

**N 69 24929**

**NASA CR 100844**

TRANSIENT CONDUCTIVITY  
OF  
SILICON

**CASE FILE  
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Final Report:

Contract NAS5-9580

Submitted to:

National Aeronautics & Space Administration  
Goddard Space Flight Center  
Greenbelt, Maryland

Date:

March 20, 1969

PRINCETON RESEARCH & DEVELOPMENT COMPANY

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# TRANSIENT CONDUCTIVITY OF SILICON

## I. INTRODUCTION

In an indirect-bandgap semiconductor like silicon momentum conservation requires that hole-electron recombination must have the participation of the crystal lattice. In practice, recombination occurs when electrons and holes are alternately captured by lattice defects, so called "recombination centers". Whenever a minority carrier is captured by a defect center there are two possible subsequent events. (1) The defect may capture a majority carrier, thus completing the recombination process for one hole-electron pair; or (2) The trapped carrier may be excited thermally back into the minority carrier band before a majority carrier can be captured. The latter "trapping" process has the effect of prolonging the net lifetime of the hole-electron pair.

The usual distinction between a recombination center and a trapping center is simply which process is more probable: majority carrier capture (recombination) or thermal re-emission of the minority carrier (trapping). Obviously, a single center may act as both a recombination center and a trapping center if the probabilities of majority carrier capture and thermal reemission of the minority carrier are comparable.

The Hall-Shockley-Read results have been applied with considerable success to Ge and Si by numerous workers. Blakemore (3) discusses the state of affairs in 1962, and gives a comprehensive bibliography of the work up to that time. Corbett (4) summarizes the work up to 1966 dealing with radiation-damage effects. The latter reference, on pp. 84-5 gives an excellent summary of the multiplicity of radiation-induced defect levels which are found in silicon.

It is apparent from a large body of evidence that many species of defects are produced when silicon is irradiated by electrons, protons, neutrons, etc. These defects are, variously, recombination centers or trapping centers, and a realistic analysis of the radiation damage behavior should be based on the simultaneous existence of more than one type of defect.

Evans and Landsberg (5) have considered transient recombination and trapping in the case where  $\Delta p$  is small and have contributed an interesting matrix formulation of the problem. Unfortunately their work stops short of providing a basis for interpreting experiment in terms of theory.

Curtis (6) has studied steady state recombination in the presence of trapping. His results are in complete agreement with the quasi-equilibrium transient recombination results which are presented here.

Among the published results is a 1963 article by the present writer (7) describing recombination and trapping in normal and electron-irradiated silicon. That article will be referred to here as (I).

We found that irradiation of silicon with high-energy electrons produces a multiplicity of defect species. This finding is consistent with a large body of evidence on the nature of radiation damage in silicon. Many different types of defects are produced, and any analysis is predicated on the existence of only a single species of defect is not realistic.

In the work described in (I) we were able to analyze samples containing numerous types of defects by making certain simplifying assumptions. These assumptions are reviewed in the present paper.

Our purpose in the present paper is: (1) to enlarge the single-level theory presented in (I) to allow both recombination and trapping by the same defect, (2) to allow the simultaneous existence of several species of trapping center, (3) to allow the existence of divalent traps, and (4) to compare the theory with experiment and resolve some inconsistencies which were previously noted, and which resulted from the simplifying assumptions of the single-level theory of (I).

## II. THEORY OF TRAPPING: Single Trap Case

Throughout the following discussion we shall assume n-type material. The treatment may be applied to p-type material by the usual process of interchanging the n-and p-notation. The crystal contains certain recombination processes which have nothing to do with the trapping with which we are here concerned. It will be sufficient for our purposes to characterize the recombination processes as a group by the single parameter  $\tau$ , the lifetime which a minority carrier would have if there were no trapping.

