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The thermal and electrical resistance of bismuth single crystals
The effects of temperature and magnetic fields

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The anomalous physical properties of bismuth, particularly as regards the reduction of the thermal and electrical conductivities in magnetic fields, have claimed the attention of a number of workers in the past. Most of the published data refers to the electrical conductivity, owing, no doubt, to the greater ease of measurement; and but little reliable work appears to have been done on the thermal conductivity, at any rate in the case of single crystals. Lounds (1902) carried out thermal-conductivity measurements employing magnetic fields up to about 5000 gauss, but the accuracy of his results was prescribed by the limitations of the method and the smallness of his crystals. Kapitza (1928) undertook an extensive investigation on the electrical conductivity of single crystals using very intense momentary fields. Banta (1932) published thermal-conductivity values using fields up to 8000 gauss, while more recently de Haas and Capel (1934) have made thermal measurements, in the absence of a field, at liquid-air and liquid-hydrogen temperatures.

The results of a preliminary investigation (Kaye and Higgins 1929*a*) at the National Physical Laboratory on the change in thermal conductivity of bismuth single crystals in transverse magnetic fields were published in 1929. In this work, specimens, which were cut in the form of disks 25 mm. in diameter and 2 mm. thick from a large crystal grown by Bridgman's method (1925), were tested in a "plate" type of apparatus, field strengths up to 11,000 gauss being employed in a 38 mm. air gap.

It will be recalled that bismuth crystallizes in the trigonal system, the principal axis (on the Bravais-Miller system) being trigonal, perpendicular to which are three binary axes including angles of 120° (fig. 1). The principal cleavage plane is perpendicular to the trigonal axis. Passing through the trigonal axis and each of the binary axes are three secondary cleavage planes each at right angles to the principal cleavage plane. The intersections of these secondary planes on the principal cleavage plane are indicated by three systems of "lines" including angles of 60°: these lines, which are parallel to the binary axes, can be detected visually on the principal cleavage plane in favourable specimens. The crystalline symmetry of a bismuth crystal is that of a rhombohedron which closely approximates to a cube.

The present paper describes an investigation, with which Mr W. F. Higgins was associated in its early stages, and which deals first with the temperature variation at moderate temperatures of the thermal and electrical conductivities (together with the Lorenz function) of bismuth single crystals. The major part of the paper is, however, concerned with a

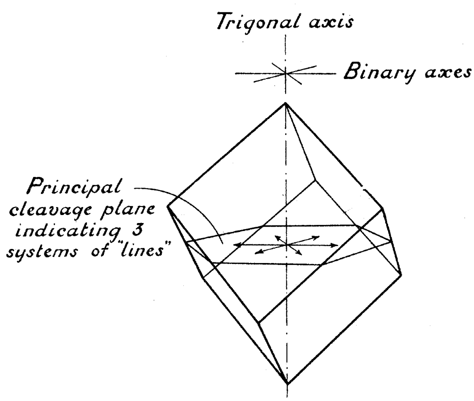

Fig. 1. Bismuth single crystal. The main trigonal axis is perpendicular to the principal cleavage plane. The three binary axes include angles of 120° and are at right angles to the trigonal axis. The three secondary cleavage planes pass through the trigonal axis and the binary axes and intersect the principal cleavage plane at right angles, the intersections or "lines" being parallel to the binary axes.

study of the two conductivities in a range of magnetic fields, as influenced by the relative orientations of the field, the crystal, and the heat or current flow respectively. This section conveniently divides itself into the measurements of the conductivities with the magnetic field oriented (*a*) transversely, and (*b*) longitudinally to the direction of the heat flow or current flow. To facilitate comparison with the electrical resistivity, it will usually be more convenient in what follows, to refer not to the thermal conductivity but to its reciprocal, the thermal resistivity.

In view of the necessarily small size of the conductivity apparatus, particularly in the magnetic observations, it was decided to take advantage of the simplification of the apparatus which would result from determining only the relative changes of conductivity. These relative values could be linked to the absolute values of the thermal resistivity which were determined in the earlier laboratory investigation: published absolute values of the electrical resistivity were similarly available.

1. Resistivity and temperature

The experience gained since the earlier work at the Laboratory, in the techniques of crystal growing and small-scale conductivity measurement, suggested, however, that it might be advantageous to repeat the basic determination of the thermal resistivity in the absence of a magnetic field and that, incidentally, it would be of interest to ascertain the influence of temperature. For the purpose, a suitable "plate" conductivity apparatus was employed of much the same type as in the work on longitudinal magnetic fields (p. 571). This was set up in a thermostatically controlled and well-stirred air enclosure, the temperature of which could be varied at will. The Kahlbaum bismuth, which was used in the work described in this paper, was of high purity, spectroscopic examination showing it to contain only traces of lead and copper, but not in sufficient quantity for chemical analysis. The density of the bismuth at room temperature was 9·78 g.cm.$^{-3}$.

The results at room temperature, which are given in Table I, proved to be in good accord with those of the 1929 work. The thermal resistivity is greatest in the direction parallel to the trigonal axis.* Fig. 2 shows that over the range from room temperature to 160° C, the curves for the relationships between thermal resistivity and temperature are approximately linear for heat flow both parallel and perpendicular to the trigonal axis, the latter having the greater (positive) temperature coefficient. If conductivity instead of resistivity is plotted against temperature, the relationships are more closely linear.

The corresponding values in Table I for the electrical resistivity (specific resistance) at room temperature were measured by means of the apparatus described on p. 567. They are in good agreement with those of Kapitza (1928) and Bridgman (1925, p. 350). The associated curves in fig. 2, which are largely deduced from Kapitza's data, again indicate an approximately linear relationship between electrical resistivity and temperature. The mean temperature coefficients (25–150° C) given in Table I, which are derived from the several curves in fig. 2, show that the electrical coefficient is roughly twice the corresponding thermal coefficient. A rise of temperature tends to reduce the disparity between the resistivities in the two directions, the electrical resistivity more rapidly than the thermal.

* de Haas and Capel (1934) find this to hold down to liquid-hydrogen temperatures.

