do not reappear unless the sample is allowed to rest at zero current for several days. Current reversal will show the effect but here again after current has passed in each direction no further bursting is observed until the specimen recovers. The details of the noise level plot as a function of time are not reproducible but the incubation time, duration, and peak noise level are consistent from trial to trial at the same current.

The quiescent noise power varies as the current squared, as shown in Fig. 4. The peak noise, however, increases approximately as the fourth power. It appears that two noise mechanisms are acting and that this particular sample separates them clearly. The high noise behavior which occurs in very heavily deformed crystals is not time dependent. For the present work, the "normal" noise level showing the square law behavior was used to compute the noise constant.

### **V. DISCUSSION**

The above results indicate that the effect of appreciable crystalline imperfection densities in germanium and silicon is to decrease the noise level through reduction in minority carrier lifetime. The good quantitative agreement is obtained even though the sample resistivity is appreciably altered by introduction of imperfections. This is so even in the case of the heavily irradiated specimens which convert from *n*-type to p-type. Probably the presence of these large imperfection densities overrides any resistivity effect.

The strong influence of minority carrier lifetime thus established appears to favor the importance of minority carriers over majority carriers in 1/f noise, as suggested by Montgomery.<sup>11</sup> However, as shown in Table III, the correlation between the noise constants and minority carrier lifetimes of the 11 supposedly identical samples before irradiation is only suggestive of this trend and is by no means a strong correlation.

## ACKNOWLEDGMENTS

The author expresses his appreciation to L. V. Azaroff, R. H. Bragg, I. Corvin, A. R. Reinberg, and C. W. Terrell for their contributions and to J. R. Madigan of Hoffman Electronics, Inc., and Federal Telecommunication Laboratories, a division of International Telephone and Telegraph Corporation, for providing the silicon crystals.

PHYSICAL REVIEW

VOLUME 115, NUMBER 5

SEPTEMBER 1, 1959

# Electron Irradiation of Indium Antimonide\*†

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The effects of 4.5-Mev electron bombardment on the electrical properties of n- and p-type InSb are studied. Isochronal annealing experiments carried out on samples bombarded at 80°K indicate three regions of rapid annealing, the first two between 80°K and 200°K and the third near room temperature. It is shown that the distribution of bombardment-produced energy levels is altered by heating a bombarded specimen to 200°K. The changes which occur as a result of this heat treatment suggest that energy levels are shifted as defects rearrange themselves into positions of greater stability. For samples bombarded at 200°K, the positions of energy levels and the rates at which they are generated are determined from careful studies of the rates at which they are generated are determined from careful studies of the temperature dependence of carrier concentration. Mobility changes are utilized to identify donor or acceptor behavior. The levels introduced into the forbidden band appear to be multiply ionized.

#### I. INTRODUCTION

HE effect of high-energy particle bombardment on the electrical properties of a semiconductor is usually interpreted in terms of the introduction of donor and acceptor sites.<sup>1</sup> According to a model by James and Lark-Horovitz,<sup>2</sup> interstitials are expected to be donors,

and vacancies are expected to be acceptors, in the case of elementary semiconductors. This model has been confirmed in its qualitative aspects for germanium<sup>3,4</sup> and silicon,<sup>5</sup> and has been utilized in the interpretation of neutron-bombarded indium antimonide<sup>6,7</sup> and gallium antimonide.8

 <sup>3</sup> Cleland, Crawford, and Pigg, Phys. Rev. 98, 1742 (1955).
<sup>4</sup> Cleland, Crawford, and Pigg, Phys. Rev. 99, 1190 (1955).
<sup>5</sup> H. Y. Fan and K. Lark-Horovitz, in *Report of the Bristol*. Conference on Defects in Crystalline Solids (The Physical Society, <sup>6</sup>H. Y. Fan and K. Lark-Horovitz, in *Effect of Radiation on* 

Materials, edited by Harwood, Hausner, Morse, and Rauch (Reinhold Publishing Corporation, New York, 1958), p. 166. J. W. Cleland and J. H. Crawford, Jr., Phys. Rev. 95, 1177

Supported by the U. S. Atomic Energy Commission.

