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THE PREPARATION AND PROPERTIES

OF

THIN FILMS OF SEMICONDUCTORS

by

E. Brock Dale

Kansas State University
Department of Physics
Manhattan, Kansas

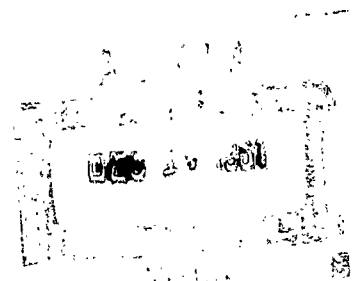
Scientific Report No. 1

Contract No. AF 19(604)-7218

September 1, 1961

Prepared for

ELECTRONICS RESEARCH DIRECTORATE
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
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THE PREPARATION AND PROPERTIES OF THIN FILMS OF SEMICONDUCTORS

ABSTRACT

InSb films have been grown on glass substrates by the vacuum evaporation of bulk InSb. The Hall coefficient and conductivity of annealed films have been measured as a function of temperature in the range 80°K to 500°K.

The variation of R and σ during annealing has been studied. In most cases, annealing below 130°C causes the conductivity to drop slightly. Annealing at 130°C causes the conductivity to rise abruptly, pass through a maximum, and then decrease at a rate several times slower than the initial rise at that temperature. Further annealing at any higher temperature causes a further decrease in σ . The Hall coefficient is usually too small to measure until the films have been annealed at 200°C or higher. At this temperature, the Hall coefficient rises toward some asymptotic value. At higher annealing temperatures, the asymptotic value is increased.

The conductivity of annealed films at room temperature varies from .04 to 68 ohm⁻¹cm⁻¹, and the Hall coefficient from 0.07 to 770 cm³/coulomb. Both n- and p-type films have been obtained, and the majority of the p-type specimens do not become n-type at any temperature below the annealing temperature. Only two of the films measured have become intrinsic within the accessible temperature range.

The Hall mobilities measured lie between 0.5 and 125 cm²/volt sec. The mobility in all films but one has increased with increasing temperature. This behavior is tentatively ascribed to the predominance of impurity scattering. Some inconsistencies between values of the intrinsic carrier concentration calculated from our data and those predicted by the theory of slightly degenerate semiconductors have been noted.

THE PREPARATION AND PROPERTIES OF THIN FILMS OF SEMICONDUCTORS

Introduction

In the work described here, InSb films have been grown on glass substrates by evaporation of the compound, and their electrical and crystalline properties have been compared with those of the bulk material.

A bewildering array of variables is always encountered in thin-film work, and these are multiplied in the case of a two-component system, such as InSb. The sensitivity of the electrical properties of semiconductors to structure and impurity concentration makes them, in a sense, well suited to the study of growth variables. This same sensitivity also complicates the study because it places stringent requirements on the degree of control that must be attained in order to render the measurements interpretable.

Freedom of the substrate from possible contaminants is of major importance. In a film 1000A thick, for example, a monatomic layer of a contaminant amounts to a substantial fraction of one per cent of the atoms in the film. Another major source of variations is the time and temperature of annealing. These conditions influence the degree to which the components react after deposition, the crystallite size, degree of agglomeration, and density of the film. A third source of variations lies in the conditions of deposition. It has been reported that, whereas rapidly deposited films tend to be homogeneous, very slowly evaporated films tend to be stratified, almost pure antimony being deposited at the beginning and almost pure indium at the end. Furthermore, at very low evaporation rates or high substrate temperatures re-evaporation of atoms from the substrate occurs before a monomolecular film has been laid down. This can affect the stoichiometry of the film, since the re-evaporated material does not find its way back to the substrate. In the work to be described, we have attempted to keep the atomic proportions of indium and antimony equal at all cost, and this has in some cases limited the conditions of preparation of the films.

Apparatus and Methods

Evaporations are carried out in a bell jar system, evacuated with a diffusion pump using silicone oil. The ultimate vacuum is about 2×10^{-6} mm. Crystalline InSb is charged to a crucible carved from reactor grade graphite. A line drawing of the crucible is shown in Figure 1. The massive wings provide a high-conductance path to the crucible and also, due to their large heat capacity, help to prevent overheating of the metal electrodes. The rim around the top of the crucible proper helps to keep the charge in the crucible. This is a problem whenever the crucible material is not wetted by the evaporant. The problem becomes more serious as the temperature of evaporation is increased or the charge of evaporant becomes smaller, e.g., near the end of an evaporation.

The crucible is outgassed by heating during evacuation. The substrate is protected from foreign materials that may boil off the crucible by a metal shield. The shield and the simple apparatus for loading the crucible under vacuum are controlled from outside the system by magnets.

The substrate is sandwiched between a mask and a heater, which is used for annealing. The hole in the mask, through which the film is deposited, is rectangular, 0.3 x 2.0 cm, with transverse slots on each side so that Hall and resistivity probes are deposited simultaneously with the film. A hole is cut in the mask near the rectangular slot to provide space for a thermocouple. The thermocouple (copper-constantan) is cemented to the part of the substrate exposed by the hole with Eccobond 58C, a high-conductivity metal-filled resin.

The heater is made of porcelain with a number of parallel grooves cut into one side. Resistance wire is threaded through the grooves and covered with ceramic cement. The ungrooved side of the porcelain is lapped flat so as to make good contact with the substrate.

