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PHYSICS

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ABSTRACT

The Hall coefficient and conductivity of silver films were measured by a DC method and comparisons with the theoretical calculations of Fuchs and Sondheimer were made. Films from 150 A. to 1500 A. in thickness were deposited by evaporation at pressures below 10^{-2} microns. The electrical properties were studied at liquid nitrogen, dry ice and acetone, and room temperatures. Film thickness measurements were made by the interferometer method. Electron diffraction and electron micrograph pictures were taken to study agregation and to check on the purity of the films. The electron micrographs show aggregation in films less than 300 A. thick. The electrical measurements also indicate this change in the thinnest films. A variation of Hall coefficient and conductivity with thickness was found but only qualitative agreement between theory and experiment was indicated.

INTRODUCTION

Theoretical calculations of the electrical characteristics of bulk metals are made, in the simplest case, in terms of the free electron theory (1). The calculations are essentially classical, assuming only from the quantum approach that the electron energies are proportional to the square of the wave vector, k, and that these energies are distributed according to Fermi-Dirac statistics. The conduction electrons are assumed free to migrate with thermal energy through the lattice, undergoing collisions much as molecules in a gas. The effects of the collisions at the surface of the solid are assumed to be negligible compared to those within. The average distance of electron travel between collisions is defined as the mean free path.

If any dimension of a metallic conductor approaches in magnitude the mean free path length, as is possible in evaporated films, surface effects must be considered. Fuchs (2) has made an analysis of this condition for the case of plane films with an electric field applied parallel to the critical surfaces. His calculation was similar to that performed for bulk materials except that new boundary conditions were applied for the solution of Boltzmann's equation of state.

For the simplest case, Fuchs assumed that all electrons striking the surfaces were scattered diffusely with a complete loss of their drift velocities. The resulting equations were solved numerically in terms of the ratio of the bulk metal conductivity, σ_o, to the thin film conductivity, σ, and the ratio of the film thickness, a, to the mean free path length, ℓ. A graphical presentation of the solution is shown in Fig. 1.

Fuchs obtained a more complete solution by introducing a parameter, ϵ, which represented the fraction of the electrons that reflected specularly at the surface. As ϵ approaches one, the curve in Fig. 1 approaches a horizontal line corresponding to a conductivity ratio of unity.

Sondheimer (3) has extended this analysis for the case of a magnetic field perpendicular to both the critical surface and the electric field. The same assumptions were made and the methods of solutions similar. For low magnetic fields (up to 15 or 20 kilogauss) Sondheimer's solutions for the conductivity ratios agreed with those obtained by Fuchs. At high fields he found that the conductivity oscillates as the field is increased. Sondheimer's solution for the ratio of the thin film Hall coefficient, A_H, to the bulk metal coefficient, A_{Ho}, with diffuse reflection of the electrons and low magnetic fields, is shown in Fig. 2. His parameter p, has the same significance as ϵ, as p approaches one, this curve also drops to a value of unity.

Since the electronic mean free path for even the best conductors is about 500 A., very thin films are necessary to study these effects. Such films may be prepared by chemical deposition, sputtering, or evaporation. Of these three processes, evaporation is the simplest and most rapid.

A few films of gold were deposited for an initial investigation, but the principal study has been made with silver. Silver is easily evaporated, is not highly active chemically, has a large electronic mean free path, and has bulk conductivity properties in agreement with calculations based on the free electron theory. These characteristics make silver a particularly suitable metal for studying thin films.

EVAPORATION OF FILMS

Glass microscope slides were used as substrates for the films. Just before use, these were carefully cleaned in Dichromate cleaning solution and then with Dreft suds in distilled water. They were rinsed with several hundred milliliters of boiling distilled water from a wash bottle and allowed to dry in a dust free atmosphere. All handling was done with forceps.