<sup>†</sup> Submitted as partial fulfillment of the requirements for the degree of Doctor of Philosophy at Purdue University, Lafayette, Indiana, 1958.

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<sup>&</sup>lt;sup>1</sup>K. Lark-Horovitz, in Semiconducting Materials, edited by H. K. Henisch (Butterworths Scientific Publications, Ltd. London,

<sup>&</sup>lt;sup>2</sup> H. M. James and K. Lark-Horovitz, Z. physik Chem. 198, 107 (1952).

<sup>(1954)</sup> <sup>8</sup> J. W. Cleland and J. H. Crawford, Jr., Phys. Rev. **100**, 1614 (1955).

In the present work, thin samples of indium antimonide were bombarded with 4.5-Mev electrons. The cross section for producing a primary displacement can be calculated with the aid of the differential cross section for Coulomb scattering, which has been determined in the relativistic range by Feshbach and McKinley.<sup>9</sup> This calculation requires a knowledge of the threshold displacement energy, the minimum energy imparted to an atom which will result in a displacement. This quantity has been determined experimentally by Klontz and Lark-Horovitz<sup>10</sup> to be  $\sim 30$  ev for germanium. More recent work<sup>11,12</sup> has indicated that permanent damage is introduced at approximately half this energy, but it has not been shown that these defects are the same type as are introduced at the higher energy. The threshold for InSb has recently been determined by Eisen et al.13 to be approximately 7 ev. Application of the theory of Snyder and Neufeld,<sup>14</sup> as modified by Seitz and Koehler,<sup>15</sup> yields for the total rate of generation of vacancy-interstitial pairs the value 24/cm for a threshold displacement energy of 7 ev. If the threshold energy were assumed to be 30 ev, the calculated rate of generating pairs would be approximately 3.2/cm.

The distribution of the defects is a factor which might influence very strongly their electrical properties. It is estimated for the present case that the primary vacancy and any secondary vacancies and interstititals produced by the primary knock-on should all lie within a diameter of approximately sixteen atomic spacings (on the average). The energy levels of such closely spaced vacancies and interstitials very likely would be perturbed. Thus an alteration of the electrical properties of bombarded samples could be effected not only by recombination of the vacancies and interstitials, but also by rearrangements of the defects into positions of greater stability.

#### **II. EXPERIMENTAL SETUP**

In the present work the Hall coefficient and conductivity of a variety of p- and n-type single crystals were determined as functions of the bombardment flux and temperature. Bombardments were carried out at liquid nitrogen and at approximately dry ice temperatures. Isochronal, or pulsed, annealing experiments were also carried out. The effect of bombardment on mobility was investigated, and compared with the theory of Brooks and Herring.<sup>16</sup>

- <sup>13</sup> F. H. Eisen, P. W. Bickel, and A. Sosin (unpublished report). <sup>14</sup> W. S. Snyder and J. Neufeld, Phys. Rev. 97, 1637 (1955), and **99**, 1326 (1955).
- <sup>15</sup> F. Seitz and J. S. Koehler, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, <sup>16</sup> P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954).

The Hall coefficient and resistivity were meaured by standard potentiometric techniques. The bombardments were carried out in a bombardment chamber, shown schematically in Fig. 1. The samples were bombarded through a hole in one of the pole pieces of the Hall magnet. This allows alternate bombardments and measurements to be made without alteration of the position of the sample. The bombardments were carried out in vacuum ( $\sim 10^{-5}$  mm Hg). The samples could be kept at any temperature above that of liquid nitrogen. The temperature of a sample was determined by means of a thermocouple placed in thermal contact with the sample. The sample and reservoir were electrically insulated from ground so that the accumulated charge could be collected to determine the bombardment flux.