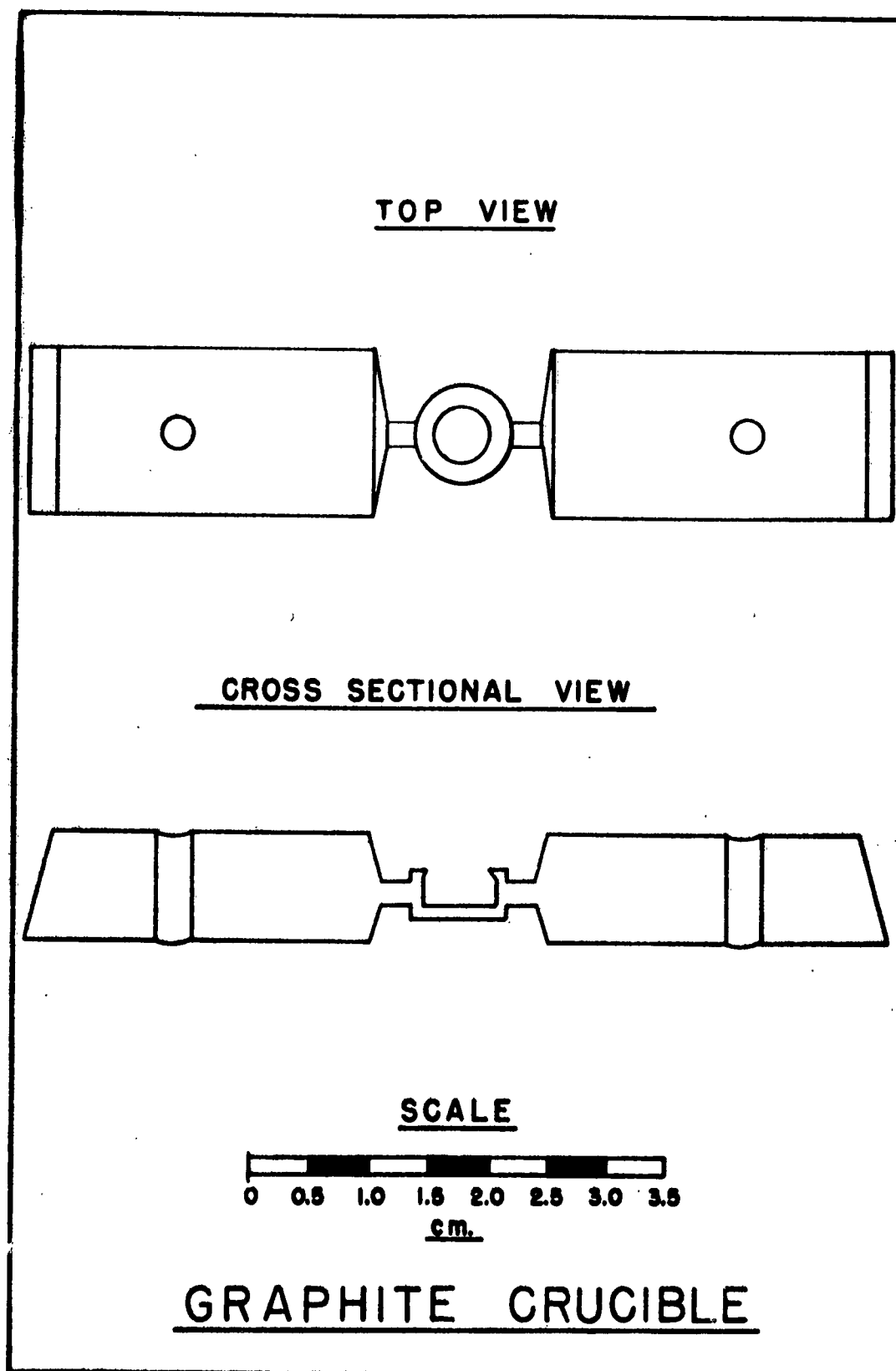


Figure 1. Graphite crucible used for evaporating InSb.

The substrates are made by cutting microscope slides into thirds. After attaching thermocouples, they are cleaned by vigorous washing in a boiling solution of strong detergent, followed by many rinses with hot distilled water. A closed glass and plastic system has been built up which allows washing and rinsing without handling the substrates. After this cleaning process, they exhibit a uniform breath figure for a short time, until contaminated by dust particles, etc., in the air. This does not imply that the surfaces are atomically clean, but it is as much as can be accomplished without ion bombardment or drastic heating. The substrates are heated under vacuum before deposition. This serves to outgas the annealing heater and to drive off vaporizable materials such as water vapor, adsorbed on the substrate.

In preparing a film, the following procedure is customarily followed: The cleaned substrate is removed from the cleaning apparatus, allowed to dry in air, and mounted in the vacuum system. Another plate is mounted alongside the substrate, an equal distance from the crucible, for subsequent use in thickness measurement. The shield is put in place over the crucible, and one or more small pieces of InSb are placed in the sample hopper. Freshly broken pieces are used, and they are not etched because, under the circumstances, etching might well introduce more impurities than it removed. After the system is pumped down to 10^{-5} mm, the crucible repeatedly is outgassed for short periods of time at 1000 degrees C or higher, and the substrate and heater are simultaneously baked out at 300 to 400 degrees C. As these cool to room temperature, the pressure in the system goes down to about 2×10^{-6} mm. The shield is then removed and the charge is dumped into the crucible. Evaporation is carried out at about 1400 degrees C. At this temperature, a film 2000 angstroms thick is evaporated in about two minutes. Higher temperatures would be desirable but are impracticable when using a crucible that is not wetted, because, as evaporation is carried out, the remaining evaporant becomes smaller and smaller in volume, and its motion about the crucible (presumably analo-

gous to the dancing of a water droplet on a hot stove) becomes more vigorous.

It has been reasonably well substantiated that, during the evaporation of InSb, the first material evaporated is antimony-rich, and the last part is indium-rich. Therefore it is essential to the stoichiometry of the film that all of the charge be evaporated, and one cannot tolerate temperatures that would cause part of the charge to be lost from the crucible during the evaporation.

After evaporation, the film is annealed. Various annealing times and temperatures have been used. This subject is discussed in detail in a later section.

After annealing, the film is mounted in the cryostat*, where copper current, voltage, and Hall leads are attached by means of silver paint. Thermal contact between the substrate and the copper cold finger of the cryostat is maintained by means of a film of Dow-Corning high vacuum grease. A drawing of the cryostat is shown in Figure 2. It is evacuated by means of a diffusion pump. A copper tube connected to the coolant (liquid nitrogen) reservoir is silver-soldered around the periphery of the cold finger to help maintain a uniform temperature distribution at liquid nitrogen temperature. Measurements between this and room temperature are made as the apparatus warms up after the nitrogen is exhausted, or by using various fixed-melting-point mixtures. Temperatures above room temperature (up to 250 degrees C.) are obtained by means of a heater similar to the annealing heater already described, cemented to the back of the cold finger.

Not all of the films discussed in this report have been prepared exactly according to the procedure just outlined, which has developed gradually over the past year. Significant deviations from this procedure, along with other pertinent data for the films discussed, are noted in Table I.

*The films discussed in the next section were annealed in the cryostat after leads had been attached.

