ance have been used in all the recent investigations on the equivalence of the two methods of treating the longitudinal electromagnetic field. As the investigations of Wentzel and others show,[12] the evaluation of the induction tensor in the theory of vacuum polarization involves a great deal of ambiguity, so that gauge invariance of quantum electrodynamics is by no means a well-established fact at the present stage of the theory. However, gauge invariance is a basic requirement of a satisfactory formulation of quantum electrodynamics, and it is reasonable to take Eqs. (9) as an assumption or to ensure their validity by means of the regularization of Pauli and Villars.

For integrals which do not satisfy the requirement (ii), further investigation is necessary before the validity and limitation of the unified treatment can be established. For example, in Schwinger's calculations of the self-energy of the electron, the results obtained by the two methods of treating the longitudinal electromagnetic field become identical only after a gauge transformation. On the other hand, the requirement (ii) is satisfied by the iterated form of the S-matrix, so that the equivalence of the two methods of evaluating the S-matrix follows immediately from the above considerations.

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Hall Coefficient and Resistivity of Thin Films of Antimony Prepared by Distillation*

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An a.c. method is described for measuring the Hall coefficient. An apparatus for the preparation of very pure evaporated metal films is also described. This apparatus eliminates such sources of contamination as hot filaments.

The effect of annealing on both Hall coefficient and resistivity of evaporated films of antimony is examined. A tentative explanation is presented for the observed increase in the Hall coefficient and decrease in the resistivity. It is based on the assumption of partial recombination of electrons and holes.

The Hall coefficient of unannealed evaporated films is 0.215_9 c.g.s.m., and of annealed films is 0.24_14 c.g.s.m. with an accuracy of one percent.

The resistivity of our annealed films is 1.28 times that of bulk antimony.

I. INTRODUCTION

If a conductor carrying a current is placed in a magnetic field at right angles to the current, a potential difference develops across the conductor in a direction perpendicular to both magnetic field and current flow. This potential difference is known as the Hall voltage

$$V=(RIH/t)\times 10^{-9},$$

where I is the current in amperes, H is the magnetic field in gauss, t is the thickness of the conductor in cm in the direction of H, and R is the Hall coefficient of the conducting material in c.g.s. magnetic units.

Examination of the literature reveals that most observers have used direct current in their determinations of the Hall coefficient. Since such a determination measures the sum of the Hall and Ettingshausen voltages, the results must be corrected by measuring the latter separately. Since the voltages are very small, the Hall voltage determined in this manner may be in serious error where the Ettingshausen voltage is large compared with the Hall voltage. The Ettingshausen voltage may be eliminated by using Hall contacts of the same material as the sample; however, this is practicable only in a limited number of cases.

In the measurements described in this paper an alternating current was used in the determination of Hall coefficients. Since the temperature gradient which leads to the Ettingshausen effect requires a time of the order of seconds to become established,[1] use of alternating current completely eliminates this effect from the observed transverse voltage. A further advantage of the a.c. method is that it is much easier to amplify very small alternating voltages than to amplify direct voltages of the same magnitude.

Despite these advantages, few observers[1–3] have used a.c. methods. Smith[1] found the Hall coefficient of bismuth to be constant within experimental error for frequencies up to 120,000 cycles per second. Wood[2] found similar results for tellurium up to 10,000 cycles per second. Busch and Labhart[3] worked only at line frequency (50 cycles). Some early observers[4–6] used a.c. of the same frequency in both the Hall sample and in the

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† Holder of National Research Council of Canada Studentship, 1948–49, 1949–50.

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electromagnet producing the magnetic field. This, of course, resulted in a direct Hall voltage and did not eliminate the Ettingshausen effect.

Since antimony has a comparatively large Hall coefficient and since there is wide disagreement as to its correct value,[7] it was decided that a careful determination of the Hall coefficient of pure antimony would serve as a test of the measuring equipment and might also serve to resolve some of the disagreement.

An examination of the expression for the Hall voltage indicates that it can be increased (for any allowable Joule heating) by reducing the thickness of the sample. This suggested preparation of the samples as thin layers by evaporation in vacuum.

II. MEASURING APPARATUS

The magnetic field is supplied by a water-cooled electromagnet with four-inch diameter flat pole faces. This magnet will produce up to 14,000 gauss with a three-quarter-inch gap. The field is measured by means of a fluxmeter and search coils. The calibration of the fluxmeter was checked by means of accurately known fields produced in nuclear magnetic moments experiments in this department.