#### III. BOMBARDMENTS CARRIED OUT AT LIQUID NITROGEN TEMPERATURE

In order to observe as much of the damage as possible, bombardments were initially carried out at liquid nitrogen temperature. Figure 2 shows the Hall coefficient and conductivity plotted as a function of the bombardment flux for a typical initially *n*-type sample. This shows that the concentration of electrons decreases, then the sample becomes p-type and the concentration of holes increases. This behavior is due to the capture of electrons or release of holes by bombardment-produced acceptor states which lie below the Fermi level. During bombardment the Fermi level is obviously shifting toward the valence band.



FIG. 1. Schematic drawing of bombardment chamber.

<sup>&</sup>lt;sup>9</sup> W. A. McKinlev and H. Feshbach, Phys. Rev. 74, 1759 (1948). <sup>10</sup> E. E. Klontz and K. Lark-Horovitz, Phys. Rev. 82, 763 (1951).

 <sup>&</sup>lt;sup>n</sup> J. J. Loferski and P. Rappaport, Phys. Rev. 98, 1861 (1955).
<sup>12</sup> W. L. Brown and W. M. Augustyniak, Bull. Am. Phys. Soc. Ser. II, 2, 156 (1957).

p-type samples undergo a monotonic change in hole concentration as long as complications due to annealing, or possibly long-lifetime trapping effects, are negligible. The concentration of holes increases if the Hall coefficient is greater than 2000 cm<sup>3</sup>/coul and decreases if the Hall coefficient is less than this value. Thus, as bombardment progresses, the Fermi level approaches a constant value which may be called the "final Fermi level." The fact that samples with a low Fermi level, or high hole concentration, lose holes as a result of bombardment, indicates the existence of donor levels above the Fermi level which give up electrons and become positively charged. These experiments thus indicate the existence of bombardment-produced donors and acceptors.

In Fig. 3 the carrier removal rates are tabulated by plotting initial removal rates,  $\Delta n/\phi$ , for small bombardment flux  $\phi$ , versus the position of the Fermi level,  $\zeta$  (plotted with solid circles).  $E_c$  is the bottom of the conduction band and  $E_v$  is the top of the valence band. Neglect, for the present, the other points which refer to bombardments at dry ice temperature. The reason for analyzing the data in this way can be seen by subtracting the neutrality equation which applies to the unbombarded specimen from the corresponding expression which applies after bombardment. The following equation is obtained if the sample is initially in the exhaustion region:

$$\frac{-\Delta n + \Delta p}{\phi} = \sum_{i} \frac{g_i}{1 + \gamma_i \exp[(E_i - \zeta)/kT]} - \text{const,} \quad (1)$$

where  $\Delta n$  or  $\Delta p$  is the carrier concentration after bombardment minus the initial carrier concentration,



FIG. 2. Variation of Hall coefficient R and conductivity  $\sigma$  with bombardment for an initially *n*-type sample bombarded at liquid nitrogen temperature.



FIG. 3. Removal rate data for bombardments at liquid nitrogen and at dry ice temperatures. Carrier concentrations were determined at  $80^{\circ}$ K.

 $g_i$  is the rate per centimeter of path of generating the centers responsible for a level at  $E_i$  above the valence band,  $\zeta$  is the Fermi level,  $\gamma_i$  is a statistical weighting factor which in the case of rather simple types of centers should be  $\frac{1}{2}$  for donors and 2 for acceptors. The bombardment flux,  $\phi$ , is the number of electrons per cm<sup>2</sup> which strike the sample. It is evident that if the introduced energy levels are several times kT apart, a plot of the left-hand side of Eq. (1) versus the Fermi level should drop rapidly in the vicinity of a bombardment-produced level, and should remain nearly constant when  $\zeta$  is not near a level. Data plotted in this manner provide what is frequently called a "removal-rate curve." This method of analysis was first used by Fan and Lark-Horovitz.<sup>5</sup>

Equation (1) implies that the value of  $\Delta n/\phi$  corresponding to a given Fermi level is independent of the amount of bombardment necessary to move the Fermi level to that position. This should be true as long as there are no other energy levels present originally in the region of the forbidden band explored, and if there are no other complicating factors such as annealing, or nonequilibrium distribution of electrons among the centers.

