Second Series *June, 1920* *Vol. XV., No. 6*

THE

PHYSICAL REVIEW.

PHYSICAL PROPERTIES OF THIN METALLIC FILMS.[1]

I. Magneto-Resistance Effects in Thin Films of Bismuth.

By J. A. Becker and L. F. Curtiss.

Synopsis.

Magneto-resistance effects in bismuth; an historical summary.—(1) *Bismuth in bulk.* This historical sketch includes allusions to the most important work which has been done on the effect of a magnetic field upon the resistance of bismuth in bulk. A complete set of references is included. (2) *Bismuth films.* A summary has also been prepared of experiments on the effect of a magnetic field on the resistance of bismuth films obtained by cathodic sputtering.

Magneto-resistance effects in films of bismuth; an experimental investigation.—Films of bismuth were deposited on glass by cathodic sputtering. These films showed initially no change of resistance when placed in a magnetic field of 16,000 gauss. It was found that by heating to a temperature near the melting point of bismuth this property could be partially restored. This change in the film as a result of heating seemed to be accompanied by a crystallization of the metal as indicated by photomicrographs. The films had a negative temperature coefficient of resistance.

Part 1. Historical Summary.

The effect of a magnetic field upon the physical properties of metals, and especially upon their electrical conductivity, has attracted the attention of physicists since 1856 when Lord Kelvin[2] discovered that beyond doubt plates of iron and nickel experienced a change in their ability to conduct electricity when they were placed in a magnetic field so that the current traversed them parallel to the lines of force. His work was rather of a qualitative nature, as was also that of Adams[3] (1876) who confirmed Lord Kelvin's results for iron.

With the discovery by Hall[4] (1879) of a new effect of a magnetic field

[1] The first of a series of articles, from the physical laboratory at Cornell University, on the properties of thin metallic films. The writers are pleased to acknowledge assistance from a grant from the Rumford Fund to Prof. F. K. Richtmyer.

[2] W. Thomson, Math. and Phys. Papers, 2, p. 307.

[3] Adams, Phil. Mag. (5), 1, p. 153, 1876.

[4] Hall, Phil. Mag. (5), 9, p. 225, 1880.

upon currents of electricity, a considerable stimulus was given to investigations of this nature. While carrying on experiments in connection with this Hall-effect, Righi[1] (1884) discovered that bismuth possessed this property of an increase of resistance in a magnetic field to an extraordinary degree compared with the results which had hitherto been obtained for iron. He noted that this increase of resistance seemed proportional to the intensity of the field, save for weaker fields, where the change of resistance increased more rapidly than the field, and that the effect was less at higher than at lower temperatures. He also found that a greater effect was produced by a transverse than by a longitudinal field in the case of this metal. His results were confirmed by the subsequent work of Hurion,[2] Leduc,[3] and v. Ettinghausen,[4] all of whom were working on the Hall-effect in bismuth. These investigations showed that the resistance of bismuth increased from twelve to sixteen per cent. in fairly strong fields. Goldhammer[5] (1887) studied the influence of magnetism on the conductivity of a number of metals in an attempt to show some relation between the increase of resistance and the Hall-effect. In the same year Lenard and Howard[6] manufactured a bismuth spiral by winding fine bismuth wire into the form of a flat, non-inductive, bifilar spiral and found that its resistance doubled in a field of 17,000 C.G.S. units. They recommended the use of similar spirals for the measurement of the intensity of magnetic fields and gave curves showing the relation between field strength and percentage increase of resistance for their own work and also for the measurements of previous investigators.

Lenard[7] (1890) discovered that the resistance of bismuth to alternating currents was less than for direct currents for fields under 6,000 gauss and that above this field strength the reverse was true.

Leduc[8] (1891) worked with bismuth between 0° and 160° in fields up to nine kilogauss and also recommended the use of spirals of bismuth for measuring magnetic fields. He proved that the purer the metal the greater the change of resistance in the magnetic field. In the same year Drude and Nernst[9] extended this temperature range to 290°, some twenty degrees above the melting point, and found that the effect was

