# Some Thermo- and Galvanomagnetic Properties of a Bismuth Crystal

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The fractional changes, due to a magnetic field, in the electrical conductivity, in the thermal conductivity, and in the thermoelectric power of a single bismuth crystal are measured in these experiments. These changes are determined as a function of the field strength, of the direction of the field, of the direction of the crystal axis, and of the direction of the heat and electric currents through the crystal. An electric current sent through the crystal cools one junction and heats the other by the Peltier effect. The temperature difference thus produced gives rise to a thermal e.m.f. in the crystal circuit. Observations of this e.m.f. allow the calculation of the fractional changes produced in the thermal conductivity and in the thermoelectric power. The change of electrical conductivity is influenced much more strongly by the crystal structure than is the change of thermal conductivity. Crystal structure and orientation of the magnetic field both affect strongly the change in the thermoelectric power. The theory of electrons in metals in its present form does not give an adequate explanation of the results, If the magnetic field changes the free electron density in bismuth some of the results may be explained in a general way.

 $\prod_{n=1}^{\infty}$  1886 Nernst and Ettingshausen<sup>1</sup> discovered that if a copper-bismuth thermocouple were put in a magnetic field, the e.m.f. of the couple was changed, In their experiments the magnetic field was perpendicular to the direction of heat How. They concluded that the effect varied with the square of the magnetic field strength and with the temperature, but was independent of the dimensions of the bismuth. Other investigators' have found that the effect exists for other orientations of the magnetic field, but that the magnitude of the effect depends on the direction of the field; that<sup>3</sup> if a single crystal is used, the magnitude of the effect depends also on the orientation of the crystalline axis.

The intimate connection between the thermoelectric power, thermal conductivity, and electricai conductivity (all three being supposed to depend on free electron concentrations) suggests that a study of their changes in a magnetic field and the relation between these changes and the position of the crystalline axis might add materially to the knowledge of the nature of galvanomagnetic and thermomagnetic effects. This paper contains an account of such a study with single crystals of pure bismuth.

#### APPARATUS AND METHOD

The method used was in general as follows:—an electric current sent through the crystal cools one junction and heats the other by the Peltier

<sup>1</sup> Nernst and Ettingshausen, Wied. Ann. 29, 343 (1886).

<sup>~</sup> Hall and Campbell, Proc. Am. Acad. 46, 625 (1911);A. W. Smith, Phys. Rev. 2, 383 (1913); Lownds, Ann. d. Physik 4, 776 (1901).

C. W. Heaps, Phys. Rev. 31, 648 (1928).

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effect. This current is broken and a very short time afterwards the crystal is connected to a potentiometer which is set to balance the thermal e.m.f. produced by the temperature difference at the junctions. This same experiment is repeated when the crystal is in a magnetic field. It is then possible to calculate the fractional change of the thermoelectric power produced in the crystal by the field. This general method was first used by la Rosa. <sup>4</sup> He did not, however, make a necessary correction for a possible effect of the field on the thermal conductivity.

The arrangement of the apparatus is shown in Fig. 1. A single crystal of bismuth was immersed in oil between the poles of a large Weiss water-cooled electromagnet. The electromagnet could be rotated so as to vary the direction of the magnetic field. The crystal was soldered to copper wires with Wood's metal. Two Burgess vacuum relays were connected to these wires.



Fig. 1, Arrangement of apparatus for measuring change of thermoelectric power and thermal conductivity in a magnetic field.

The relays were operated by a rotary switch running at constant speed. They were so arranged that both were never closed at the same time. From Fig. <sup>1</sup> it is seen that relay 1 controlled the current through the crystal, and relay 2 connected the crystal across the potentiometer. The galvanometer used with the potentiometer, of the astatic moving magnet type, was adjusted to a sensitivity of about 300 mm per microvolt.

