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THE EMITTANCE OF GERMANIUM AND SILICON AT LOW TEMPERATURE

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Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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THE EMITTANCE OF GERMANIUM AND SILICON AT LOW TEMPERATURE

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FOREWORD

This is the summary technical report describing work performed under MIPR AS-7-146, "Low Temperature Emittance Techniques and Measurements." The contract as initiated under Project Nr. 7360, "Chemistry and Physics of Materials", Task Nr. 736001, "Thermodynamics and Heat Transfer", and administered by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Mr. Hyman Marcus (MAYT), Project Engineer.

This report covers research conducted from 28 February 1967 to 28 February 1968. Mr. E.R. Schleiger was the principal investigator.

This report was submitted by the authors in July 1968.

The authors express their appreciation to John R. Nichols, who designed the resistivity capsule; to William J. Parker, Raymond S. Alger, James D. Mitchell, and C.P. Butler, who provided technical assistance and advice during the course of the experiment; and, to the members of the Cryogenic Target Group at the University of California Lawrence Radiation Laboratory, who provided the assistance and facilities which made possible the resistance thermometer calibration at the liquid hydrogen point.

This report has been reviewed and is approved.

Hyman Marcus

HYMAN MARCUS, Acting Chief
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ABSTRACT

Emittance measurements as a function of temperature have been performed on germanium and silicon samples representing a wide range of resistivities. In general, emittance was found to increase with increasing temperature and increasing impurity level. The emittance of germanium (p and n-types) at 360°K ranged from approximately 0.2 for a resistivity of 30 ohm-cm to approximately 0.6 for a resistivity of 0.1 ohm-cm. At 34°K, the emittance decreased to approximately one half the above values. Silicon (p and n-types) had comparable values of emittance at 360°K for resistivities of 200 ohm-cm and 0.001 ohm-cm, but at 30°K the emittance values were reduced to approximately 0.03 and 0.1 respectively. Germanium and silicon of intermediate resistivity were found to have intermediate emittance at the high and low temperature extremes, but anomalies were observed in the temperature-emittance relations at temperatures between the two extremes.

The general relation between emittance, temperature, and impurity level has been explained in terms of charge carrier densities. An explanation of the emittance-temperature anomalies has been suggested in terms of the relations between carrier density, carrier lifetime, and emittance.

Distribution of this abstract is unlimited.

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SECTION I

INTRODUCTION

It is very desirable that the emittance characteristics be known for any window material used to fabricate viewing ports for infrared instrumentation in spacecraft. Technical Report AFML-TR-66-148[1] describes a method developed at this laboratory for measurement of total hemispherical emittance of transparent materials over the temperature range 75°K to 312°K. Technical Report AFML-TR-67-200[2] describes refinements of the method which extend its useful temperature range down to 44°K.

The present report presents the results of emittance measurements of two semiconductor materials, germanium and silicon, over the temperature range 25°K to 360°K. The extension of the emittance measurements to a temperature of 25°K was made possible by a comparable extension of the temperature range of the thermocouple calibration. The semiconductors on which the emittance measurements were performed included wide ranges of impurity level and the results thus provide an opportunity to examine the effect of impurity concentration on the emittance-temperature relationships.

SECTION II

EXPERIMENT

Thermocouple Calibration

Technical Report AFML-TR-67-200[2] contains a discussion of the factors which necessitated an "in place" calibration of the alumel-chromel P thermocouples used in the emittance measurements and describes the method used. A brief summary of this discussion follows.

If a thermocouple is to be used to make precise temperature measurements, it is necessary to calibrate the thermocouple wire which is used. The calibration must be made under conditions which reproduce the temperature gradients that exist during the experimental temperature measurements. In this case the calibration consisted of comparing

thermocouple emfs with the temperature as indicated by a platinum resistance thermometer with which the couples were in thermal contact. The desired reduction of temperature gradients was accomplished by placing both the platinum resistance thermometer and the couples in a copper capsule suspended from the trapeze within the same experimental chamber which was used in the emittance measurements. Thus at any given capsule temperature the thermal gradients in the thermocouple circuit were the same as those existing when the temperature of the emittance specimen was being measured.

The procedure used in the calibration was that previously described[2] except that the thermocouple calibration was made over a greater range (20°K to 367°K) than was covered in the previous work (40°K to 308°K). The 40°K lower limit of the earlier thermocouple calibration represented the estimated limit of reliability in extrapolating the platinum resistance thermometer calibration below the liquid nitrogen fixed point (77°K). As part of the current work the resistance thermometer calibration was extended to approximately 20°K by measuring its resistance at the liquid hydrogen boiling point (20.19°K). It thus became possible to calibrate the thermocouples down to this same temperature.

A total of 15 thermocouples was needed for the emittance measurements. Continuous lengths of wire needed for this number of couples were taken from the chromel P and alumel spools and divided into three parts. Samples taken from each of the three segments were used to fabricate the three thermocouples which were subsequently calibrated. Thus each calibration thermocouple was representative of five of the couples used in the emittance measurements. Results of the calibrations are presented in Section III.

Samples and Sample Preparations

Emittance measurements were made on a total of 15 specimens. Table I describes the samples in terms of impurity, type, and nominal resistivity.

The specimens were prepared in the form of disks approximately 1 mm thick by 18 to 25 mm diameter. The germanium was received from the manufacturer* in the form of sections cut from horizontal zone levelled single crystals having the desired impurities and resistivities. Each specimen was prepared from one of these sections by cutting with a silicon carbide wheel a slice of about 1.2 mm in thickness perpendicular to the long axis of the crystal. This orientation was chosen since it gives the

*NPC Metals and Chemicals Company, 3133 E. 12th Street, Los Angeles, California 90023.

greatest homogeneity of impurity concentration. To prevent fracturing of the slice each piece was backed with a metal block during the cut-off process[3] after which it was lapped with No. 600 silicon carbide to remove all saw marks and to bring its thickness to nearly 1 mm. The samples were reduced to the shape of a circular disk by means of a diamond core drill and were then optically polished on both faces on a Pellon polishing pad* with 0.05μ alumina. Holes of diameter 0.010" for mounting the thermocouple wires were drilled in the samples with a supersonic drill. Finally, the samples were etched for one minute in a freshly prepared etching solution consisting of 5 parts nitric and 3 parts hydrofluoric acids. This etching process removed about 0.001 cm of the surface. Investigators have reported that the disturbed layer on the surface of germanium due to grinding and polishing extends to a depth of about 0.0001 cm, hence, this etching treatment completely removes this layer which would affect the measurement of the emittance of the normal material.

The silicon samples were prepared in the same manner except that they were procured from the manufacturer** in the form of disks approximately 1 mm in thickness cut in the same crystal orientation as the germanium. The samples were lapped, polished, trued, drilled and etched as previously described. The etching bath used on the silicon samples consisted of 5 parts nitric, 3 parts hydrofluoric, and 3 parts acetic acids. Final weights and dimensions were obtained after the etching was completed. Mounting of the thermocouples and installation of the specimens followed the procedures described in AFML-TR-66-148.[1]

Emittance Measurements

The characteristics of the emittance samples are described in Table I. The emittance measurements were accomplished with the apparatus and methods previously described.[1,2] Specimens were heated radiantly by electrical filaments. At the lower temperatures helium gas was temporarily introduced into the dewar to provide the thermal switching necessary to temporarily increase the cooling rate between those temperatures at which emittance was determined. Both the filament heating and the thermal switching techniques were those previously used with the Irtran filters.[2] Results of the emittance measurements are presented in Section III.

*Manufactured by Geoscience Instruments Corporation, 110 Beekman St., New York, New York.