[1] Righi, Jour. de Phys. (2), 3, p. 355, 1884.
[2] Hurion, Comptes Rendus, 98, p. 1257.
[3] Leduc, Comptes Rendus, 98, p. 673; 102, p. 358, 1886.
[4] v. Ettinghausen and Nernst, Wien. Ber., 94, II., p. 560, 1886.
[5] Goldhammer, Wied. Ann., 31, p. 360, 1887.
[6] Lenard and Howard, Electrotechn. Zeitschr., 9 p. 340, 1888.
[7] Lenard, Wied. Ann. 39, p. 619, 1890.
[8] Leduc, Comptes Rendus, 110, p. 130; 111, p. 737, 1891.
[9] Drude and Nernst, Gött. Nachrichten, No. 14, p. 471, 1890.

still undeniably present in the molten metal, although very much slighter. Henderson[1] (1894) also studied the effect of temperature between 18° and 80° in fields up to thirty-six kilogauss using a small spiral and a du Bois ring electromagnet for the purpose. He proposed the following equation showing the relation between R, the resistance of the metal in the field, R_0, its resistance out of the field at 0°, as a function of the field strength, H, and temperature, θ:

$$R/R_0 = f(H, \theta).$$

He also emphasized the necessity, for even approximate measurements by means of bismuth spirals, of taking the temperature accurately into account. For this purpose he proposed the winding of spirals of copper or platinum side by side with the bismuth spiral for measuring the temperature.

v. Aubel[2] (1889–1897) also investigated the influence of temperature in weak fields and compared preparations of bismuth of different origins. As a result of his investigations he was led to regard the temperature-resistance curve for the metal outside the field as the best criterion of purity, surpassing even the spectroscopic test. The fact that traces of certain metals, as lead and tin, had a great influence on this curve had also been demonstrated by Righi.[3] By Dewar and Fleming[4] (1895–1897) the temperature range was extended down to −190° and at this temperature they found the effect very large, dr/r being equal to 150 in a Hartmann & Braun bismuth spiral in a field of twenty-two kilogauss. Du Bois and Wills[5] (1899) working at the same temperature in stronger fields found this ratio to have a value as high as 230.

During this time considerable attention had been given to the crystalline structure of the bismuth and a number of investigators worked with plates cut from large crystals in a definite manner with respect to the principal crystallographic axis. Experiments of this nature were carried on by Lebret[6] and nominally by v. Everdingen at the Leiden Laboratory. In these experiments the relation between the increase of resistance and the Hall-effect was investigated. Yamaguchi[7] (1900) working also at −190° found a "close relation between the increase of resistance and the thermomagnetic transversal effect." Lownds[8]

[1] Henderson, Phil. Mag. (5), 38, p. 488.
[2] v. Aubel, Ann. de Chim. et de Phys. (7), 18, p. 433, 1889.
[3] Righi, Jour. de Phys. (2), 3, p. 355, 1884.
[4] Dewar and Fleming, Phil. Mag. (5), 40, p. 303; Proc. Roy. Soc., 60, p. 72, 425, 1897.
[5] Du Bois and Wills, Verh. d. Deut. Phys. Gesell., 1, p. 169, 1899.
[6] v. Everdingen, Arch. Neerl. (2), 4, p. 371.
[7] Yamaguchi, Ann. d. Phys., 1, p. 214, 1900.
[8] Lownds, Ann. d. Phys., 6, p. 146, 1901; 9, p. 677, 1902.

(1902) working with an oriented bismuth plate cut from a large bismuth crystal concluded that this relation, if it indeed existed, was by no means a simple one. A chemical analysis was not made and this is particularly unfortunate in view of the fact that some of his data seems to indicate that the plate with which he worked may not have been of very great purity.

In the same year Patterson,[1] at the suggestion of J. J. Thomson, undertook some accurate measurements of this effect in various metals in order to obtain the mean free path, the mean velocity, and the pressure of electrons, in accordance with the theory of metallic conduction developed by Thomson[2] in a paper presented before the International Congress of Physics at Paris (1900). Prof. Thomson showed that

$$dr/r = 1/3H^2u_0^2$$

where dr is the increase of resistance in a field of strength H, r the resistance outside the field, and u_0 the average velocity of drift of an electron in an electrostatic field equal to unity. From his measurements Patterson deduced values for the mean velocity, the mean free path, the pressure in atmospheres, the number in unit volume, the time between collisions, and the rate of dissociation for the electrons in the metals studied.

Laws[3] (1910), likewise working from the point of view of the electron theory, carried on measurements at the temperature of steam and of liquid air in fields up to thirteen kilogauss for cadmium, zinc, and graphite. He found that dr/r is practically proportional to H^2 at all temperatures, as it should be according to Thomson's theory, and that its value increases considerably as the temperature falls. It is to be noted that for these substances dr/r is small even for strong fields.