In the position shown the rotary switch allows a current  $i$  to pass through the crystal. This current, because of the Peltier effect, produces a temperature difference between the junctions on the crystal. Rotating the rotary switch cuts off this current by operating relay 1. At an adjustable time  $t$  later, by operating relay 2, the rotary switch connects the crystal to the potentiometer for a very short time. Farther rotation turns on the current  $i$ , and the cycle is repeated in the next revolution of the rotary switch. If the potentiometer is not adjusted to the e.m.f. of the crystal, the galvanometer will be deHected once during each cycle. By adjusting the potentiometer till the galvanometer is not deHected, the thermal e.m.f. in the crystal circuit could be measured. The rotary switch was arranged so that the e.m.f.'s  $E_1$  and  $E_2$ 

<sup>4</sup> La Rosa, Nuovo Cim. 1S, 26 (1919).

at two times  $t_1$  and  $t_2$  after the current was cut off could be determined.  $E_1$ and  $E<sub>2</sub>$  were determined with and without the magnetic field. The apparatus was capable of measuring an e.m.f. to a tenth of a microvolt; but variable stray thermal and contact e.m.f.'s make the accuracy of observation somewhat less than this.

#### THEQRY oF THE METHoD

The heat generated at the hot junction, for example, raises the temperature of that junction, and is then conducted partly through the crystal to the cold junction and partly into the oil around the junction. If the electric current has been flowing long enough for the crystal junctions to reach an equilibrium temperature difference, the heat is conducted away as fast as it is liberated. If the heat conducted through the oil from one junction to the other be neglected. the heat conducted through the crystal will be equal to the Peltier heat liberated at the hot junction plus the difference between the Joule heats developed at the hot and cold junctions. Hence

$$
i\pi + i^2(r_2 - r_1) = kB d\theta/dx \tag{1}
$$

where i is the electric current,  $\pi$  the Peltier coefficient,  $r_1$  and  $r_2$  the resistances of the cold and hot junctions respectively, k the thermal conductivity,  $B$  a constant depending on the dimensions of the crystal, and  $d\theta/dx$  the temperature gradient along the crystal. The term  $i^{2}(r_{2} - r_{1})$  is the difference between the Joule heats developed at the two junctions, which must be conducted through the crystal. Let  $d\theta/dx = \Delta\theta/l$ , *l* being the length of the crystal and  $\Delta\theta$  the temperature difference between the junctions. In a magnetic field certain of these quantities will be changed. Denoting by a subscript  $H$  the values of these quantities in a magnetic field  $H$ , we have

$$
i\pi_H + i^2(r_2 - r_1)_H = k_H B(\Delta\theta_H/l);
$$

whence

$$
\Delta \theta_H/\Delta \theta = k/k_H \frac{i\pi_H + i^2(r_2 - r_1)}{i\pi + i^2(r_2 - r_1)}.
$$
\n(2)

When *i* is reversed the heat  $i\pi$  is reversed in sign, but the heat  $i^2(r_2 - r_1)$  remains unchanged. It is thus possible by reversing  $i$  to estimate the magnitude of  $i^2(r_2 - r_1)/i\pi$ . For example,  $E_1$  was 76 microvolts; when the current was reversed  $E_1$  was 84 microvolts. Thus the Joule heats developed at the two junctions contributed 4 microvolts to the observed e.m.f. In every case experiments gave  $i^{2}(r_{2}-r_{1})/i\pi$  less than 0.1. Thus to a good approximation

$$
\Delta \theta_H / \Delta \theta = (k / k_H) (\pi_H / \pi). \tag{3}
$$

Substituting  $E = P\Delta\theta$  and  $P = \pi/\theta$ , where E is the e.m.f. of the crystal thermocouple and  $P$  its thermoelectric power, we get

$$
\frac{E_H}{E} = \frac{P_H}{P} \frac{\Delta \theta_H}{\Delta \theta} = \frac{P_H}{P} \frac{k}{k_H} \frac{\pi_H}{\pi} = \frac{P_H^2}{P^2} \frac{k}{k_H} \,. \tag{4}
$$

Putting  $\Delta E = E_H - E$  and  $\Delta k = k_H - k$  this relation gives

$$
\Delta P/P = (1 + (\Delta E/E)_0 + \Delta k/k + (\Delta E/E)_0 \Delta k/k)^{1/2} - 1 \tag{5}
$$

where  $(\Delta E/E)$ <sub>0</sub> is the value of  $\Delta E/E$  at time  $t=0$ , immediately after the electric current is cut off, but before sufficient heat has been conducted away through the crystal to diminish  $\Delta\theta$  appreciably. In order to calculate  $\Delta P/P$ it is necessary to calculate  $\Delta k/k$  and  $(\Delta E/E)_0$ .