The clean slides were placed in an RCA, EMV-1A vacuum chamber, and a layer of silver approximately 1500 A. thick was deposited around a thin monel metal mask to provide current and Hall contacts as shown in Fig. 3a. A second mask of monel with a rectangular opening 5.07 cm. by 1.27 cm. was placed over the slide before evaporating the main film as shown in Fig. 3b.

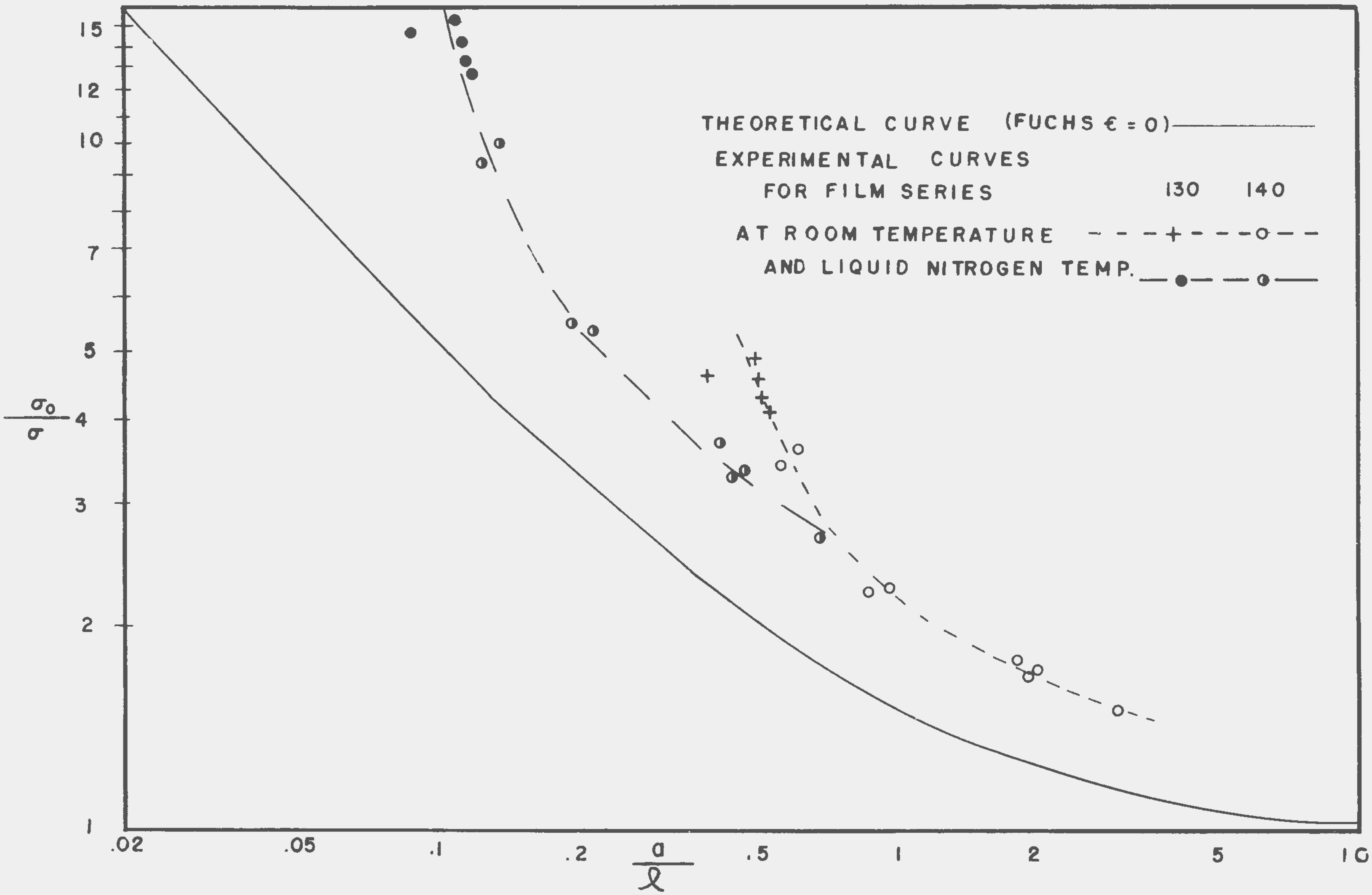

FIG. 1. ELECTRICAL CONDUCTIVITY OF THIN SILVER FILMS.