In (I) we considered a sample having recombination and one single species of trap. The traps were assumed not to contribute to recombination; i. e., they were purely trapping centers. Our fundamental approach was similar to the earlier approach of Hornbeck and Haynes<sup>(8)</sup>. We assumed that a condition of quasi thermal equilibrium was established between the

traps and the valence band. On this assumption the trap and valence band populations may be characterized by a single quasi-Fermi level. The calculations and results of (I) are summarized in Appendix A. Our conclusion was that in the single-trap case the excess conductivity decays in two stages, an early stage during which the excess carrier concentration is large compared with the trap density and a final stage during which it is small compared with the trap density, with a broad transition (the "initial" decay) region between the two limiting cases. In the large-injection limit, the recovery is purely exponential, with a time constant  $\tau$ . In the small-injection limit (the "final" decay) the recovery is also purely exponential, with a time constant equal to

Although the theoretical treatment in (I) was limited to the case of a single species of trap it is possible to extend the treatment to many traps provided they are well separated. In this context two traps are "well separated" provided the value of  $p_t/N_t$  for the shallow trap is large compared with the value for the deep trap, and provided the shallow trap concentration is somewhat larger than the deep trap concentration. The value of  $p_t$  depends exponentially on the trap's energy level, and for the separations observed in silicon the values of  $p_t$  for adjacent traps are usually different by orders of magnitude. If adjacent traps have similar concentrations, or if a deep trap is present in a concentration that exceeds that of a shallow trap there are two possible consequences: (1) the shallow trap (with small concentration) may be totally masked by the deep trap, and hence it may be overlooked; (2) the shallow trap, although unresolved, may produce an observable effect which must be taken into account in any analysis of the deep trap.

In our treatment of this problem in (I) we neglected the possibility that recombination might occur at the trapping centers; our assumption was that the traps were able to communicate only with the minority carrier band. If we allow for recombination via this channel the differential equation governing the hole recombination, Equation A1, becomes

$$-\frac{d}{dt}(\Delta p) = \frac{a}{\tau} \Delta p + (1-a) \Delta p (n_0 + \Delta n) v_e \sigma_e \quad (1)$$

where  $\sigma_e$  is the electron capture cross section of the trap when it is occupied by a hole.

We consider two limits: (1)  $p$  large compared with  $N_t$ , and (2)  $p$  small compared with  $N_t$ . We furthermore restrict ourselves to  $p, n$  small compared with  $n_0$ . In this consideration the second term on the right hand side of eq. (1) will be treated as a perturbation of the total recombination rate. It turns out that this is not always the case, especially at low temperatures.

(1) In the limit  $p \gg N_t$ ,

$$-\frac{d}{dt}(\Delta p) = \frac{1}{\tau}(\Delta p) + N_t n_0 v_e \sigma_e \quad (2)$$

This may be integrated directly to give

$$\Delta p = \left( \Delta p_0 + \frac{n_0 \tau}{\tau'} \right) e^{-\frac{t}{\tau}} - \frac{n_0 \tau}{\tau'} \quad (3)$$

where  $\tau = \left[ N_t v_e \sigma_e \right]^{-1}$  and  $\Delta p_0$  is the initial excess hole concentration.

(2) In the limit  $\ll N_t$ ,  $a \rightarrow \frac{p_t}{p_t + N_t}$  and

$$-\frac{d}{dt}(\Delta p) = \frac{a}{\tau} \Delta p + (1-a) \Delta p n_0 v_e \sigma_e \quad (4)$$

Equation (4) may be integrated directly. The decay of  $\Delta p$  is again a pure exponential with a new time constant

$$\tau_1 = \tau \left[ 1 + \frac{N_t}{p_t} \right] \left[ 1 + \frac{n_0 \tau}{p_t \tau'} \right]^{-1}$$

We now wish to compare the large signal and small signal perturbations of the total recombination rate. In the large injection limit the amplitude is perturbed and the order of the perturbation is given by  $n_0 \tau / \Delta p_0 \tau'$ . In the small injection case the characteristic time constant is perturbed and the perturbation is proportional to  $n_0 \tau / p_t \tau'$ . The ratio of these two perturbation factors is simply  $p_t / \Delta p_0$ . For all cases of interest in silicon this ratio is very small. Therefore, the effect of recombination at the traps is more important in the latter stages of the decay than in the early stages.