The above paragraphs rather hastily summarize the most important work which has been done with bismuth in bulk in connection with the phenomenon of an increase of resistance in a magnetic field. Turning to the experiments which have been performed with bismuth films obtained by cathodic sputtering we find that they are very few, and the results of different experimenters seem to disagree widely. Patterson[4] (1901) reports that he found the change of resistance in bismuth films obtained by this process to decrease with the thickness. He came to this conclusion from measurements which he made on three sets of films of different thicknesses from 10^{-5} cm. to 4×10^{-6} cm., the thickness being

[1] Patterson, Phil. Mag. (6), 3, p. 643, 1902.

[2] J. J. Thomson, Rapports presėntės au Congrès International de Physique, 1900.

[3] Laws, Phil. Mag. (6), 19, p. 685, 1910.

[4] Patterson, Proc. Camb. Phil. Soc., 11, p. 118.

measured by Wiener's interference method. For the thicker of these films he obtained an increase of 0.27 per cent. in a field of 26.2 kilogauss and for the thinner in the same field an increase of only 0.01 per cent. In a later paper,[1] in which he gives a detailed account of his work, he reports having difficulty measuring the specific resistance of the thicker films because of the fact that they soon lost their metallic luster and became dull and powdery in appearance. For the same reason he found it impossible to make films of this metal thicker than 10^{-5} cm. His films all gradually increased in resistance with time, although films of other metals decreased in resistance on standing. He tried to effect a rapid aging and to decrease the resistance of his bismuth films by heating, as Longden and others had done with platinum films, but in every case on heating in air the resistance increased greatly. He tried baths of different oils without success. However, by heating a film in an evacuated glass tube with leads sealed through the glass he found that he could hasten the increase of resistance so that after standing for a considerable period there was very little change of resistance. During these heatings he made measurements of resistance which indicated a negative temperature coefficient for this film. This was measured accurately and found to be -0.002.

Houllevigue[2] (1902) reports that a bismuth film prepared by this process and placed normally in a field of 2.25 kilogauss showed no change of resistance whatever from its value of 26.9 ohms. Leduc[3] had previously observed that bismuth is most sensitive to magnetism when its crystalline structure is most marked. It seems that bismuth obtained by cathodic sputtering ought to be completely amorphous, Houllevigue concludes, and he made some attempts to give it a crystalline structure by heating to 350°, which failed since the metal was altered by the process.

In a brief note in connection with a piece of work on bismuth in bulk, Jewett[4] (1905) makes the following observation: "In thin plates of non-crystalline bismuth, formed by means of the cathode stream, no evidence of any magnetic effect on the resistance was observable even at field strengths as high as 27,000."

In order to investigate this effect in bismuth films more fully, work was begun in the laboratory at Cornell University in the summer of 1917 by L. J. Sivian. He verified Houllevigue's results and found a negative

[1] Patterson, Phil. Mag. (6), 4, p. 652, 1902.
[2] Houllevigue, Comptes Rendus, 135, p. 626.
[3] Leduc, Jour. de Phys., II., 3, p. 133, 1884.
[4] Jewett, Phys. Rev., 16, p. 51, 1903.

temperature coefficient for his films. The war prevented him from completing his work, but in the following year one of us (J. A. B.) undertook the continuation of it, a description of which makes up the following part of this paper.

Part 2. Experimental Investigation.

The films were prepared by sputtering upon microscope slides from a cathode of cast bismuth in a gallon bell-jar sealed to a steel bed-plate by means of mercury. The rate of deposition was such that twenty minutes were required for a film which was practically opaque. The films were usually so thick that they transmitted only a small amount of light. The contact for the resistance measurements was made by sputtering a thicker film over the edges, copper plating these, winding a few turns of copper wire over the plating, and then plating again. The resistance was measured by means of a Wheatstone bridge with which a change of resistance of .02 per cent. could be detected. The maximum field strength used was 15,000 gauss produced by a large electromagnet from the Société Genevoise.