**Electronic Space Products, Inc., 854 So Robertson Blvd., Los Angeles, California 90035.

Resistivity Measurements

In selected cases, measurements of resistivity were made as a function of temperature on small samples cut from the emittance specimens. The resistivity samples were small bars approximately 2.0 cm x 0.3 cm x 0.1 cm prepared by the techniques and apparatus described in the previous section. A thin layer of copper was electroplated on each end of the specimen to provide ohmic contact during the resistivity measurements by the familiar four-point contact method. Figure 1 shows the apparatus with three specimens clamped between the current contacts and three sets of needle point probes arranged to measure the potential drop along the sample. The resistivity is calculated from the expression

$$\rho = \frac{Ea}{I\ell}$$

where E is the potential drop across the needles

I is the current through the specimens

a is the cross sectional area

ℓ is the spacing between the needles.

Temperatures are measured with a thermocouple imbedded in the fourth or dummy sample. Preliminary experiments over the expected temperature range confirmed that temperature gradients within such a specimen are negligible and that the temperature at its center may be assumed to be that of the other three specimens for small rates of temperature change.

The resistivity of the specimens was measured as a function of temperature as they were slowly warmed from approximately 20°K to 400°K. This range of temperatures was attained by use of the same dewar as that used for emittance measurements. The capsule was placed in the experimental chamber and liquid helium used to cool the chamber and the resistivity capsule to the starting temperature of approximately 20°K. About four hours were required to cool the capsule and samples. Cooling occurs primarily by conduction to the trapeze base. Starting at 20°K both the experimental chamber and the resistivity capsule are

allowed to warm to 77°K, the temperature of the liquid nitrogen-cooled shield which surrounds the experimental chamber. This warming occurs naturally as soon as the liquid helium is purged from the experimental chamber. Further warming of the capsule is accomplished by purging the liquid nitrogen from the shield and the walls of the dewar and thus allowing the entire internal structure to warm to room temperature. The rate of warming can be increased as desired by the use of a small heater in the base of the capsule, by introducing helium gas to break the vacuum of the dewar, or by blowing warm air into the liquid helium or liquid nitrogen chambers. Warming the capsule above room temperature is accomplished by restoring the dewar vacuum and supplying heat by the capsule heater and by the passage of hot air through the hollow walls of the liquid helium chamber.

During the entire warming process the emf of the thermocouple in the dummy specimen and the voltage drops across the needle probes of each resistivity specimen is recorded by the same read-out system used in the emittance measurements.[1,2] The current in the series connected specimens (1 milliamp) was provided by a Quan-Tech Laboratories Model S-108 constant current supply and monitored by a Hewlett Packard Model 410C electronic voltameter. The time required for the entire warming process is approximately 48 hours of which about 12 hours requires supervision -- namely the warming from 20°K to 77°K and the warming above room temperature. Results of the resistivity measurements are contained in Section III.

SECTION III

RESULTS

Thermocouple Calibration

Figure 2 shows the calibrations of the three chromel P-alumel thermocouples expressed as adjustments to the NBS tables[5] of thermal emf. Each of the plotted points represents the emf which must be algebraically added to the NBS value to make it agree with the observed thermocouple emf at the temperature indicated by the platinum resistance thermometer. In general, the three calibrations agree within the experimental error of the measurements. In the temperature range 89°K to 127°K, however, the differences between the three curves are large enough to be significant. The corrections applied to any individual thermocouple were therefore based on the calibration applicable to the wire segments from which that couple was fabricated. It will be noted that the adjustments for these three thermocouples are comparable to those reported for TC-3 in Fig. 4 of Technical Report AFML-TR-67-200,[2] a thermocouple which was fabricated from the same lot of thermocouple wire.

Emittance Measurements

Emittances of the 15 specimens listed in Table I are shown in Figs. 3 through 7. The plotted emittance values were calculated from the observed cooling rates by the method described in Technical Reports AFML-TR-66-148[4] and AFML-TR-67-200.[2] Specific heat values used in the calculations for germanium were those shown by Flubacher[6] et al., for temperatures below 300°K and by Gerlich[7] et al., for temperatures above 300°K. Silicon specific heats below 300°K were also obtained from the Flubacher data; above 300°K they were obtained from a compilation by Y. S. Touloukian.[8]

In general, the emittance values shown in any one figure are for specimens that were mounted together on the trapeze and thus represent data taken in the same run. The emittance curves on a given figure do not always extend down to the same low temperature, either because the liquid helium supply was exhausted or because the ratio of emitting power to thermal capacity became so low that temperature changes could no longer be measured with sufficient accuracy to justify data taking. Thus in Fig. 3 the rate of cooling of the G-3 specimen below 30°K was too small to be successfully measured, and the G-1 specimen had cooled so slowly during the run that the entire amount of liquid helium available for this run had been used by the time it reached approximately 40°K. In the case of sample S-1, Fig. 6, a second run was made to extend data down to 34°K. The agreement between the two runs is excellent.

The anomalies in emittance which may be noted in a number of cases at the temperatures of 64°K and 74°K are believed to result from anomalies in the routine calibrations of the thermocouple emf read-out system which were also noted in the same temperature range. The emittance curves have therefore been drawn to ignore any implied inflections at these two data points.

Several features of the emittance-temperature relations displayed by these curves are noteworthy. The following comments summarize these features and Section V contains a discussion of the significance of these relations.

At temperatures above 60°K for germanium and above 240°K for silicon, the emittance-resistivity relationship is quite consistent. The highest resistivity samples have the lowest emittances, the lowest resistivity ones have the highest emittances, and those with intermediate resistivities have intermediate emittances. The only possible exception to this generalization is in the 30 and 1 ohm-cm n-type germanium samples which at temperatures above 100°K show identical emittances within experimental errors. At temperatures between 100° and 40°, however, even these two samples fit the above generalization.

At temperatures below 60°K for germanium and below 240°K for silicon, however, the resistivity-emittance relationship differs. All the intermediate resistivity (1 ohm-cm) samples show an increase in emittance with decreasing temperature until an emittance maximum is reached which is greater than that of the corresponding low resistivity samples. This can be seen in Figs. 6 and 7 with p and n type silicon, where the intermediate resistivity samples show an emittance peak at 120°K and 80°K respectively. Intermediate resistivity p and n type germanium also show this characteristic but at a lower temperature. The p type, Fig. 3, shows an emittance peak at 35°K while the n type, Fig. 4, shows the emittance still rising at 20°K and would presumably peak at a temperature somewhere below this value.

Resistivity Measurements

Figures 8 and 9 show the results of resistivity measurements of three germanium specimens. The curves are typical of semiconductor resistivity behavior - the negative temperature coefficient at low temperatures being the result of increasing impurity conduction with temperature, the second negative temperature coefficient at higher temperatures being the result of increasing intrinsic conduction with temperature. It will be noted that Fig. 8, the curve for G-1 has a different ordinate scale than that used for the curves of Fig. 9. A portion of the G-1 curve has been plotted on Fig. 9 for comparative purposes.

Resistivity measurements were attempted on the germanium n-type specimens and on the silicon specimens but the results are considered unreliable at the lower temperatures and so are not included in this report. The chief source of unreliability below room temperature was apparently AC pickup which, after rectification in the semiconductor, was superimposed on the measured potential drop across the two potential probes. The presence of the extraneous voltage was evidenced by a change in the magnitude of the inter-probe potential drop when the current through the semiconductor was reversed. In view of the fact that temperature-resistivity relations are well known for the semiconductors concerned, the value of additional data was not believed great enough to justify the time and effort involved in providing the more sophisticated measuring techniques which are required.

SECTION IV

ERRORS

The sources of errors and the estimated effect of these errors on the emittance values are shown in Table II. A general discussion of the error sources may be found in Technical Reports AFML-TR-66-148[4] and AFML-TR-67-200.[3] Three of the errors mentioned in the Table require additional comments. The thermocouple calibration error is now considered to be a constant ± 2% over the entire temperature range in view of the improvement in the calibration of the platinum resistance thermometer at the liquid hydrogen boiling point. The estimates of specific heat errors are based on the accuracies stated in the appropriate literature references. In the case of silicon specific heats above 300°K, no estimate of accuracy was included with the data but experimental methods of measuring specific heat in the 300°K to 400°K region can be expected to have errors not greater than ± 3%.