Determination of  $\Delta k/k$ .

To determine  $\Delta k/k$  we utilize the fact that  $\Delta \theta$  is decreased after the electric current is stopped by conduction of heat through the crystal. Let  $d/dt(\Delta\theta) = -Ak\Delta\theta$ , A being a constant. This equation gives log  $(\Delta\theta/\Delta\theta_0) =$  $-Akt$ , where  $\Delta\theta_0$  is the value of  $\Delta\theta$  when  $t = 0$ . Since  $E/E_0 = \Delta\theta/\Delta\theta_0$ , we have  $log (E/E_0) = -Akt$ . It is impossible to observe  $E_0$  experimentally. However, let  $E_1$  and  $E_2$  be the values of E at times  $t_1$  and  $t_0$  respectively. Then

$$
\log (E_2/E_1) = - A k(t_2 - t_1); \log (E_2/E_1)_H = - A k_H(t_2 - t_1), \qquad (6)
$$

the  $H$  subscripts again denoting values obtained in a magnetic field. Dividing the second of these equations by the first and setting  $\Delta k = k_H - k$  gives

$$
\Delta k/k = \frac{\log (E_2/E_1)_H}{\log (E_2/E_1)} - 1.
$$
 (7)

Determination of  $(\Delta E/E)_{0}$ .

To determine  $(\Delta E/E)_{0}$  we combine the two equations log  $(E_{1}/E_{0})_{H}$  $=-Ak<sub>H</sub>t<sub>1</sub>$  and log  $(E<sub>1</sub>/E<sub>0</sub>)=-Ak<sub>t<sub>1</sub></sub>$ , getting

$$
E_{0H}/E_0 = E_{1H}/E_1 e^{A(k_H - k)t_1} = E_{1H}/E_1 e^{A k \Delta k / k t_1}.
$$
 (8)

A similar relation holds for  $t_2$ , which combined with (8) gives

$$
(1/t_2 - 1/t_2) \log (E_{0H}/E_0) = 1/t_1 \log (E_{1H}/E_1) - 1/t_2 \log (E_{2H}/E_2).
$$
 (9)

This relation gives  $(\Delta E/E)_0$ , since  $E_{0H}/E_0 = (\Delta E/E)_0 + 1$ .

Thermal equilibrium must be reached in the crystal before the electric current is stopped if Eq.  $(1)$  is to apply. This condition was satisfied by increasing the time during which  $i$  flowed till further increase did not increase the values of the e.m.f.'s obtained. This made the time of one revolution of the rotary switch about 5 seconds. Then the e.m.f.'s were observed to be proportional to the current, as would be expected from equation (1) if the Joule heat be neglected. It was estimated from the magnitude of the observed e.m.f.'s that  $\Delta\theta$  was about 1°C. P,  $\pi$ , and perhaps k are functions of the temperature, but it was assumed that the temperature changes duringan experiment are so small that these quantities can be regarded as constant, A few observations were made with different currents; but within the limits of experimental error  $\Delta E/E$ ,  $\Delta k/k$ , and  $\Delta P/P$  were found independent of i.

With the direction of heat flow perpendicular to the crystalline axis and with a magnetic field of 8000 gauss perpendicular to both the crystalline axis and the heat flow, it was found that  $E_1 = 85.0$  microvolts,  $E_2 = 58.0$ microvolts,  $E_{1H} = 61.8$  microvolts, and  $E_{2H} = 45.3$  microvolts. If these values be substituted in Eq. (7), it is found that  $\Delta k/k = -0.190$ . From Eq. (9), with  $t_1 = 0.129$  sec. and  $t_2 = 0.662$  sec., it is found that  $(\Delta E/E)_0 = -0.285$ . The variation of  $\Delta E/E$  with the time is clearly seen here, since  $(\Delta E/E)_t$ , =  $-0.273$  and  $(\Delta E/E)_{t_2} = -0.219$ . If the above values be substituted in Eq. (5),  $\Delta P/P = -0.245$  is obtained. These values are plotted in Figs. 4 and 6.