Current is supplied to the Hall sample by a 210-cycle R.C. oscillator. This frequency was chosen to minimize pick-up of harmonics of 60 cycles.

The amplifier for the Hall voltage has a high gain (up to 10^7) and is sharply tuned at 210 cycles ($Q>200$). The input impedance is high so that negligible current flows through the Hall contacts. The sharp frequency characteristic, obtained by using a parallel T feedback network, reduces the amount of tube noise amplified. The Hall voltage can be applied directly to the grid of the first tube or through a step-up transformer. The latter feature should be valuable in measuring very small Hall voltages, for the transformer will raise the signal voltage above the noise level of the first tube, thus improving the signal to noise ratio.

To measure the Hall voltage the sample is mounted on a piece of insulating board and held in place by clamping the ends between layers of tin foil. The clamps serve as electrodes for the primary current. The contacts for the Hall voltage are constructed as shown in Fig. 1. The ball bearing, free to roll in its mounting sleeve, makes a point contact which can be moved along the metal layer without scratching it. The Hall contacts are held at a fixed separation somewhat less than the width of the sample. Spring mounting assures good electrical contact. With current flowing but no magnetic field, the Hall contacts are adjusted so that their potential difference is small compared to the Hall voltage. This residual voltage (as well as the total voltage with magnetic field) is measured by noting the amplifier output and then substituting for the unknown voltage a known voltage which may be varied to give the same amplifier output. This calibration voltage is developed across a standard resistance and may be calculated by measuring the current flowing through the standard resistance. This is repeated for each determination. By this method the accuracy of the measurements of Hall voltage does not depend on the long-time stability of the amplifier.

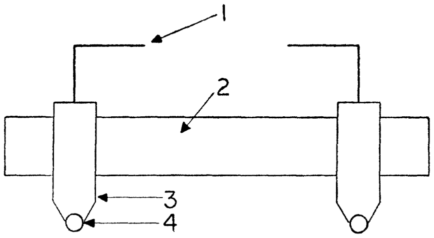

FIG. 1. Schematic diagram of movable Hall contacts. (1) Lead to amplifier; (2) lucite support; (3) brass sleeve; (4) steel ball bearing 1 mm in diameter. Distance between contacts is 2 cm.

The same ammeter is used to measure both the current through the Hall sample and the calibration voltage. Since in the expression for the Hall coefficient the Hall voltage appears in the numerator and the primary current in the denominator, this arrangement tends to cancel any error in the ammeter calibration.

III. PREPARATION OF SAMPLES

The layers of antimony were prepared by evaporation in vacuum using glass microscope slides 2.5×7.5 cm as targets. At first a conventional vacuum evaporating apparatus with removable glass bell jar was used. To ensure uniformity of metal thickness along the sample multiple sources were used. The sources were 20-mil molybdenum wire wound in funnel-shaped spirals. The nominal thickness of the metal layers was determined by weighing and using the known sample area and the density of antimony in bulk. Layers from 0.2 to 10 microns in thickness were prepared with this apparatus. Their electrical resistivities ranged from 10 to 20 times greater than that for antimony in bulk. The layers were bright and highly reflecting but had a finely mottled or banded appearance. Annealing in vacuum reduced the resistivity somewhat but was limited by the fact that at temperatures above 400°C the antimony re-evaporated from the slides. Annealing at 500°C in an atmosphere of 20 to 25 cm Hg of carbon dioxide gas reduced the resistivity to five or six times that of antimony in bulk with only a small loss of metal due to re-evaporation.

Because of their high resistivities, these layers were considered unsatisfactory. In an effort to produce better layers, the vacuum evaporating apparatus shown in Fig. 2 was constructed. It is made entirely of Pyrex glass. Heat necessary for evaporation of the metal is supplied by a 700-watt furnace which is lowered over the apparatus down to level AA. This apparatus has several advantages over the conventional vacuum evaporating apparatus:

(1) It can be completely outgassed permitting more complete evacuation.