The solid lines in Fig. 3 represent  $-\Delta n/\phi$  or  $\Delta p/\phi$  values during bombardment of the same sample. In constructing Fig. 3 the following constants were used: effective mass of electrons,  $0.015m_0$ ; effective mass of holes,  $0.17m_0$ ; energy gap,  $(0.29-3.9\times10^{-4}T)$  ev. These values are reported by Hrostowski *et al.*<sup>17</sup> and are in reasonably good agreement with other sources. In all

<sup>&</sup>lt;sup>17</sup> Hrostowski, Morin, Geballe, and Wheatley, Phys. Rev. 100, 1672 (1955).

TABLE I. Comparison of measured mobility changes with the calculated changes based on the Brooks-Herring formula and the assumption that all levels are single-ionization levels.

Туре	Carrier concentration (10 <sup>15</sup> cm <sup>-3</sup> )	$\Delta(1/\mu)/\phi$ initial (measured at 80°K) (10 <sup>-20</sup> volt sec)	$\begin{array}{c} \Delta(1/\mu)/\phi\\ \text{calculated}\\ (10^{-20} \text{ volt sec}) \end{array}$	Temperature of bombardment (°K)
n	3.4	1.6	0.21	80
Þ	3.6	4.5	1.30	80
'n	1.3	0.8	0.11	200
Þ	4.5	6.0	0.88	200

cases except where the specimens were degenerate, the carrier concentration was determined according to the formula  $n = (3\pi/8)(1/Re)$ , where R is the Hall coefficient in cm<sup>3</sup>/coul. In cases of degeneracy the carrier concentration was calculated from the transport equation using quantum statistics and assuming 100% impurity scattering. This latter calculation was used only in cases where the conductivity and Hall coefficient were nearly constant over a large temperature range.

The middle section of the removal-rate curve for liquid nitrogen bombardments is not included because of slow changes with time (probably annealing) which become more pronounced as the Fermi level is lowered from the conduction band.

The Bohr model applied to donors and acceptors predicts the first ionization potential of each to be 0.0008 ev. and 0.009 ev, respectively. These levels do not show up on the removal rate curve, as is evidenced by the nearly constant removal rates in the vicinity of the band edges. It is very likely that these levels are suppressed by the large carrier concentrations. The introduced levels in the forbidden band are very likely the result of multiply ionized states. This fact is also borne out by considering the change in the reciprocal of mobility with bombardment in Table I. The calculated changes in mobility, obtained by assuming all centers to be only singly ionized and by applying the Brooks-Herring formula for impurity scattering,<sup>16</sup> are not large enough to account for the observed changes.

According to the removal rate curve, Fig. 3, there appears to be a level in the vicinity of 0.03 ev above the valence band, and several levels near the middle of the gap. The rate of generation of the centers responsible for the 0.03-ev level, as estimated from the change in removal rate, is approximately 3.5/cm. Plots of logR versus 1/T confirm the existence of a level at 0.03 ev in partially annealed samples.

A remarkable feature of these bombardments is the decidedly greater removal rate for *n*-type samples as compared to p-type samples. This could be an indication either that many more acceptors than donors are introduced, or that the acceptors tend to be more highly ionized.

Isochronal annealing experiments were performed on p- and n-type samples of varying initial concentrations. The term "isochronal annealing" is intended to imply that the sample is annealed at different temperatures but kept at each temperature the same amount of time. Then after each annealing period the sample is returned to a low temperature, in this case liquid nitrogen temperature, for measurement of the property of interest, in this case the Hall coefficient and resistivity.

The results for mildy bombarded *n*-type samples are easier to understand, since for these samples the Fermi level did not approach any bombardment-produced energy levels (i.e., the carrier concentration was linear with flux). The results are plotted in Fig. 4. The quantity  $n_A$  is the carrier concentration at liquid nitrogen temperature after the sample has been annealed to the temperature  $T_A$ , but not above it.  $n_0$  is the initial carrier concentration. The change in carrier concentration is divided by the amount of flux the sample has received so that all samples could be compared conveniently. The shapes of the curves are not critically dependent on the selection of annealing period, or the temperature interval.