#### RESULTS

It was found much easier to determine accurately  $\Delta E/E$  than  $\Delta k/k$ , since  $\Delta k/k$  is calculated from the ratio of the logs of two quantities differing little from unity. Since the rate of cooling of the crystal couple depended on the physical dimensions of the crystal, it was found desirable for the crystal to have a cross-sectional area of about  $1 \text{ mm}^2$ ; hence it was necessary to use two different specimens in order to secure all the desired orientations with



Fig. 2. Fractional change of thermal conductivity as a function of magnetic field strength.

respect to the crystalline axis. Both crystals were grown from the same very pure bismuth, supplied by Eimer and Amend. The direction of the crystalline axis was determined by observing reflections from cleavage planes by Bridgman's<sup>5</sup> method. The three-dimensional direction diagrams accompanying all the curves show the angles between the crystal axis  $a$ , the heat flow  $h$ , and the magnetic field  $H$ . The data for  $h$  parallel to  $a$  were obtained with one crystal, for h perpendicular to a with the other crystal.

The fractional changes in the thermal conductivity as a function of the magnetic field strength for several different orientations of the crystal axis a, heat flow  $h$ , and magnetic field  $H$  are shown in Fig. 2. It is of interest to note that the longitudinal effect, in which  $h$  is parallel to  $H$  (see the two top direction diagrams) is too small to measure.

It was found that when  $h$  was along  $a$  and  $H$  was perpendicular to both a and h, a rotation of H in this normal plane made no difference in the magnitude of the observed effects. This fact is indicated in the direction diagrams next to the bottom by showing  $H$  in two positions. The differences between

<sup>5</sup> Bridgman, Proc. Am. Acad. 60, 305 (1905).

the curves for the cases in which the effect is measurable are about the same as the magnitude of the errors of observation. The values at 8000 gauss, however, are averages of several sets of observations, and it is believed that they show a real effect of the orientation of a on the value of  $\Delta k/k$ . In general it appears that the orientation of  $H$  with respect to the heat flow is of considerably greater importance than the orientation of  $H$  with respect to the crystal axis.

So far as is known to the author  $\Delta k/k$  has not been measured before for a single crystal. If a bismuth plate consists of small crystals randomly oriented, the magnitude of the transverse effect should be the same as that shown here for the transverse orientations,  $(H$  perpendicular to h) which are approximately equal. The mean of two such values obtained for polycrystalline bismuth plates by Leduc<sup>6</sup> and Van Everdingen<sup>7</sup> at 6000 gauss is  $-0.0575$ . The mean of the values shown in Fig. 2 for this field is  $-0.056$ . The agreement is very good.



Fig. 3. Fractional change of thermoelectric power as a function of magnetic field strength.

As has been indicated, the fractional change in the thermoelectric power of the crystal couple can be calculated from the same four observations that gave  $\Delta k/k$ . The results obtained in this way are shown in Fig. 3. A similar set of results has been obtained by C. W. Heaps, who obtained  $\Delta P/P$  by a more direct method. For h parallel to a, and H perpendicular to both a and h, his curve is almost a straight line rising to a value of 0.08 at 8000 gauss. The corresponding curve in Fig. 3 agrees with this up to about 4000 gauss. The lack of agreement between his curve and the one given here is probably due to a small angle between  $a$  and  $h$ , which would introduce components of all the negative values of  $\Delta P/P$  shown in Fig. 3. A lack of uniformity in the evo-1ution of heat over the ends of the relatively short crystals would result in a heat flow not strictly along the length of the crystal, which in this case was along  $a$ . Obviously a very small departure from parallelism of  $a$  and  $h$  would suffice to produce an appreciable decrease in the value of  $\Delta P/P$ . For the other curves of Fig. 3 the agreement with those of Heaps is as good as one might

<sup>&#</sup>x27; Leduc, Compt. Rend. 104, 783 (1887).

<sup>&#</sup>x27; Van Everdingen, Jour. de Physique (3) 10, 217 (1901).

expect, considering the difhculty of exact adjustment and the impossibility of securing crystals without Haws.

 $\Delta P/P$  was observed to be a function of the temperature, but observations were only made between 18<sup>o</sup>C and 40<sup>o</sup>C. The results for  $\Delta P/P$  are in general agreement with the experiments of A. W. Smith, $\frac{3}{7}$  showing a decrease of  $\Delta P/P$  with increasing temperature. The values of  $\Delta P/P$ ,  $\Delta k/k$ , and the fractional changes of electrical conductivity given in this paper were all taken at 25°C.