The errors due to uncorrected heat losses through the support wires and residual gases become significant at specimen temperatures below 50°K. This results from the fact that the specimen cooling rate due to radiation losses is decreasing much more rapidly than the losses due to the wire and gas conduction. For example, when the specimen temperature is decreased from 50°K to 25°K its loss by radiation is decreased by a factor of 16, while the wire conduction loss is estimated to decrease by a factor of 5. The wire loss is not linear with temperature because it is affected by other factors besides gradient, namely the decrease in conductivity as temperature decreases and the decrease in radiation loss from the wire itself as its mean temperature decreases. Gas conduction losses are a linear function of specimen

temperature and also become relatively significant at very low temperatures. Thus for a specimen with emittance 0.5, these uncorrected heat losses are estimated to cause 1% error in emittance at 50°K and 4% error at 25°K. For a specimen with emittance 0.1, the errors at 50°K and 25°K would be 5% and 20% respectively.

No values of total hemispherical emittance of germanium or silicon were found in the literature, so it is not possible to compare the presented data with other results. On the basis of the estimated errors shown in Table II, it is believed that the data shown is accurate within ± 5% for temperatures above 50°K. Below 50°K, the possibility of systematic errors increases until at the lowest temperature the low emittance values may include a systematic error as great as 20% superimposed on the random errors.

SECTION V

DISCUSSION OF RESULTS

The results which have been obtained in the emittance measurements will be discussed from two points of view - first from the standpoint of their significance with respect to the use of silicon and germanium in IR devices, and secondly from the standpoint of possible theoretical explanations of the emittance-temperature relations.

Relevance to IR Devices

IR devices are currently used in a variety of guidance, detection and surveillance systems aboard aircraft, missiles and satellites. Silicon and germanium commonly perform two types of functions in these devices. Externally they serve as flat windows and curved IR domes. Internally they serve as (1) correction plates in mirror optical systems, (2) lenses and prisms particularly in immersion optics, and (3) filters both in the form of coatings and as substrates. In these applications the IR transmission is the characteristic of principle concern. Since the optical elements fill a sizeable fraction of the detecting elements field of view, the emittance also becomes important because of its influence on the heat transferred to the detector from the local environment.

The optical properties of most materials are influenced by imperfections, impurities, and defects in the host material; consequently, it is not surprising that the emittance of silicon and germanium is sensitive to the doping levels. Moderately pure silicon

and germanium (typical resistivities 5 ohm-cm and 30 ohm-cm, respectively) are considered adequate for IR optics. Figures 3 through 7 show that these purities are adequate for the respective material at room temperature and at low temperatures for germanium; however, 5 ohm-cm silicon probably exhibits an emittance characteristic that reaches rather high levels at low temperature. At comparable impurity levels (e.g., 1 ohm-cm in Figs. 3 through 5) germanium exhibits a similar increase in emittance at low temperatures. This behavior is contrary to the usual assumption that optical materials become more transparent at low temperatures. Obviously these low temperature absorption peaks become an important factor in determining acceptable impurity levels for cryogenically cooled optical systems. In addition, the controllable emittance provides an additional design variable.

Comments on Emittance at Low Temperatures

Several features of the curves in Figs. 3 through 7 go beyond our current understanding. First, all of the curves for intermediate doped silicon and germanium exhibit an emittance that reaches a peak at low temperatures, i.e., about 80 to 120°K for silicon and ~ 35°K for germanium. Second, highly doped germanium has a nearly constant emittance from about 75°K up to the maximum temperature. Both of these characteristics can be explained in terms of existing models; however, the available evidence does not permit identification of the process.

In general, emittance can be described in terms of (1) the number of emittees, (2) the efficiency or frequency of exciting the emittors, and (3) the relative probabilities of radiation vs radiationless transitions back to the lower energy state. Dumke[9] has expressed the transitions involved in free absorption in terms of the Hamiltonian $H = H^{f} + H^{L} + H^{s} + H^{fL} + H^{fs}$

where

H^{f} = the unperturbed Hamiltonian of an electron in a perfect lattice

H^{L} = the photon or electromagnetic field contribution

H^{s} = the scattering mechanism which is necessary to conserve crystal momentum

H^{fL} = the interaction Hamiltonian involving the electron and the electromagnetic field

H^{fs} = the interaction Hamiltonian involving the electron and the scattering mechanism.

Since emittance is the inverse of absorption and Kirchhoff's low equates the two quantities at a given wavelength, the interactions specified in

this Hamiltonian apply also to the emittance of free carriers in semiconductors. In considering the data in Figures 3 through 7 we will look at processes that affect the number and types of emittors, this interaction with photons and their scattering by the crystalene lattice.

The curves for n and p type germanium of resistivity 30 ohm-cm are very similar. The same is true for the n and p type silicon of resistivity 200 ohm-cm. These curves represent fairly pure crystals i.e. no intentional doping. Values of emittance higher than those shown by these curves are due to the donors or acceptors added to control the electrical conductivity. The state of the donor or acceptor depends both on the concentration of centers and the lattice temperature. At room temperature both silicon and germanium are in their exhaustion region where all of the doping atoms are ionized; therefore, the increase in emittance with electrical conductivity reflects the increased number of ionized centers i.e. free electrons and holes. As the temperature is reduced the behavior of the ionized centers depends on the impurity concentration. In the highly doped degenerate samples (curves for G-3, G-6, S-3 and S-6) the centers remain ionized over the temperature range of these experiments; consequently the number of emitting centers remains essentially constant in number and type. The 0.001 ohm-cm silicon exhibits a temperature dependence similar to metals where the decrease reflects reduced interaction with the crystal lattice i.e. H^{e_L} and H^{e_S}. In contrast the emittance for 0.01 ohm-cm germanium remains nearly constant between 20 and 360°K implying a constant interaction with the lattice.

When the intermediate (about 1 ohm-cm) doped crystals are cooled below the exhaustion range, electrons and holes become trapped to form neutral donor and acceptor atoms respectively. Both the number and type of emitting center are changing and now the enhanced emittance can be attributed to either the increased number of neutral impurity atoms or to a change in the interaction between the ionized doping atoms and the lattice. The first case depends upon the classical color-center model for the absorption or emission of energy and so will not be discussed in further detail. The second case involves a change in rate of interaction between the lattice and the free carriers and will be discussed in some detail in the following paragraphs.

Many investigators[10,11,12] have reported free carrier absorption to be one of the major components of optical absorption in germanium and silicon. If in the emission process the thermal energy of the crystal lattice is transmitted to the free carriers which in turn are scattered by phonons or impurity ions and emit quanta of infrared radiation, then the efficiency of this process should be

roughly proportional to the concentration of the charge carriers. Thus, the experimental observation that the low resistivity, highly doped samples with a high concentration of charge carriers show higher values of emittance than do the high resistivity, low doped samples with relatively few charge carriers is consistent with theory.

This simple charge carrier theory, however, fails to hold in the previously described emittance behavior of the intermediate resistivity, 1 ohm-cm, samples at low temperatures. Morin and Maita and others[11,13] have observed that the charge carrier densities in similar samples of silicon and germanium show no anomalies at these temperatures. According to their data both p and n type materials of all resistivities show smooth and consistent relationships between temperature and carrier concentration. Energy considerations indicate that such an emittance increase could not be due to a latent heat type of energy storage. No known change of state process permits the absorption of heat energy with decreasing temperature. Nor is it possible to have a carrier trapping process wherein the charge carriers are trapped in high energy levels and "frozen" out by a decrease in temperature. Analysis also indicates that the energies involved in such processes are not sufficient to account for the increase in emittance. All of the charge carriers, 10^{16}, present in a 1 ohm-cm, p type silicon sample if trapped at a high, 1 ev level, could absorb only enough thermal energy to change the temperature by .004 degrees i.e. not enough to effect significantly the measured emittance. A modification of the charge carrier theory based on our emittance measurements suggests that at certain charge carrier densities and temperatures there is an increase in the efficiency of energy transfer from the crystal lattice to the charge carriers.