The following comments are pertinent to the annealing of *n*-type InSb: (1) Annealing occurs in the direction of restoring the initial concentration and mobility. (2) By the time a sample has reached room temperature (or slightly above) the initial concentration and mobility are almost completely restored. (3) Most of the annealing occurs in three rather well-defined temperature regions:  $80-85^{\circ}$ ,  $120-150^{\circ}$ , and  $250-330^{\circ}$ K. This suggests three different annealing processes, which will be referred to as number one, two, and three, starting with the one at the lowest temperature. (4) The low-temperature process (number one) is very likely made less conspicuous by annealing which occurs during bombardment.

The results of the same experiment performed on



FIG. 4. Annealing of *n*-type InSb, measurements at 80°K.

*p*-type samples are indicated in Fig. 5. One observes the following: (1) There seems to be general agreement with *n*-type samples as to the regions of rapid annealing, except that the regions seem not so well defined in the case of the p-type experiments. This could be caused by the presence of bombardment-produced levels which lie close to the Fermi level during certain stages of annealing. The process which occurs at the intermediate temperature appears to be shifted slightly to higher temperature; therefore, this might be a different process from the second process mentioned above for the *n*-type samples. (2) The first two processes, except for the most pure sample, occur opposite to the direction of restoring the initial concentration (compare the first two processes in the case of *n*-type specimens). Only process three occurs in the direction of restoring the initial concentration. Thus, annealing is not, in general, the reverse of bombardment. (3) Annealing to as high as 373°K does not restore the initial concentration and mobility of the p-type samples.

Changes in mobility occur along with changes in carrier concentration. During the first two processes the mobility of p-type samples actually becomes smaller. Only in the third annealing stage does the mobility increase. On the other hand, as an *n*-type sample is annealed its mobility increases along with the increases in carrier concentration.

The annealing processes between 80° and 200°K always consist of either a decrease in hole concentration or an increase in electron concentration. This means that the total bound charge becomes more positive or less negative. Thus, either many more acceptors than donors anneal out, or there is a general shifting of energy



FIG. 5. Annealing of p-type InSb, measurements at 80°K.

levels toward the conduction band. It is believed that these first two processes are the result of rearrangements of defects which lie very close to each other, and possibly also of recombination of very close vacancyinterstitial pairs.

The mobility of *n*-type samples increases during the first two annealing processes. The mobility of the p-type samples decreases, in spite of the fact that the number of defects, and consequently the number of scattering centers, appear to be decreasing. These changes in mobility might be partially explained by the accompying changes in carrier concentration, which would produce more screening in the case of the *n*-type samples and less screening in the case of the p-type samples. However, in comparing changes in the reciprocal of mobility for samples of comparable carrier concentration bombarded at two temperatures (see Table I), it is found that this quantity changes more rapidly for p-type samples bombarded at dry ice temperature than for *p*-type samples bombarded at liquid nitrogen temperature. Some mechanism which works opposite to the decrease in the number of scattering centers must be responsible for this effect. There are two such mechanisms possible: a shifting of donor levels toward the conduction band, thus making the donors more highly ionized; or a separation of closely spaced donors and acceptors, the effect of which would be to decrease their mutual shielding.