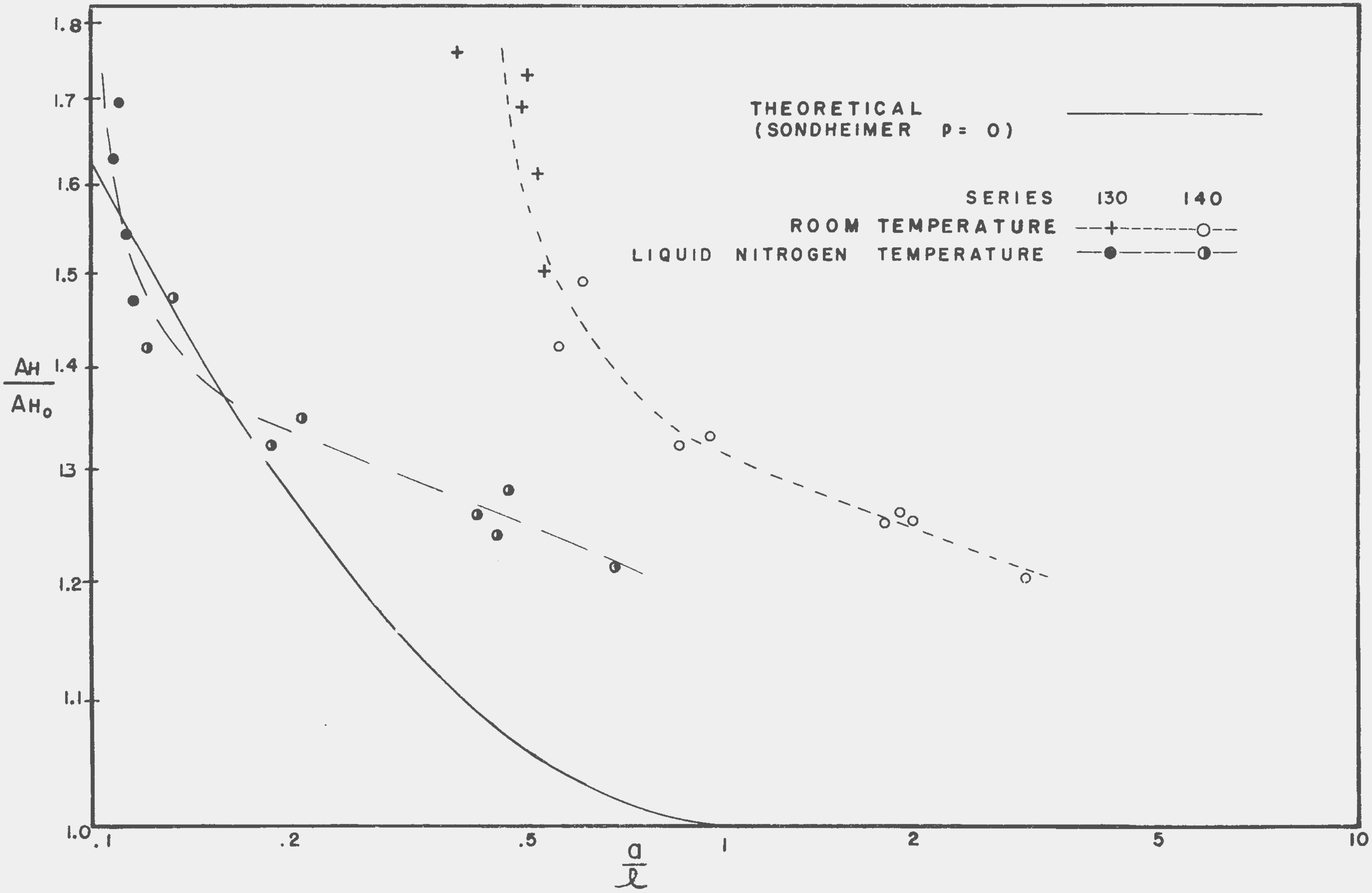

FIG. 2 HALL COEFFICIENTS OF THIN SILVER FILMS.