If we examine the temperature dependence of the small signal perturbation it is easy to show how the error introduced by neglecting recombination at the traps will vary with temperature. In our experiment we measure  $\tau_1$ , which is smaller than the expression for the terminal time constant in the case where recombination is neglected,  $\tau \left[ 1 + \frac{N_t}{p_t} \right]$ . Assuming again for the sake of simplicity that  $p_t \ll N_t$ , the apparent experimental value of  $N_t/p_t$  will be systematically lower than its true value, and the apparent value of  $p_t$  will be larger than its true value. Consequently the trap energy level, which is computed from the apparent  $p_t$  will appear to be closer to the valence band than it really is. Since the principal temperature dependence occurs in the factor  $p_t$  the error will increase with decreasing temperature. As we will point out in the following sections this is qualitatively what has been



observed for the sample reported in (I) and in other samples studied since.

An example of this effect is the hole trap at  $E_v + 0.29$  eV which was produced by electron irradiation of sample 1160 in (I). The apparent energy level of this trap was 0.29 eV when the sample was at  $-47^\circ\text{C}$ , and 0.25 eV when the sample was cooled to  $-75^\circ\text{C}$ . Following our discussion above, as the sample is cooled, and recombination begins to dominate, our analysis no longer yields  $p_t/N_t$  for the ratio of fast/slow time constants. We begin to observe, instead,  $(1 - p_t/N_t) n_0 v_e \sigma_e$ . This being the case, we can obtain a value for the electron-capture cross section of the trap  $\sigma_e$ . This cross section is a property of the trap which is not observable in any other manner.

For the "0.29 eV" trap,  $\sigma_e = 6 \times 10^{-18} \text{cm}^2$ . This cross section is probably too large for a divalent acceptor (which one would predict to have  $\sigma_e = 10^{-20} \text{cm}^2$ ) so the trap is most likely a monovalent acceptor.

In the same sample, 1160, the trap at 0.39 eV exhibits the same phenomenon: a shift in the apparent energy level with sample temperature. For this trap, the electron capture cross section necessary to account for the shift is  $\sigma_e = 2 \times 10^{-20} \text{cm}^2$ . This value is probably indicative of a divalent acceptor.

### III. MULTIPLE TRAPS

The theoretical treatment of trapping outlined above is restricted to samples containing only one species of trap. We estimated that the single trap theory was applicable to samples containing more than one species, provided the traps are well separated, as defined above. In order to verify this estimation, and to extend the treatment to cases where the traps are not well separated, we now consider samples containing two species of traps.

As in the single-trap case, we consider a sample of n-type material. At time  $t = 0$  the excess hole concentration is  $\Delta p_0$ . The recombination processes in the crystal (exclusive of the traps being studied) are represented by the lifetime  $\tau$ . There are two sets of traps:  $N_1$  traps per unit volume having

energy level  $E_1$ , and  $N_2$  traps per unit volume having energy level  $E_2$ . Both are assumed to act purely as hole traps, capturing holes from the valence band, and re-emitting holes back into the valence band. It is assumed that the traps are non-interacting; a hole cannot move from one trap to another without passing first into the valence band.

We assume quasi-thermal equilibrium between each of the sets of traps and the valence band; the charge populations of the traps and the valence band may be described by a single quasi-Fermi level (q.f.l.)  $F_t$ . This assumption means that the excess holes are exchanged freely and rapidly between the two sets of traps and the valence band. It is essentially a condition of multiple trapping, in which the holes are captured and freed many times on average before recombination occurs. We wish to calculate for any given set of crystal parameters (including the excess carrier concentration) the quasi-thermal equilibrium distribution of the excess carriers among the two sets of traps and the valence band.

Under these conditions the populations of traps and valence band are given by the following equations. The number of traps #1 which are occupied by holes is:

$$\beta_1 \Delta p = N_1 e^{\frac{E_1 - F_t}{kT}} \left[ 1 + e^{\frac{E_1 - F_t}{kT}} \right] \quad (5)$$

Similarly, the number of traps #2 which are occupied by holes is

$$\beta_2 \Delta p = N_2 e^{\frac{E_2 - F_t}{kT}} \left[ 1 + e^{\frac{E_2 - F_t}{kT}} \right] \quad (6)$$

The number of free holes is given by

$$\begin{aligned} \propto \Delta p &= (1 - \beta_1 - \beta_2) \Delta p = N_v e^{\frac{E_v - F_t}{kT}} \\ &= p_1 e^{\frac{E_1 - F_t}{kT}} \end{aligned} \quad (7)$$