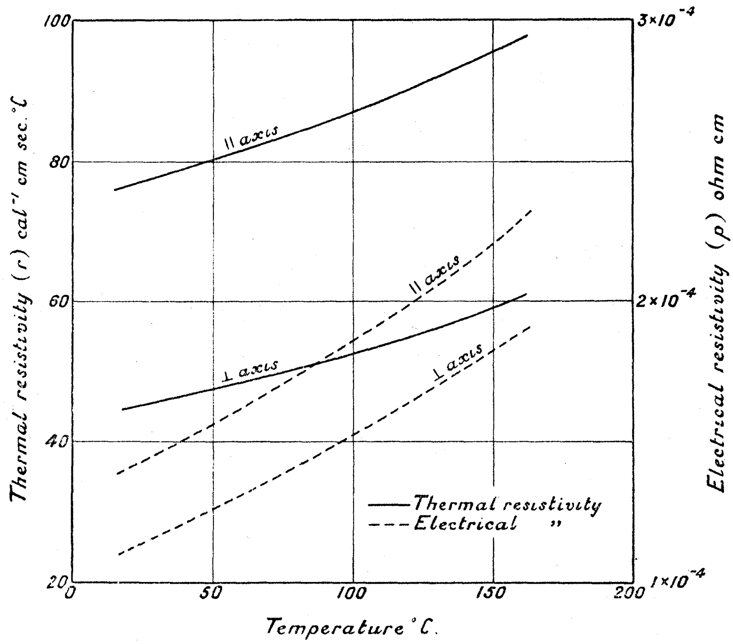

FIG. 2. Variation with temperature of thermal and electrical resistivity of a single bismuth crystal parallel and perpendicular to the trigonal axis.

TABLE I. THERMAL AND ELECTRICAL RESISTIVITY AND TEMPERATURE COEFFICIENTS OF A BISMUTH SINGLE CRYSTAL

Direction of heat flow	Thermal resistivity, r, at 25° C	Mean temperature-coefficient, α, in $r_t = r_0(1+\alpha_t)$
∥ trigonal axis	77·5 cal.$^{-1}$ cm. sec. °C	c. 0·0019
⊥ trigonal axis	45·2 cal.$^{-1}$ cm. sec. °C	c. 0·0025

Direction of current	Electrical resistivity, ρ, at 25° C	Mean temperature-coefficient, α, in $\rho_t = \rho_0(1+\alpha_t)$
∥ trigonal axis	$1·44 \times 10^{-4}$ ohm-cm.	c. 0·0042
⊥ trigonal axis	$1·14 \times 10^{-4}$ ohm-cm.	c. 0·0048

It follows from the foregoing that the Lorenz function (ρ/rT, where T is the absolute temperature) for a bismuth crystal has the following values at room temperature:

$$\parallel \text{ trigonal axis, } 0{\cdot}63 \times 10^{-8},$$

$$\perp \text{ trigonal axis, } 0{\cdot}86 \times 10^{-8}.$$

As the temperature is raised, these values diminish, and, in common with the Lorenz functions for many other metals, tend to converge towards the "normal" electronic figure of $0{\cdot}59 \times 10^{-8}$ which Sommerfeld's theory indicates. Here, one may be reminded that the number of free electrons in bismuth is accepted as being much smaller than in most metals, being of the order of 1/20 the number of atoms, instead of the order of one per atom. Incidentally, this accounts for the high diamagnetism which is some ten times that of a normal metal.

With reference to the thermal resistivity at right angles to the trigonal axis, an attempt was made to detect the variation, if any, of the resistivity in relation to the positions of the binary axes. With the aid of appropriate specimens, measurements were made in directions both parallel and at right angles to a binary axis, but no difference greater than the order of accuracy ($\frac{1}{2}$ %) was detectable in the results at ordinary temperatures. It is interesting to note, however, that de Haas and Capel (1934) found, that at liquid-air temperatures, the thermal resistivity parallel to a binary axis (|| line) is some 20 % less than that at right angles ($\perp$ line).

2. Resistivity and magnetic fields

A. *Transverse magnetic fields*

As regards the effect of magnetic fields on the thermal and electrical resistivities of a bismuth crystal, it was decided to begin this section of the work by checking the preliminary observations with transverse fields and also by using stronger fields. The air gap in the electromagnet previously used was accordingly reduced to 12·5 mm., when a series of uniform fields up to about 23,000 gauss could be obtained between pole pieces measuring 100×84 mm. A "bar" type of conductivity apparatus was adopted, as being well suited to the restricted space between the pole pieces. Moreover, bismuth single crystals of bar shape and suitable size can be readily grown, and require little mechanical working, thus reducing the likelihood of distortion and the formation of polycrystalline surface layers.

Goetz's method (1930) of growing crystals was adopted, as providing the minimum of external mechanical constraint. As is well known, the method is based on the progressive freezing of molten bismuth, the orientation of the specimen being controlled by inoculation with a seed crystal. The bismuth was contained in a horizontal graphite trough of 90° V section, the process being carried out in a stream of hydrogen. In view of Goetz's insistence on the necessity for extreme purity of the hydrogen, elaborate arrangements were set up for the purpose. Later, however, the purifying system was temporarily dispensed with, and as the results were no less successful, hydrogen direct from a gas cylinder was used thenceforward.

With experience, it was presently found possible to grow crystals in any orientation desired, though the production of specimens in which the axis was parallel to the trigonal axis was always the most troublesome. On removal from the graphite trough, the bismuth rods were first etched with dilute nitric acid to determine whether or not the inoculation had succeeded, and to what extent it had proceeded without interruption. The rods used for the transverse-field measurements had a V section about 5 mm. across, the test specimens, some 10 cm. long, being cut from these.

Thermal-resistance measurements in transverse magnetic fields.

If, as is well known, a rod which is heated at one end is allowed to radiate to its surroundings, then, on the assumption of Newton's law of cooling,

$$\theta = Ae^{\mu x} + Be^{-\mu x},$$

where θ is the excess temperature above the surroundings at a point x of the rod, A and B are constants, and μ is inversely proportional to the square root of the conductivity of the rod. If now we derive the temperature gradient in the rod by measuring the excess temperatures θ_1, θ_2 and θ_3 at three points along the rod, spaced at equal intervals each of length c, then denoting the value of $\frac{\theta_1+\theta_3}{2\theta_2}$ by n, we have

$$\mu c = \log_e (n + \sqrt{(n^2 - 1)}).$$

It follows that
$$\frac{r_H}{r_0} = \left\{\frac{\log_e (n_H + \sqrt{(n_H^2 - 1)})}{\log_e (n_0 + \sqrt{(n_0^2 - 1)})}\right\}^2,$$

where r_H and r_0 are the thermal resistivities of the rod in field H and zero field respectively.

The conductivity apparatus based on the above method is shown in section in fig. 3. The bismuth rod was surrounded by a constant-temperature enclosure in the form of a copper jacket fitted at the ends with copper blocks round which circulated cold water supplied at constant pressure and temperature. The "cold" end of the bismuth rod fitted tightly into one of the copper blocks through the intermediary of a copper clip. At the "hot" end, the bismuth was sheathed by a small heating coil of platinum mounted in an ebonite bush. The space between the bismuth rod and the copper jacket was filled with silocel powder.