Fig. 4. Fractional change of thermal conductivity as a function of the varying angle  $\phi$  shown in the three-dimensional direction diagrams.

Fig. 4 shows the effect on  $\Delta k/k$  of rotating a constant magnetic field of 8000 gauss about h as an axis, about  $a$  as an axis, and about an axis perpendicular to both  $\alpha$  and  $\hbar$ . Maxima and minima are found where they would be expected from the curves of Fig. 2. The flat maximum of the curve with  $H$ perpendicular to  $\alpha$  seemed peculiar, so the curve was repeated with another crystal and improved apparatus. All values obtained were negative; these results are shown by the dotted curve in Fig. 4. These last results are considered much more dependable than the first obtained. Hence no significance



Fig. 5. Fractional changes in thermoelectric power as a function of the varying angle  $\phi$  shown in the three-dimensional direction diagrams.

is to be attached to the small positive values of  $\Delta k/k$  for the solid curve in Fig. 4, nor to the wide range through which they were obtained.

The values of  $\Delta P/P$  were calculated from the data giving  $\Delta k/k$  in Fig. 4. The results are shown in Fig. 5. For one direction of rotation the points fall approximately along a straight line. The outstanding feature of the other two curves is their lack of symmetry about 0' or 90'. The maxima and minima do not occur in the transverse or longitudinal positions, and one of the curves is not symmetrical about its maximum or minimum. It was found that changing the direction of the magnetic field by 180' did not alter the magnitude of any of the effects observed, so all of these curves are repeated in the next 180'.

The curve through the black points was repeated with another crystal. The values of  $E_{0t_1}$ ,  $E_{Ht_1}$ , and  $\Delta P/P$  obtained are shown in the polar chart of Fig. 6. The variation in  $\Delta P/P$  is not as large as that in Fig. 5, but the curve in Fig. 6 giving  $\Delta P/P$  has the same general features as the corresponding one in Fig. 5.

bismuth crystallizes in the dihexagonal alternating class of the hexagonal system. The plane of easy cleavage is parallel to the (111) planes and is per-



Fig. 6. Polar chart showing  $E_{ot_1}$ ,  $E_{Ht_1}$ , and  $\Delta P/P$  as a function of the varying angle 0 shown in the three-dimensional direction diagram.

pendicular to the trigonal axis. There is also fair cleavage parallel to the  $(111)$  planes. The crystal used to obtain Fig. 6 was found to have the magnetic field along the  $(11\bar{1})$  planes as well as along the  $(111)$  planes at 165°. A maximum in  $\Delta P/P$  occurs here. The (111) and (111) planes intersect the (111) plane so that one is parallel to  $H$  at 105°, and the other at 45°. There is in Fig. 6 a minimum of  $\Delta P/P$  at 105, but there is no similar feature at 45.

It appears from these considerations that the  $\Delta P/P$  curve in Fig. 6 is not symmetrical about 0° or 90° because there are structure factors in the crystal which produce a distortion. The plane perpendicular to the crystal axis can thus not be considered as possessing circular symmetry about  $a$ . The separation in this plane of the two effects—namely, the structure effect and the

effect due to the direction of h with respect to  $H$ —appears to be impossible without a much more detailed investigation.

The fractional changes produced by the magnetic field in the electrical conductivity are shown as  $\Delta c/c$  in Fig. 7. These results were obtained by soldering two more copper wires to the crystal where the current leads were soldered on, and by measuring with a potentiometer the potential drop V along the crystal. The current being held constant, the change  $\Delta V$  produced in V by the field was determined, whence  $\Delta c/c$  could be calculated. It was found that the temperature difference caused by the Peltier effect produced an appreciable error in these results; but since  $E_0$  and  $(\Delta E/E)_0$  could be calculated, the necessary correction could be applied.



Fig. 7. Fractional changes of electrical conductivity as a function of magnetic field strength. Electric current direction is indicated by  $i$ , crystal axis by  $a$ , and magnetic field by  $H$ .