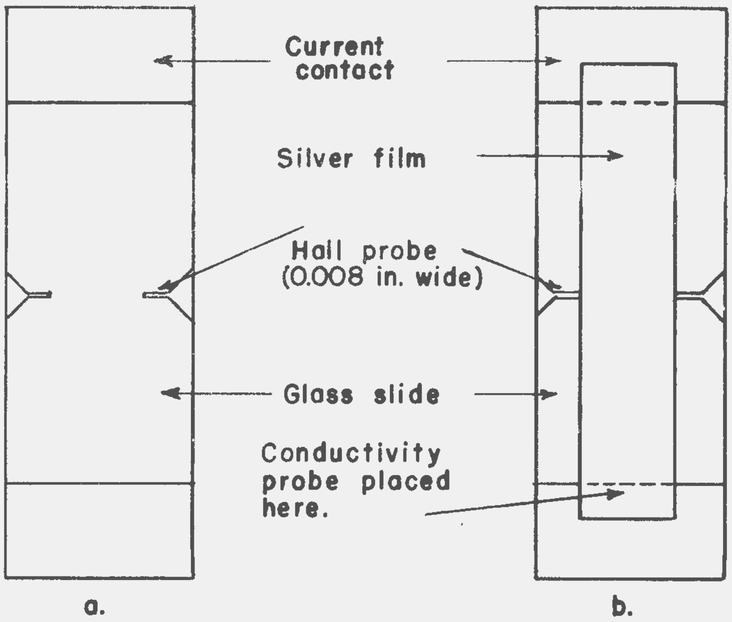

Fig. 3. Arrangement of silver film on glass slide.

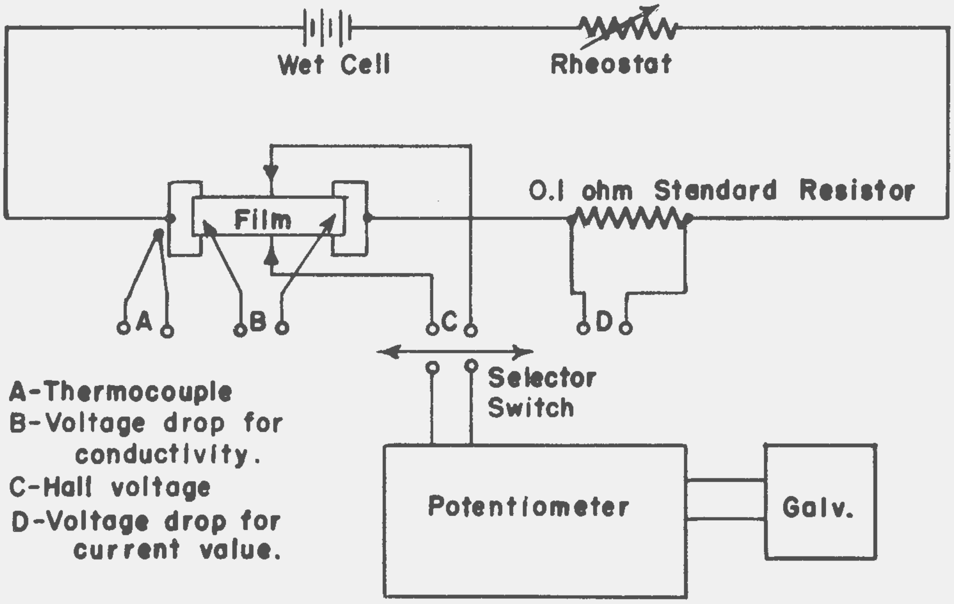

Fig. 4. Circuit for electrical measurements. Magnetic field perpendicular to plane of film.