The temperature gradient in the rod was measured by small copper-constantan thermocouples made of 36 s.w.g. wires. A small hole about 1 mm. deep and 0·5 mm. in diameter was drilled at each of the three selected points in the rod, and the couples were cemented in the holes by means of Wood's alloy, the rod being momentarily dipped in hot water for the purpose. It appeared from microscopic examination after etching the regions round the holes, that the disturbance caused by the drilling was negligible. The temperature of a couple which was soldered to the outside of the copper jacket, served as the "zero" for the couples on the rod. Each couple was calibrated before it was mounted in the apparatus.

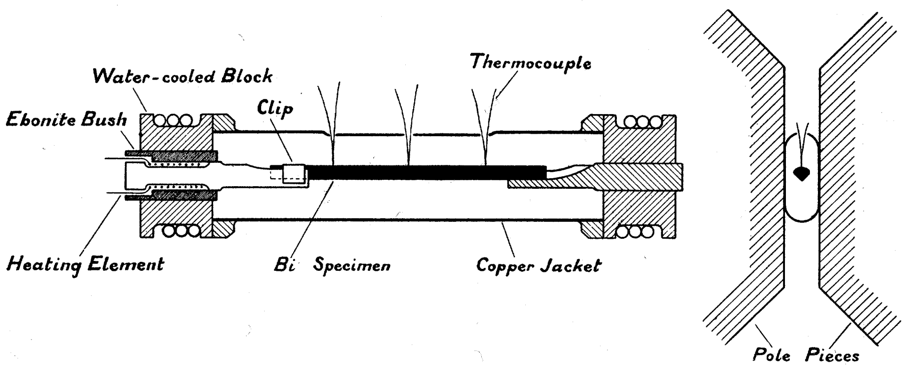

FIG. 3. "Bar" thermal-resistivity apparatus for use in transverse magnetic fields.

For the purpose of the thermal-conductivity measurements, a bismuth rod of the particular orientation required was mounted in the apparatus, the axis of the rod being parallel to the faces of the pole pieces of the magnet. The water flow was adjusted to a convenient amount, and the heating current was set to give a suitable temperature gradient along the rod, the difference between the readings of the two remote couples being normally about 10° C for a mean temperature of the bismuth of about 22° C. The steady state was reached after about 15 min., when a series of readings was taken both for zero field and for a variety of transverse field strengths. The magnetic fields were measured with a calibrated search coil and a Grassot fluxmeter, the accuracy being of the order of 100 gauss.

For convenience, the four main orientations of a bismuth crystal with respect to the directions of heat flow and transverse magnetic field may be designated as in Table II, in which the lower part shows graphically the directions of the magnetic field and the heat flow, relative to the trigonal and binary axes.

TABLE II. TRANSVERSE MAGNETIC FIELD (HEAT FLOW $\perp$ H)

Crystal orientation	Orientation of trigonal axis with reference to: Heat flow	Magnetic field H
A	$\perp$	$\perp$
B	$\perp$	$\parallel$
C_1 (line $\perp$ H)	$\parallel$	$\perp$
C_2 (line $\parallel$ H)		

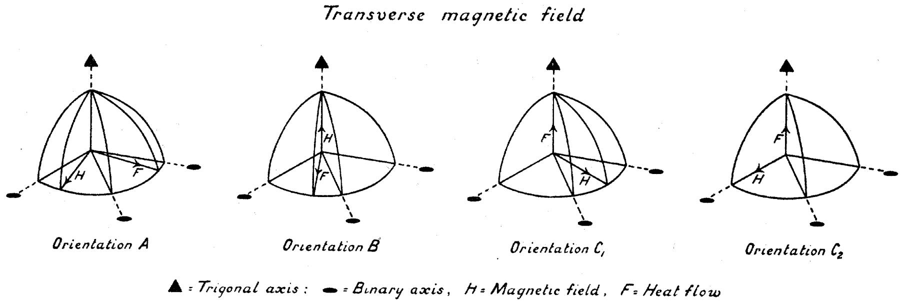

FIG. 4.

In the case of the crystal orientations C_1 and C_2, it was found that on rotating a crystal round its trigonal axis, the thermal resistance varied sinusoidally over a range which depended on the field strength, reaching a minimum whenever the direction of the field coincided with one of the binary axes (i.e. line $\parallel$ H), and a maximum at each of the mid-way positions (line $\perp$ H). Later, corresponding maxima and minima were also found in the electrical-resistance measurements (p. 569). Kapitza (1928) noted a similar effect in the electrical resistance of bismuth with very intense magnetic fields of the order of 300 kilogauss. Fig. 5 gives a polar representation of the present magnetic and electrical results for a field of 20,000 gauss.

In fig. 6 are shown the mean curves (omitting the numerous observation points) for the four orientations, the field strength being plotted against the ratio of the thermal resistivity in a field of strength H to that in zero field, r_H/r_0. The values of r_H/r_0 for the smaller fields are in fair accord with the preliminary results.* For the larger fields, the curves for orientations A and B become linear and parallel, while, on the contrary, those for orientation C are steadily separating, and tending to become "saturated".

* Kaye and Higgins (1929 a). Incidentally, in this paper, the notation of the two curves in fig. 1 should be interchanged, as also should the first and second values in column 3 of the table on p. 1059.

Electrical-resistance measurements in transverse magnetic fields.

The measurement of electrical resistivity was carried out by comparing the fall in potential over a measured length of the bismuth rod with that over a standard low resistance in series. The current leads were attached to the ends of the rod; while for the potential leads, thin copper wires were