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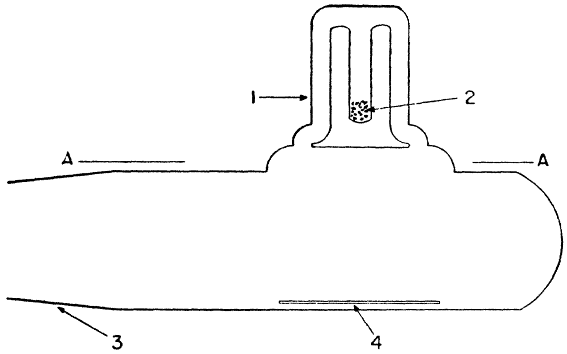

FIG. 2. Schematic diagram of evaporating apparatus. (1) 8 mm o.d. Pyrex glass tubing; (2) metal to be evaporated; (3) ground glass joint to liquid air trap and pumping system; (4) target (1×3-in. glass microscope slide).

(2) Metals other than that being evaporated, rubber gaskets, and hot filaments are eliminated, thus reducing the possibility of contamination.

(3) Impurities with boiling points lower than that of the metal to be evaporated tend to evaporate more rapidly and are concentrated in the first portion evaporated; impurities with higher boiling points tend to remain in the residual metal. Because of this fractional distillation, by discarding the initial and final portions, appreciable purification is achieved.

This apparatus will withstand temperatures up to 600°C. For evaporation at higher temperatures a similar apparatus could be constructed of fused quartz.

The thickness of layers prepared in this apparatus was uniform within one percent along the length of the sample. This was determined by weighing the antimony deposited on several small targets of known area placed at intervals along a 2.5×7.5 cm slide.

Layers of antimony from 0.1 to 3.0 microns in thickness have been prepared using this apparatus. All were highly reflecting and none showed any structure. Their electrical resistivities before annealing ranged from 1.8 to 2.2 times greater than that for antimony in bulk (1.2 to 1.4 after annealing in carbon dioxide).

During evaporation, the gas pressure was kept below 10^{-5} mm Hg and the antimony was heated to 580 to 600°C. Antimony was deposited at rates ranging from 2.6 to 33 micrograms/cm^2/min. No variation of resistivity with thickness or rate of deposition was observed.

IV. PURITY OF SAMPLES

The antimony used was 99.8 percent pure. Maximum limits of impurities (in percent) were listed as arsenic 0.10, copper 0.03, iron 0.05, lead 0.04, tin 0.030, zinc 0.010.

Examination of the arc spectra of several of the evaporated layers showed that the concentration of each of these impurities was considerably lower than in the original bulk antimony. Arsenic and zinc were concentrated in the first fraction sublimed while copper, iron, lead, and tin were concentrated in the residual melt. The first fraction of each melt (about five percent of the total melt) produced a layer with resistivity from 3 to 11 times that of bulk antimony. This high resistivity was probably due to the increased concentration of arsenic.

V. EXPERIMENTAL RESULTS

1. Hall Coefficient

Unannealed Samples

The Hall coefficient R was measured in five unannealed samples of antimony. The voltage measured is that developed across the Hall contacts and must be multiplied by the ratio of sample width to separation of Hall contacts in order to obtain the Hall voltage. This ratio was 1.26_7.

There appears to be no variation of R with sample thickness from 0.7 to 1.1 microns, strength of applied magnetic field from 4000 to 12,000 gauss, nor with current density from 180 to 500 amp./cm^2. The mean value of R for these samples (22 determinations) was $+0.215_9$ c.g.s.m. at 20°C. The probable error of the mean was 0.000_4 c.g.s.m.

Annealed Samples

Antimony samples annealed in carbon dioxide at 20 cm Hg and 510°C for 45 minutes had a larger Hall coefficient than before annealing. Repeated annealing caused no further change in R. The Hall coefficient does not vary with thickness (0.8 to 1.9 microns), applied magnetic field (3000 to 12,000 gauss), or current density (140 to 460 amp./cm^2).

The mean value of R for five annealed samples (35 determinations) was $+0.244_1$ c.g.s.m. at 20°C. The probable error of the mean was 0.000_2 c.g.s.m. The increase in R caused by annealing was 13 percent.

The accuracy of the measurement of the Hall coefficient is estimated to be within ±one percent, the chief sources of error being the determination of the uniformity of thickness of the layers (0.5 percent) and the measurement of the magnetic field (0.5 percent).

Impure Sample

As noted previously, the first sample prepared from each melt contained considerably more arsenic and zinc than did the original bulk antimony. The Hall coefficient of one of these impure samples was measured as follows, at 20°C.