It will be noted that the third annealing process can be explained in terms of vacancy-interstitial recombination, since in both n- and p-type samples the changes tend to restore the initial conditions. But the p-type samples, in contrast to the n-type samples, are not completely restored to their initial conditions. This indicates that after the third anneal there is either an excess of introduced donors over acceptors, or an equal number of each, the introduced donors and acceptors being unequally ionized only when the Fermi level is near the valence band.

p-type samples, while remaining p-type during the first two annealing stages, have been observed to convert to *n*-type after the third stage of annealing. This fact is consistent with the observations of Cleland and Crawford<sup>7</sup> who observed conversion of p-type to *n*-type when InSb was bombarded with high-energy neutrons at room temperature. These authors also noted a decrease in mobility during annealing of p-type gallium antimonide.<sup>8</sup>

#### IV. BOMBARDMENTS CARRIED OUT AT DRY ICE TEMPERATURE

In the above annealing experiments the first two processes are difficult to interpret; however, the third process might consist of recombination of some of the vacancy-interstitial pairs. Bombardments were therefore carried out at a temperature slightly below the onset of the third annealing stage (200°K, or approximately dry ice temperature) in order to obtain more



FIG. 6. Temperature variation of Hall coefficient of a p-type sample with various amounts of bombardment as a parameter, bombarded at 200°K.

information concerning the defects stable at this temperature.

At 200°K most samples are nearly intrinsic; therefore, all removal rate and Fermi level determinations were made at liquid nitrogen temperature. The samples were kept at 200°K only during bombardment. This procedure also allows comparison of the removal rate curves for the two types of bombardments. Samples bombarded at this temperature are more stable than samples bombarded at liquid nitrogen temperature, as far as long-period stability is concerned.

*n*-type samples still become *p*-type when bombarded at this temperature; however, the final Fermi level (determined at 80°K) has shifted from 0.03 ev in the case of samples bombarded at liquid nitrogen temperature to approximately 0.08 ev for samples bombarded at 200°K. The removal-rate curve, constructed from bombardments carried out on several samples, is shown in Fig. 3. The open circles are initial removal rate values for different samples, and each solid line represents  $\Delta n/\phi$  values for the same sample, as before. The triangles separated by dotted lines represent values too far apart to justify connection with a solid line. The crosses represent  $\Delta n/\phi$  values for samples after they had been bombarded at liquid nitrogen temperature, warmed to 200°K for at least 30 min, and then cooled back to liquid nitrogen temperature.

A comparison of removal-rate curves for liquid nitrogen and dry ice bombardments shows that the latter do not exhibit the marked asymmetry of the former. The distribution of energy levels introduced at dry ice temperature is quite different from that produced at liquid nitrogen temperature. Apparently the levels most effected by warming from 80° to 200°K lie between  $E_v$ +0.05 ev and  $E_c$ -0.03 ev.

From the shape of the removal-rate curve it is possible to make rather crude estimates of the positions of the levels introduced at 200°K. On the p-type side there appears to be a level in the vicinity of 0.04 ev and possibly another one near 0.08 ev. On the *n*-type side there are certainly levels present in the range 0.03 to 0.10 ev, but  $\Delta n/\phi$  changes almost linearly over this range which amounts to approximately 10kT. If this change were the result of a single level, it would occur over a range of approximately 4kT. It therefore appears that there are at least two and possibly more levels in this range which are separated by less than 4kT and are consequently unresolved. These curves also suggest that the level which was at 0.03 ev in the case of liquid nitrogen bombarded samples has shifted to approximately 0.04 ev, if these two levels result from the same type of defect.

Another method of determining energy levels consists of analyzing the variation of carrier concentration, or Hall coefficient, with temperature after a known amount of bombardment. This amounts to fitting Eq. (1) to data in which the variables are carrier concentration and temperature, the flux being constant. In general this equation is too complicated to handle; but if in certain cases the Fermi level remains sufficiently close to a given level over a reasonable temperature range, and if there are no other levels close to the level under consideration, Eq. (1) can be simplified to the following form:

$$\exp(E_{0j}/kT)$$

$$= \{A_j N_v/p\} \{ (g_i - C_j - \Delta p/\phi)/(C_j + \Delta p/\phi) \}, \quad (2)$$

where

$$E_j = E_{0j} + \alpha_j T, \quad A_j = \gamma_j e^{\alpha_j/k}.$$

 $E_{0j}$  is the activation energy (at T=0) of the level under consideration,  $A_j$  is a constant involving the statistical weight factor and the temperature coefficient  $\alpha_j$  of the energy level, and  $C_j$  is a constant involving some of the rates of generating other levels and can usually be determined from the removal-rate curve. The quantity  $N_v$  is the effective density of states,

$$N_v = 2(2\pi m^* kT)^{\frac{3}{2}}/h^3$$

The parameters adjusted in making a fit are  $g_i$  and  $C_j$ .