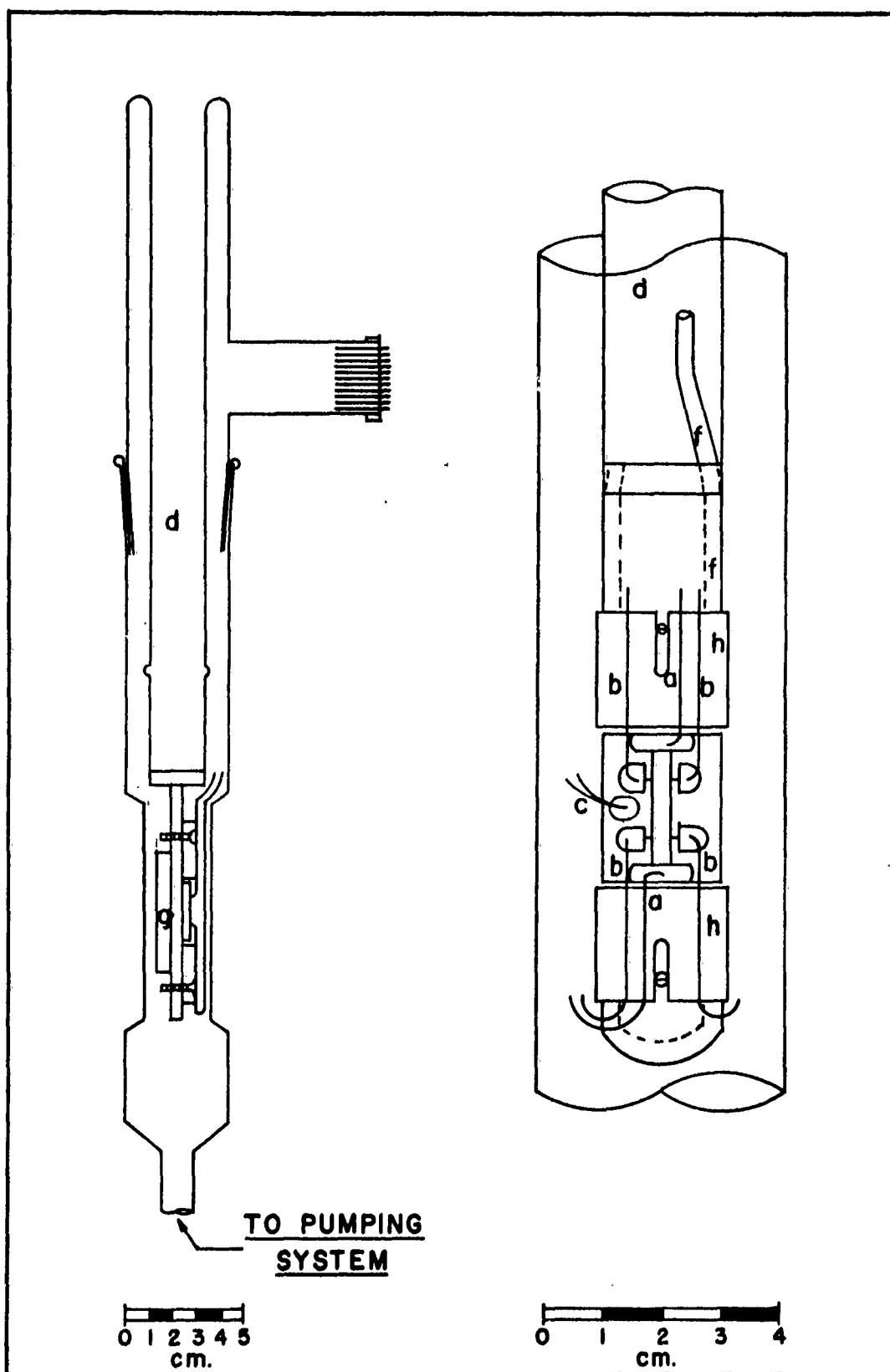


Figure 2. Liquid nitrogen cryostat and heating assembly for measuring Hall Coefficient and conductivity as a function of temperature. (a) Current probes. (b) Voltage probes. (c) Thermocouple. (d) Nitrogen reservoir. (e) Cold finger. (f) Copper tube silver-soldered around periphery of cold finger. (g) Heater (not shown on enlarged drawing.) (h) Ceramic slabs. Probes are cemented into grooves in these slabs.

Table I. Summary of film properties and preparation data

Film No.	Type	Thick- ness, A	Annealing Time and Temp.	R at 27°C.	σ at 27°C.	R at 27°C.	Evap. Time	Remarks
S-103	n	1400	30 min., 250°C.	0.6	125	125	80 sec.	Crucible outgassed 30 min. below 500°C. Substrate out- gassed briefly at 250°C.
S-113	p	3750	2 hr., 250- 270°C	7.4	2.8	21	200 sec.	Substrate and Crucible not outgassed
S-119	p	1460	See Fig. 3	1.5	5.3	8	135 sec.	Ditto
S-S	p	1200	See Fig. 3	34	0.9	31		
S-127	p	1400	See Fig. 4	21*	0.69	15*	180 sec.	Substrate not outgassed.
S-143	p	550	See Fig. 4	770*	0.04	32*	95 sec.	
D-1	n	1170	See Fig. 3	105	0.15	15.5	120 sec.	
D-13	p	2950	See Fig. 4	0.066 before 237° anneal, 0.093 after.	6.8	0.5, 0.7	120 sec.	

*Stray emf's in the measuring circuit interfered with these Hall measurements, which probably are meaningless.

Effects of Annealing Thin Films of InSb

When a freshly deposited film of InSb is heated, its properties are irreversibly changed. This effect has been commented upon by Launay and Columbani, (1) who report that the conductivity decreases abruptly and irreversibly when the films are heated to about 150°C . These authors also report that after a film has been heated to a given temperature, its conductivity changes in a reversible fashion as the temperature is changed, at all temperatures below the maximum temperature. We have found this to be approximately the case, as long as one does not skirt the maximum temperature too closely.

We have investigated the changes that take place in the films as they are annealed in a stepwise fashion. The temperature was increased in steps, and the change in the conductivity and Hall coefficient with time at each temperature was monitored. Annealing curves for the films discussed are shown in Figures 3 and 4.

It was found that each time the temperature is raised, there is an immediate increase in the conductance. At 130°C and below, the initial increase usually is followed by a nearly exponential decrease toward some equilibrium value. When the temperature is raised above 130°C , the initial increase as the temperature is raised is followed by a further rapid increase of conductance with time, reaching a maximum after two to three hours. After reaching the maximum, the conductivity begins to decrease toward some asymptotic value. Any further stepwise increases of the temperature cause an immediate increase in the conductivity, followed by an increased rate of decline.

These further increases in the temperature (i.e., beyond 135°) may cause either an increase or a decrease in the asymptotic (i.e., equilibrium) value of the conductivity, but the increase in the asymptotic value, when it occurs, is always less than the increase in conductivity that takes place simultaneously with the rais-

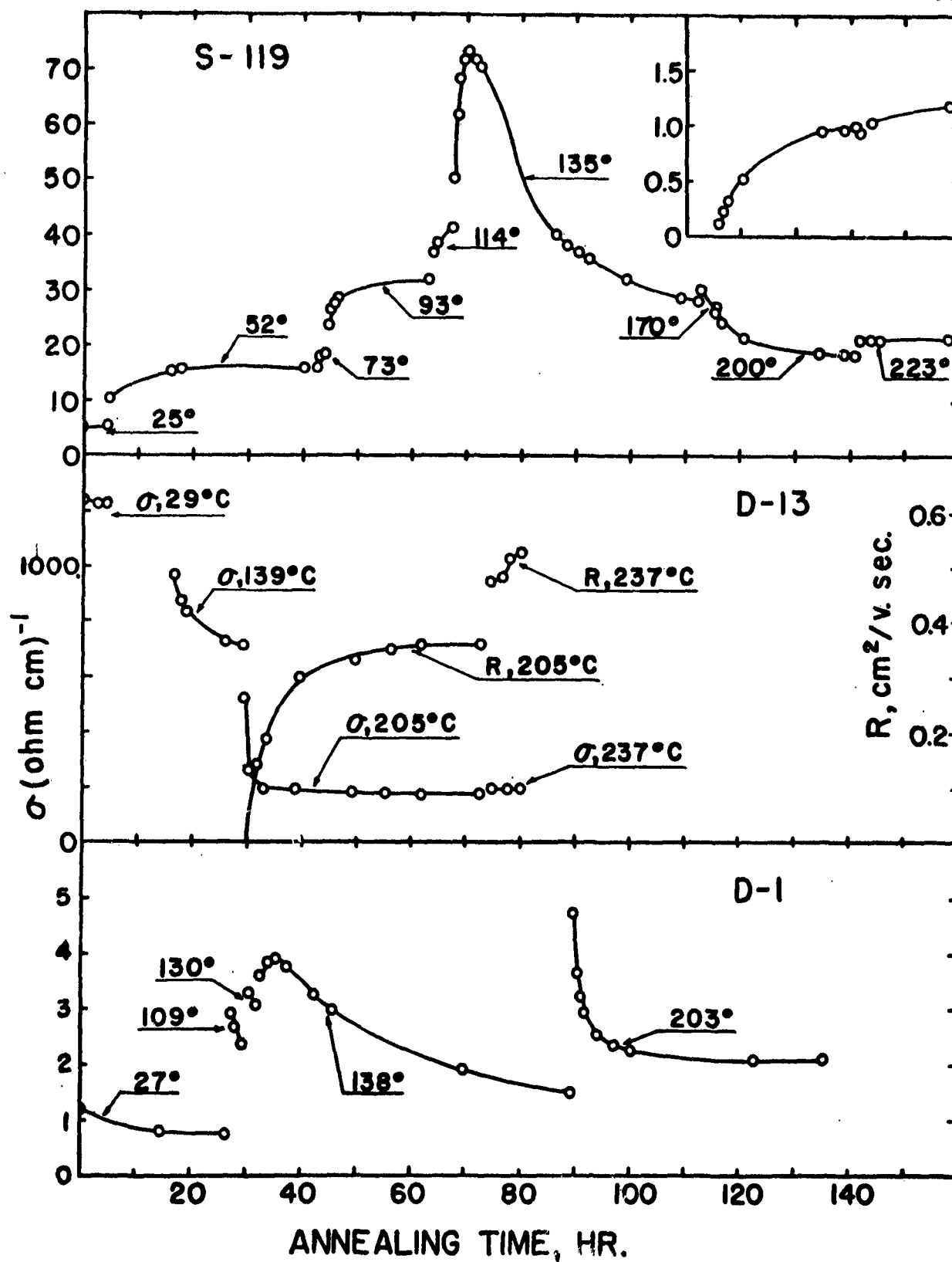


Figure 3. Annealing curves for InSb films S-119, D-13, and D-1.