Therefore we have three equations (5 - 7) in three unknowns ( $\beta_1$ ,  $\beta_2$  &  $F_t$ ). We can completely specify the free vs trapped hole concentrations in terms of  $F_t$ . Consequently our attention here will be on the behavior of  $F_t$  as a function of the sample parameters. We can accomplish this by adding equations (5) through (7).

$$p = N_1 \left( \frac{x}{1+x} \right) + N_2 \left( \frac{Ax}{1+Ax} \right) + p_1 x \quad (8)$$

Where  $x \equiv e^{\frac{E_1 - F_t}{kT}}$  and  $A \equiv e^{\frac{E_2 - E_1}{kT}}$

We have here eliminated  $\beta_1$  &  $\beta_2$ .

If Equation (8) is expanded, we obtain

$$(1+x)(1+Ax) \Delta p = N_1 x (1+Ax) + N_2 Ax (1+x) + p_1 x (1+x)(1+Ax) \quad (9)$$

If we further substitute  $B \equiv \frac{p_1}{N_1}$   $C \equiv \frac{N_2}{N_1}$  and D we have:

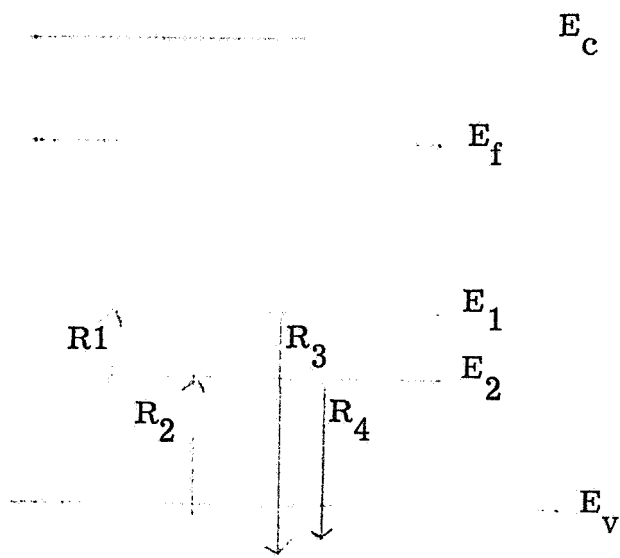
$$ABx^3 + [B(1+A) + A(1+C) - AD] x^2 + [B + AC + 1 - D - AD] x - D = 0$$

This equation is cubic in  $x$ . It has three roots, all of which are real, one positive, and the other two negative. According to our definition of  $x$ , only the positive root is physically meaningful. Once we have determined the positive root for any given set of parameters,  $N_1$ ,  $N_2$ ,  $E_1$ ,  $E_2$ , and  $\Delta p$  we can calculate  $F_t$  and determine the distribution of the excess holes. Knowing the lifetime  $\tau$  we can then calculate the instantaneous recombination rate as a function of  $\Delta p$ , and thus compute the transient excess conductivity of the sample.

#### IV. DIVALENT TRAPS

We next consider the case of a sample containing a single species of divalent trap. As in the previous cases, we represent the recombination processes by the lifetime  $\tau$ . We again assume quasi equilibrium, but as Sah and Shockley have pointed out<sup>(9)</sup>, one cannot describe the populations of a multivalent defect by means of a quasi-Fermi level. Our approach is formally the same as for the multiple trap calculation, except that instead of characterizing the system by a q.f.l. we write detailed balance equations for the various states.

The system is illustrated in the following figure:



DEFINITIONS:

$N_t$  = the trap concentration

$(E_1 - E_v)$  = the binding energy of a single hole to the trap

$(E_2 - E_v)$  = the binding energy of a second hole to the trap

$\sigma_1$  = the cross section of the trap for capture of a hole when the trap is empty

$\sigma_2$  = the cross section of the trap for capture of a second hole when it is occupied by one hole

$\tau_1$  = the mean time for a hole to be thermally excited into the valence band when it is single trapped (emission energy =  $E_1 - E_v$ )

$\tau_2$  = the mean time for thermal excitation from the trap to the valence band when there are two holes on the trap