One possible cause of such an increase in energy transfer efficiency could be that there is an increase in the lattice-carrier coupling brought about by a resonance phenomenum induced at a given temperature in a certain sized crystal domain whose boundaries are determined by impurities. If this is the case then one would expect a change in free carrier mobilities corresponding to a change in the lattice-carrier coupling. Analysis of carrier mobility data[11,13,14], however, reveals no such relationship. Carrier mobilities at all concentrations show only a monotonic change with temperature with no anomalies matching those of emittance.

Another possibility for increased energy transfer from crystal lattice to the charge carrier could be an increase in the lifetime of the charge carrier which would permit them to undergo many more thermal-to-radiation energy transfer processes. Moss[15] in studies made on InSb has found that the lifetime of the charge carriers depends on their

concentration and follows a bell-shaped curve which reaches a maximum at about 2×10^{18} carriers per cm^3. By coincidence the charge carrier density of our 1 ohm-cm p type silicon sample reaches $2 \times 10^{18}/cm^3$ at 120°K. This is the temperature at which the emittance of this sample reaches a maximun. Experimental data at this point is very incomplete but evidence indicates some relationship between carrier concentration, carrier lifetime and emittance.

Figure 10 shows an emittance model of an n type material based on this free carrier emittance theory. Thermal energy from the crystal lattice is transferred to the charge carriers exciting them to a higher energy level. These excited carriers are then scattered by phonons or impurity centers. Some of the energy lost in the scattering process is emitted as a broad spectrum bremsstrahlung type of radiation and some is absorbed by the scattering center and is returned to the crystal lattice as heat energy. Multiple scattering finally returns the charge carrier to its initial energy state. The net result of this process is that some of the heat energy of the crystal lattice is converted to radiant energy and is emitted. This process can occur over again many times with the same charge carrier. It is estimated that in a one cm^3 crystal cooling from 360° to 20°K each of the 10^{18} charge carriers would undergo an average of about 10^7 of these energy transfer processes. Because of the great number of processes necessary a longer lifetime for the charge carriers would result in a more efficient heat transfer and a higher emittance. Figure 11 shows an emittance model for a p type material. Here thermal energy from the crystal lattice is absorbed generating excess holes in the material. Part of this energy is given up by the freed electron by interaction with scattering centers. Some of this energy is emitted and some is returned via the scattering centers to the crystal lattice as thermal energy. The remainder of the absorbed energy is given off as a band type of radiation generated when one of the holes is filled by the electron. Here again the net result of this process is that thermal energy from the crystal lattice is converted into radiant energy and is emitted. And here again the efficiency of this thermal energy transfer depends upon the number and the lifetime of the charge carriers. It is perhaps significant that at the temperatures of maximum emittance for the two 1 ohm-cm p and n type silicon samples the number of carrier electrons (minority carriers in the case of the p type material) is the same in both cases, namely, 2×10^{15}.

The mechanism of energy transfer from crystal lattice to charge carrier is not fully understood but must be related to the thermal oscillation amplitude of the atoms in the crystal lattice. Our results show that for germanium and silicon samples of equal carrier densities, the former gives consistently higher values of

emittance. The temperature-emittance relationship which characterizes silicon below 300°K is also evident for germanium but occurs at temperatures below 80°K. This behavior can be explained on the basis of data presented by Collins and Fan[12] who indicate that at a given temperature the thermal vibrational displacement of the atoms in germanium is greater than for those in silicon. Thus in germanium the efficiency of energy transfer by means of the crystal lattice interaction with the carriers is greater and can occur at lower temperatures than in silicon.

The emittance models of Figures 10 and 11 explain several experimental phenomena:

1. Emittance values approach zero at very low temperatures. Because the thermal vibrations of the atoms in the crystal lattice are reduced to zero at very low temperatures energy transfer to the charge carriers is impossible.

2. N type materials give a broad spectrum emittance. P type materials give a band type of spectral emittance.

3. Germanium gives consistently higher values of emittance than does silicon.

4. Emittance depends upon number and lifetimes of the charge carriers.

5. The models are compatible with one of the suggested explanations for the anomalous emittance behavior of the intermediate resistivity samples.

The following experimentation should be conducted to determine the cause of the anomalous emittance-temperature relationship of the intermediate resistivity samples:

1. Emittance measurements should be made on samples having different resistivities near 1 ohm-cm to determine whether or not the emittance peak shifts on the temperature scale with a change of resistivity. As an example, the emittance maximum of the 1 ohm-cm boron doped, p type silicon sample occurs at about 120°K. If measurements were to be made on samples of the same material having resistivities of about 0.5 ohm-cm and 0.1 ohm-cm, one of two possible results could be expected: either the emittance maximum would retain its shape but would shift to lower temperatures with decreasing resistivities or it would greatly broaden but remain at more or less the same temperature. If such a temperature shift does occur, it would present

strong evidence that the anomalous effect takes place at an optimum charge carrier concentration corresponding to a maximum carrier lifetime. If such a shift does not occur then the carrier lifetime theory of emittance can be discounted. If the emittance maximum broadens but does not shift appreciably with changes in resistivity, then the neutral impurity atom color center theory would gain credence.

2. Studies should be made on the intermediate resistivity materials relating charge carrier lifetime to concentration to determine if the lifetime maxima do correlate with the emittance.

3. Spectral emittance studies should be made on the intermediate resistivity samples at the temperatures of maximum emittance to determine the energies of the emitted radiation. Such studies would be valuable in determining the energy levels involved in the charge carrier transitions.

4. Emittance measurements should be made on samples of different physical dimensions to insure that the results are not due to some interaction between the carrier concentration and the physical dimensions of the sample.

5. Emittance measurements should be made on samples having the same carrier concentration but different neutral atom concentration to determine if the anomalies effect could be due to neutral atoms as mentioned previously.

6. Studies should be made to determine if the emittance anomalies could be due to some hysteresis effect between emittance and temperature during the cooling process. The cooling should be reversed over short intervals of temperature to determine any possible emittance lag.

SECTION VI

FUTURE WORK

This concludes the work of the present contract on the emittance of semiconducting materials. However, in view of the results obtained further studies should be pursued in order to better understand the mechanism of semiconductor emittance and which could lead to a further understanding of the solid state. The suggested

experiments, which are described in Section V, could lead to some very useful methods of controlling the temperature-emittance relationship in germanium and silicon by varying the impurity levels.

SECTION VII

CONCLUSIONS

Emittance-temperature relations have been established for samples of germanium and silicon having several different resistivities. The experimental data substantiate the general theory that emittance in a semiconducting material depends upon the concentration of charge carriers present in the sample. The emittance behavior of the intermediate resistivity materials, however, indicates that at least one other factor is influential. Available experimental data indicates that this factor could be either charge carrier lifetime or neutral impurity atom concentration. Additional experimental data are required to substantiate or disprove the effects of either or both of these possibilities.

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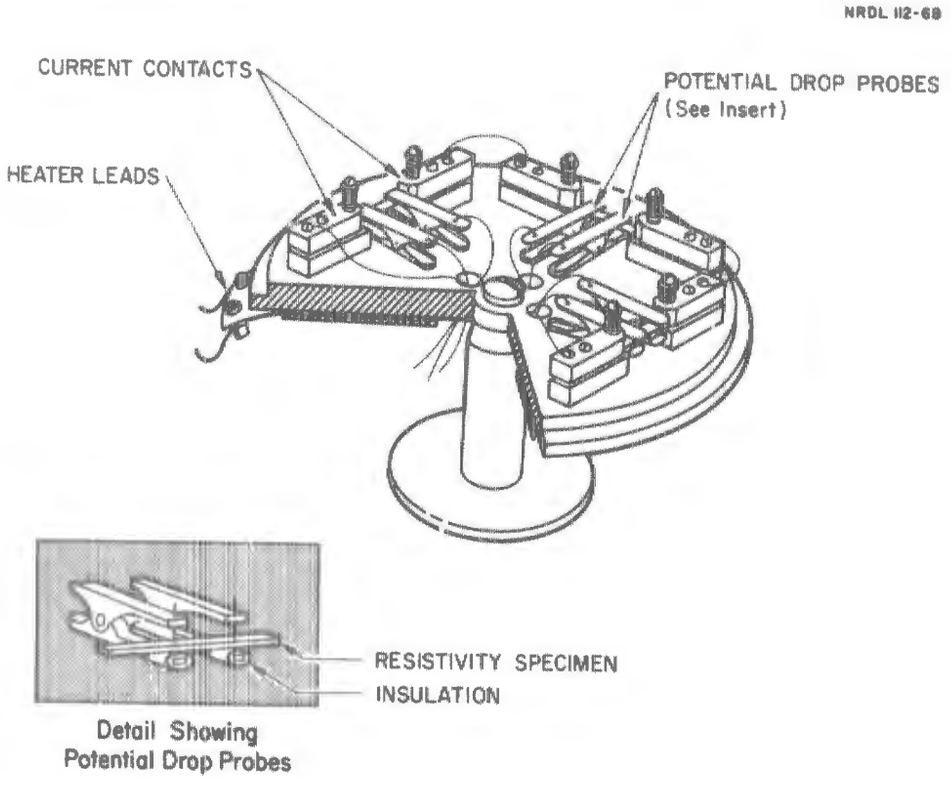