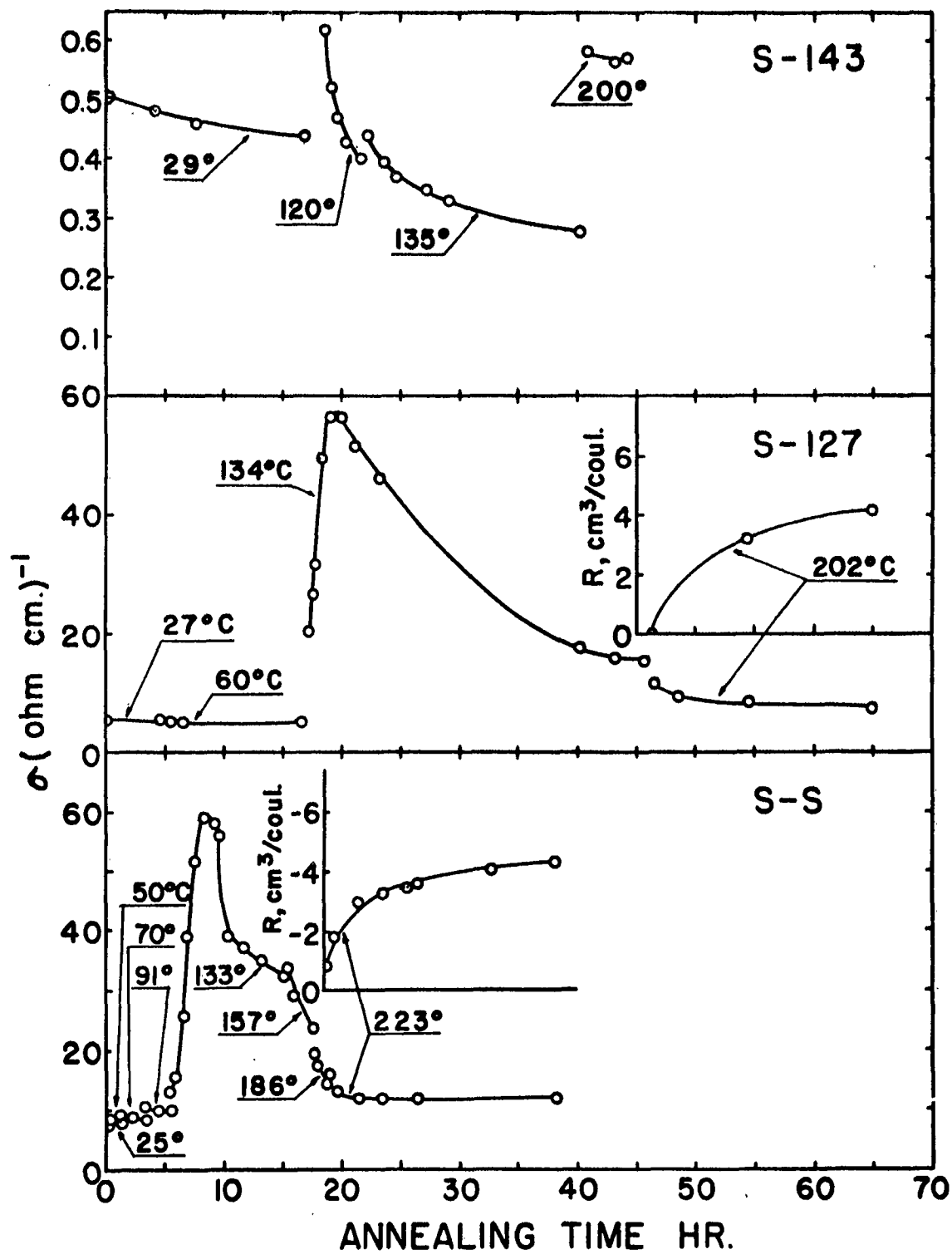


Figure 4. Annealing curves for InSb films S-143, S-127, and S-S.

ing of the temperature. The net effect of raising the temperature of annealing, after one has passed the 135-degree maximum, is usually a decrease in the final conductance at a given temperature. In film D-13 (Figure 8) the conductivity curves after annealing at 205°C and 237°C cross each other, the curve made after annealing at 237°C being slightly higher at the ends of the curve, and the curve taken between the 205°C anneal and the 237°C anneal slightly higher near the center of the curves, in the region near room temperature.

The Hall coefficient remains near zero until an annealing temperature in the neighborhood of 200°C is reached. It then begins to increase toward some asymptotic value, (positive or negative). Increasing the annealing temperature causes an increase in the asymptotic value of the Hall coefficient, and in the Hall coefficient at temperatures below the annealing temperature (Figure 9).

We have not observed an instance of change of sign of the Hall coefficient during these final stages of annealing.

As previously implied, the behavior just described is representative of that of most, but not all of the films that have been monitored during annealing. The most drastic deviations are noted in films S-119, S-143, and D-13. Whereas the conductivity of the "normal" films decreases with time at any temperature below 130°C, that of film S-119 increased with time. As with all other films, its conductivity tended to level off after sufficient time at a given temperature. Film S-143 did not pass through a maximum of conductivity at 130°C. Rather, its conductivity decreased with time after the initial rise that took place while the temperature was being raised from 29 to 120°C. We believe that in this case the maximum was traversed while the temperature was still rising. It may be significant that film S-143 is the thinnest one (550A) for which annealing effects have been studied.

Film D-13 did not pass through a conductivity maximum at all. Its conductivity at room temperature before annealing was higher than at any subsequent time. Its initial conductivity ($605 \text{ ohm}^{-1}\text{cm}^{-1}$) was two orders of magnitude greater than that of any of our other films. In common with film S-143 (initial conductivity, $0.5 \text{ ohm}^{-1}\text{cm}^{-1}$), its conductivity decreased upon aging at room temperature. Even so, it is not likely that any appreciable amount of annealing took place during the deposition of the film, since the maximum temperature reached during deposition was 31°C .