As thus produced the films showed initially no change in resistance even in a field of 15,000 gauss, in which bismuth spirals double their

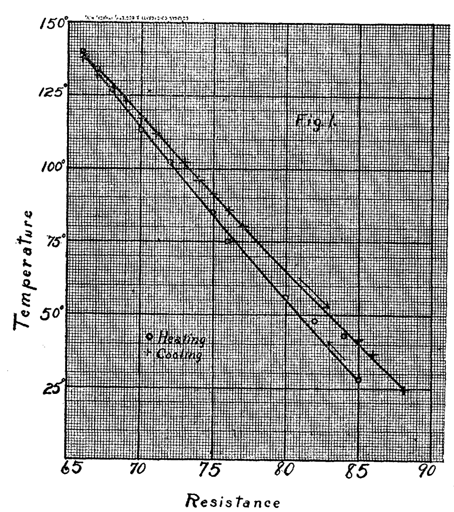

Fig. 1.

Showing graphically the results given in the above table.

resistance. The films were then placed in a beaker of oil, which was heated by means of a Bunsen burner to a definite temperature, allowed to cool, reheated and recooled several times. Resistance measurements were made during this treatment. The film was then placed between the poles of the electromagnet and the resistance measurements made at various field strengths. This whole process was then repeated, heating to a higher maximum temperature. Photomicrographs were taken before and after heating some of the films and showed crystal growth due to heating.

Table I. gives a typical temperature-resistance run.

Table I.

Temperature, °C. = T:	28	43	48	56	75	85	102	113	127	133
Resistance, Ohms = R:	85.0	84.0	82.0	80.0	76.0	75.0	72.0	70.0	68.0	67.0
T:	140	138	132	127	123	117.5	112	107.2	102	
R:	66.0	66.0	67.0	68.0	69.0	70.0	71.0	72.0	73.0	
T:	96.0	91	85.5	80.5	43	41	36.6	32.5	31.3	24.5
R:	74.0	75.0	76.0	77.0	84.5	85.0	86.0	86.5	86.75	88.5

The results given in the above table are represented graphically in Fig. 1.

Table II. shows how the resistance of a film, which had been raised to a maximum temperature of 256° C., changed with the field strength.

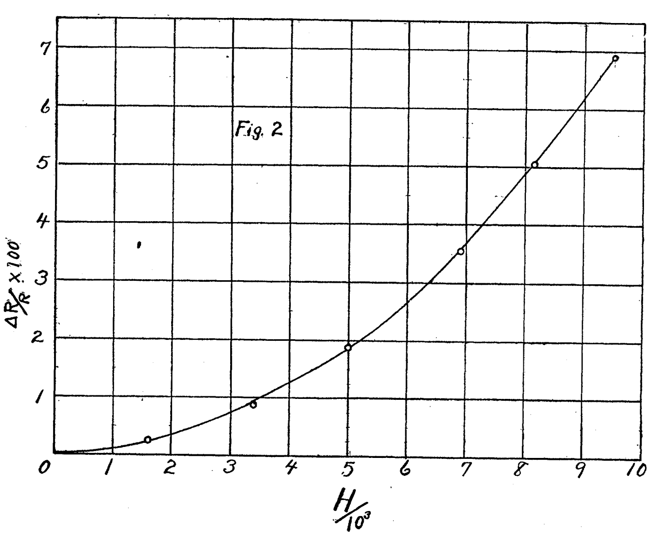

Fig. 2.

Showing the effect of heating upon the increase of resistance in the magnetic field.

TABLE II.

Field in Gauss $= H$:	0	1,740	3,400	5,000	7,550	8,150
Resistance of film $= R$:	79.7	79.9	80.4	81.2	83.2	83.7
Per cent. change of resistance $\frac{\Delta R}{R} \times 100$:	.00	.25	.88	1.88	4.4	5.02
H:	9,500	8,150	6,900	3,400	0	
R:	85.2	83.7	82.6	80.4	79.7	
$\frac{\Delta R}{R} \times 100$:	6.90	5.02	3.64	.88	0	

The results given in the above table are shown graphically below in Fig. 2.

SUMMARY.

The following conclusions are the result of the investigation:

1. Bismuth films obtained by cathode sputtering have a negative temperature coefficient of about .001 to .003 ohms per ohm per ° C. This coefficient decreases with temperature.

2. At about 240° C. the resistance begins to decrease rapidly until the film melts at about 260° C.

3. Heating and cooling the film cyclically crystallizes the metal. This was indicated by photomicrographs taken before and after heating.

4. Heating the films to temperatures well below the melting point of bismuth partially restores the property of the change of resistance in a magnetic field. The percentage change in resistance in a given field increases rapidly with the maximum temperature to which the film has been heated. Temperatures just below the melting point are particularly effective.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY.