GALVOMAGNETIC PROPERTIES

of

EVAPORATED BISMUTH FILMS

by

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in the Department

of

Physics

We accept this thesis as conforming to the standard required from candidates for the degree of MASTER OF APPLIED SCIENCE

Members of the Department of Physics

THE UNIVERSITY OF BRITISH COLUMBIA

September 1951

ABSTRACT

A study has been made of the Hall coefficient and resistivity of evaporated bismuth films. Special attention has been given to the determination of the effects of the conditions of preparation on the resultant properties. A suggestion has been offered to explain the strong dependence of these properties on the temperature of the substrate during deposition.

Critical points have been found in the curves of the resistivity and its magnetic field dependance versus thickness. This critical thickness is thought to be that at which a previously reported abrupt change in crystallite size occurs.

ACKNOWLEDGEMENTS

The research described in this thesis was supported by the Defence Research Board of Canada.

The problem was directed by Doctor A. J. Dekker whose assistance and advice are sincerely appreciated.

W. Peria

September 1951.

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ILLUSTRATIONS

I. INTRODUCTION

During a study of the electrical properties of evaporated bismuth films, (1) in this department, it became apparent that the trapping of current carriers in localized energy levels plays an important role in determining these properties. The research described in this thesis was carried out to investigate the effects of the conditions of preparation of the films, on the amount and type of trapping which occurs. The influence of the film thickness, the rate of evaporation and the temperature of the substrate during evaporation, were studied. The properties measured to this end were the Hall constant, the conductivity and the variation of these quantities with magnetic field.

By a trapped current carrier we signify one situated in an energy level which is provided by some deformation of the lattice potential (crystallite boundaries, surface states) (2,3) such that the carrier does not take part in the conduction process.

The Hall coefficient, R, is defined by the relation

$$R = \frac{E_y}{I_x H_z}$$

where E_y is the transverse electric field developed in a conductor which carries longitudinally a current density I_x , perpendicular to a magnetic field H_z . E_y is perpendicular to both I_x and H_z .

II. EXPERIMENTAL

Preparation of the Samples.

Bismuth was deposited by vacuum evaporation onto glass targets about 7.5 x 2.5 x 0.1 cm. The metal used was Johnson, Matthey & Co., spectroscopically standardized. Table I is the list of impurities as supplied by the company.

Table 1 - List of Impurities.

	Chemical	Spectroscopic
Fe	.0011%	Barely visible
Cu	.0024%	Very faintly visible
Ag	Trace	Very faintly visible
Ca	Not detected	Faintly visible
Mg	Not detected	Faintly visible

The vacuum vessel A (fig. 1) is that employed in the previous work (1) except that the geometry has been somewhat altered to secure more uniform samples. It consists entirely of Vycor, a high-silica glass usable up to 1100°C. The construction is such that effectively the target B receives metal from two sources.

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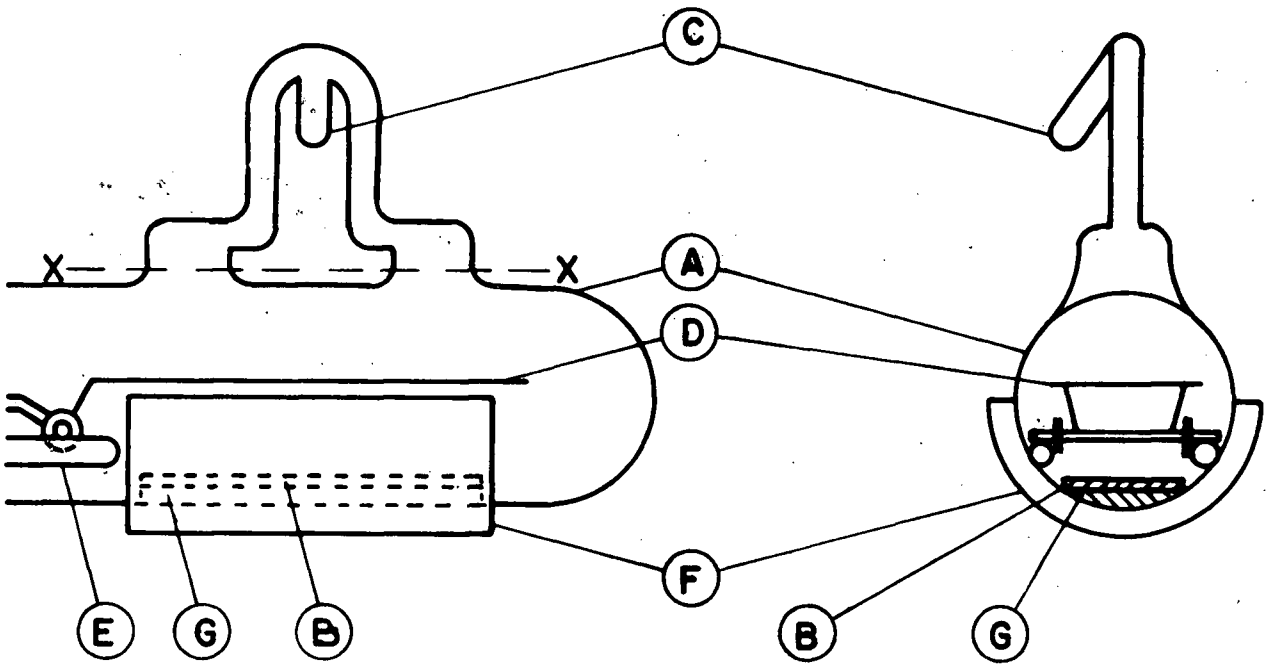

FIG. 1

In use a furnace already at the desired temperature is lowered to the level x-x . When temperature equilibrium has been established in the crucible C, (fig. 1) the externally manipulated glass baffle D is withdrawn along the rails E and condensation on the target begins.

The thickness of the film was determined by weighing the target before and after deposition and assuming the density of bulk bismuth. All samples were weighed immediately after removal from the vacuum system in order to minimize errors due to absorption from the atmosphere. This effect was measured for one sample; an increase in weight of 0.2 mg. in 20 min. was observed for this 6 mg. sample.

The uniformity of the films was investigated by weighing the quantity of metal deposited on several bits of glass, of known area, occupying the space ordinarily occupied by the target proper. The samples were found to have a cross-section which was uniform to 1% but which was not rectangular i.e. the films are thicker in the centre than on the sides by about 10%. This fact does not alter the value of any of the calculated constants since they involve only the current density. However, the value of thickness to which they apply must be taken as the average thickness of the film.

The target may be cooled to some extent by placing refrigerant in the double-walled brass container F. The joint between this container and the Vycor vessel is made leak-proof with paper gaskets previously soaked in water.

The cooling process was made slightly more efficient by clamping the target to a brass plate G (fig. 1) whose under surface conformed to the inner surface of the vacuum vessel.

The temperature of the target as a function of time after the furnace was placed on was measured by simulating the conditions of an evaporation, except that (i) the crucible was empty (ii) the "target" was a bismuth film of known resistance-temperature relation. A rough measure of the surface temperature of the target was then obtained by measuring the film resistance.

Measuring Apparatus.

The magnetic field was produced by a water-cooled electromagnet with 4-inch diameter pole faces and an adjustable gap width. A maximum field of 10 kilogauss could be obtained with a 1-inch gap and was uniform within 0.5 percent over the volume between the pole faces.

The field was measured by means of a search coil

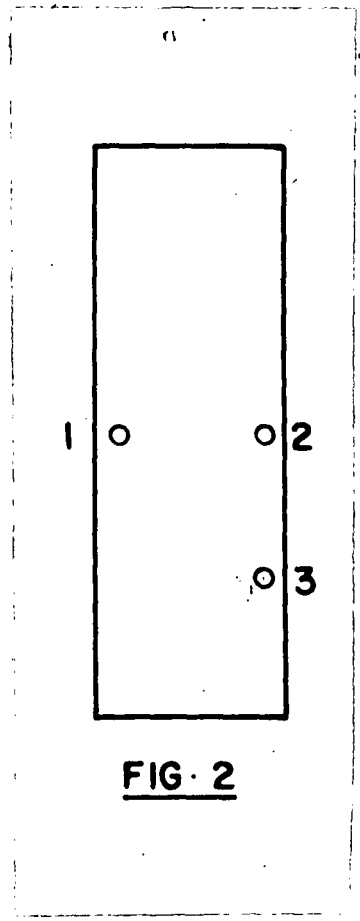

FIG. 2

To face page 5.

and fluxmeter, calibrated in the accurately known fields of the nuclear magnetic resonance spectrometer in this department. The search coil was mounted on a spring-loaded spindle so that its plane was parallel to the pole faces when in its equilibrium position. To measure the field, the spindle was rotated through 180°, the fluxmeter adjusted to zero and the spindle released.

For the one sample measured at dry ice temperatures, a search coil N (fig. 5) was fixed within the vacuum chamber and the field measured by switching the magnet current off or on.

The small field remaining for zero magnet current was cancelled by adjusting a small current in the reverse direction until a compass needle between the pole faces just changes orientation.

For the meaasurements at room temperature the sample was clamped to an insulating board, as in the previous work, between strips of tinfoil which also served as current electrodes. The insulating sheet was supported vertically so that all measurements were made with the magnetic field normal to the plane of the sample. Three probes were used, placed on the sample as shown in fig. 2. Probes 1 and 2 served to measure the Hall voltage, probes 2 and 3 the resistance.

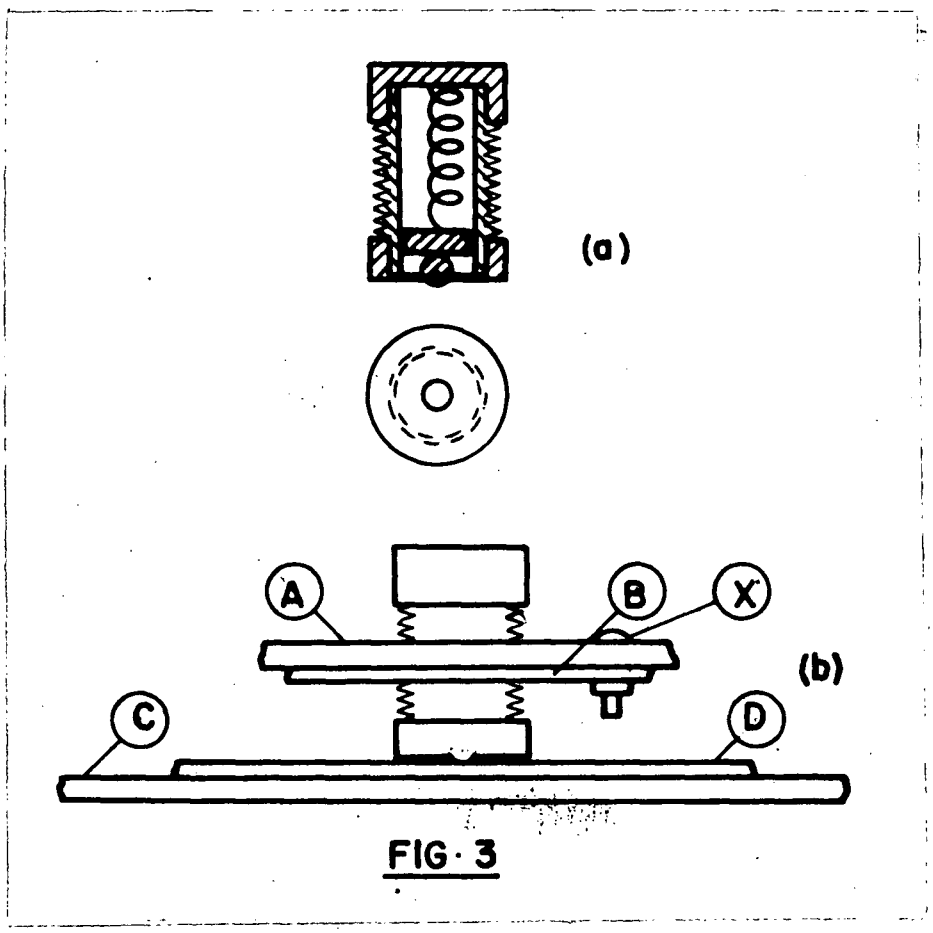

FIG. 3

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The probes consisted of 1/8 inch bronze bearings mounted in a brass assembly (fig. 3a). These were threaded into a bakelite sheet A, (fig. 3b) pivoting about point X on an aluminium sheet B which was firmly bolted to the same insulating sheet C as was the sample D.

Between probes 1 and 2, there appears, as well as the Hall voltage, the IR drop between them if they are not situated on the same equipotential. This could be made small relative to the Hall voltage by rotating the whole contact assembly about point X. Before making this adjustment the probes were withdrawn so that the sample was not scratched. To replace the probes, a direct current was passed through the sample and each probe in turn was screwed down until contact was indicated by the deflection of a galvanometer. In an average case the IR drop could be made 10% or less of the Hall voltage without difficulty. The damage sustained by the sample during this adjustment consisted of two or three small holes (about 0.1 mm.) in the region of probes 1 and 2 and one at probe 3.

The fundamental difference between this type of probe and those previously employed, is that the two operations of fastening down the probe assembly and making contact between probe and film, are distinct.

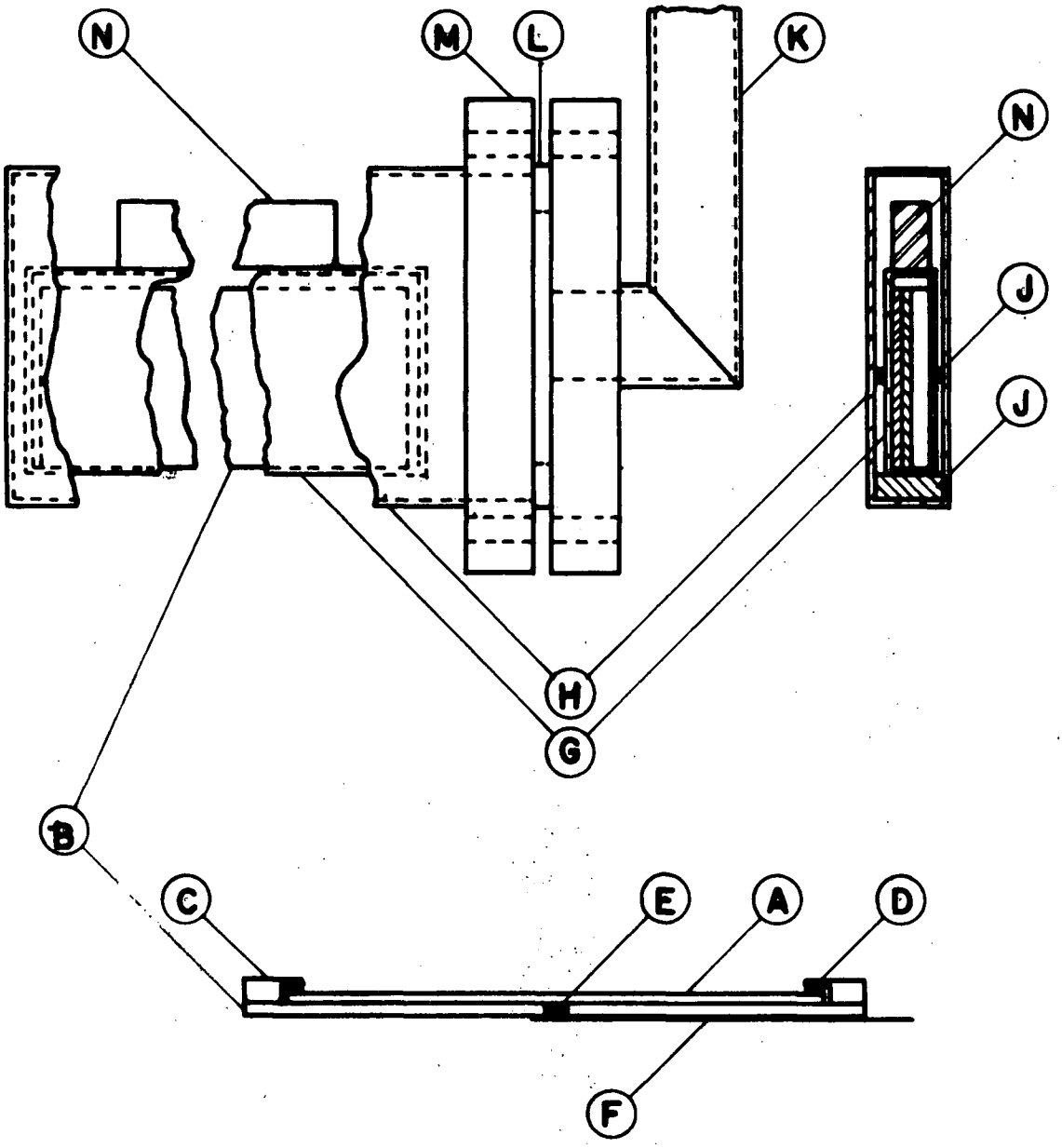

FIG. 5

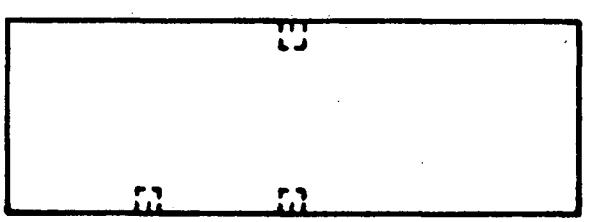

FIG. 6

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The sample which was measured at low temperatures (A, fig. 5) was clamped to a lucite strip B by lucite blocks C and strips of tinfoil D which served as current electrodes. The previously described probes are too bulky for use in this situation and were replaced by silver paint (Dupont #4817) electrodes which terminated, on the under side of the sample, in a wide patch (fig. 6). When the sample, was in position these three patches each made contact with a drop of mercury E, contained in a 1/8 inch hole drilled in a corresponding position in the lucite strip B (fig. 5). These holes were closed on the other side by strips of copper foil F cemented to the lucite strip and running longitudinally past the end of it, where connections were made to copper wires. Current leads were brought out from the tinfoil electrodes in a similar fashion.

Temperatures were measured by means of two copper-constantan thermocouples cemented in grooves between the specimen and strip B. A third thermocouple between B and the copper wall G was for control purposes.

Chamber G was wound with a copper heating coil to enable readings to be taken above the temperature of the brass wall H. Heat exchange between containers

G and H was made small by using lucite spacers J and by evacuating the outer container through pipe K. The demountable vacuum joint was sealed with a lead gasket L between flanges M.

The whole apparatus was set in a CO_2-alcohol mixture in a Styrofoam container. Styrofoam (Dow) is an insulating material made by "foaming" liquid polystyrene and was easily formed to the shape needed to fit between the pole faces of the magnet.

Measuring Apparatus.

The AC method and equipment previously employed (1) were used for the measurement of Hall voltages. In all cases the voltage between probes 1 and 2 for zero field was corrected to allow for its increase in the magnetic field, before being added algebraically to the voltage with field. The sign of the Hall coefficient was determined for each sample by using DC in the sample and measuring the voltage between probes 1 and 2 with a potentiometer.

The resistivity was determined using a DC method. Current was obtained from a regulated 300 volt supply through a high resistance, so that the sample current is constant irrespective of applied magnetic field. The voltage between probes 2 and 3 was measured with a Rubicon

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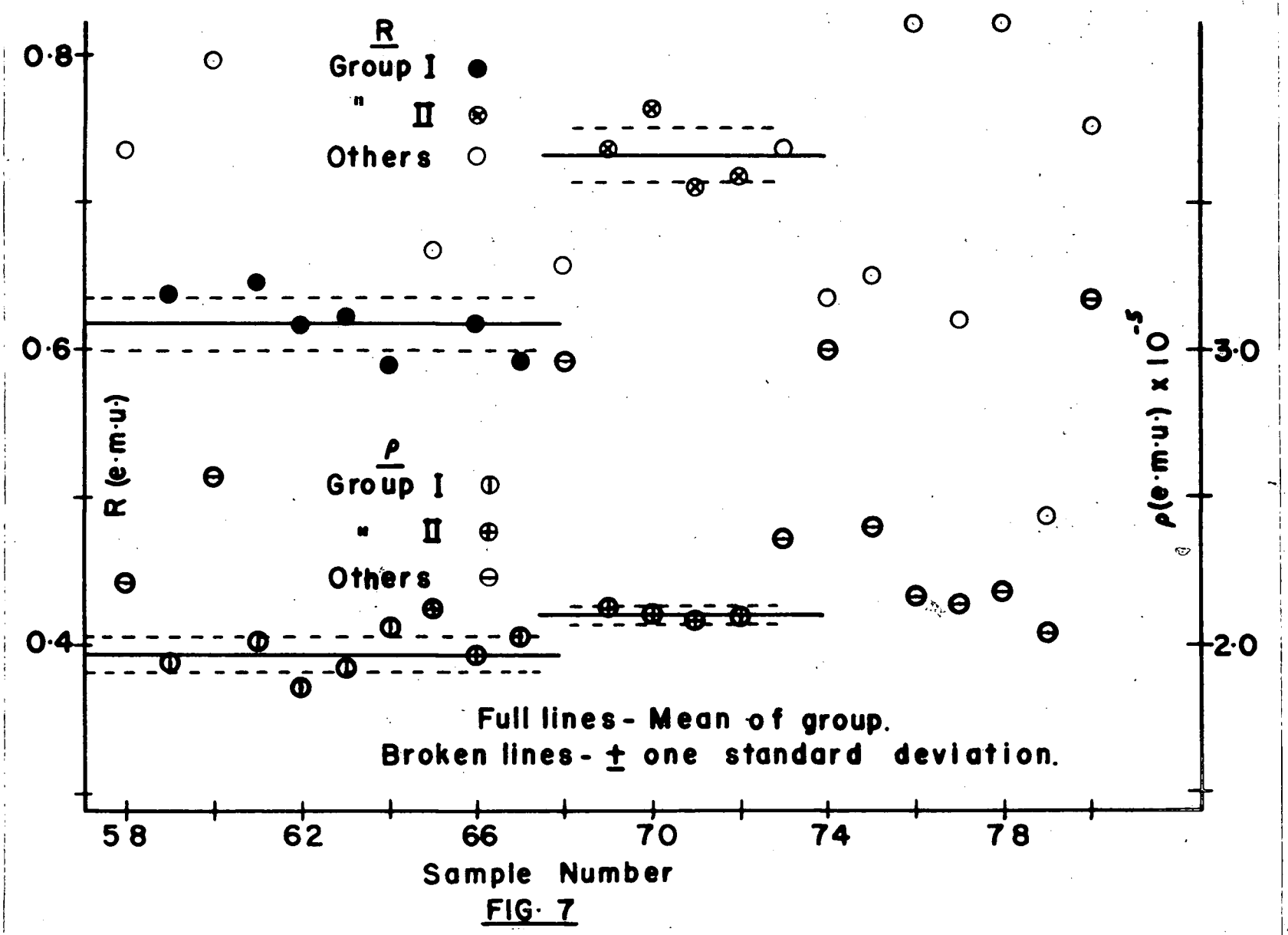


FIG. 7

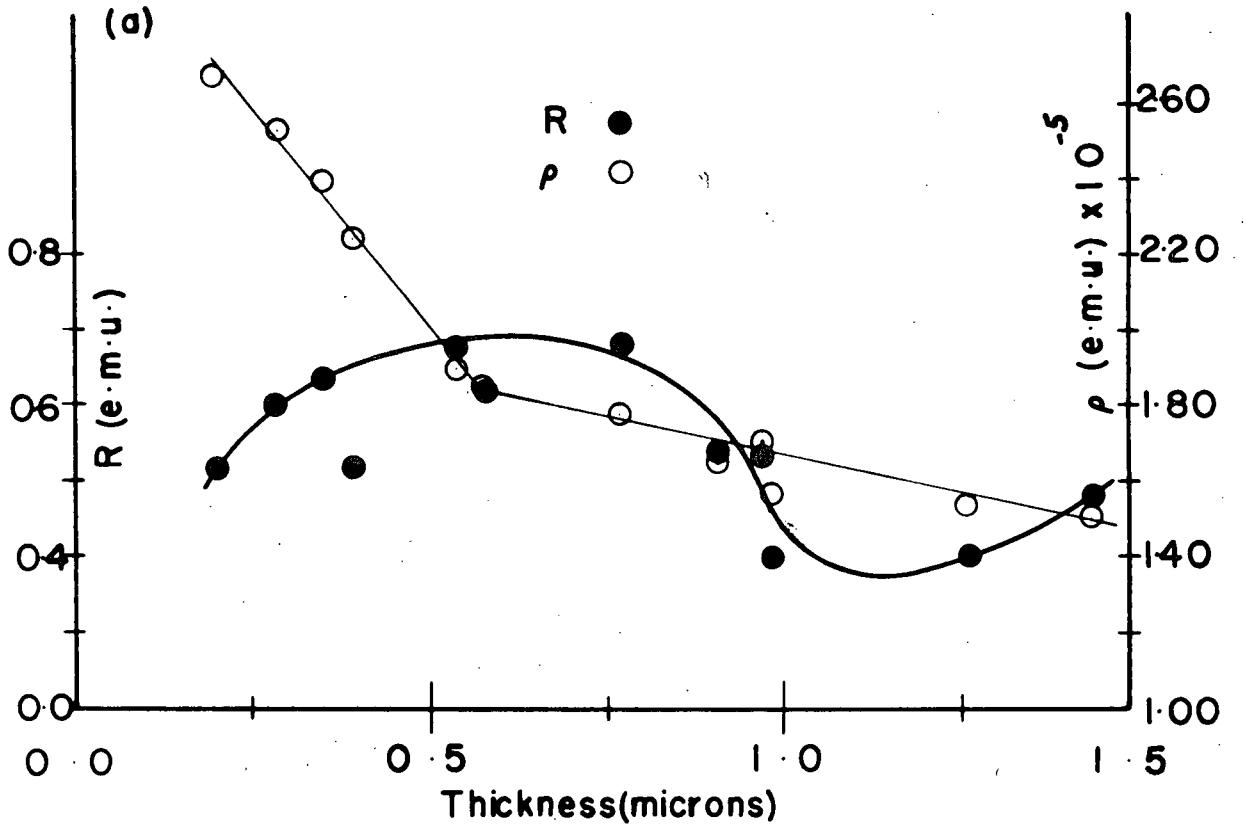
portable potentiometer.

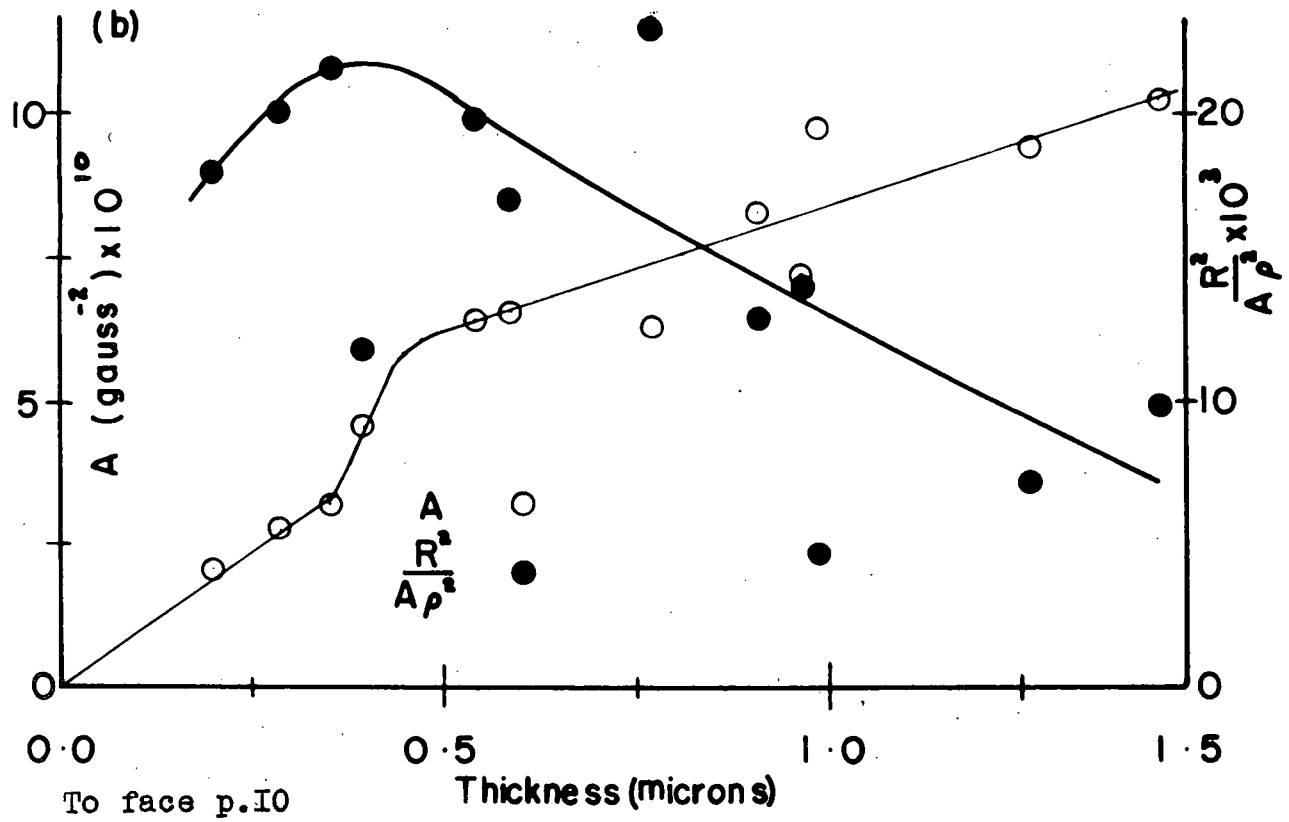
III. RESULTS

A. Reproducibility.

In order to test the reproducibility of the results, a series of samples (nos. 58-80) were made from a single melt under as nearly similar conditions as possible. That is to say the target was never cooled, the furnace was always preheated to the same temperature and the baffle always withdrawn for the same length of time. Fig. 7 is a chart of the results obtained.

Note that with certain exceptions the samples up to #72 may be divided roughly into two groups with respect to the Hall coefficient and the resistivity. In every case the values of R and ρ falling outside these two groups belong either to (i) the first sample of the melt or (ii) the first sample evaporated after leaving the melt in vacuum for one or more days. In addition each of these exceptions is thinner than groups I and II although the conditions of preparation were the same. The high values of ρ indicated for these films (fig. 7) must be ascribed to this latter cause, but in view of the results of the following section their high Hall coefficients cannot be so explained. For nos. 73-80 the results are scattered and all are thinner than would be expected on comparison with groups I and II.





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FIG·8

In subsequent experiments a quantity of bismuth corresponding to 0.5μ on the target was always evaporated with the baffle covering the target, before any samples were prepared. In addition, evaporation was never carried beyond a point corresponding to the end of group I. (i.e. less than one half of each melt was used).

B. Variation of the Properties with Thickness.

A series of samples was prepared all under identical conditions except that the bismuth was heated to a different temperature for each of them. Films from 0.2 to 1.4μ thick were obtained by varying this temperature from 800°C to 880°C. The rates of evaporation ranged from 1.7 to 9.5 ug/cm^2-sec. The results of this experiment are shown in fig. 8 and Table II.

The fractional change of resistivity appears to depend on the magnetic field according to an expression of the form

$$\frac{\Delta\rho}{\rho} = AH^2$$

where A is a constant. The values of A quoted are the best ones in the sense of least squares.

Table II - Variation of the Properties with Thickness (at 200C).

No.	t(μ)	R_6	$\rho \times 10^{-5}$	$A \times 10^{10}$	$R^2/A\rho^2 \times 10^3$
113	0.200	+0.519	2.69	2.06	18.0
111	0.288	0.602	2.55	2.76	20.2
110	0.354	0.637	2.40	3.24	21.7
112	0.396	0.522	2.25	4.56	11.8
108	0.541	0.680	1.90	6.43	19.9
109	0.584	0.621	1.86	6.58	17.0
106	0.771	0.684	1.78	6.36	23.1
107	0.908	0.540	1.65	8.30	12.9
115	0.966	0.534	1.71	7.20	14.0
114	0.985	0.399	1.57	9.80	6.6
104	1.260	0.403	1.54	9.48	7.2
105	1.431	0.483	1.51	10.30	9.9

t = thickness of sample in microns
R_6 = Hall coefficient (e.m.u.) in a field of 6 kilogauss
ρ = resistivity in electromagnetic units.

A series of samples of varying thickness was also prepared by heating the melt to the same temperature in each case but withdrawing the baffle for various lengths of time. Quite a different variation of the properties was obtained for this series but the results are not considered significant in view of the fact that the temperature of the target would be higher for thicker films. The temperature of the target during deposition is a vital factor in determining the properties, as is shown in part C.

C. Cooling the Target.

Two samples were prepared under the same conditions as those of part A except that the targets were cooled by placing a CO_2-alcohol mixture in the

cooling box F of fig. 1. The properties of these samples are listed in table III along with some prepared at the same time without cooling the target.

Table III - Effect of Cooling the Target
(Measurements at 20°C).

No	t(μ)	T(°C)	R_6	$\rho \times 10^{-5}$	$A \times 10^{10}$	$R^2/A\rho^2 \times 10^3$
84	0.658	30	+0.626	1.86	5.89	19.3
85	0.777	-18	+0.054	2.19	6.02	0.10
119#	0.657	37	+1.06	2.00	4.66	13.1
120#	0.525	-6	+0.255	3.44	1.97	2.9

T = estimated surface temperature of the target at the instant deposition begins.
# indicates that the substrate is mica.

Notice that in both cases cooling the target decreased R_6 and A and increased ρ compared to a sample of the same thickness whose target was not cooled. The magnitudes of the changes are such that the quantity $R^2/A\rho^2$ decreases.

D. Negative Hall Coefficients.

Several specimens were prepared on cooled targets by preheating the furnace to 950°C or more and omitting the baffle altogether. In this way the bismuth could be very quickly raised to a temperature at which appreciable evaporation occurred and the furnace could be removed after a short time interval. Thus the target temperatures for these samples were less than for those of part C. The results for 2 such samples are shown in Table IV.

Table IV - Negative Hall Coefficients (at 20°C).

No.	t(μ)	T(°C)	R_6	$\rho \times 10^{-5}$	$A \times 10^{10}$	$\delta \times 10^{9}$
29	0.923	30	-3.59	4.47		
121	1.23	0	-3.11	3.57	6.1	2.4

T = estimated surface temperature of the target when the deposition ended.

These samples are found not to obey the quadratic law mentioned in part B, but to approximate a law

$$\frac{\Delta\rho}{\rho} = \frac{AH^2}{1+\delta H^2}$$

In addition the Hall constant for these films increases as the field increases and seems to reach a rather ill-defined maximum or a constant value at about 6 kilogauss.

E. Variation of the Properties with Temperature.

One sample from the group described in part B (thickness 0.908μ) was measured down to dry ice temperatures. (see Table V).

Table V - Variation of the Properties with Temperature (#107).

Temp.(°C)	R_o	$\rho \times 10^{-5}$	$A \times 10^{10}$	$B \times 10^{10}$	$R^2/A\rho^2 \times 10^3$
20	.540(6 Kgauss.)	1.65	8.32		12.9
0	.597	1.66	11.8	6.7	10.9
-20	.619	1.68	15.2	3.3	8.9
-40	.654	1.70	18.6		7.9
-60	.480	1.78	24.2	1.1	3.0
-70	.028	1.85	26.8		0.1

Here R_o is the Hall coefficient for zero magnetic field except where otherwise indicated. B is defined by the

expression

$$R(H) = R_o - BH^2$$

which is known to hold (1) for this type of layer at room temperature. R_o and B were calculated from values of R measured at 3 kilogauss and 5 kilogauss.

G. The Effect of Annealing.

Several samples were annealed in vacuum or in 20 cm. Hg. pressure of CO_2. No loss in weight could be detected for films annealed in either manner. Since no difference could be detected between the effects achieved by the two methods of annealing, they are not distinguished in what follows.

Table VI - Effect of Annealing.

No.	t(μ)	R_6	$\rho \times 10^5$	$A \times 10^{10}$	$R^2/A\rho^2 \times 10^3$
(a)					
59	0.533	+0.637	1.94	6.29	17.2
59*		+0.764	1.74	8.82	21.8
61	0.546	+0.645	2.01	6.08	16.9
61*		+0.696	1.79	9.05	16.7
62	0.576	+0.616	1.86	8.05	13.6
62*		+0.610	1.68	10.0	13.2
83	0.731	+0.633	1.87	6.87	16.7
83*		+0.724	1.61	9.65	20.9
86	0.560	+0.547	2.20	5.39	11.5
86*		+0.743	1.84	8.12	20.0
(b)					
85	0.776	+0.054	2.19	6.01	0.10
85*		+0.285	1.92	8.55	2.6
(See Table III)					
(c)					
29	0.924	-3.59	4.47		
29*		-3.98	3.08		
(See Table IV)					

* signifies that the sample was annealed approximately 40 min. at 260°C.

Because the change in R on annealing varied from sample to sample and because the sign of the change is in contradiction to the results of Leverton and Dekker (1), one sample was annealed in several stages, and measured at 20°C after each annealing. The results appear in Table VII.

Table VII - Step-by-step Annealing.

No.	t(μ)	Time(min.)	Temp.(°C)	R_o(e.m.u.)	$Bx10^{10}$	$\rho x10^{-5}$	$Ax10^{10}$
64	0.544			+0.618	7.2	2.06	5.95
64_1		10	150	0.616	7.0	2.04	6.39
64_2		3	<240	0.645	7.0	1.97	7.40
64_3		13	247	0.659	6.6	1.92	6.90
64_4		20	258	0.616	5.1	1.87	7.16
64_5		30	258	0.679	5.5	1.86	7.62
64_6		40	268	0.701		1.86	7.48

Colums 3 and 4 indicate the annealing which produced the changes between any given row and the row preceding it.

Notice theddecrease in A occurring after the third anneal and the decrease in R_o after the fourth.

H. Calculations.

Jones (4) has presented a model by means of which most of the galvanomagnetic effects observed in bulk bismuth can be explained. The two assumptions on which his calculations are based are (i) the surfaces of constant energy in k-space take the form of ellipsoids and (ii) the relaxation time of the current carriers is independent of

their energy. Two equations are presented which take the form

$$\frac{\Delta\rho}{\rho} = \frac{AH^2}{1+\delta H^2} \qquad (1)$$

$$R = \frac{R_0 - BH^2}{1+\delta H^2} \qquad (2)$$

If our films are assumed to consist of crystallites whose principal axis is perpendicular to the substrate as found by Lane (5), then all the measurements previously listed are for current flow perpendicular to and magnetic field parallel to this axis. Under these circumstances, Jones gives for ρ, A, R_0, B and δ;

$$\frac{1}{\rho} = \sigma = \frac{e}{c}(n_1 v_1 + n_2 v_2) \qquad (3)$$

$$A = \frac{\sigma_1 \sigma_2}{\sigma^2}\left(\frac{\sigma_2}{n_2} + \frac{\sigma_1}{n_1}\right)^2 \frac{c^2}{e^2} \qquad (4)$$

$$R_0 = \frac{c}{e}\left(\frac{\sigma_1^2}{n_1} - \frac{\sigma_2^2}{n_2}\right)\frac{1}{\sigma^2} \qquad (5)$$

$$B = \frac{\sigma_1^2 \sigma_2^2}{(n_1 n_2)^2 \sigma^2}(n_1 - n_2)\frac{c^3}{e^3} \qquad (6)$$

$$\delta = \frac{\sigma_1^2 \sigma_2^2}{(n_1 n_2)^2 \sigma^2}(n_1 - n_2)^2 \frac{c^2}{e^2} \qquad (7)$$

Here σ is the total conductivity perpendicular to the principal axis, σ_1 that due to electrons alone and σ_2 to holes alone. n_1, n_2 are the density of electrons and holes respectively. Therefore $\sigma_1 = \frac{e}{c} n_1 v_1$, $\sigma_2 = \frac{e}{c} n_2 v_2$

where v_1 and v_2 are the carrier mobilities. Note that the use of a single symbol for the conductivity perpendicular to the principal axis implies circular symmetry about this axis. Actually there is only trigonal symmetry.

Since those of our samples which were deposited on uncooled targets follow, for the fields used, laws of the types (1) and (2) with $\delta H^2 << 1$, equations 3, 4, 5, and 6 were solved for n_1, n_2, v_1 and v_2 for a few of these samples. The quantity $\frac{AR_o}{B}$ was formed from equations 4, 5 and 6 and the quantity $\frac{R_o^2}{\overline{\rho^2 A}}$ from equations 3, 4, and 5. Both are dimensionless quantities and may be expressed in terms of $\gamma = \frac{n_2}{n_1}$ and $\beta = \frac{v_2}{v_1}$ as follows;

$$\frac{AR_o}{B} = \frac{\gamma(1+\beta)^2(\gamma\beta^2-1)}{\beta(1+\gamma\beta)^2(\gamma-1)} \qquad (8)$$

$$\frac{R_o^2}{\overline{\rho^2 A}} = \frac{(\gamma\beta^2-1)^2}{\gamma\beta(\beta+1)^2} \qquad (9)$$

Equations 8 and 9 were solved for γ & β by trial and error. These were substituted into 5 written in the form,

$$n_1 = \frac{c}{e R_o} \frac{\gamma\beta^2-1}{(\gamma\beta+1)^2} \qquad (10)$$

and in (3) in the form

$$v_1 = \frac{c}{e\rho(n_1+\beta n_2)} \qquad (11)$$

and hence n_2 and v_2 obtained.

As mentioned previously the change of resistance with magnetic field was not quadratic for those films with negative Hall coefficients. An equation of the form (1) fitted the experimental results much better and a rough value of δ could be evaluated.

In this case the quantities $\frac{R_o^2}{A\rho^2}$ and δ/A were expressed in terms of γ and β. n_1, n_2, v_1 and v_2 were then evaluated as before. It should be emphasized that δ is not accurately known. However, even if δ were 50% lower than the value used in this calculation one is still led to the conclusion that the density of holes is much less than that of the electrons. (Table VIII (d)).

Table VIII - Calculated Carrier Densities and Mobilities.

No	$n_1 \times 10^{-18}$ (cm^{-3})	$n_2 \times 10^{-18}$ (cm^{-3})	$v_1 \times 10^{5}$ (e.m.u.)	$v_2 \times 10^{5}$ (e.m.u.)
(a)				
62*	7.5	11.5	2.2	2.2
(b)				
64	4.6	7.1	2.8	2.5
64^1	5.5	9.0	2.2	2.0
64^2	4.5	6.2	3.0	2.9
64^3	5.2	7.5	2.6	2.5
64^4	5.4	7.1	2.7	2.7
64^5	5.1	6.8	2.8	2.8
(c)				
107				
0°C	4.5	5.4	3.8	3.8
-20°C	4.7	5.0	3.7	3.9
-60°C	3.1	3.1	5.5	5.8
(d)				
121	8.4	0.4	1.9	5.7

For sections (a) and (b) of this table refer to part G, for section (c) to part E and for section (d) to part D.

IV DISCUSSION OF RESULTS

A. Reproducibility.

The observation that the first sample of a melt possessed different properties than succeeding ones is very likely due to a concentration of the low boiling point impurities in this sample. Leverton and Dekker (1) observed this concentration of impurities to occur in the case of antimony films prepared by a similar technique.