Fig. 1 Resistivity Apparatus

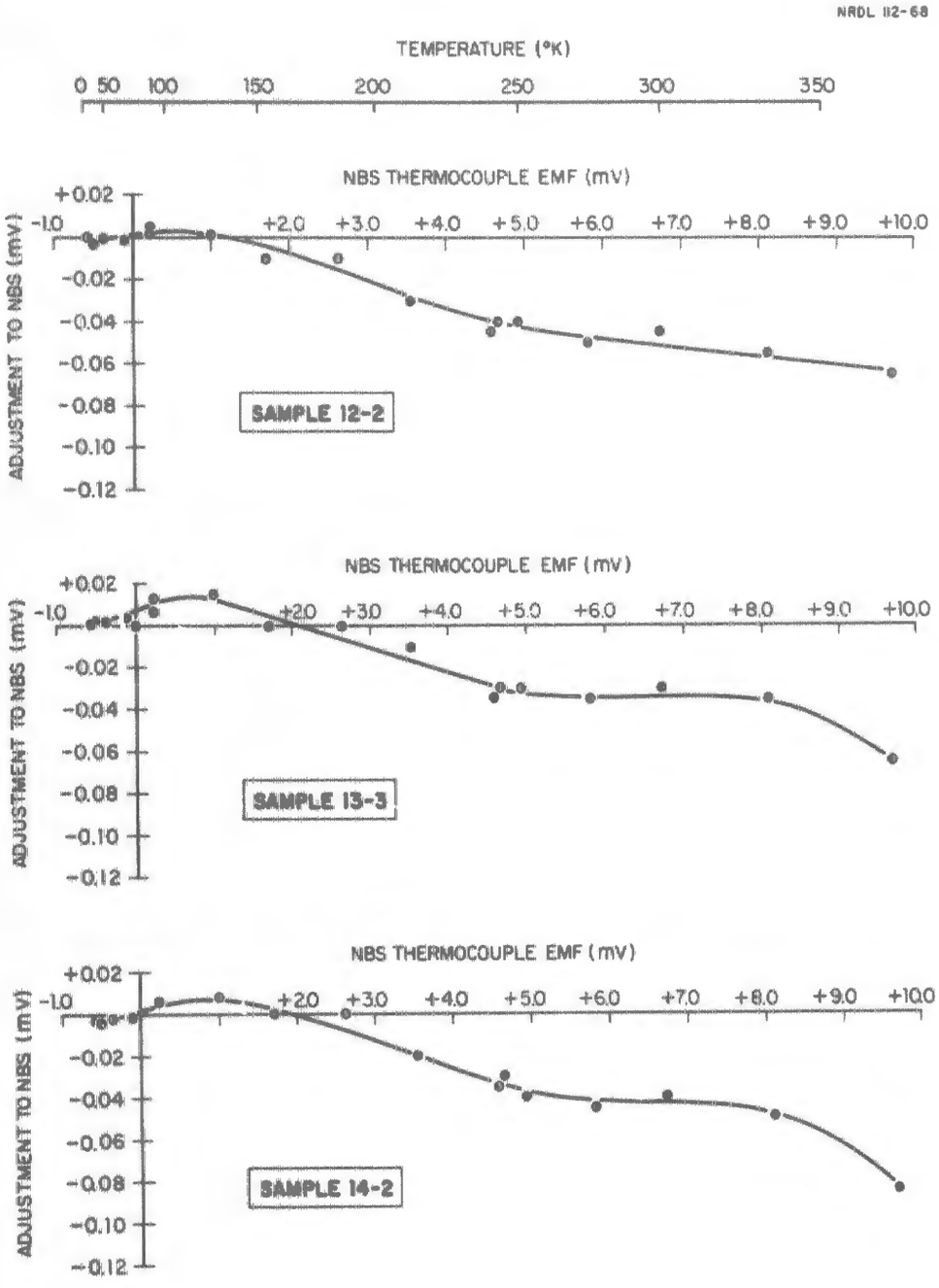

Fig. 2 Thermocouple Correction Curves

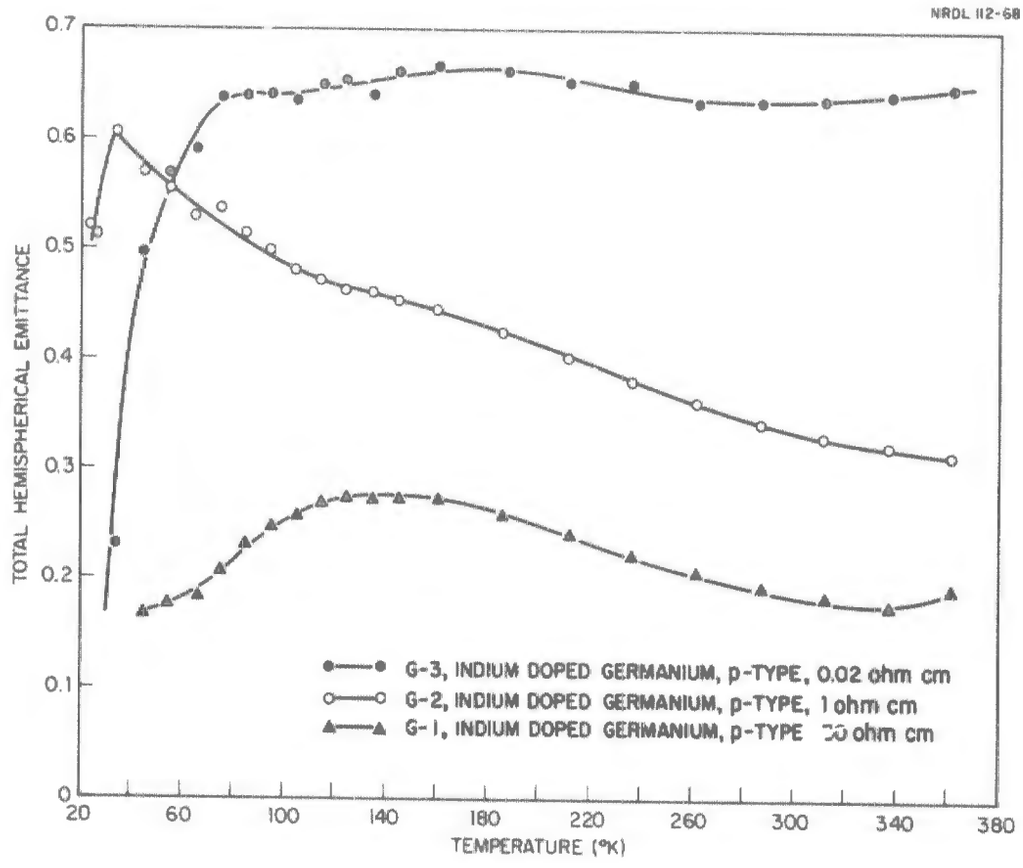

Fig. 3 Emittance of p-Type Germanium

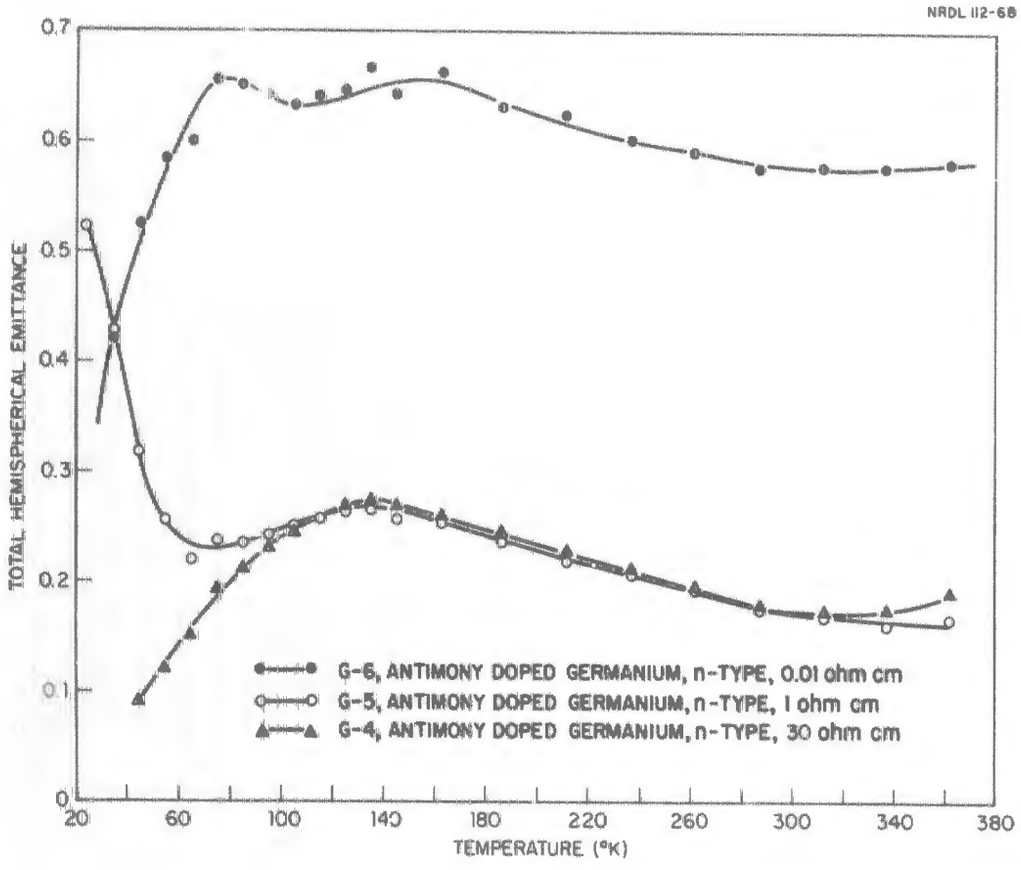

Fig. 4 Emittance of n-Type Germanium

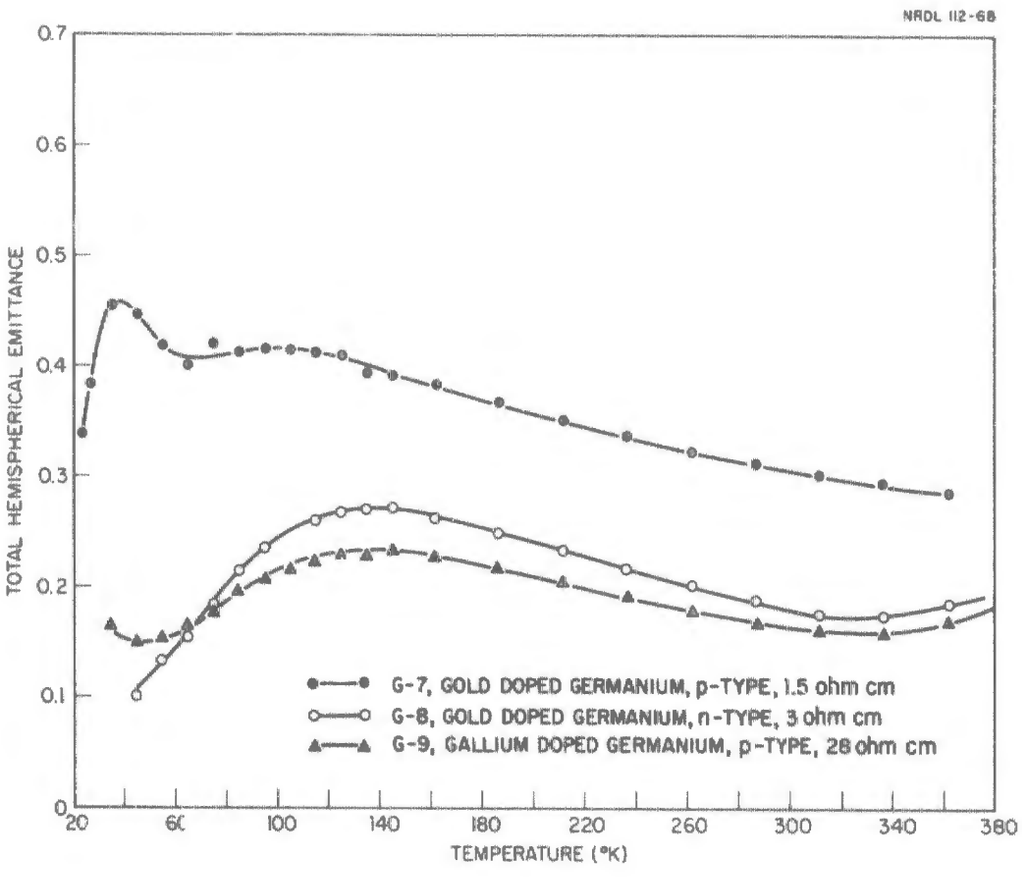

Fig. 5 Emittance of Gallium and Gold Doped Germanium

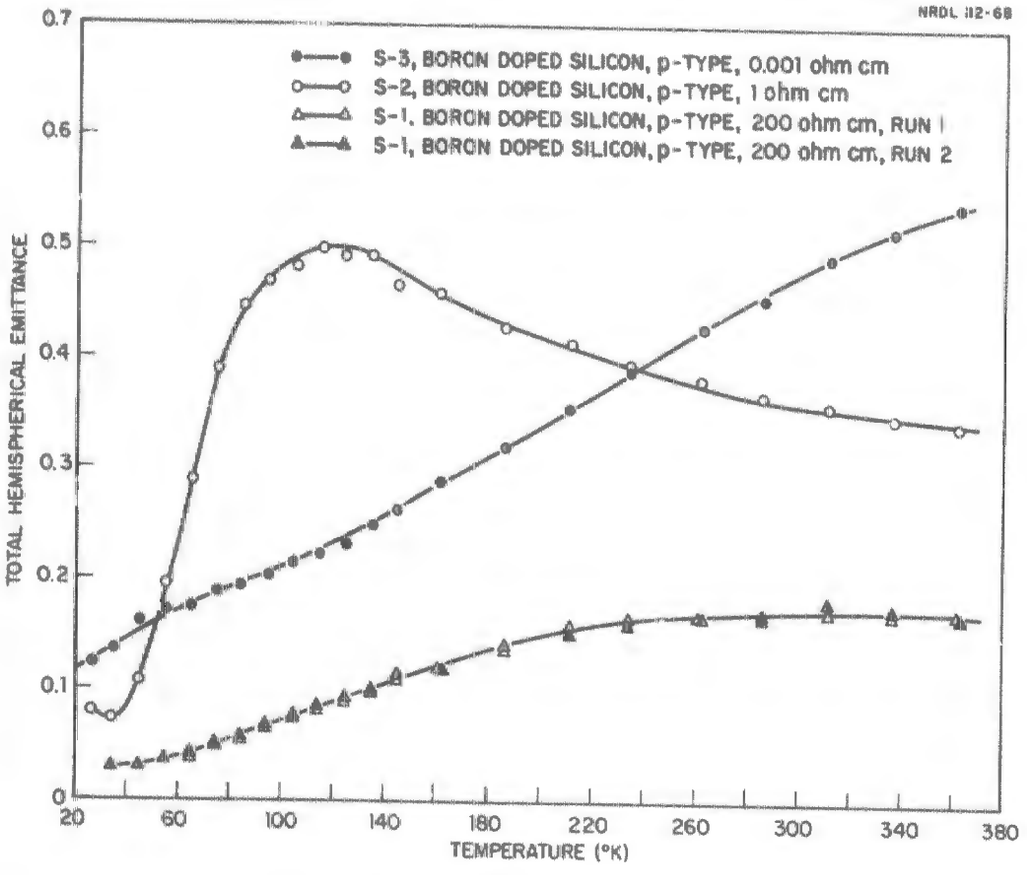

Fig. 6 Emittance of p-Type Silicon

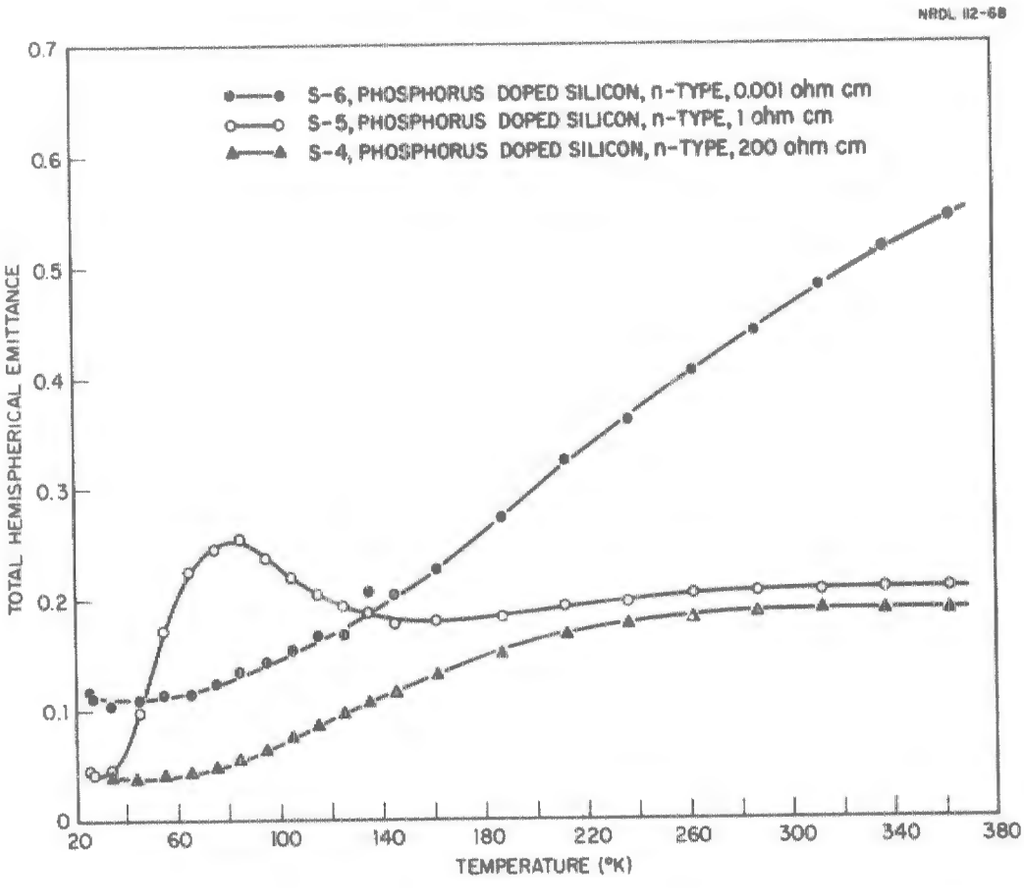

Fig. 7 Emittance of n-Type Silicon

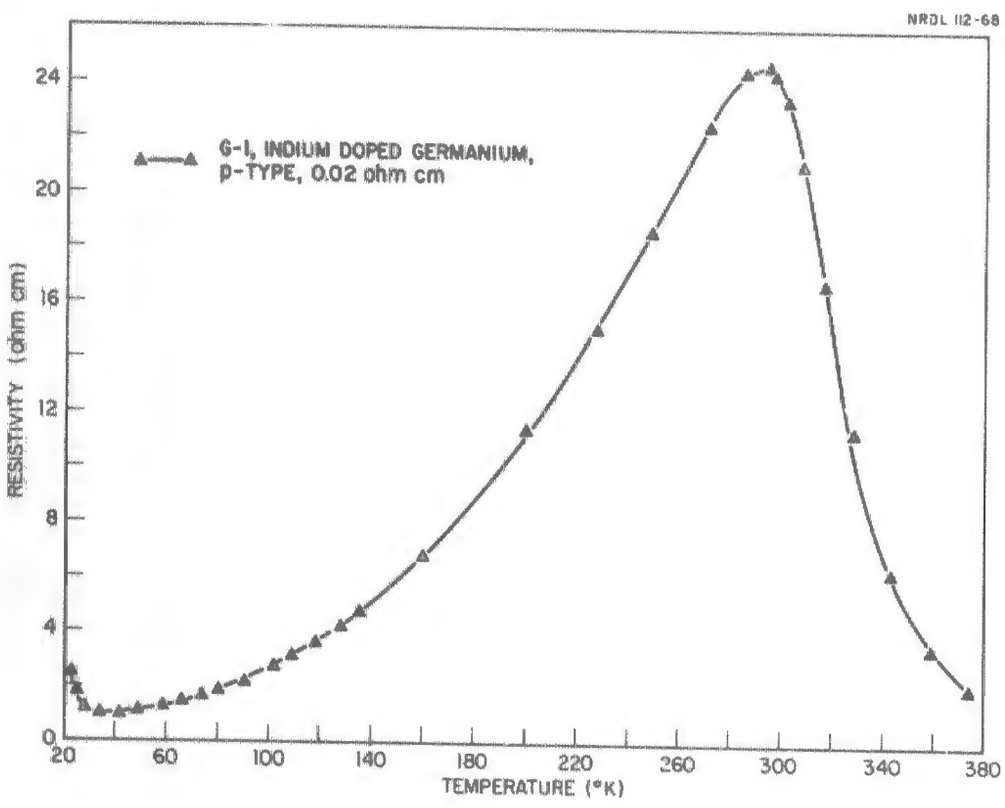

Fig. 8 Resistivity of Low Impurity Level Germanium

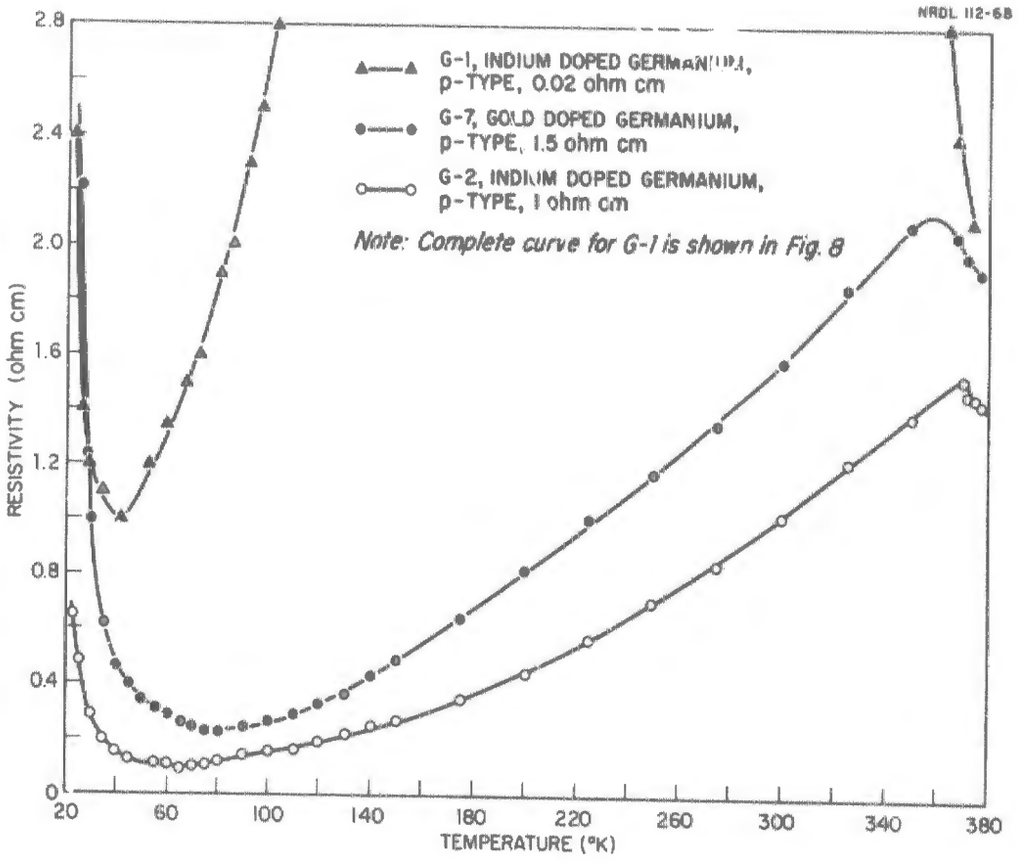

Fig. 9 Resistivity of Low and Intermediate Impurity Level Germanium

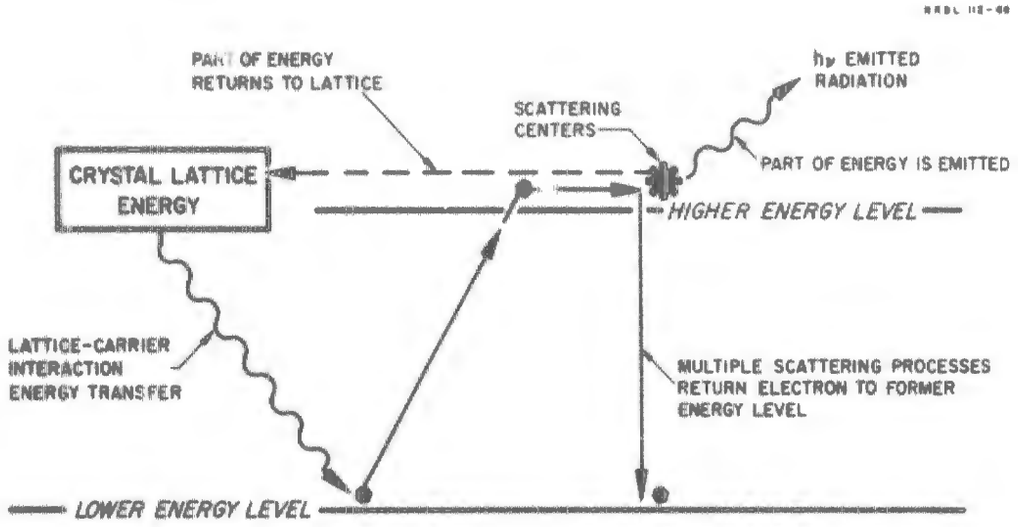

Fig. 10 Emittance Model for n-Type Material

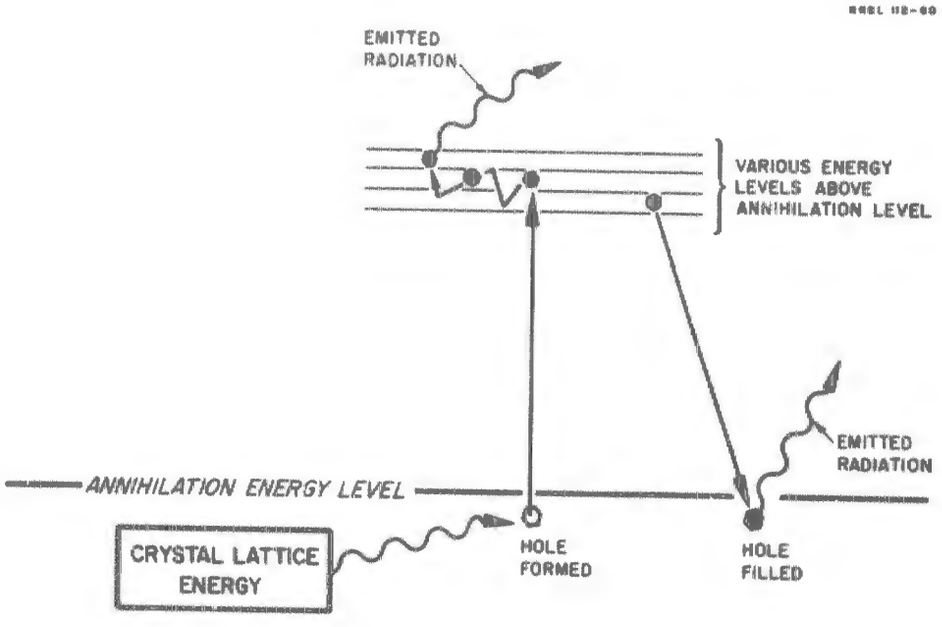

Fig. 11 Emittance Model for p-Type Material