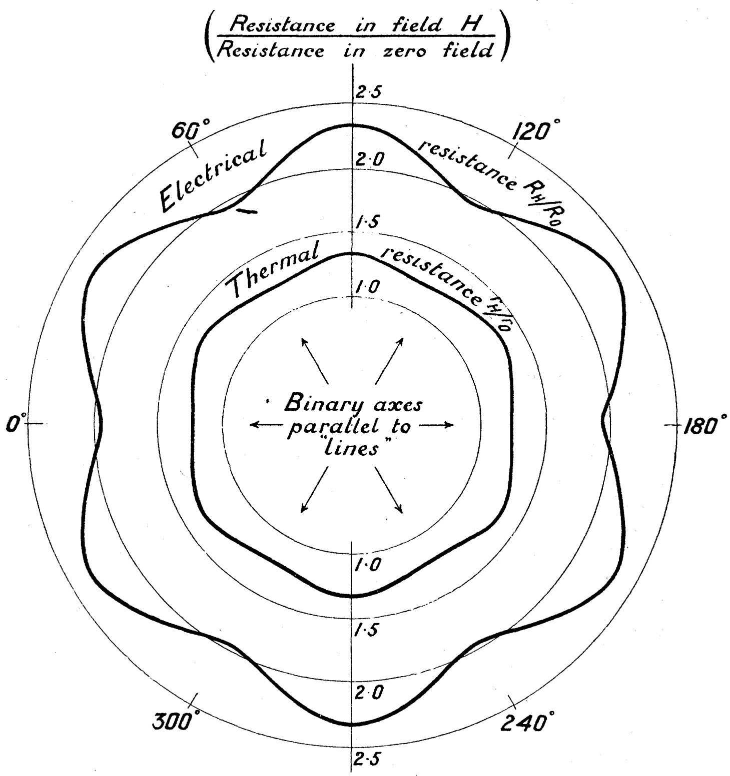

FIG. 5. Heat flow or current flow parallel to trigonal axis (i.e. perpendicular to principal cleavage plane) of bismuth single crystal. Magnetic field perpendicular to axis. Polar representation of cleavage plane showing that as the crystal is rotated round its trigonal axis the thermal and electrical resistivities reach a minimum when the direction of the field coincides with one of the three binary axes or lines. Field strength 20,000 gauss.

fixed in the holes previously used for the outer thermocouples. To minimize any thermoelectric effects at the points of attachment of the leads, the entire rod was immersed in a constant-temperature bath of acid-free paraffin oil. Any residual effect was cancelled out by reversing the current in the rod and taking the mean reading. The mean temperature of the bismuth rod was 16° C.

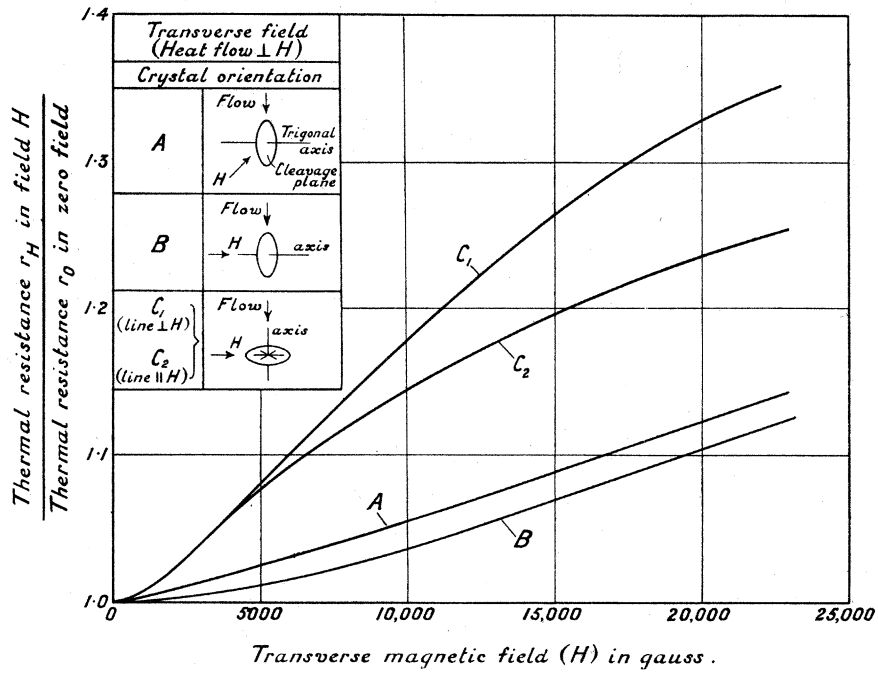

FIG. 6. Variation of thermal resistance of a bismuth single crystal in a transverse magnetic field.

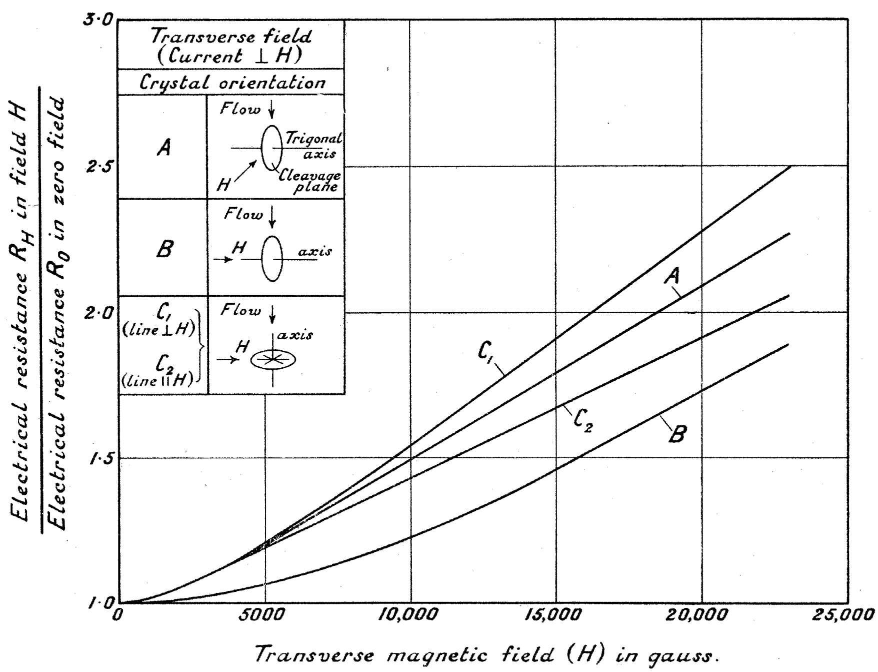

FIG. 7. Variation of electrical resistance of a bismuth single crystal in a transverse magnetic field.

The several crystal orientations are as in Table II, "heat flow" being replaced by "current". The mean values of the ratio of electrical resistivity in a transverse field of strength H to that in zero field, R_H/R_0, are shown plotted against field strength, in fig. 7. For the larger fields, all the curves become linear, those for orientations A and B being parallel, as was the case with the corresponding thermal curves. Incidentally, in the case of orientations A and B, two different specimens were used, one for each orientation. It was found that axial rotation of either specimen through 90° gave points which lay closely on the curve for the other. As already mentioned, axial rotation of a specimen in orientation C resulted in alternating maximum and minimum values of the electrical resistance.

B. *Longitudinal magnetic fields*

For the measurement of thermal-resistance changes with the magnetic field parallel to the heat flow, the air gap of the electromagnet was increased to 25 mm., affording a maximum field of about 16,000 gauss. Even with the wider gap, it was not practicable, however, to construct a "bar" type of apparatus which would go "end on" in so small a space, and accordingly a "plate" method was adopted. For convenience, the electromagnet was set up with its pole faces horizontal.