Structure Changes During Annealing

Films deposited on collodion substrates, so that they can be observed by transmitted electron diffraction, show only the broad, diffuse, rings characteristic of amorphous films. After a few seconds exposure to the electron beam, the characteristic lines of InSb appear, and after a few minutes, these lines have broken up into spots, indicating that the beam is being diffracted by a few single crystals. Films deposited on glass substrates are examined by reflected electron diffraction. In this case, the unannealed film is not initially amorphous, but shows a clear InSb ring pattern, with extra rings showing the presence of indium in the film. The pattern does not change over a few minutes time. Partially annealed films, in which the annealing was stopped near the point of maximum conductivity, show only rings due to InSb. Films that have been carried through the entire process described above, frequently exhibit only the amorphous pattern. On occasion, a rather poorly defined, complicated ring structure is found superimposed on the amorphous pattern. We have not yet been able to identify this structure, other than to ascertain that it is not In, Sb, or InSb. However, the films, which usually do not show interference colors before annealing, frequently do show such colors after annealing, and it seems not improbable that both the interference colors and the unidentified electron diffraction pattern are due to oxides formed on the surface during annealing.

Electrical Properties of some Selected InSb Films

In bulk InSb, even highly impure material, one finds that the Hall coefficient and the conductivity become essentially independent of the temperature at low temperatures. In many of our films R continues to increase and σ to decrease monotonically, all the way down to liquid nitrogen temperature. This effect is observed in the conductivity curves for films S-103, S-119, S-113, S-S, and D-1, Figure 5. The temperature variation of the Hall coefficient of the same films is shown in Figure 6. These curves do not extend much below room temperature because instrumental difficulties cast some doubt on the validity of such Hall measurements as we were able to make at low temperature. Low temperature Hall measurements are frequently impossible because the film resistance becomes so large that the sensitivity of the potentiometer is inadequate for the measurement of small voltages.

Film D-113 is p-type at room temperature. Its Hall coefficient changes sign at about 300°K. The maximum of R at $1000/T \approx 2.1$ is probably spurious, since the Hall coefficient of this film at all temperatures was found to have decreased after the high temperature measurement. Film S-S is still p-type at the highest temperature at which it was measured, as is S-119.

Films S-103 and D-1 appear to be intrinsic in the 300-500°K range. The carrier concentration $n = 1/eR$ at 400°K is 9.2×10^{16} for S-103 and 1.95×10^{17} for D-1. These are reasonably near the value of $n_i = 8.7 \times 10^{16}$ calculated on the basis of Howarth's estimate: (2)

$$n_i^2 = 1.8 \times 10^{32} (T/290)^3 \exp \left(-0.255/k \right) \left((1/T) - (1/290) \right)$$

The energy gap computed from $\Delta E_0 = \frac{2k}{\log_{10} e} \frac{d}{d(1/T)} (\log_{10} RT^{3/2})$ is 0.24 ev

for S-103 and 0.27 for D-1. These values compare quite well with the value

$\Delta E_0 = 0.255$ ev given in the equation above. The low mobility in these films suggests that, even though intrinsic at 400°K, they are quite impure. The shapes of the

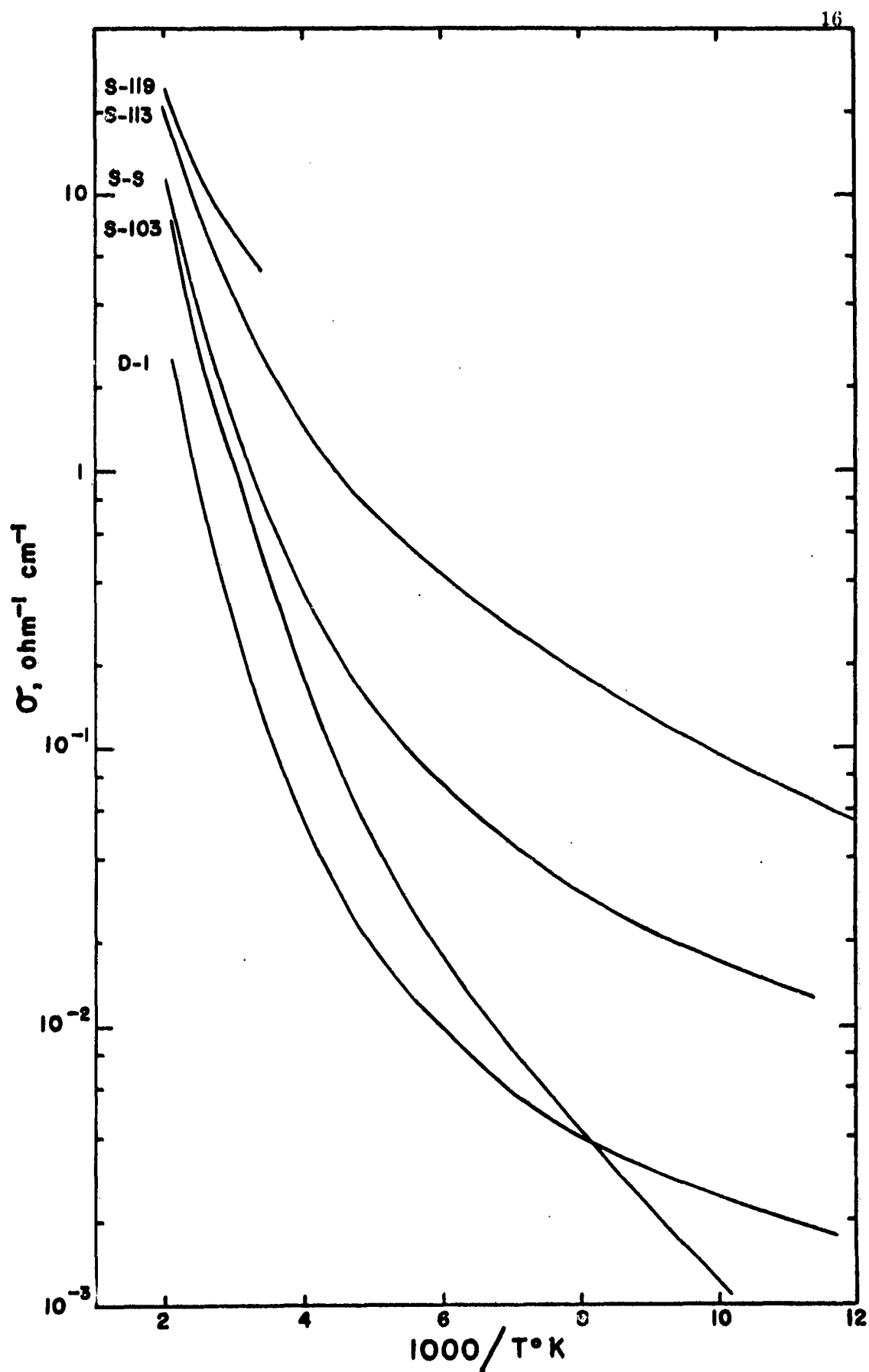


Figure 5. Variation with temperature of the conductivity of several annealed InSb films.