A filament was constructed by winding approximately two feet of 0.010 in. diameter, 98+% purity, Makepeace, silver wire on a 6 or 7 turn, 0.3 in. diameter, tungsten helix of 0.030 in. diameter wire. A coil of 0.008 in. diameter molybdenum wire was loosely wound over the silver. When the silver melted, surface tension caused it to form membranes stretched between the tungsten and molybdenum wires. The filament was thus able to hold a greater charge of silver and more surface area was provided for evaporation.

After the filament and shielded substrates had been loaded into the vacuum chamber and a vacuum of about 100 microns had been attained, a gas discharge of 70 ma. at about 3000 volts was maintained for 15 min. to further clean the substrates by ion bombardment.

When the vacuum had reached 1 micron a shutter was swung between the filament and the substrates by moving a magnet outside the bell jar. Then the filament was heated just above the melting point of silver for 5 to 10 sec. to prefuse the silver and outgas the filament structure.

Following this, the system was allowed to pump for 10 to 12 hours to allow further outgassing. At the end of this time the vacuum was below the minimum gauge reading, 10^{-2} microns. The shutter was then opened and the films deposited by heating the filament to the evaporation point for 10 sec. or less, depending on the film thicknesses desired. During this heating the gauge continued to indicate a pressure of less than 10^{-2} microns.

Three sets of films including thicknesses from 150 to 1500 A. were prepared by this method and labeled series 130, 140, and 150. The films were stored in a dessicator at normal pressures and temperatures except while measurements were being made.

ELECTRICAL MEASUREMENTS

All electrical measurements were made with the simple DC potentiometer circuit shown in Fig. 4. A Rubicon, Type B Potentiometer was used with a Rubicon, lamp enclosed type galvanometer having a sensitivity of 0.02 microamps. per mm.

For the measurements, the substrate was mounted on a small masonite board which had been sprayed with plastic for waterproofing. Current contact with the film was made through flat, phosphor-bronze clips and connections for Hall voltage and conductivity were made with spring-brass wire clips. It was found necessary to place several layers of aluminum foil between each clip and the evaporated silver contacts to attain a firm, stable connection. A thick layer of General Cement silver paint No. 21-2, an air drying paint, between the evaporated silver and the clips also provided excellent contact at room temperature but tended to flake off when the assembly was cooled.

The electrical measurements were made in two stages.

First, a film was mounted in the holder and the assembly placed in the magnetic field. A current of 0.01 amps. to 0.2 amps. was allowed to flow for several minutes to insure that a stable condition existed. No heating of the film was ever detected. Readings were then taken of the voltage drop across the film, the voltage drop across the standard resistor, and the Hall voltage. The Hall voltage measurement was repeated with the magnetic field reversed. Three sets of data were taken with the order of the readings varied in order to eliminate any residual voltage drift effects. The film and holder were then immersed in liquid nitrogen contained in a dewar located between the poles of the magnet and the series of measurements repeated at this temperature. After being removed from the liquid nitrogen, the sample was warmed to room temperature and the condensed moisture evaporated off by a small blower. The room temperature measurements were repeated to check for any irreversible effects of the cooling.

After being stored in a dessicator for a period of time from one to three weeks, the film was remounted in the holder and carried through a similar process with the liquid nitrogen being replaced by a dry ice and acetone mixture. A polyethylene bag was used to protect the film and holder from the destructive effect of the acetone. Since the Hall coefficient changes only slightly between room and dry ice temperatures the Hall measurements were not repeated.

Later, several of the films were mounted in the holder at room temperature, measured, dismounted, and then the cycle repeated several times to check the reproducibility of the measurements.