This effect is well known, and has been extensively investigated for polycrystalline bismuth. Lownds<sup>8</sup> gives two values of  $\Delta c/c$  for a single crystal with different orientations in a magnetic field, and Borelius and Lindh' give several values which can be compared with the values of  $\Delta c/c$  shown in Fig. 7. Their values were obtained at an average temperature of 18'C. The comparisons are made in Table I. The values given by Lownds, and by

Orientation	۵L. н	٠a.	łН	a	ti tH а	t a
Field H (gauss)	5000	5000	2300	2300	2300	2.300
Lownds	$-0.198$	$-0.143$				
Borelius & Lindh			$-0.039$	$-0.053$	$-0.026$	$-0.085$
Banta	-0.160	$-0.103$	$-0.015$	$-0.015$	$-0.004$	-0.055

TABLE I. Values of  $\Delta c/c$ . Comparison with the results of others.

Borelius and Lindh, are larger than the corresponding values found by the present experiments. Part of these differences can be explained as a tempera-

<sup>8</sup> Lownds, Ann. d. Physik (4) 9, 677 (1902).

<sup>9</sup> Borelius and Lindh, Ann. d. Physik $(4)$  53, 97 (1917).

ture difference, since Drude and Nernst<sup>10</sup> found that  $\Delta c/c$  decreased rapidly with increasing temperature. As before, some of the differences may be due to imperfections in the crystals.

### CONCLUSIONS

The results reported here are difhcult to fit into any simple theory. There is at present no theory of electrons in metals which adequately accounts for all of the observed facts of thermoelectricity in crystals. Any theoretical result for  $\Delta c/c$ ,  $\Delta k/k$ , or  $\Delta P/P$  should be an even function of H, since the direction of H can be changed by  $180^{\circ}$  without affecting the magnitude of any of these quantities. Such a result has been obtained for  $\Delta c/c$  with transverse fields by Sommerfeld<sup>11</sup> and Frank,<sup>12</sup> who get  $\Delta c/c = -BH^2/(1+CH^2)$ , B and C being positive constants. In obtaining this expression it is assumed that the magnetic field does not change the density of free electrons in the metal, but does disturb the distribution function. This equation has been found to fit the experimental results very well for ordinary polycrystalline metals. It is not, however, so successful in dealing with bismuth, which in many respects is abnormal; and it cannot be expected, in the form derived, to account for the important effect of-crystalline structure. It might be expected that  $\Delta c/c$  and  $\Delta k/k$  would have their smallest values for H parallel to h and i respectively, since then the electron flow is along  $H$ . In general, this seems to be true. While the direction of the crystalline axis with respect to  $H$  or  $h$ is relatively unimportant for  $\Delta k/k$ , it is of decided importance for  $\Delta c/c$ .

Sommerfeld and Frank state that in the adiabatic case their calculations indicate that  $\Delta k/k$  is only about two percent of  $\Delta c/c$ . Thus bismuth apparently has a much larger  $\Delta k/k$  than can be accounted for by the Sommerfeld theory.

There is no satisfactory theory to account for the change in thermoelectric power in a magnetic field. If the classical result<sup>13</sup>  $Pe = R \log (n_1/n_2)$  is assumed to hold approximately, then the only way to account for the change in P is to suppose that the density n of free electrons in bismuth is changed by the magnetic field. Possibly this change is indicated by the divergence of  $\Delta c/c$  and  $\Delta k/k$  from the values predicted by Sommerfeld's theory, which does not allow for a change of n. Suppose then that  $n_1$  is the electron density in bismuth, and  $n_2$  the electron density in copper. Then, since copper is a normal conductor and does not have its thermal e.m.f. affected by a magnetic field,  $P_{H}e=R \log (n_{1H}/n_{2}).$ 

Thus

$$
P_H/P = \log (n_{1H}/n_2)/\log (n_1/n_2).
$$

Let

$$
n_{1H}=n_1+\Delta n_1.
$$

<sup>&</sup>lt;sup>10</sup> Drude and Nernst, Wied. Ann. 42, 568 (1891).

 $n$  Sommerfeld, Zeits. f. Physik 47, 1 (1928).

<sup>&</sup>lt;sup>12</sup> Sommerfeld and Frank, Rev. Mod. Phys. 3, 1 (1931).

<sup>&</sup>lt;sup>13</sup> O. W. Richardon, Electron Theory of Matter, p. 461.