It is more difficult to explain the observations on the first sample prepared after leaving the melt in vacuum for a day or more. However, it seems feasible that, if a surface film of oxide forms on the melt, the vapour pressure over the melt will be lower than over an unoxidized melt and that the vapour will contain oxide molecules. If this is the case we may expect a specimen made from such a melt to be thinner than otherwise and to possess a higher resistivity and a different Hall constant.

The difference between groups I and II (fig. 7) with respect to R_6 and ρ may be attributed to the concentration of the higher boiling point impurities (Fe, Cu) in the samples of group II. The erratic

results obtained from samples 73 - 80 are probably due to relatively large amounts of impurities evaporated, as the end of the melt is approached.

It is believed that subsequent samples prepared as described in section III-A, are as pure as can be obtained by this technique and therefore that any postulated inequality in the numbers of positive and negative carriers must be explained by the removal of one or the other type of carrier (or both) by trapping (see Section I.)

B. Variation of the Properties with Thickness.

The maximum in the curve of $\frac{R_0^2}{A\rho^2}$ versus thickness (fig. 8b) occurs at a thickness of about 0.4μ. Lane (5), working also with evaporated bismuth films, has plotted the temperature dependence of the increase of resistivity in a magnetic field versus film thickness and found an abrupt change in slope to occur at about 0.4μ. He identifies this critical thickness as that at which Goetz (6) reported the crystallites in evaporated bismuth films to undergo a sudden increase in size. The work of Gross (7) and Levinstein (8) shows that below the critical thickness the average crystallite size increases as the thickness is increased. The shape of our $\frac{R_0^2}{A\rho^2}$ curve is not inconsistent with this evidence.

$\frac{R_0^2}{a\rho^2}$ is a function of γ and β only

(see eq. 9). If we postulate with Leverton and Dekker (1) that a certain number of the current carriers may be trapped in localized levels at crystallite boundaries then clearly the number of trapped carriers will decrease as the crystallite size increases. Also the carrier mobilities will increase with increasing thickness since they depend to some extent on scattering at crystallite boundaries. We may expect then that at least small changes will occur in γ and β as the thickness is varied. Inspection of equation 9 shows that only small changes in γ and β are required to produce the observed variation in $\frac{R_\square^2}{\overline{A\rho^2}}$.

C. - Cooling the Target.

The experimental results presented in sections II-C and D indicate that the main effect achieved by cooling the substrate during deposition is the trapping of a large fraction (see table VIII (d)) of the available positive current carriers or "holes".

It is impossible, on the postulate of section IV-B, to explain why the trapping of holes should predominate in these specimens. The effect cannot be due merely to a reduced crystallite size for, as we have seen (section IV-B) the ratio of the carrier densities does not appear to depend very strongly on this variable. However, if we postulate that the

cooling of the target results in a less perfect lattice, (i.e. more lattice defects) then the observations may be explained by assuming that holes become trapped in vacant lattice points. That is to say we assume that the potential for an electron in the immediate neighbourhood of a lattice point vacated by a positive ion core is such that there is a tendency to repel as many electrons (i.e. attract as many holes) as correspond to the valency of the core.

This postulate is analogous to that advanced (9) in connection with F-centres in ionic crystals. These are thought to be electrons trapped in negative ion vacancies.

D. - Variation of the Properties with Temperature.

The only fact worthy of comment in this section is the negative temperature coefficient of resistance. Lane (5) and Leverton and Dekker (1) find this same result but negative temperature coefficients are never found for other metal films of comparable thickness. (10) Table VIII(c) shows that for this sample at least the effect is due to a reduction in the number of carriers, since the mobilities increase with decreasing temperature as in bulk bismuth.

Mott and Jones (11) suggest that the

negative temperature coefficient of resistance observed in dilute solutions of tin and lead in bismuth is due to a reduction in the number of overlapping electrons. This would result in a lowering of the Fermi level so that for a certain range of temperatures it would be possible for the number of carriers to increase with increasing temperature as in semiconductors.

This idea may apply to thin films of bismuth where the electron density is presumably lower than in bulk bismuth due to trapping. It is to be noted however that in our case the hole density also appears to increase with increasing temperature (Table VIII(c)). It is not possible to discuss this effect further on the basis of the few measurements made.

E. - Effect of Annealing.

It is difficult to be certain, on the basis of the few calculations made, but the result of annealing at 260°C appears (table VIII(b)) to be an increase in the density of negative carriers and a decrease in the density of positive carriers. If this is the case, a combination of the explanations advanced by Leverton and Dekker (1) for antimony and bismuth films would be consistent with the observations.

These authors postulated that (i) annealing antimony films increased the crystallite size,

thereby decreasing the extent of overlapping of the two conduction bands and effectively "recombining" some of the electrons and holes; (ii) that annealing bismuth films released some of the trapped carriers. If both these processes are operative the change in R on annealing would be expected to depend even more strongly on the conditions of preparation than the Hall constant itself. A comparison of the results for different samples, both in this and the previous work shows that indeed R may increase or decrease on annealing.

Annealing those samples with negative Hall coefficients causes the coefficient to become more negative (table VI(c)). On the other hand those specimens deposited on cooled plates and having small positive Hall coefficients were found to suffer an increase in the coefficient on annealing. Lacking enough data to calculate the actual carrier densities in these samples we cannot say whether or not these changes are consistent with the foregoing postulates. It should be noted however that a change in n_1 or n_2 may produce a change of either sign in R, (eq. 5), depending on the initial value of these densities.

F. - Calculations.

Table VIII shows that the number of free electrons in a "normal" (i.e. deposited on an uncooled target) annealed film is about 7×10^{18} per cm^3. and that

the carrier mobility is about 3000 cm^2-$volt^{-1}$-sec^{-1}. at room temperature.

Mott and Jones (10) estimate the electron (and hence also the hole) density to be 3×10^{18} per cm^3. on the basis of some measurements on the specific magnetic moment of bismuth single crystals. We consider our value to be in excellent agreement with this one. So far as we know no other experimental value has been quoted for the carrier mobility in bismuth.

V. CONCLUSION.

The electrical properties of evaporated bismuth films depend strongly on the temperature of the substrate during deposition and on the thickness of the film. Values of the constants defining these properties depend therefore on the sample measured and are not applicable to bismuth in bulk.

The observed results can be qualitatively explained by assuming that carriers (positive or negative) may be trapped in localized levels at crystallite boundaries and that positive carriers may be trapped in vacant lattice points. One other assumption may or may not be necessary, viz., that the extent of the average overlap of the two highest energy bands depends on the average crystallite size.

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