FIG. 7. A fitting of p-type data to Eq. (2).  $g_1=1.54$  cm<sup>-1</sup> and  $C_1=2.44$  cm<sup>-1</sup>. The slope of the solid line corresponds to  $E_{01}=0.048$  ev.

This method of determining energy levels could not be applied to samples bombarded at liquid nitrogen (which anneal upon warming) since the apparatus was not designed to achieve the required low temperature. Figure 6 shows a plot of  $\log R$  versus 1/T with flux as a parameter for a *p*-type sample bombarded at 200°K. The above analysis (see Fig. 7) was made for curve *B* and for similar curves obtained from other *p*-type samples.

The ordinate of the graph of Fig. 7 is proportional to the right-hand side of Eq. (2). The quantities plotted were calculated from experimental  $\Delta p/\phi$  values, using a value of  $C_1 = 2.44$  cm<sup>-1</sup>. It can be shown that if the level under consideration is the first level above the valence band,  $C_1$  must equal the initial carrier removal rate of a sample whose Fermi level is very near the edge of the valence band, i.e.,  $C_1 \cong 2.5$  cm<sup>-1</sup> (see Fig. 3).  $g_1$  was adjusted to make the points lie on a straight line. The straight line drawn in Fig. 7 corresponds to  $g_1=1.54$ cm<sup>-1</sup> and  $E_{01}=0.048$  ev. The estimated uncertainties in  $g_1$  and  $E_{01}$  are, respectively,  $\pm 0.1$  cm<sup>-1</sup> and  $\pm 0.005$  ev.

Curves E, F, and G of Fig. 6 demonstrate very clearly the level near 0.08 ev which was barely resolved by the removal rate curve. This will be called the second level. Analysis of these curves yields  $g_2=1.3\pm0.3$  cm<sup>-1</sup>, and  $E_{02}=0.081\pm0.003$  ev.

An equation analogous to Eq. (2) can be written for *n*-type samples. Figure 8 shows a set of temperature curves for an *n*-type sample with flux as a parameter. An attempt to analyze these curves and similar curves from other *n*-type samples gave conflicting results. This



FIG. 8. Temperature variation of Hall coefficient of an initially n-type sample with various amounts of bombardment as a parameter, bombarded at 200°K.



FIG. 9. Change in the reciprocal of Hall mobility with bombardment for an *n*-type sample bombarded at 200°K. Measurements were made at  $80^{\circ}$ K.

is not surprising in view of the fact that the shape of the removal-rate curve suggests that the levels on the *n*-type side are too closely spaced to enable an analysis. The only estimation of the number of centers responsible for this group of levels is obtained from the drop in  $-\Delta n/\phi$  as the Fermi level passes through them. This is approximately 1.7 cm<sup>-1</sup>. Thus, each of the three sets of levels are introduced at approximately the same rate, i.e., at approximately 1.5/cm.

