HALL EFFECT AND SPECIFIC RESISTANCE OF SILVER FILMS.

BY G. R. WAIT.

SYNOPSIS.

Hall Effect and Specific Resistance of Silver Films, 200 to 20 μμ. Thick.—In agreement with previous results, the specific resistance increased more and more rapidly with decreasing thickness, becoming infinite for about 20 μμ. On the other hand the Hall coefficient was found to be the same in the films as in the bulk metal. The thicknesses were computed from the weight of silver in each film, assuming the density that of the bulk metal. The films were obtained by chemical deposition.

Theory of Electrical Conduction in Thin Films.—After discussing various proposed theories in the light of the above results, it is concluded that these and other facts are in harmony with the simple conception that the film consists of granules, each having the properties of the bulk metal, and that conduction occurs only along strings of granules in contact.

Brashear Method of Depositing Silver Films.—Exceptionally hard films whose resistance, instead of decreasing, increased slightly with time, were obtained by using about four times the amount of sodium hydroxide specified.

HISTORICAL.

Miss Stone[1] in 1898 found that the specific resistance of thin silver films was greater than that of bulk metal, and that it increased with decreasing thickness of the film down to a thickness between 50 μμ and 60 μμ, where it almost suddenly became very great. Other workers in the field of films, since that time, have obtained similar results. Among the contributions to this field may be mentioned the work of Vincent,[2] Longden,[3] Patterson,[4] Reide,[5] Swann,[6] Pogany[7], Weber and Oosterhuis,[8] and King.[9]

Moreau[10] made an investigation of the Hall effect in silver and nickel films. He found that the coefficient of the Hall effect in the films was not constant for various thicknesses, being much greater than the value in bulk metal for the smaller thicknesses and decreasing to smaller values than that in bulk metal at a thickness greater than about 60 μμ.

[1] PHYS. REV., (1), vi, p. 1, 1898.
[2] Ann. d. Chim. et Phys., 7, p. 421, 1900.
[3] PHYS. REV., (1), xi, p. 40 and p. 84, 1900.
[4] Phil. Mag., 4, p. 652, 1902.
[5] Ann. d. Physik, 6, p. 881, 1914.
[6] Phil. Mag., 28, p. 467, 1914.
[7] Phys. Zeitsch., 15, p. 563, 1914.
[8] K. Akad. Amsterd. Proc., 19, p. 597, 1917.
[9] PHYS. REV., (2), x, p. 291, 1917.
[10] Journ. de Physique, 10, p. 478, 1901.

EXPERIMENTAL METHODS.

Deposition of Films.—The resistance of films, obtained by the Brashear[1] method of chemical deposition, decreased with time, a phenomenon experienced by other investigators. By increasing to about four times the amount of sodium hydroxide specified in this method, exceptionally hard films were obtained, their resistances increasing slightly with time, occasioned probably by a combination of the film with gases of the air. Cleanliness of the glass surface and purity of chemicals were extremely important in the production of satisfactory films.

Determination of Thickness.—The thickness of a film was determined from the weight of the silver composing it and, as a check, from the weight of silver iodide after the film was transformed. The densities of silver and silver iodide were assumed to be those of bulk silver and ordinary silver iodide respectively. Determinations of thickness by the two methods of weighing were used only after they had been proved superior to the Newton ring method by a rather extensive investigation.

Measurement of Resistance.—The resistance of the films was measured as soon as possible after they were dry, or usually a few minutes after being removed from the solution. In order to determine the contact resistance between the electrode and the film, four electrodes were placed upon the film. Let a, b, c, d represent the four electrodes, c and b being placed very near to each other at one end of the film and a and d near each other at the opposite end; then using the measurements of resistances between a and b, a and c, a and d, b and c, b and d, c and d, six equations were formed from which two independent values of the film's resistance were found.

Measurement of the Hall Effect.—The films were cut into the shape shown in Fig. 1, the electrodes for the primary current being connected at A and B, while those for the measurement of the Hall effect were connected at C and D. The latter electrodes could be shifted accurately by removing some of the film at one or both of the narrow necks. The equipotential points could thus be easily found and permanently retained.

The film under investigation was placed in a holder made of insulating fiber (Fig. 2) upon which had been fastened three electrodes and a groove

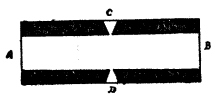

Fig. 1.

