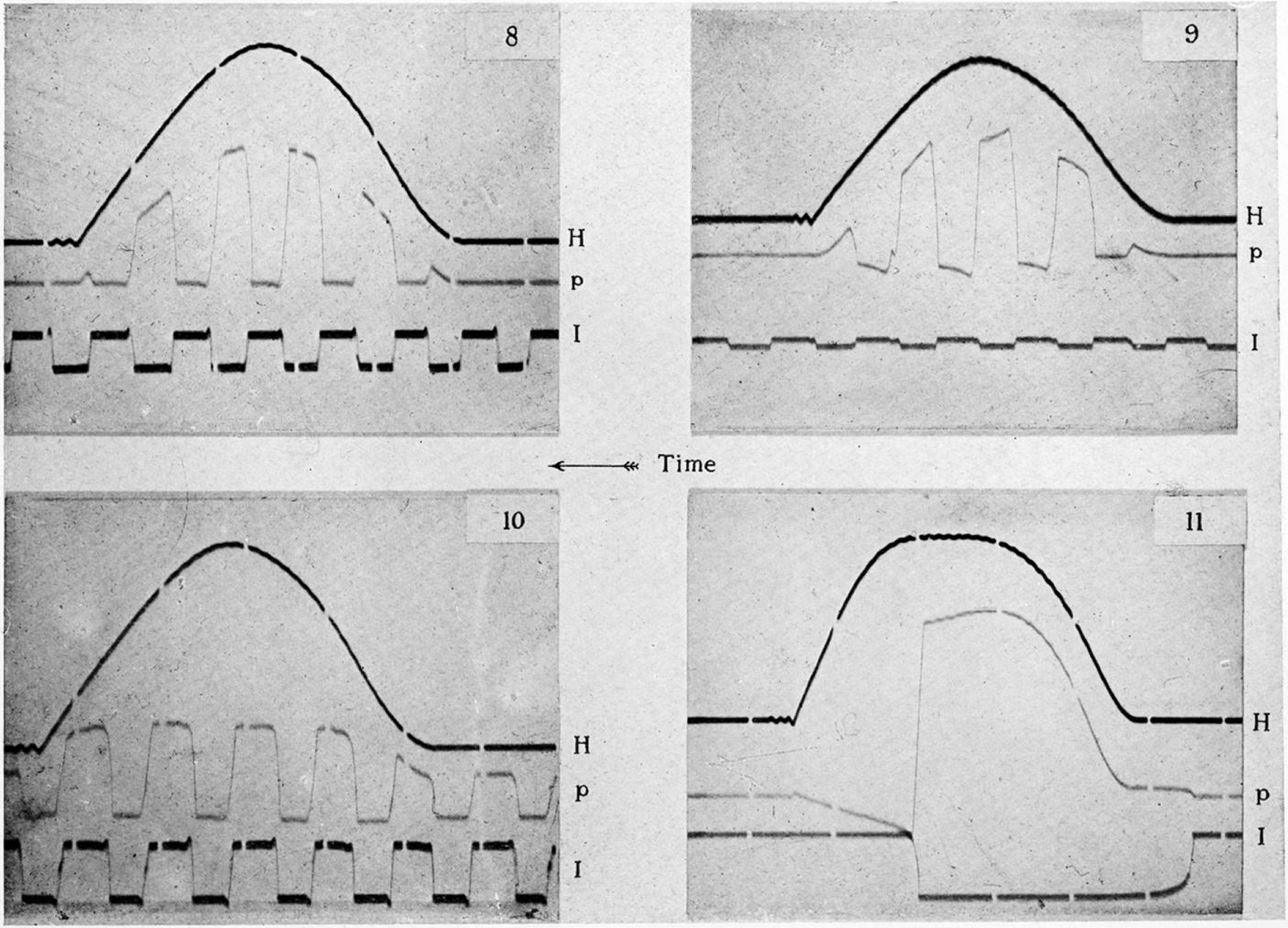
OSCILLOGRAM No. 12.—Crystal K. (I $\perp$ H) and (I || Axis). (Line || H). Holder fig. 9 B. $R_0 = 0\cdot0053\ \Omega$. Temperature = 23·5° C. $H_{max.} = 194$ kilogauss. I = 3 amps. $r = 5\cdot05\ \Omega$. $n = 0\cdot10$.