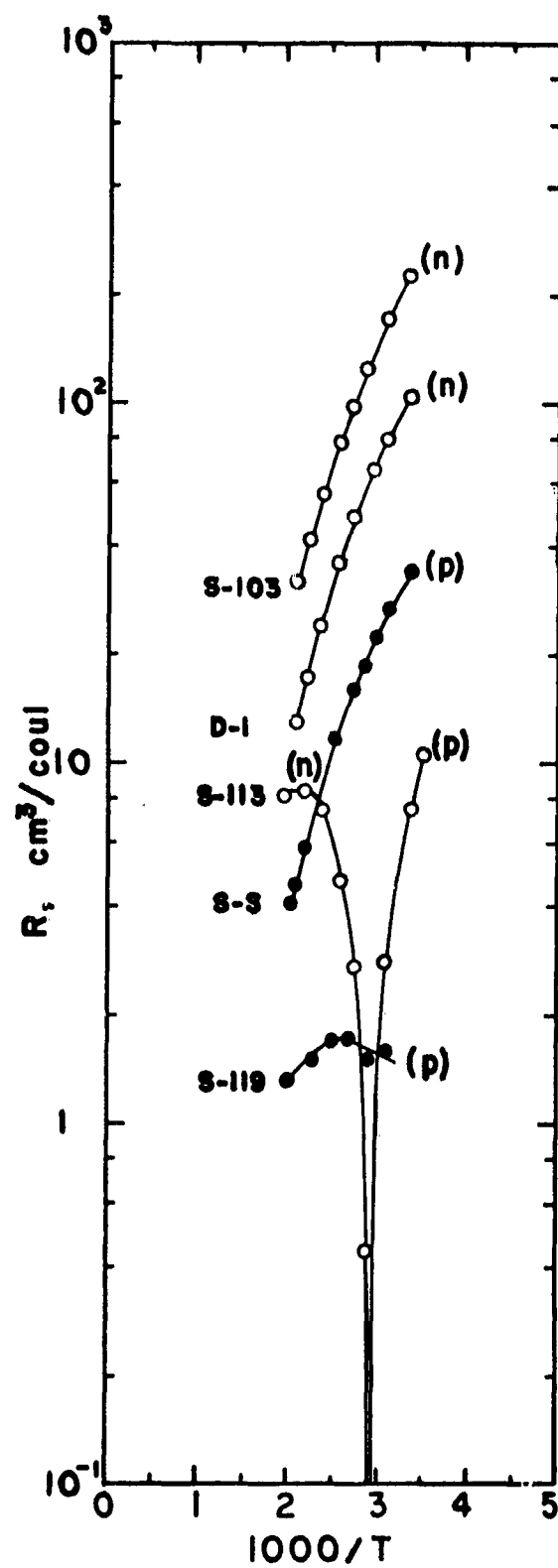


Figure 6. Variation with temperature of the Hall Coefficient of several annealed InSb films.

mobility curves for these two films (Fig. 7) are quite similar, although the mobility in S-103 is nearly an order of magnitude greater than that in D-1. In both films, the mobility increases with increasing temperature, as one would expect if impurity scattering were predominant. The logarithmic slope, $d(\log R\sigma)/d(\log T)$, is 2.5 for D-1 and 2.8 for S-103 at the low-temperature end of the curves. The slopes are near unity for both curves at the high-temperature end.

The thinness of the films does not directly influence the mobility in our films. The mean free path, given in terms of the mobility, is $L = 10^{-7}(\mu/4e)(2\pi m^*kT)^{1/2}$, or about $10^{-9}\mu$ for $m^* = .03$ electron masses and $T = 300^\circ\text{K}$. Thus for observed mobilities of 10 to 1000 $\text{cm}^2/\text{v sec}$, the mean free path is 10^{-8} to 10^{-6}cm , and consequently one would expect the contribution of the surface to scattering to be negligible in our films, which are of the order of 10^{-5}cm thick. If films are produced in which the mobility is upwards of 10,000 $\text{cm}^2/\text{v sec}$, a measurable effect due to surface scattering can, of course, be expected.

The possibility exists that the low mobility is due to scattering at the crystallite boundaries. In this case, the mean free path would be independent of the temperature, and the mobility would be proportional to $[T^{1/2}m^*(T)]^{-1}$. We plan to make a detailed investigation of this possibility.

In recent weeks, the sensitivity of the Hall apparatus has been improved somewhat, facilitating measurements at low temperature, and better control of the annealing procedure has been achieved by monitoring the conductivity and the Hall coefficient as annealing proceeds. Some recent results are illustrated in Figures 8 and 9, which show curves for film D-13 in two stages of annealing. These curves resemble, at least superficially, the corresponding curves for bulk InSb. From the Hall coefficient in the exhaustion region, the excess acceptor concentration in the film, after annealing at 205°C , is calculated to be

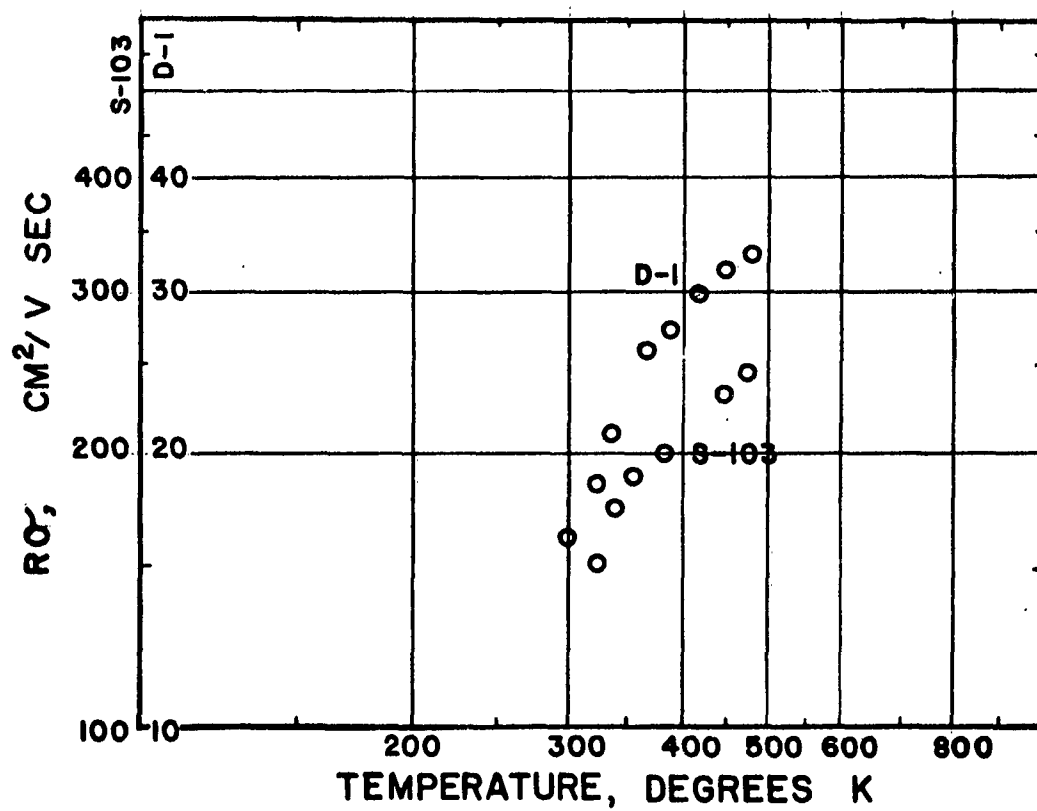


Figure 7. Variation with temperature of the Hall mobility of nearly-intrinsic n-type InSb films.