$\Delta p$  = the excess hole concentration

$\alpha$  = the fraction of  $\Delta p$  that are free

$\beta_1$  = the fraction of the traps occupied by one hole

$\beta_2$  = the fraction of the traps occupied by two holes

$v_h$  = the thermal velocity of a free hole

$R_1$  = the rate at which empty traps capture holes

$R_2$  = the rate at which singly-occupied traps capture holes

$R_3$  = the rate of thermal emission into the valence band from singly-occupied traps

$R_4$  = the rate of thermal emission from doubly-occupied holes

Under our condition of quasi-thermal equilibrium the trap populations are nearly constant, and detailed balance requires that  $R_1 = R_3$  and  $R_2 = R_4$ .

The four rates can be determined:

$$R_1 = \alpha \Delta p (1 - \beta_1 - \beta_2) N_t v_h \sigma_1 \quad (11a)$$

$$R_2 = \alpha \Delta p \beta_1 N_t v_h \sigma_2 \quad (11b)$$

$$R_3 = \beta_1 N_t / \tau_1 \quad (11c)$$

$$R_4 = 2 \beta_2 N_t / \tau_2$$

The two thermal emission times  $\tau_1$  and  $\tau_2$  can be shown from detailed balance at thermal equilibrium to be equal to

$$\tau_1 = (p_1 v_h \sigma_1)^{-1} \quad (12a)$$

$$\tau_2 = (p_2 v_h \sigma_2)^{-1} \quad (12b)$$

where  $p_1$  and  $p_2$  are the usual Shockley-Read parameters ( $p_1 = N_v e^{(E_v - E_1)/kT}$  and  $p_2 = N_v e^{(E_v - E_2)/kT}$ ).

Equating  $R_1$  to  $R_3$  and  $R_2$  to  $R_4$ :

$$\alpha \Delta p (1 - \beta_1 - \beta_2) N_t v_h \sigma_1 = \beta_1 N_t p_1 v_h \sigma_1 \quad (13a)$$

$$\alpha \Delta p \beta_1 N_t v_h \sigma_2 = 2 \beta_2 N_t p_2 v_h \sigma_2 \quad (13b)$$

and simplifying:

$$\alpha \Delta p (1 - \beta_1 - \beta_2) = \beta_1 p_1 \quad (14a)$$

$$\alpha \Delta p \beta_1 = 2 \beta_2 p_2$$

These two equations relate the instantaneous population distribution parameters  $\alpha$ ,  $\beta_1$ , and  $\beta_2$  to the physical quantities describing the crystal. We can write a third equation relating these quantities using the requirement that the total free plus trapped hole concentration must add up to  $\Delta p$ .

$$(1 - \alpha) \Delta p = (\beta_1 + 2\beta_2) N_t. \quad (15)$$

We can eliminate  $\beta_1$  and  $\beta_2$  from these three equations, and we obtain:

$$\frac{1}{2} \alpha^3 \Delta p^2 + \alpha^2 \Delta p (N_t + p_2 - \frac{1}{2} \Delta p) + p_2 (p_1 - \Delta p + N_t) - p_1 p_2 = 0 \quad (16)$$

As in the two-trap case, we obtain a cubic equation for the occupancy fraction in terms of the crystal parameters. If we again make the substitutions for A, B, and D defined on page 9 equation (16) becomes:

$$\alpha^3 D^2 + \alpha^2 D (2 + 2\frac{B}{A} - D) + 2\alpha \frac{B}{A} (1 - D + B) - 2\frac{B^2}{A} = 0 \quad (17)$$

For comparison, if we write the cubic equation for the two-trap case in terms of A, B, C and D, we have:

$$\alpha^3 D^2 + \alpha^2 D (\frac{B}{A} + B + 1 + C - D) + \alpha \frac{B}{A} (1 - D + B + AC - AD) - \frac{B^2}{A} = 0$$

It is interesting to note that in the divalent case the cubic equation for  $\alpha$  does not contain the two capture cross sections,  $\sigma_1$  and  $\sigma_2$ .