FILM THICKNESS MEASUREMENTS

After all electrical measurements had been completed the thickness of each film was measured by the interferometer method that has been adequately discussed and described by Tolansky (4). The step in the film was produced by making a scratch with the sharp corner of a microscope slide. This produced a sharp break in the film without damaging the substrate.

Some evidence was obtained to indicate that errors can be introduced into the thickness measurements if the top layer of silver is more than 800 or 900 A. thick. This problem should be studied further.

The equipment used here for these measurements has been described by Bearinger (5).

ELECTRON DIFFRACTION AND MICROSCOPY

A study of some of the chemical and physical properties of the thinner films was undertaken to check the continuity and purity of the films. Samples for study were obtained by placing on each substrate several nickel, electron-microscope screens covered with a thin collodian film. Sennett and Scott (6) have indicated that the physical character of deposited films is the same for all smooth, amorphous substrates so a film on collodian will reveal the nature of the film on glass. The covered screens were examined in an RCA, EMU Electron Microscope which could be used for either microscopy or diffraction.

EXPERIMENTAL RESULTS

The electron microscope screens were examined immediately following the deposition of the films, after several weeks aging, and after immersion in liquid nitrogen. The diffraction studies revealed a small amount of impurity which has been tentatively identified as WO_3 in the films of series 130 but none in the films of the other series. This is presumably due to the fact that the tungsten filament was maintained at a higher temperature and for a longer period of time for the series 130 evaporation than for the others.

The electron micrographs of the films were similar to those of Sennett and Scott. Aggregation was evident in films below 200 A. in thickness, although enough contact was maintained between the individual particles to allow films as thin as 150 A, to conduct. The particles of the films thinner than 150A. were about 100A. in diameter.

No changes were noticed in the films after aging or immersion in liquid nitrogen. The effects of immersion on films deposited on collodian and on glass are probably different however because of the differences in the expansion coefficients.

Summaries of the results of the electrical measurements are shown plotted in Figs. 5 and 6. The thickness of each film was measured to within 3% or less. At any one time the electrical measurements could be reproduced to within 2%. Over the period of aging and immersion some values changed as much as 5%, however no trends predominated in the changes of the Hall coefficients or the conductivities; some varied monotonically up or down, some randomly, and some not at all.

The values for the resistivity of bulk silver shown in Fig. 5 were taken from The Handbook of Chemistry and Physics (7). The values for the Hall coefficient of the bulk material in Table I were averaged from those given in The International Critical Tables (8). In Table I are given the values of the constants for bulk silver which are necessary for the experimental plots shown in Figs. 1 and 2.