The chief disadvantage of a "plate" method lies in the necessity for machining and polishing the specimens, though every precaution was taken to minimize any mechanical disturbances which might be so caused. Disks 25 mm. in diameter and 2·5 mm. thick were carefully sawn and turned from a large single crystal of bismuth grown, as described above, in the orientation required. The final polishing was carried out in the optics workshop of the Laboratory, the surface being made flat to about 1/10,000 in.

The superficial structure of the specimens so prepared was afterwards examined by X-ray reflexion at the principal cleavage plane of the crystal. It was found that the surface consisted of a mosaic of small crystals whose linear dimensions were of the order of 0·05 mm. In order to reveal the depth of this disturbance the surface was etched away in stages, an X-ray examination being made at each stage. The multicrystalline structure finally disappeared after the removal of about 1 % of the thickness of the plate.

Thermal-resistance measurements in longitudinal magnetic fields.

A vertical section of the apparatus is shown somewhat diagrammatically in fig. 8. The bismuth disk was horizontal and below it was a hollow water-cooled "cold" plate of copper 25 mm. in diameter and mounted in an ebonite base. Above the disk was the "hot" plate, also of copper, which was heated at its upper face by a platinum heating grid wound on mica, the whole being mounted in an ebonite block. The grid was provided with current and potential leads for power measurement.

The temperatures of the hot and cold plates were measured by a pair of copper-constantan thermocouples pegged flush with each surface, the copper plate serving as one element. The constantan wires entered through small insulated holes in the plates, as shown in fig. 8. The faces of the plates with the couples in position were then ground flat to a high degree of

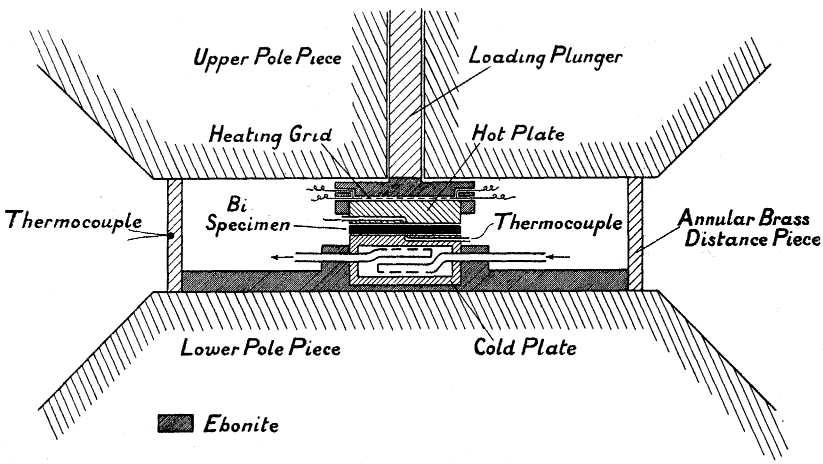

FIG. 8. "Plate" thermal-resistivity apparatus for use in longitudinal magnetic fields.

accuracy and polished. Thermal contact between the bismuth and the hot and cold plates was further improved by the use of glycerine films (see Kaye and Higgins 1926). To ensure uniformity of thickness of the films, an axial load of about 8 kg. was applied to the system by means of a mild-steel plunger passing through the upper pole piece of the electromagnet, the lower end of the plunger being arranged to be co-planar with the pole face.

A constant-temperature enclosure was provided by a brass cylinder 25 mm. long, which also acted as a distance piece for the poles of the magnet. Its temperature was measured by two couples. A steady temperature for the cold plate was maintained, as previously, by a constant-temperature water flow. The surplus space in the enclosure was filled with asbestos wool.

The extraneous heat loss from the hot plate, which was determined by substituting balsa wood of known conductivity for the bismuth (Kaye and Higgins 1928), was of the order of 1 %. The temperature drop across the glycerine films, which was ascertained by replacing the bismuth by a polished copper disk (Kaye and Higgins 1926), amounted to approximately 8 % of the total temperature drop between the hot and cold plates.

For the purpose of the thermal-conductivity measurements, the current in the heating grid was adjusted to give a temperature drop of about 4° C across the bismuth plate at a mean temperature of 25° C. Thermal equilibrium was very soon established, when a series of readings was taken both for zero field and for a range of longitudinal magnetic fields. Each time the conditions were changed, a lapse of a few minutes was allowed for the re-establishment of thermal equilibrium.

The three main orientations of the crystal may for convenience be designated as in Table III, of which the lower part is similar to the lower part of Table II.

TABLE III. LONGITUDINAL MAGNETIC FIELDS (HEAT FLOW || H)

Crystal orientation	Orientation of trigonal axis with reference to heat flow and magnetic field H
Y	$\parallel$
Z_1 (line $\perp$ H)	$\perp$
Z_2 (line $\parallel$ H)	$\perp$

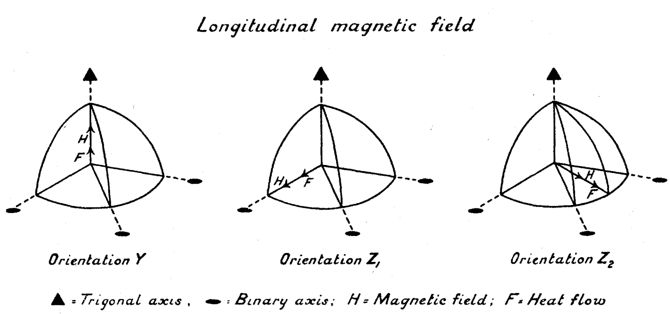

FIG. 9.

Three bismuth specimens, each of a different thickness, were examined in both the Y and Z orientations. The results, which showed no systematic dependence on the thickness, indicate that the effect of the longitudinal field on the thermal resistance is very nearly the same in all three orientations and much less than with a transverse field. In fig. 10, orientations Z_1 and Z_2 are represented sufficiently accurately by one mean curve, which for high fields becomes linear and parallel to the curve for orientation Y.

As we shall see presently, the corresponding electrical-resistance values show marked differences between all three orientations.

Electrical-resistance measurements in longitudinal magnetic fields.

For the electrical-resistance measurements, bismuth rods such as were used with the transverse fields were employed, their length, however, being just under 25 mm. Current leads were soldered to the two extremities of the rod, while the potential leads (of platinum) were similarly attached at about 5 mm. from each end. The rod was mounted vertically within a shallow cylindrical brass container 25 mm. deep. This container, which was filled with acid-free paraffin oil to assist in the establishment of thermal equilibrium, served also as a distance piece for the magnet poles.