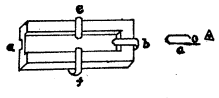

Fig. 2.

for the fourth. The electrodes were made of spring phosphor bronze

[1] Astrophys. Journal I, p. 252, 1898.

and shaped as shown in Fig. 2. In order to secure the best contact between the electrode and the film, the point o of the electrode was fitted into a small dent of a triangular piece of copper whose underside had been made plane. This triangular piece of copper was placed upon the film with a small piece of aluminum foil separating the two. The above holder and design of electrodes were used in the measurements of the resistance as well as the Hall effect.

The experimental arrangement for the measurement of the Hall effect consisted of a double potentiometer and is shown in Fig. 3, A, B, C, and D are resistance boxes, the resistances in B and in C being large in comparison with the resistances in A and in D, respectively. The drop across the box D was so adjusted that it was just equal to the Hall effect. G_1 is a Leeds and Northrup galvanometer having a sensitiveness of about 10^{-8} volts per mm. scale deflection. B_2 is a storage cell furnishing the primary current for F. A_1 is an ammeter for the measurement of this current, which was varied (by altering R) from approximately 0.0015 to 0.03 ampere, the thicker films permitting the larger currents.

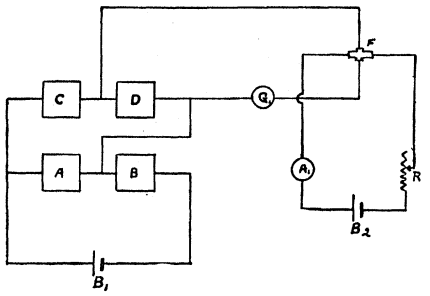

Fig. 3.

Since the Hall effect was measured by taking the drop in potential across D necessary to prevent a deflection of the galvanometer G_1, then $E = \frac{A V \frac{1}{2} (D_1 - D_2)}{(A + B)(C + D)}$, where E is the value of the Hall effect in c.g.s. units, D_1 and D_2 are the values of D necessary to prevent a deflection of G_1 with the magnetic field in opposite directions, A, B and C are the resistances shown and V s the potential difference of the cell B_1, measured in c.g.s. units.

The magnetic field was furnished by a large electro-magnet, the faces of whose pole pieces were four centimeters in diameter and one centimeter apart. The field strength was measured by means of a bismuth spiral calibrated for this purpose. The measurement of the field for different currents through the magnet over a duration of five years using

two different spirals gave differences of only 0.8 per cent. The fields used were from 5,000 to 12,000 lines per cm.[2]

TABLE I.

Film	ϵ.	*E/HI.*	R	Residuals.	Film	ϵ.	*E/HI.*	R	Residuals.
42	21	320	805	30	9	40	216	20.7	19
34	21	...	3 x 10″	..	33	43	164	3.5	2
28	22	...	3 x 10″	..	37	46	188	8.3	..
36	23	321	200	..	27	47	118	3.9	6
41	28	325	9.7	3	31	50	138	3.8	4
33	29	314	10.8	9	7	51	143	12	11
35	31	284	5.8	17	4	51	170	8.8	7
23	33	295	8.5	6	30	54	185	5	11
32	36	232	8.6	2	40	89	108	2.8	2
18	38	182	10	13	29	109	74	3.7	5
26	38	202	9.4	18	10	182	47	2.6	7
43	40	212	9.3	8					

EXPERIMENTAL RESULTS.

In Table I. are given the results of the present investigation. In column one is given the film number; in column two, its thickness in millimicrons, the mean of the thickness obtained upon the basis of the weight of the silver and its weight after it had been transformed into silver iodide. The third column gives E, the Hall e.m.f. divided by the product of the magnetic field H, in e.m.u. and the primary current I in c.g.s.u. In most instances four different strengths of the magnetic field were used, in which case there were four values for E/HI; the one given in column three is the mean of the four. The mean residual for each film is recorded in column five. A particular residual was obtained by taking the differences between the mean E/HI and the E/HI for that particular field and current. Column four contains the resistance in 10^{-6} ohms per cm.[3] of each film. For two films the Hall effect is not given, this being due to the fact that it was not possible to obtain measurements of the effect for films having such high resistances. Although considerable data have been obtained by various investigators upon the variation of specific resistance of films with their thickness, and also som data upon coefficients of the Hall effect, the author, is not aware that the two phenomena have ever been studied for the same film. It is important, if results upon the two phenomena be used in conjunction with each other, that they be obtained from the same film. This would be even more important for films that change with time.