Table I

Description of Samples

Sample	Semi-conductor	Impurity	Type	Nominal Resistivity ohm cm
G-1	germanium	indium	P	24
G-2		indium	P	1
G-3		indium	P	0.02
G-4		antimony	N	30
G-5		antimony	N	1
G-6		antimony	N	0.01
G-7		gold	P	1.5
G-8		gold	N	3
G-9		gallium	P	28
S-1	silicon	boron	P	200
S-2		boron	P	1
S-3		boron	P	0.001
S-4		phosphorus	N	200
S-5		phosphorus	N	1
S-6		phosphorus	N	0.001

Table II

Estimated Errors

Source or Type of Error	Maximum Contribution in Terms of Emittance Error(a)
Temperature gradients in the specimen	- 1.0%
Lack of "blackness" in chamber	- 0.1%
Instrumentation errors, i.e., errors in measuring thermocouple emf	
above 77°K	± 2%
below 77°K	± 3%
Mass and dimensional errors in specimens	± 0.2%
Thermocouple calibration errors	± 2%
Errors in specimen specific heat	
above 300°K	± 3% (b)
below 300°K	± 0.2%
Uncorrected heat losses through the support wires and residual gases	+ 1% to + 20% (c)

(a) The + errors give too large an emittance value, the - errors too small a value, and the ± errors are considered to have a random effect.

(b) The value shown is for germanium; no estimate was obtained for silicon.

(c) For specimens with low emittance values this error becomes quite large at low temperatures. See discussion in Section IV.

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13. ABSTRACT

Emittance measurements as a function of temperature have been performed on germanium and silicon samples representing a wide range of resistivities. In general, emittance was found to increase with increasing temperature and increasing impurity level. The emittance of germanium (p and n-types) at 360°K ranged from approximately 0.2 for a resistivity of 30 ohm-cm to approximately 0.6 for a resistivity of 0.1 ohm-cm. At 34°K, the emittance decreased to approximately one half the above values. Silicon (p and n-types) had comparable values of emittance at 360°K for resistivities of 200 ohm-cm and 0.001 ohm-cm, but at 30°K the emittance values were reduced to approximately 0.03 and 0.1 respectively. Germanium and silicon of intermediate resistivity were found to have intermediate emittance at the high and low temperature extremes, but anomalies were observed in the temperature-emittance relations at temperatures between the two extremes.

The general relation between emittance, temperature, and impurity level has been explained in terms of charge carrier densities. An explanation of the emittance-temperature anomalies has been suggested in terms of the relations between carrier density, carrier lifetime, and emittance.

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