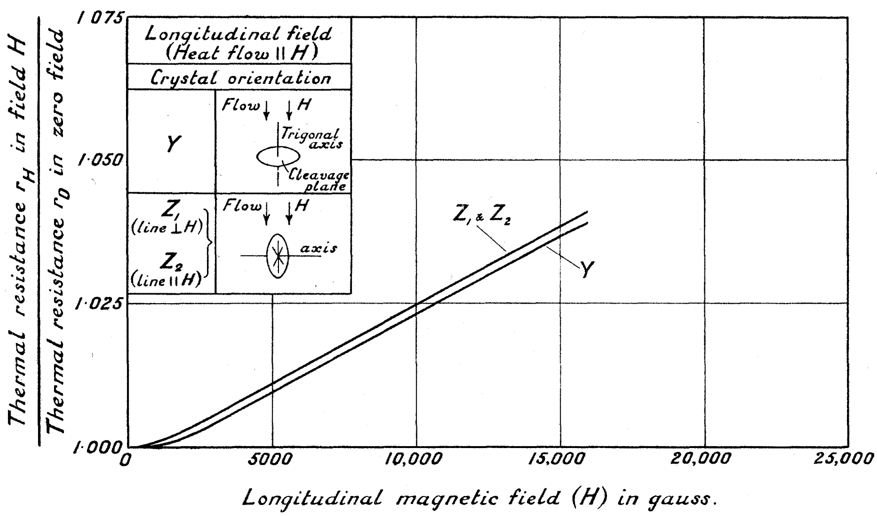

FIG. 10. Variation of thermal resistance of a bismuth single crystal in a longitudinal magnetic field.

In the measurements, the current traversing the bismuth was first adjusted to a suitable value, generally about 0·3 amp. The measured potential drop was then about 400 μV, in the absence of a magnetic field. For each value of the field strength, the potential drop was determined for both directions of the current, the two readings rarely differing by more than 1 part in 400. The mean temperature of the bismuth was 16° C.

The main orientations are the same as those given in Table III, "heat flow" being replaced by "current". The several mean curves for the different orientations, which are given in fig. 11, are quite distinct and so do not resemble the corresponding thermal-resistance curves. The graphs for the Y and Z_2 orientations become straight lines for the greater part of the range, but in the case of the Z_1 orientation there is a definite tendency towards saturation for the higher fields.

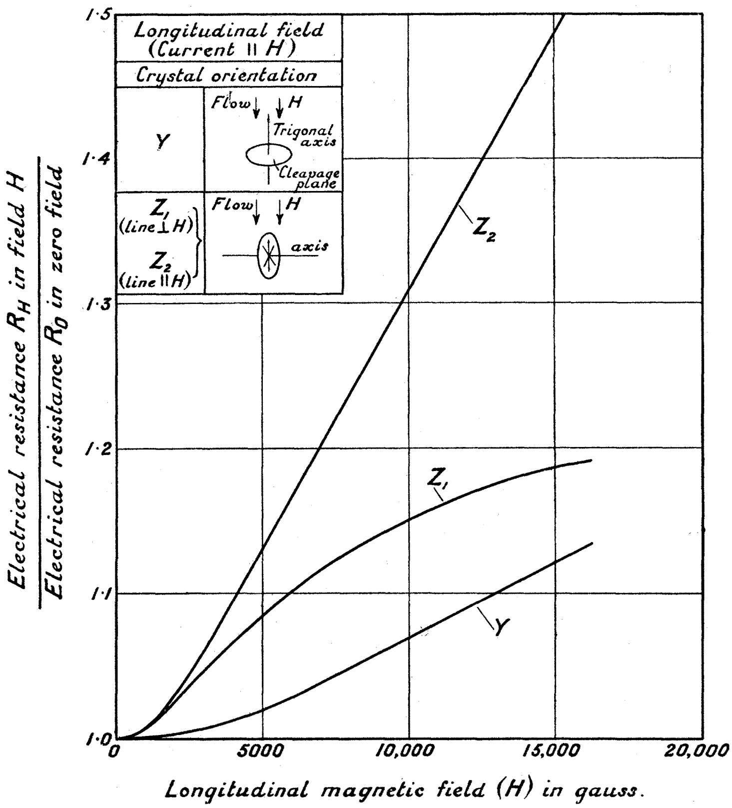

FIG. 11. Variation of electrical resistance of a bismuth single crystal in a longitudinal magnetic field.

Summary of results

The numerical values of the resistivity ratios for various orientations of a single bismuth crystal subjected to fields of 10,000 and 20,000 gauss (extrapolated where necessary) are summarized for purposes of illustration in Table IV, which is derived from figs. 6, 7, 10 and 11. A study of the various data and curves indicates that for a bismuth single crystal at ordinary temperatures:

(1) For all orientations of magnetic field, in relation to the electrical or thermal flow and the trigonal axis, the invariable effect, under like con-

ditions, is to increase the electrical resistivity more than the thermal resistivity, usually substantially so.

(2) The effect of a magnetic field is most pronounced when the electrical or thermal flow is at right angles to the field and parallel to the trigonal axis (i.e. at right angles to the principal cleavage plane), orientation C. Under such conditions, the effect reaches a maximum when the magnetic field is at right angles to one of the three "lines" (i.e. at right angles to one of the three secondary cleavage planes)—orientation C_1. The electrical and thermal effects simultaneously reach minima in the mid-way positions, i.e. when the magnetic field is parallel to one of the lines—orientation C_2.

TABLE IV. SUMMARY OF MAGNETIC-FIELD RESULTS

Magnetic field	Crystal orientation	Resistivity in field H / Resistivity in zero field: Thermal flow, 10,000 gauss	Thermal flow, 20,000 gauss	Electrical flow, 10,000 gauss	Electrical flow, 20,000 gauss
Transverse ($H \perp$ flow)	A (flow $\perp$ axis) ($H \perp$ axis)	$1{\cdot}05_5$	$1{\cdot}12_5$	1·50	2·09
	B (flow $\perp$ axis) ($H \parallel$ axis)	$1{\cdot}03_5$	$1{\cdot}10_5$	$1{\cdot}22_5$	1·73
	C_1 (flow $\parallel$ axis) ($H \perp$ axis) ($H \perp$ line)	1·18	1·33	1·54	2·28
	C_2 (flow $\parallel$ axis) ($H \perp$ axis) ($H \parallel$ line)	$1{\cdot}14_5$	$1{\cdot}23_5$	1·43	1·91
	C (mean of C_1 and C_2)	1·16	1·28	1·49	2·09
Longitudinal ($H \parallel$ flow)	Y ($H \parallel$ axis)	$1{\cdot}02_5$	(1·05)	1·07	(1·17)
	Z_1 ($H \perp$ axis) ($H \perp$ line)	$1{\cdot}02_5$	(1·05)	1·15	(1·20)
	Z_2 ($H \perp$ axis) ($H \parallel$ line)	$1{\cdot}02_5$	(1·05)	1·31	(1·66)

(3) The effect of a magnetic field is least pronounced when the field is parallel to the electrical or thermal flow and also to the trigonal axis (orientation Y), though in the case of the thermal flow the extent of the effect is much the same for all three orientations Y, Z_1 and Z_2.