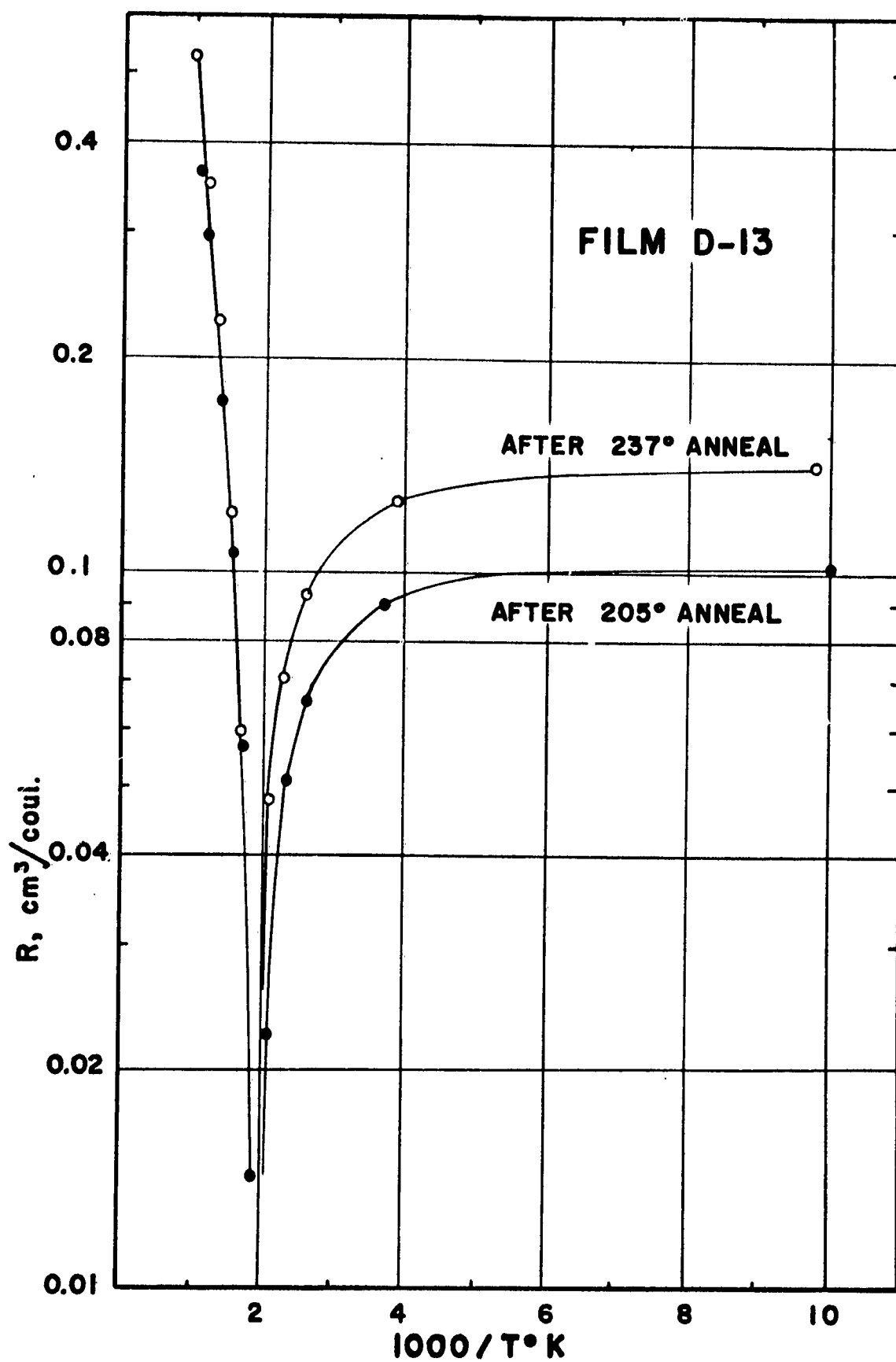


Figure 8. Comparison of the temperature dependence of the Hall Coefficient in InSb film D-13 after annealing at 205°C and at 237°C .

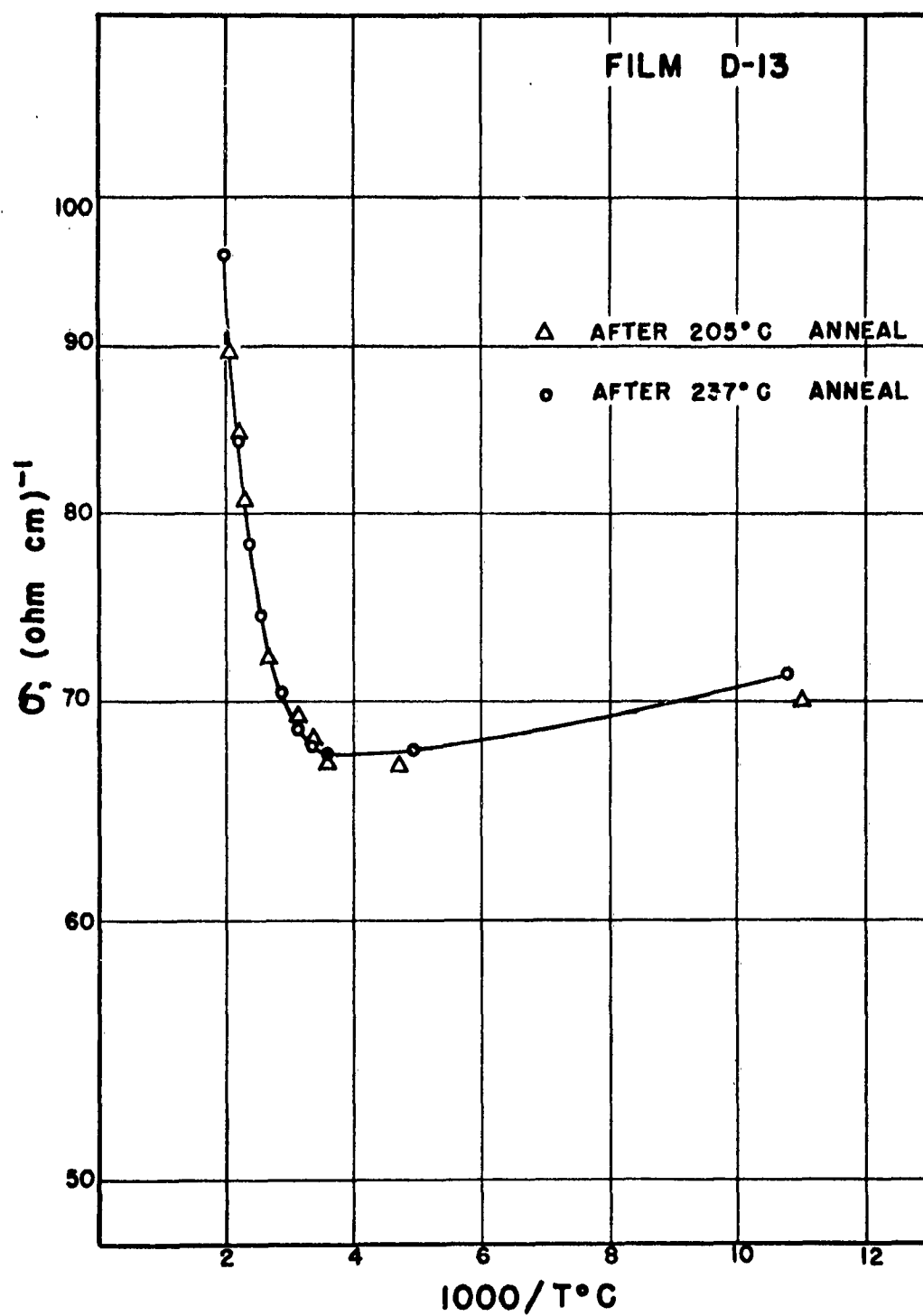


Figure 9. Comparison of the temperature dependence of the conductivity of InSb film D-13 after annealing at 205°C and at 237°C.

$N_a - N_d = 1/eR = 6.3 \times 10^{19}$. An impurity concentration of this magnitude places the material so far into the degenerate region that the asymptotic formulas valid for non-degenerate or slightly degenerate semiconductors can scarcely be expected to apply. However, an order-of magnitude comparison of constants derived on the basis of these curves is of interest.