To determine which levels are donors and which are acceptors it is necessary to rely on mobility changes. Both n- and p-type samples which showed a negative slope of  $\log(R/\rho)$  versus  $\log T$  before bombardment showed a positive slope after appreciable bombardment, thus demonstrating the introduction of ionized scattering centers by bombardment. Figure 9 shows a plot of the reciprocal of Hall mobility,  $\rho/R$ , against flux for the n-type sample of Fig. 8. Positions of the Fermi level are also listed. The initial rise is almost linear and is apparently due to the introduction of ionized defects. After a flux of approximately  $50 \times 10^{13}$ /cm<sup>2</sup> the carrier concentration is dropping very rapidly. This produces less free-carrier shielding and consequently greater scattering which results in an upward curvature of  $\rho/R$ . With larger fluxes the curve levels off, in spite of the fact that the carrier concentration in this range is still decreasing. This leveling off occurs while the Fermi level passes through the range 0.03 to 0.085 ev which is exactly the range in which  $-\Delta n/\phi$  decreases in Fig. 3. This leveling off is interpreted to mean that the scattering per introduced defect is decreasing, or the magnitude of the charge on the centers responsible for the levels on the *n*-type side is decreasing as the Fermi level is lowered through these levels. This behavior indicates that these centers are acceptors. Similar behavior is observed for the p-type sample of Fig. 6, and by the same reasoning it is inferred that the level at approximately  $E_v + 0.048$  ev is a donor. The character of level number 2 remains undecided. It should be pointed out that the above interpretation does not consider the

screening effect which closely spaced donors and acceptors might have on each other.

The initial change of the reciprocal of Hall mobility with flux for both n- and p-type samples is greater than the value calculated assuming all centers singly ionized (see Table I). Thus, the centers must be multiply ionized. The calculated values would be decreased still further by considering the effect of mutual screening due to the proximity of the donors and acceptors.

# **V. CONCLUSIONS**

Electron bombardment of indium antimonide produces remarkably different effects, depending on the temperature of bombardment, or the temperature to which a sample has been raised after bombardment. The greater value of the final Fermi level for samples bombarded at dry ice temperature as compared with samples bombarded at liquid nitrogen temperature, and the different shapes of the removal-rate curves in the two cases, this curve in the latter case being quite asymmetrical, point to a change in the distribution of levels as a sample is heated from liquid nitrogen temperature to dry ice temperature. There is further evidence from the annealing data that after the samples were warmed to room temperature there existed a still different level distribution, possibly all donors.

The levels which lie within the forbidden band, or sufficiently far into the forbidden band to be detected, are associated with multiply ionized states. The level picture for liquid nitrogen bombardments is incomplete, but one level was detected at 0.03 ev above the valence band. The sites responsible for this level are introduced at an estimated rate of 3.5/cm The calculated rate is 24/cm for a threshold displacement energy of 7 ev. If this is the correct threshold value for calculating the number of displacements introduced by 4.5-Mev electrons, then one must assume either that only a fraction of the total number of defects are detected by changes in carrier concentration, or that many of the defects introduced anneal rapidly at liquid nitrogen temperature. In view of the fact that annealing does occur at liquid nitrogen temperature, irradiations at a still lower temperature would be of considerable interest.

The energy level picture is more complete for bombardments at dry ice temperature than for those at liquid nitrogen temperature. There are two levels on the p-type side at 0.048 ev and 0.081 ev, and a group of levels in the region 0.03 to 0.10 ev below the conduction band. Each of these three sets of levels is introduced at approximately the same rate, 1.5/cm. The level at 0.03 ev above the valence band appears to be a donor and the group of levels below the conduction band appears to be acceptors.

Apparently many of the defects introduced at liquid nitrogen temperature are not stable at dry ice temperature, since the rate of generating defects appears to be considerably smaller at the higher temperature.

Samples bombarded at liquid nitrogen temperature and gradually annealed to higher and higher temperature showed three stages of rapid annealing, the first two occurring between liquid nitrogen and dry ice temperature, the latter near room temperature. The annealing changes which occur between liquid nitrogen and dry ice temperature cannot be explained in terms of recombination of vacancies and interstitials only. It is felt that geometrical rearrangements of some of the defects which are not annihilated plays an important role in these annealing processes.

## ACKNOWLEDGMENTS

The author wishes to acknowledge his indebtedness to the late Dr. K. Lark-Horovitz who suggested the problem and offered many timely comments and criticisms. He also wishes to express his gratitude to Dr. H. Y. Fan for suggesting many thought-provoking ideas and to Dr. E. E. Klontz and Dr. J. W. MacKay who rendered considerable guidance throughout the experiments. The crystals were grown by Miss Louise Roth.