Magnetic field (10^3 gauss)	Hall coefficient (c.g.s.m.)
3.96	$0.188_8 \pm 0.001_9$
12.24	$0.195_6 \pm 0.000_6$
Mean	0.192_2

The Hall coefficient of this sample was 11 percent lower than that of more pure samples (unannealed) and appeared to vary somewhat with magnetic field strength.

2. Resistivity Measurements

The resistivity ρ of a number of samples was measured at temperatures of 77 and 293°K.

Electron diffraction studies[8, 9] have shown that evaporated antimony deposits are oriented with the principal axis perpendicular to the substrate; hence, the resistivity measurements were actually made perpendicular to the principal axis. The resistivity of bulk antimony perpendicular to the principal axis is[10] 42.6×10^{-6} ohm-cm at 293°K and[11] 8.2×10^{-6} ohm-cm at 77°K, hence

$$\Delta\rho/\Delta T = 0.159\times10^{-6}\ \text{ohm-cm/°K}$$

over this temperature range. The mean value of $\Delta\rho/\Delta T$ for the unannealed samples was 0.154×10^{-6} ohm-cm/°K and for the unannealed samples 0.168×10^{-6} ohm-cm/°K.

In Fig. 3 resistivity is plotted against temperature for unannealed samples, annealed samples, and bulk antimony.

The resistivity of the evaporated layers can be represented conveniently as the sum of a temperature independent resistivity, ρ_0, and a temperature dependent resistivity, ρ^T, which varies approximately linearly with the absolute temperature

$$\rho = \rho_0 + \rho^T.$$

ρ_0 was obtained by extrapolating the resistivity-temperature plot to 0°K.

The resistivity measurements are summarized in Table I.

Annealing greatly reduced ρ_0, but slightly increased ρ^T.

The mean room temperature resistivity of the annealed samples was 1.28 times that of bulk antimony. The lowest resistivity previously reported for evaporated layers was 1.35 times that of bulk antimony by Harris and Shaffer.[12] The resistivity of their samples was considerably more temperature dependent than that of bulk antimony, the smallest value of $\Delta\rho/\Delta T$ they reported was 0.185×10^{-6} ohm-cm/°K.

VI. DISCUSSION OF RESULTS

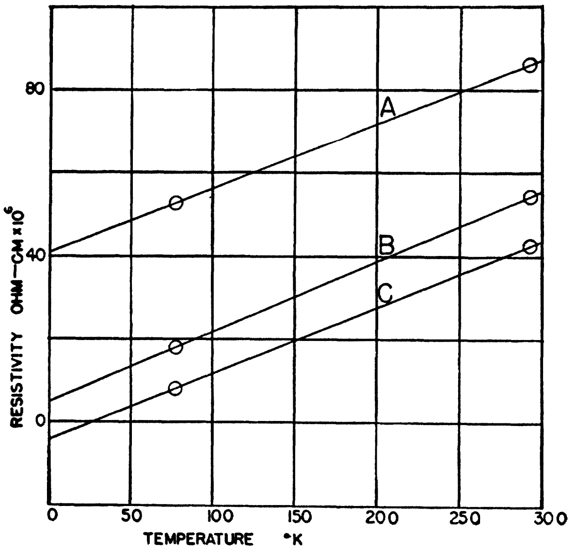

FIG. 3. Resistivity of evaporated deposits of antimony as a function of temperature. *A*—unannealed deposits; *B*—annealed deposits; *C*—single crystals, resistivity perpendicular to principal axis.

Antimony crystallizes in a trigonal structure. This structure differs from that of most other metals in that there are two atoms per elementary cell. According to the modern electron theory of solids, each energy band provides two possible energy states per elementary cell. Hence, a contribution of one electron per atom would completely fill a Brillouin zone. Antimony has five valence electrons per atom and it is generally assumed that these fill four bands completely, while the fifth band is nearly filled and the sixth nearly empty. The amount of overlapping of the fifth and sixth bands has been estimated by Brown and Lane[13] from measurements of the magnetic anisotropy of tin-antimony alloys. They conclude that there is about 1 free electron per 100 antimony atoms or 3.3×10^{20} electrons and an equal number of holes per cm^3.

TABLE I. Resistivity data. (Resistivities in units of 10^{-6} ohm-cm.)