(4) When the electrical or thermal flow is at right angles to the trigonal axis, the effect of a transverse magnetic field is least when it is parallel to the axis (orientation B), and greatest when the field is at right angles to

both axis and flow (orientation A). Kapitza (1928, p. 413) using very much stronger fields found, on the contrary, that the electrical effect was greater in orientation B.

(5) In all the orientations for both thermal and electrical flow, the curves in figs. 6, 7, 10 and 11 indicate relatively small and approximately parabolic effects for small fields up to 1000–2000 gauss. As the fields are increased, the curves become considerably steeper, so that if extended backwards they do not pass through the origin. At high fields, all the thermal-flow curves become linear, except those for orientations C_1 and C_2, which tend to show signs of "saturation", while the corresponding electrical-flow curves are also all linear, showing no signs of saturation, except in the one case of orientation Z_1. The linear portions of the thermal curves for orientations A and B are parallel to each other (or nearly so), while the corresponding electrical curves are not only parallel to each other but also to that for mean orientation C. The thermal curves for orientations Y and Z are parallel and bear no resemblance to the corresponding electrical curves.

(6) It follows from the above, that the Lorenz function at ordinary temperatures and zero field, which already exceeds the "normal" value, steadily increases with a magnetic field for all orientations, the rate of increase being greatest (e.g. 90 % for 20,000 gauss) when the field, flow and trigonal axis are all mutually at right angles (orientation A), and least (e.g. 10 % for 20,000 gauss) when the field, flow and axis are all parallel (orientation Y). This progressive departure with increasing field from Sommerfeld's theoretical value would appear to withhold support for his basic assumption that electrical and thermal conduction are both due solely to the same electronic agency. It is apparent, too, that the nature of the conducting mechanism is bound up with the direction of measurement in the crystal.

Discussion

Electrical conduction in transverse fields

According to Sommerfeld's wave-mechanical modification of the theory of free electrons in metals, developed originally by J. J. Thomson, Drude and others, the electrons have the velocity distribution of a degenerate gas. Sommerfeld's theory, which accounts satisfactorily for many of the electrical properties of metals, was used by N. H. Franck (1930), and later by H. Jones and his collaborators (1934, 1936), to calculate the alteration of electrical resistance in a metal subjected to a transverse magnetic field, assuming the electron-gas to obey the Fermi-Dirac statistics. Franck's argument takes account only of the electrons, and ignores their possible interactions with the atoms, so that it makes no explicit reference to the lattice and predicts no variation with orientation. Jones makes allowance for the interactions between the free electrons and the electric field due to the atoms of a cubic lattice. Both workers conclude that the fractional change of electrical resistance, x_e, is related to the square of the field H, by a formula of the type

$$x_e = \alpha H^2/(1+\beta H^2),$$

where α and β are functions of both the temperature and the mean free path of the electrons.

The formula predicts that when H is small, so that βH^2 is negligible in comparison with unity, x_e should vary as H^2, whereas for large fields, when the denominator is effectively βH^2, x_e should become constant. The first of these predictions is in agreement with the results of both Kapitza (1928) and the present investigation on bismuth crystals, but the second is not. On the contrary, in both sets of observations the increase in electrical resistance at high transverse fields is approximately a linear function of the field. Kapitza, it may be remembered, was led to suggest that different mechanisms were needed to account for the results in high and low fields respectively.

If, however, we suitably modify the above "H^2" formula to read

$$x_e = \gamma H^2/(1+\delta \mid H \mid),$$

this new "$\mid H \mid$" formula reduces to a quadratic law for small transverse fields, while at high fields it indicates a linear variation of x_e with H, as found experimentally. That the formula fits the present observations satisfactorily at all fields, is shown in fig. 12, where H^2/x_e is seen to be a linear function of H. Furthermore, the formula also gives good quantitative agreement with Kapitza's observations on electrical flow, as is demonstrated in fig. 13.

From the curves in fig. 12 the values of γ and δ have been calculated. They vary with the orientation of the specimen, and no doubt also with its purity and state of strain. Indeed, if it may be assumed that, like the parameters α and β of the "H^2" formula, γ and δ are functions of temperature and mean free path, then, at constant temperature, they should depend only on the mean free path. This would explain the variation with orientation, and suggests that γ and δ, being functions of a single variable, should be closely related to each other, a suggestion which is supported by plotting the values of γ against those of δ for the four orientations, when we find that not only do the four points lie on a smooth curve, but the values of γ and δ calculated for Kapitza's crystal also fall on the same curve.

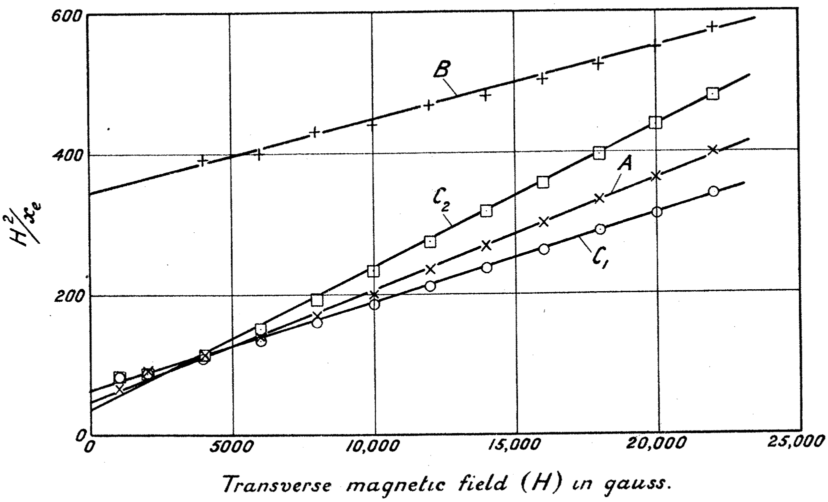

FIG. 12.