Then

$$
P_H/P = \frac{\log (1 + \Delta n_1/n_1) + \log (n_1/n_2)}{\log (n_1/n_2)}
$$
  
= 1 + A log (1 + \Delta n\_1/n\_1). (10)

So  $\Delta P/P = A \log (1 + \Delta n_1/n_1)$ , where  $A = 1/\log (n_1/n_2)$ .

From the curves of Fig. 3,  $\Delta n_1$  is seen to be a function of both the magnetic field strength and the direction in the crystal. If we suppose that  $n_2$  is greater than  $n_1$  which seems a reasonable assumption in view of the relative electrical conductivities of the two metals, then A is negative. So, again from Fig. 3,  $\Delta n_1$  is positive for three orientations of a, h, and H in the crystal, and negative for two orientations. The largest change in  $n_1$  is for a, h, and H mutually perpendicular, and is an increase.

Classical electron theory<sup>14</sup> indicates that  $k = Dn\lambda$  and  $c = En\lambda$ ,  $\lambda$  being the mean free path of the electrons and  $D$  and  $E$  being constant at a given tempermean free path of the electrons and  $D$  and  $E$  being constant at a given temper<br>ature.<sup>15</sup> It seems possible that a magnetic field, in addition to affecting  $\emph{n}$ , may produce changes of molecular configuration which would alter  $\lambda$ . Changes of  $\lambda$  produced in this way would be distinct from any changes produced by such effects as curving of the free paths in the magnetic field, etc. Thus

and  

$$
\Delta c/c = \Delta n/n + \Delta \lambda/\lambda
$$

$$
\Delta k/k = \Delta n/n + \Delta \lambda/\lambda.
$$

So  $\Delta c/c = \Delta k/k$ . According to Sommerfeld's theory,  $\Delta k/k$  is only a small fraction of  $\Delta c/c$ . Thus the above result is more nearly in agreement with experiment than is Sommerfeld's theory. If it be assumed that the change in electrical conductivity c is due to a change in n and  $\lambda$  of the character indicated above, with the change predicted by Sommerfeld's theory in addition, then  $\Delta c/c = \Delta n/n + \Delta \lambda / \lambda - BH^2/(1 + CH^2)$ . Since  $\Delta k/k$  is very small according to Sommerfeld's theory, the whole effect may be given by  $\Delta k/k = \Delta n/\lambda$  $+\Delta\lambda/\lambda$ .

Thus

$$
\Delta c/c = \Delta k/k - BH^2/(1 + CH^2). \tag{11}
$$

The experimental results indicate that this result is hardly satisfactory. According to Sommerfeld  $B$  is a positive constant; but if Eq. (11) is true,  $B$ must be negative for one orientation: namely, with H along a, and i and h respectively perpendicular to a. For these curves in Figs. 2 and 7,  $\Delta k/k$  is less than  $\Delta c/c$  at 8000 gauss. Another objection is based on the shape of the curves: it is hard to see how the addition of a square function of  $H$  to the curves of Fig. 2 could give the curves of Fig. 7. Also, the result of the theory of Sommerfeld and Frank is supposed to hold for transverse fields, and the quantity  $BH^2/(1+CH^2)$  is thus zero for longitudinal fields—a result con-

<sup>14</sup> O. W. Richardson, Electron Theory of Matter, pp. 410–421.<br><sup>15</sup> If Sommerfeld's formulae are used instead of the classical ones the results deduced are not essentially different from these above.

tradicted by these experimental results, although the longitudinal values of  $\Delta k/k$  and  $\Delta c/c$  are in general the smallest obtained.

Consideration of the results leads to the following conclusions: Theory indicates that  $\Delta c/c$  should be negative for transverse fields. It is found negative, but the value is found to be dependent on the orientation of the crystalline axis with respect to the current and the magnetic Geld. The curves of Figs. 2 and 4 appear to indicate that there is some unrecognized but essential difference between the mechanisms of heat conduction and electric conduction in bismuth crystals. This conclusion is indicated by the fact that the  $\Delta c/c$ curves are strongly influenced by crystal structure; the  $\Delta k/k$  curves, on the other hand, appear to be roughly all the same for all cases where  $H$  is perpendicular to  $h$ . When  $H$  is parallel to  $h$  there is no measurable effect produced in  $\Delta k/k$ . There is some evidence that strong magnetic fields change the density of free electrons in the bismuth crystals.

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