## V. DISCUSSION OF RESULTS OF CALCULATIONS

### A. Two Well-Separated Traps

The theoretical dependence of  $\propto$  vs.  $\Delta p$  for a representative two-trap example is shown in Fig. 1. The curve clearly has three distinct regions. In region I the two traps are saturated, and the electron-hole recombination proceeds as though the traps were absent. In region II the deep traps are still saturated, but the population of the shallow traps changes rapidly with  $\Delta p$ . In region III the shallow traps are almost all empty and the population of the deep traps varies rapidly with  $\Delta p$ .

Fig. 2 shows  $x$  vs.  $\Delta p$  for the same trap parameters. Since the logarithm of  $x$  is proportional to the position of the q. f. l. this Figure shows how the position of the q. f. l. varies with  $\Delta p$ . Two ordinates are labelled  $E_1$  and  $E_2$ ; these are the points at which the q. f. l. lies at the energy level of the two traps, respectively. The curve is linear at the two extremes, region I and region III. These are regions in which the q. f. l. moves linearly time during the recovery, and the recovery curve is approximately a pure exponential. If the separation between  $E_1$  and  $E_2$  were sufficient we would expect to see a third linear region between  $E_1$  and  $E_2$ , but this is not visible in the example chosen.

In this example, the single-level theory can be applied without introducing significant error.

### B. Two Poorly-Separated Traps.

Several examples of two poorly-separated traps are shown in Figs. 3. In Fig. 3a the trap parameters are the following:

$$A = .003$$

$$B = .001$$

$$C = 3.3$$



This corresponds to  $p_1/N_1 = .001$ ,  $p_2/N_2 = .1$ ,  $N_2/N_1 = 3.3$ . For comparison, we have also plotted the single-trap curve, for a trap with the same value of  $p/N$  as the deep trap in the example being considered. Clearly, the shape of the curve for the two-trap example is different from the single-trap comparison, but it is equally clear that any determination of the parameters describing the shallow trap is made very difficult by the presence of the deep trap. In practice, if one mistakenly applied the single-trap theory to this two-trap example, one would make virtually no error in determining the energy level (of the deep trap), but one would err in determining the trap concentration by a factor of about 1.5.

Fig. 3b shows  $\chi$  vs.  $\Delta p$  for the following trap parameters:  $A = .003$ ,  $B = .001$ ,  $C = 1.0$ . This corresponds to the case where the shallow trap is present in the same concentration as the deep trap. In this figure we have again plotted the single-trap curve for  $p/N = .001$ . Obviously the single-trap curve and the two-trap curve are almost indistinguishable.

Fig. 3c shows  $\chi$  vs.  $\Delta p$  for the trap parameters:  $A = .003$ ,  $B = .001$ ,  $C = 0.3$ , and for comparison the same single-trap curve as in the previous two figures. In this example, the shallow trap has lower concentration than the deep trap, and the single-trap curve is totally indistinguishable from the two-trap curve.

### C. Divalent Traps

A number of selected examples of divalent traps are shown in Figs. 4 and 5. The behavior can be summarized as follows: if the shallow level associated with the divalent trap is quite shallow the divalent trap is totally indistinguishable from a single monovalent trap.

As the shallow energy level approaches the deep level, ( $A \rightarrow 1$ ) the sample gives the appearance of a single trap, lying at the deeper energy level of the divalent pair, with a slight apparent exaggeration of the trap concentration.

We conclude, therefore, that the structure that we have observed in the transient conductivity (see, for example, (I) and the following section of this paper) cannot be ascribed to one single species of divalent trap in our samples. The recovery structure is caused by the existence of several distinct species of traps. There is no basis in our observations for distinguishing between monovalent and divalent traps.

## VI COMPARISON WITH EXPERIMENT

A number of samples have been studied using the same experimental technique as described in I. Each wafer of material was prepared with ohmic contacts, placed in series with a battery and a load resistor, and exposed to short bursts of electrons from a 1-MeV Van-de-Graaff generator. The transient excess conductivity was observed oscillographically. The switching time of the high-energy electron beam was very short (less than 1 nanosecond) compared with the samples' transient time constants.

All of the samples studied evidenced multiple traps, though in many of the samples at some temperatures only one trap was effective. In such cases the single trap theory was adequate. In most of the samples exhibiting multiple traps the single level theory could be applied with no significant errors. We will show examples of this. In such cases, where the traps are quite well separated, the single-level theory gives the same trap parameter assignments as the two-trap theory. In a few instances the separate species of traps were sufficiently well separated to indicate clearly that multiple traps were present, but the single-level analysis gave erroneous results. In these cases we have applied the 2-trap theory, fitting the theoretical curves to the experimental results to give the trap parameters.