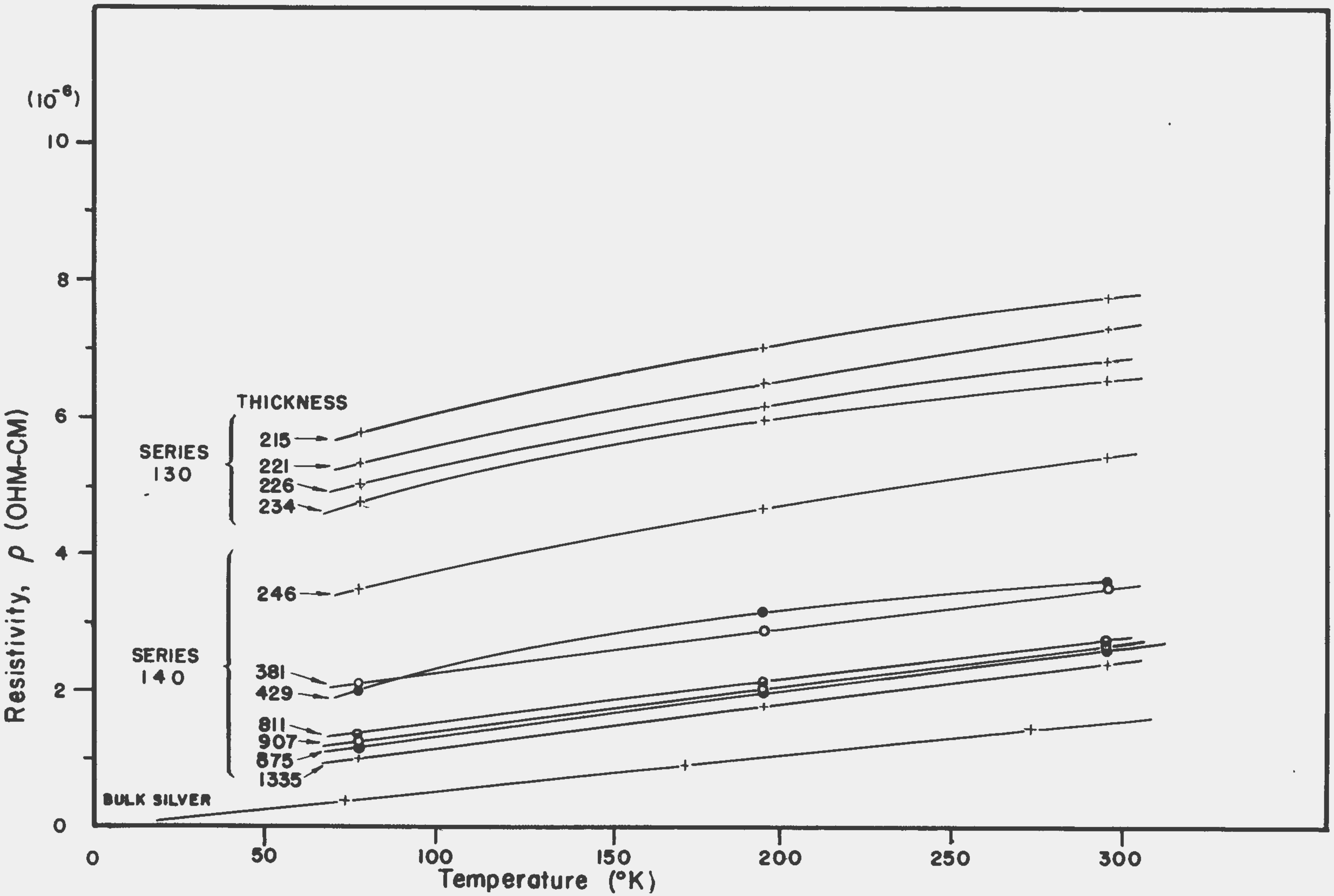

FIG. 5. TEMPERATURE DEPENDENCE OF RESISTIVITY OF THIN SILVER FILMS

TABLE I
Electrical Constants for Bulk Silver

Temperature ($^\circ$K)	77	195	295
ρ_0 (ohm-cm)	$.38(10^{-6})$	$1.02(10^{-6})$	$1.60(10^{-6})$
A_{H_0} (cm^3/coulomb)	$.92(10^{-4})$	$.88(10^{-4})$	$.84(10^{-4})$
μ (cm^2/volt-sec)	240	86	53
n (electrons/cm^3)	$6.8\ (10^{22})$	$7.1(10^{22})$	$7.4(10^{22})$
$n^{1/3}$ (1/cm)	$4.1\ (10^{7})$	$4.1(10^{7})$	$4.2(10^{7})$
ℓ (Angstroms)	450	710	2000

It is interesting to note that for the linear portion of the curves in Fig. 6, the change in Hall coefficient with temperature is nearly the same as for bulk materials and that the change is independent of thickness. If the Sondheimer prediction were true, one would expect the change to be larger for the thinner films.

The sharp break in the region of 300 A. in the curves which show conductivity or Hall effect as a function of thickness is probably due to aggregation causing a physical change in the films. In this region the data are a function of the contact between particles as well as the properties of the particles themselves. A project is now being planned in which films will be deposited on substrates at liquid nitrogen temperatures and maintained at that temperature while electrical measurements are made.