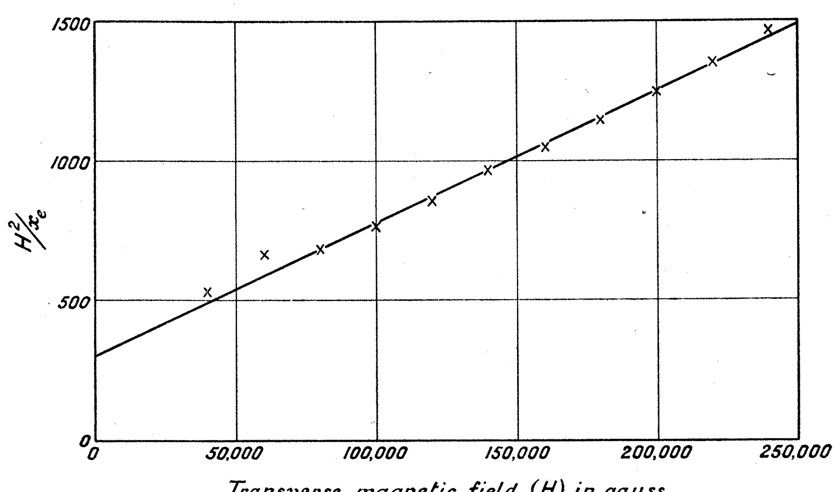

FIG. 13. (Kapitza.)

Thermal conduction in transverse fields

As regards the mechanism of thermal conduction in metals, there appears to be no complete mathematical theory available, and, in particular, none in which lattices other than cubic are considered. Nevertheless if thermal conduction is attributable, in the main, to the energy carried by the same free electrons as those which transport electrical charge and thus account for electrical conduction, we should expect the two in general to follow parallel relations. It seems to be generally accepted, however, that the thermal process is of a dual nature, i.e. an "electronic" (metallic) component bound up with the mean path of the electrons; and a "lattice" (non-metallic) component conveyed as elastic waves in the atomic lattice. There is disagreement as to how the effects of the two components implement each other; Grüneisen regards the thermal resistivities as additive, Eucken, on the other hand, looks upon the conductivities as additive, while more recently Peierls rejects both assumptions, on the score that the two components are not independent.

Extreme examples of lattice conduction are provided by such materials as sulphur, which while having so extremely small an electrical conductivity as to indicate a virtual absence of free electrons, yet have a thermal conductivity which, although only small, is readily measurable (Kaye and Higgins 1929*b*). We must look to the energy transferred through the medium of the atomic lattice as almost wholly accounting for the thermal conduction in such high electrical insulators.

We should anticipate that the nature and complexity of the two conducting mechanisms would be bound up with the direction of flow in a metal crystal such as bismuth, since the electronic mean free path is presumably less in those directions which are rich in atoms. This is supported by the present experiments, which show that the influence of a transverse magnetic field on both electrical and thermal conductivity is least when the flow is parallel to the cleavage plane, and the magnetic field is at right angles to this plane, so that the lines of flow remain parallel to the cleavage plane.

Furthermore, we note from Table I that, while for zero field the mean electrical conductivity at right angles to the cleavage plane (orientation C) is 80 % of that along the plane (orientation A), the corresponding figure for thermal flow is under 60 %. The effect of a high transverse magnetic field, say 20,000 gauss, is to leave the electrical ratio unchanged, while the thermal ratio is reduced to 50 % (Table IV). This seems to indicate that the lattice contribution to heat flow is appreciably greater in the direction richest in atoms, unless the dimensions of the lattice in the two directions are differentially influenced by a magnetic field to an extent sufficient to affect the relative number of electronic collisions.

In the light of the above, and in view of the success with which the "$|H|$"

formula interpreted the electrical observations, we are led to try whether a similar formula

$$x_t = \gamma H^2/(1+\delta \mid H \mid)$$

will fit the thermal observations (x_t being the fractional alteration of thermal resistance in a transverse magnetic field $\mid H \mid$, and γ and δ are constants). Plotting H^2/x_t against H as before, we find that the formula holds excellently for orientation A, reasonably well for C_1 and C_2, and poorly for B. Furthermore, if the "best" straight lines are drawn to represent these ordinates for all four orientations, the derived values of γ and δ again fall on a smooth curve.

On the other hand, if we adopt a similar procedure with the "H^2" formula, so that we now plot H^2/x_t against H^2, we find that the linearity fails completely for orientation A, gives only a poor representation for C_1 and C_2, but represents moderately well orientation B. The mean values of α and β in this formula are no longer functions one of the other.

The present experiments may thus be looked upon as confirming the view that there are two mechanisms by which a transverse magnetic field can affect the conductivity of a bismuth crystal, one leading to an "$\mid H \mid$" relation, and the other to an "H^2" relation: the former is predominant for electrical conduction, while both appear to be operative in the thermal case, their relative contributions varying with the orientation.

Electrical and thermal conduction in longitudinal fields

As regards the electrical and thermal changes of bismuth in a longitudinal magnetic field, the present results show that they are much smaller than in a transverse field, as would be anticipated on the usual assumptions as to the behaviour of free electrons travelling parallel to the field. It would appear that a longitudinal field can influence the free paths of only those electrons which have components of transverse velocity, since the field is directly effective only on electrons with such motions.

One should not ignore, however, the possibility of appreciable parasitic effects in the experimental observations due to the considerable mechanical working necessitated by the choice of "plate" specimens for the longitudinal fields. Be that as it may, the extreme complexity of the phenomena in such fields may be gauged from the fact that while there is no theoretical prediction available as to the type of formula which should govern the longitudinal resistances, in point of fact, we find that, by comparison with the transverse-field results, the electrical resistance follows an "H^2" formula for orientations Z_1 and Z_2, the corresponding thermal resistance obeys very closely an "H" formula, while both resistances for orientation Y subscribe to neither formula.

I wish to express my acknowledgements to Mr D. E. A. Jones for valuable and efficient assistance throughout the work. I am also greatly indebted to Mr J. H. Awbery for helpful discussion.

Summary

The thermal and electrical resistivities of bismuth single crystals have been studied at a series of temperatures from 25 up to 160° C. In either case, the values for a direction parallel to the trigonal axis are greater than for those at right angles. The temperature coefficient is positive in every case, being roughly twice as large for the electrical resistivity as for the thermal.

The effects produced on the resistivities of bismuth crystals by magnetic fields up to about 20,000 gauss have been measured for various crystal orientations using fields both parallel and at right angles to the thermal or electrical flow. In all circumstances, the resistivity is increased by an amount which is invariably greater (usually substantially) for the electrical resistivity than for the thermal. The effects are most pronounced when the thermal or electrical flow is parallel to the trigonal axis, and the field is at right angles to one of the three "lines" or secondary axes. The effects are least pronounced when the field, the flow and the trigonal axis are all parallel. In all the orientations, the effects are relatively small and approximately parabolic for fields up to about 2000 gauss, thereafter becoming linear and more pronounced for stronger fields, except for one or two orientations where there is a tendency to "saturation".

The observations lend support to the view that there are two conducting mechanisms through the medium of which a magnetic field can affect the conductivity, one predominating for electrical conduction while both appear to be operative for thermal conduction, their relative contributions varying with the orientation.

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