Specific Resistance.—In Fig. 4 is plotted ρ, the specific resistance, against

ϵ, the thickness of the films. It will be seen that for films having the greater thickness the ρ is very little greater than its value in bulk silver, and seems to approach asymptotically to that value. The value of ρ gradually increases toward decreasing thickness until about 50 $\mu\mu$ is reached, when it increases much more rapidly. It will be seen that the value of ρ seems to approach ∞ in the neigh- borhood of 20 $\mu\mu$.

Hall Effect.—As is well known, the Hall e.m.f., E, is given by the rela-

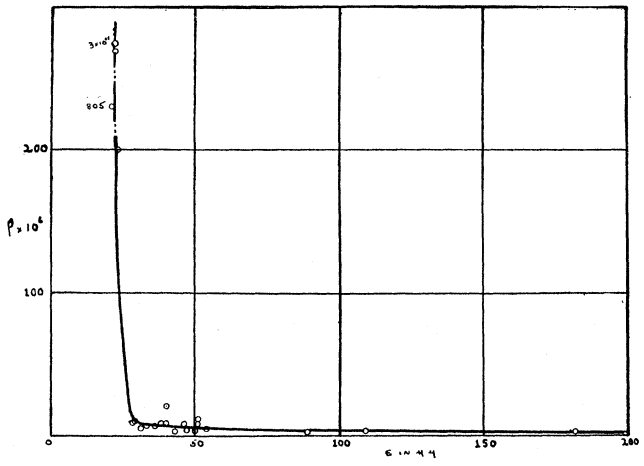

Fig. 4.

tion $E = (HI/\epsilon)\alpha$ wherein α is the Hall coefficient. In numerous tests with silver films herein described, E was found to be proportional to H and I. The values of E/HI for various values of ϵ, given in Table I., are

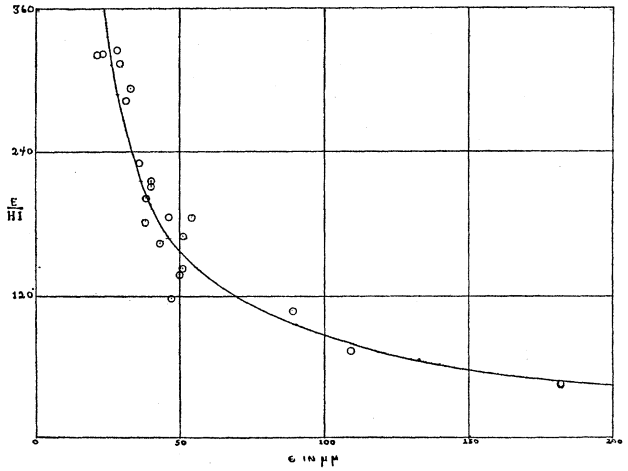

Fig. 5.

plotted in Fig. 5 in which is drawn a hyperbola with $\alpha = 0.00084$, the accepted value of the Hall coefficient in silver. It will be seen that the curve fairly represents their mean. Thus the value of α, the Hall coefficient, in the films is the same as in bulk silver and is constant for all thicknesses investigated greater than 23 $\mu\mu$.

THEORETICAL CONSIDERATIONS.

Assuming that there is a diffusion of negative electrons through the spaces between the atoms, that the electrical properties of the metal arise entirely in the average motion impressed by external circumstances on the swarm of electrons which are otherwise moving about quite freely in the spaces between the atoms, and that the distribution of velocities among them at any instant is precisely that specified by Maxwell's law, the electron theory of the Hall effect leads to the following well-known result for the electric field in the z-direction at right angles to the direction of current density in the y-direction J_y, and to the magnetic field of intensity H in the x-direction:

$$E_z = -\frac{3\pi}{8\,Nec} HJ_y.$$

E_z is the electric field of uniform intensity produced in the z-direction, the current density, J_z, being supposed zero; N is the number of free electrons per unit volume, e the charge on the electron, and c the ratio of units. This result is in accord with experiments in a large number of cases. Without further assumptions it is not possible to apply the result of the theoretical investigation to a thin film wherein the material is supposed to consist of granules not in the intimate contact obtaining in bulk form.