The Hall mobility, $R\sigma$, in the exhaustion region decreases as T increases; however, this decrease is associated with the change of sign of R . One can calculate a different value of μ from R and σ , assuming that $p-n = N$, the excess acceptor concentration over the donor concentration.* This procedure results in a nearly constant mobility between 100°K and 400°K. The two mobility curves are shown in Figure 10.

In p-type InSb, the Hall coefficient goes through a maximum as the temperature is raised beyond that at which R changes sign. At the maximum $\frac{\partial R}{\partial n} = 0$ and the value of R at the maximum can be shown to be $R_{\max} = -(b-1)^2/4b(N_A - N_D)$. Breckenridge (3) has used this relation and the fact that, in the exhaustion range, $R_{\text{ex}} = \frac{1}{e(N_D - N_A)}$ to obtain the mobility ratio $b = \mu_n/\mu_p$; thus, $R_{\max}/R_{\text{ex}} = -(b-1)^2/4b$. For bulk InSb, b lies between 30 and 100. The measurements on film D-13 do not extend to the maximum of R ; however, a lower limit to b can be calculated by using the highest measured value of R instead of $R_{\max}$. This shows b to be greater than 15. At the temperature at which $R = 0$, (335°K for D-13,) $p = nb^2$. Using Howarth's values (2) for m_n , m_p , and the variation of ΔE with temperature as before, $n_i = 3.2 \times 10^{16}$ at 335°K. From these two equa-

* $\mu = R_{\text{ex}}\sigma \frac{b-1}{b} + \frac{R\sigma}{b-1}$ For these calculations and those that follow, we have used the data for the film after annealing at 237°C. The value of R_{ex} is taken to be that at the lowest temperature at which it was measured (93°K,) i.e., $R_{\text{ex}} = 0.14 = 1/Ne$. For Figure 10, we have assumed $b = 15$.

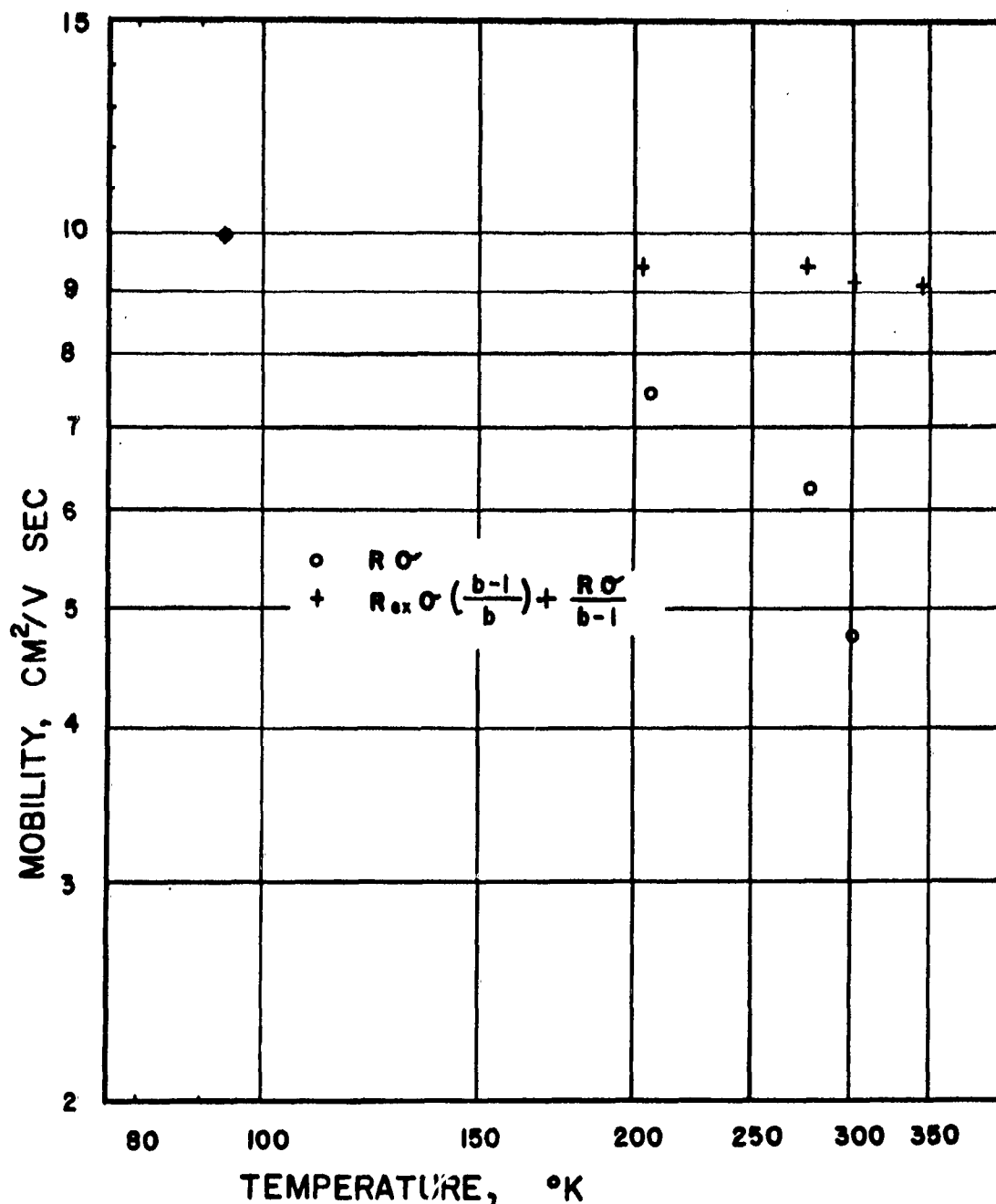


Figure 10. Hall mobility in (1-type) film D-13. Ordinates of the lower points (circles) are the product $R\sigma$. The upper points are computed by assuming $p-n = N_A - N_D$, $R = (p-nb^2)/e(p+nb)^2$, $\mu = \sigma / (nb+p)e$, with $b \approx 30$.

tions, the following values for n and p can be calculated:

<u>Assumed b</u>	<u>n</u>	<u>p</u>
15	2.2×10^{15}	4.8×10^{17}
30	1.1×10^{15}	9.6×10^{17}
100	3.2×10^{14}	3.2×10^{18}

These values are obviously in conflict with the value of $N_a - N_d = 4.5 \times 10^{19}$ calculated from the Hall coefficient at exhaustion.

If one assumes that the observations are correct, and that, at 335°K, $p-n = 4.5 \times 10^{19}$, one obtains $n_i = 4.5 \times 10^{19} b/(b^2-1)$ resulting in values of n_i equal to 3×10^{18} , 1.5×10^{18} and 4.5×10^{17} for b equal to 15, 30, and 100, respectively.

Several plausible explanations of this discrepancy can be formulated: We have used relations for R and n_i outside their range of validity. It is probable that rectification of this error would bring our calculations nearer to consistency within themselves. On the other hand, it is known that the films are agglomerated. Thus the measured properties may represent an average over many microcrystals with different properties, perhaps even of different conductivity types. If this is the case, calculations of impurity concentration based on measurements of R and σ are meaningless. A third explanation is possible in terms of a broad impurity band which overlaps the valence band, and finally, one cannot avoid consideration of surface effects, e.g., an inversion layer, which would be expected to be strongly evident in a thin film. The choice between these alternatives must await the accumulation of more extensive data.

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