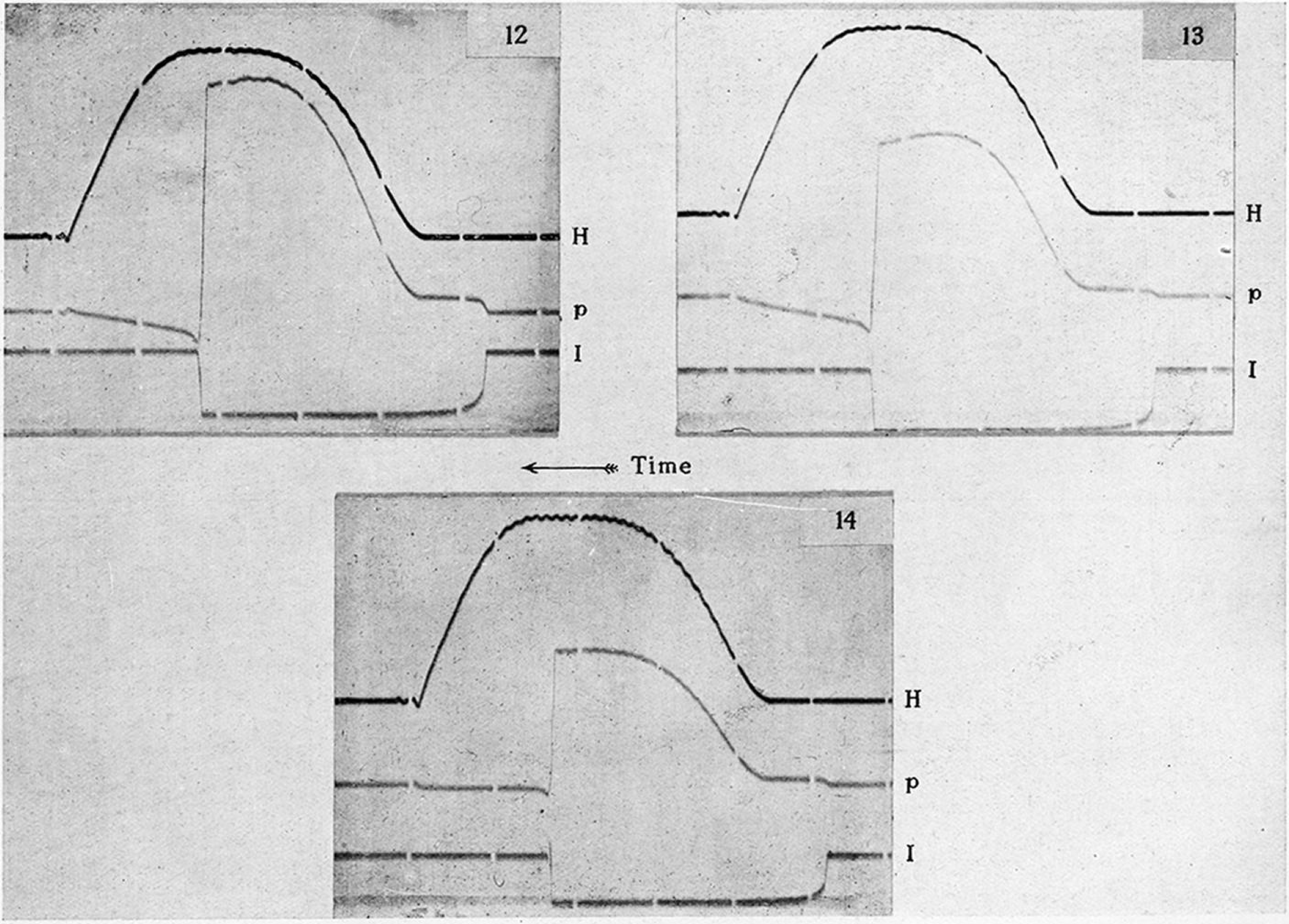
OSCILLOGRAM No. 13.—Crystal B. (I $\perp$ H) and (I || Axis). Holder fig. 9 B. (Line $\perp$ H). $R_0 = 0\cdot00463\ \Omega$. Temperature = 22° C. $H_{max.} = 194$ kilogauss. I = 3 amps. $r = 10\cdot05\ \Omega$. $n = 0\cdot17$.

OSCILLOGRAM No. 14.—Crystal B. (I $\perp$ H) and (I || Axis). Holder fig. 9 B. (Line || H). $R_0 = 0\cdot00385\ \Omega$. Temperature = 193° absolute. $H_{max.} = 93$ kilogauss. I= 3 amps. $r = 10\cdot05\ \Omega$. $n = 0\cdot03$.


1
H
p
T
y
x
2
H
p
I
Time
3
H
p
I
4
T
p
H


5
H
p
I
6
H
p
I
Time
7
H
p
I


8
9
10
11
H
p
I
Time


12
H
p
I
13
H
p
I
Time
14
H
p
I