	ρ_{77}	ρ_{293}	$\Delta\rho/\Delta T$	$\rho_{293}{}^T$	ρ_0	$(\rho/\rho_{\text{Sb}})_{293}$
Unannealed samples	53	86	0.154	45	41	2.02
Annealed samples	18	54.5	0.168	49	5.5	1.28
Bulk antimony	8.2	42.6	0.159	46.6	−4.0	1.00

$\rho_{293}{}^T$ is the value of ρ^T at 293°K.
(ρ/ρ_{Sb}) is the ratio of resistivity to that of bulk antimony.

Apart from the relatively large number of free electrons and holes (even at $T=0$), which leads to a positive temperature coefficient of resistance, antimony may, in certain respects, be considered as a semiconductor. Its Hall coefficient should be given by the same formula which holds for a semiconductor with combined electron and hole conduction:

$$R = +\frac{3\pi}{8e}\cdot\frac{n_h b_h^2 - n_e b_e^2}{(n_h b_h + n_e b_e)^2}, \tag{1}$$

where e is the electronic charge, n_h, n_e are the densities of holes and electrons respectively, and b_h, b_e are their mobilities. For pure antimony, $n_h = n_e$ and since the Hall coefficient is positive, $b_h > b_e$.

Our result for the Hall coefficient of unannealed antimony, $+0.215_9$ c.g.s.m. at 20°C, is in agreement with the value +0.219 c.g.s.m. reported by Barlow[14] and by Zahn[15] but is in poor agreement with the value

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+0.192 c.g.s.m. by Ettingshausen and Nernst,[16] and +0.125 c.g.s.m. by Alterthum.[17]

For annealed antimony samples we obtain a Hall coefficient of $+0.244_1$ c.g.s.m. at 20°C, which is 13 percent higher than that of the unannealed samples. Since the increase in the Hall coefficient due to annealing does not vary with the thickness of the antimony layer, the increase must be due to a bulk effect and cannot be attributed to a surface effect such as partial oxidation of the antimony.

From Eq. (1), assuming the ratio b_e/b_h to remain constant, it can be shown that in the neighborhood of n_e/n_h an increase in the Hall coefficient can be obtained only by reducing n_e and/or n_h. It is very unlikely that annealing would have the effect of trapping either electrons or holes. On the contrary, one would expect the small crystallites to form larger crystals upon annealing, thereby reducing the number of possible surface traps.

It is interesting to refer to an observation made by Stephens[18] on antimony in bulk. Stephens measured the Hall coefficient of two antimony plates 0.5 cm in thickness, one consisting of large crystals, the other of smaller crystals. He found that the Hall coefficient of the first plate was 9 percent greater than that of the second.

On the basis of the foregoing discussion it seems reasonable to exclude an explanation based on trapping electrons or holes at the crystal boundaries. The following is suggested as a tentative explanation of the increase in R. The ratio b_e/b_h is assumed to remain practically constant during the annealing process. Our antimony layers as well as the plates used by Stephens were of very high purity; we will therefore assume that trapping by impurities may be neglected. (In any case we should not expect such trapping to be increased by annealing the samples.) Since trapping at crystal boundaries is also excluded, $n_e = n_h$. It is clear that the amount of overlapping of the fifth and sixth bands depends on the crystal structure. Since the behavior of the potential at the crystal boundaries will be different from that within the crystals, one might expect the extent of "average overlapping" to depend on the size of the crystals composing the sample. If we assume that crystal boundaries tend to increase the average overlapping, annealing would result in the recombination of a fraction of the free electrons and holes. Annealing would then have the effect of reducing the number of both electrons and holes and hence would increase the Hall coefficient.

Any interpretation of the effect of annealing on R must be in accord with the observed decrease in resistivity. The latter is an effect which is generally observed in evaporated layers. It is commonly assumed that by increasing the size of the crystallites, annealing reduces scattering by crystal boundaries. This would lead to a decrease in ρ_0, the temperature independent part of the resistivity. However, in addition to the decrease in ρ_0, we observed an increase of about nine percent in ρ^T, the temperature dependent part of the resistivity. This increase is consistent with the tentative explanation given above for the behavior of the Hall coefficient. If a number of free electrons and holes recombine upon annealing, ρ^T will increase.

One would expect the percentage increase in R and ρ^T on annealing to be the same. In view of the simplifying assumptions made, the observed increases of 13 percent and nine percent, respectively, seem to be in satisfactory agreement.

The authors wish to thank Dr. A. van der Ziel for his assistance in the design of the electronic equipment.

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