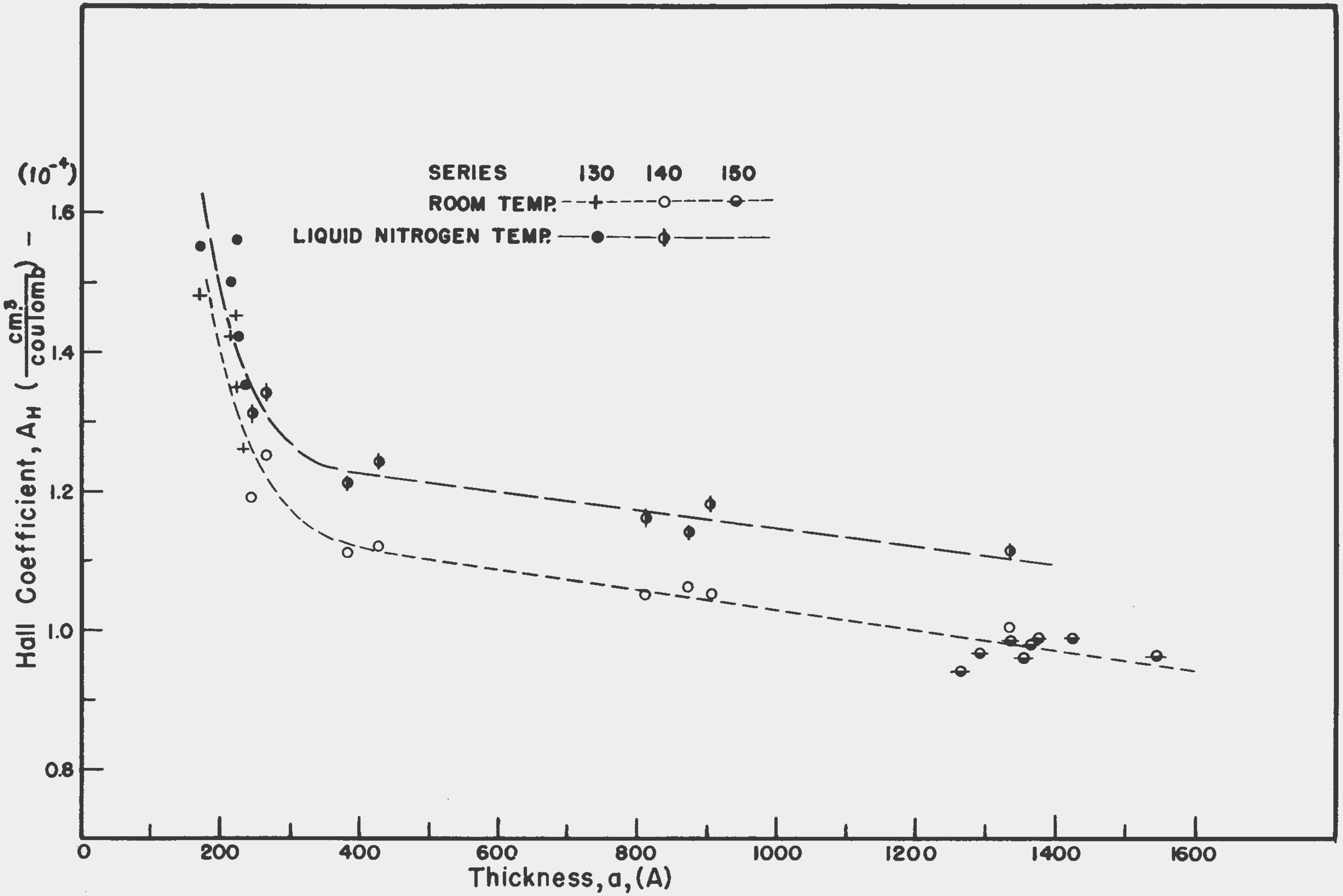

FIG. 6. HALL COEFFICIENTS OF THIN SILVER FILMS.

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