Let us assume that J_y' is constant through the xz cross-section of any granule and that the packing of granules is sufficiently close to warrant the approximate statement that the current through the film cross-section is carried by the granules and not by gaps. Consider the xz cross-section. We are concerned with a gross result rather than what occurs in the individual granule, and consequently we are induced to idealize the location of these granules in order to simplify our own thinking. Let us assume that we have a layer of similar granules of thickness Δx. All of them may not be carrying current and in those that do, the current densities are not the same. The total difference of potential across this film will be $\Sigma E_z' \cdot \Delta z$ where Δz is the approximate width of the granules, and $\Delta x.\Delta z$ is the area of the granule in cross-section. But,

$$\Sigma E_z' \Delta z = -\frac{3\pi}{8\,Nec} H\Sigma J_y' \Delta z = -\frac{3\pi}{8\,Nec} H\Sigma J_y' \frac{\Delta x \cdot \Delta z}{\Delta x}$$

or

$$E = -\frac{3\pi}{8\,Nec} HJ,$$

where J is the current per unit thickness.

In the expression for E_z, the value of current density J_y was introduced by assuming that in the granule $J_y = \sigma E_y$, where σ is the conductivity determined by the same assumptions as to electrons, and E_z is the electric field. In applying this theory to the granule, we have thus assumed consistently that the theory applies to the granules the same as to the bulk metal. Our conclusion is that the coefficient should be constant irrespective of the specific resistance or thickness of the film, and that it should be the same as in bulk metal. Both of these points are verified by experiment as already shown. The assumptions seem therefore to be in agreement with the experimental facts, and the author will assume the correctness of this simple theory of thin films, namely that they are composed of granules having the property of bulk metal and of conducting gaps which give resistance only.

J. J. Thomson[1] explained the variation of specific resistance of films with thickness by assuming that the mean free path of the conducting electron was less in the film than in the bulk metal. The curve drawn based upon such an assumption, however, is not so steep as the experimental curve. Patterson suggests that this may be due to a gradation in the density of electrons from the inner part of the film toward the outer boundaries. Swann[2] assumed that the mean free path of the conducting electron varied with temperature the same in the film as it does in bulk metal. By measuring the specific resistance of platinum films over a wide range of temperature he obtained results which show that Thomson's explanation is not in agreement with experimental facts. The present investigation furnishes direct information regarding Patterson's suggestion pertaining to the change in the number of conducting electrons per unit volume. From Patterson's assumptions alone, the thinner films should show the greater value for the coefficient and its value should approach that in bulk metal as the thickness is increased. Instead of this, however, the Hall coefficient is always constant, having the same value as in bulk metal.

Moreau[3] explained his results for the Hall effect in films by means of Vincent's transition layer theory. The results of the present investigation, however, are not in accord with Moreau's results nor with Vincent's theory. Now Vincent was able to explain the rapid increase in specific

[1] Phil. Mag. (4), p. 675, 1902.

[2] Loc. cit.

[3] Phil. Mag. (4), p. 675, 1902.

resistance upon the assumption that the specific resistance of the film of metal between the transition layers was that of ordinary metal, while the resistance of the layers was constant and quite great. Obviously, the Hall coefficient, which depends upon the number of conducting electrons per cm.^{3} would therefore change at the thicknesses where the increase in specific resistance is so marked. No such change was detected experimentally.

Swann,[1] found the three following interesting facts: (*a*) Thick films underwent an increase in resistance with increase in temperature, (*b*) thin films underwent a decrease in resistance with increase in temperature, and (*c*) films having a thickness between these had an apparent zero temperature coefficient of resistance over most of its range. Now, the change in a film's resistance, when its temperature is increased slightly, will depend at least upon the three following factors: (1) Expansion of the glass, upon which the film is deposited. (2) Expansion of metal composing the groups bringing them into more intimate contact. (3) The regular temperature coefficient of the metal. For very thin films the effect of (2) will be to decrease the resistance, as the temperature is increased; for thicker films this effect may be very small as may be seen from the following considerations. In the case of very thin films it was seen that a very small addition of groups produced a great decrease in the resistance, but that the addition of the same number of groups to a thick film decreased the resistance very much less. Similarly an expansion of groups might be expected to produce a great change of resistance in the case of thin films, and a small change in the case of the thicker ones. The above considerations make possible an explanation of the so-called temperature coefficients, and permits the simple assumption that the addition of groups have the effect of decreasing the number of conducting paths through the film, by combining many that are already present and making them straighter and wider.

The general conclusion is that the experiments herein recorded and all others in thin films are in harmony with the simple theory here proposed, namely that we are dealing with granules which have the same electrical properties as bulk metal and with conducting gaps.

The author wishes to express his appreciation to the Physics Department of the State University of Iowa for valuable assistance received, and especially to Professor G. W. Stewart under whose direction this work was carried on, and whose encouragement and criticisms made the work possible.

PHYSICAL LABORATORY, STATE UNIVERSITY OF IOWA.

[1] Phil. Mag. (4), p. 675, 1902.