For example, Fig. 6 shows sample #1160,  $T = 75^{\circ}\text{C}$ , sample illuminated with a tungsten lamp. We have plotted  $\frac{1}{v} \frac{dv}{dt}$  vs.  $V$ , which corresponds to our theoretical  $\alpha$  vs.  $\Delta p$ . The points are experimental, taken from oscillographs, and the solid curve is a theoretical two-trap solution. The 2-trap parameters were estimated from a single-level analysis of the oscillographs. The agreement between theory and experiment is excellent, and illustrates the validity of the single-level theory when the traps are well-separated.

In Fig. 7 we show the same sample at the same temperature,  $-75^{\circ}\text{C}$ , with no illumination. Here again, we have plotted the experimental points and a theoretical 2-trap curve, using parameters determined from a single-level analysis. Although the apparent trap separation is less good than in Fig. 6, the agreement between theory and experiment is quite good.

The effect of illumination is interesting. Analysis of Figs. 6 and 7 leads to practically identical determinations of the trap energy levels. The principal effect of the light is to change the apparent concentrations of the two species of traps. In altering the apparent trap concentrations in this specimen the two traps are better separated under illumination than in the dark. This suggests the value of illumination in future work in unravelling complicated multiple-trap samples. It also suggests the possibility that tungsten light may not be the best to use; the dependence of this phenomenon on the spectral content of the light source should be investigated.

Fig. 8 shows the results obtained with another sample of n-type material. The points are experimental, and the curve is theoretical. The theoretical 2-trap parameters were selected to give the best experimental fit. This sample is interesting, since the single-level analysis gave significantly different trap parameters from the final 2-trap results.

Experimental measurements consisting of oscillographic recordings at various sample temperatures, before and after electron-irradiation, have been carried out using a total of four samples, in addition to the sample previously reported in (I). The results of our analysis of these samples are summarized in the tables below.

In Tables 1-5, each entry consists of (a) the trap concentration, and (b) the trap energy level, measured from the minority carrier band edge.

Table 1 shows the results of sample 1160, taken from (I). As previously determined, there are two levels existing before irradiation, and one level produced by irradiation. There is a deviation from the true energy levels at low sample temperatures due to the effect of recombination as described in Section II above. The deviating energy level values are indicated in parentheses.

Table 2 shows the results of another n-type sample, Number 37B. The first three measurements were made before irradiation, and the last three were made after irradiation by a flux of  $6 \times 10^{14}$  electrons/cm<sup>2</sup> at an energy of 1 MeV. There are clearly four, and probably five, traps present in the sample. Three of the traps, at  $E_V + .22$  eV,  $E_V + .30$  eV, and  $E_V + .34$  eV were present before and after irradiation. The trap at  $E_V + .37$  eV was only observed after irradiation, as was the probably trap at  $E_V + .44$  eV. The production rate for the .37 eV trap is about  $.09 \text{ cm}^{-1}$  for 1 MeV electrons.

Table 3 shows the results of another n-type sample, number ZL83. One trap, at  $E_V + .40$  eV, has a concentration that is independent of irradiation. A second trap at  $E_V + .30$  eV increases in concentration linearly with irradiation flux. Its introduction rate by 1 MeV electrons is  $.01 \text{ cm}^{-1}$ .

Table 4 shows the results of a p-type sample, number 852. There are two traps present before irradiation, at  $E_C - .34$  eV is produced by irradiation. Its introduction rate by 1 MeV electrons is  $.01 \text{ cm}^{-1}$ .

Table 5 shows another p-type sample, number SG1. Its resistivity was 0.5 ohm-cm. The first specimen of this crystal showed three distinct traps, at  $E_C - .32$  eV,  $E_C - .36$  eV, and  $E_C - .46$  eV. The total trap density was about  $4 \times 10^{14} \text{ cm}^{-3}$ . The lifetime (i. e., the recovery time constant at such injection levels that all traps were saturated) was 2 microseconds.

The sample was then subjected to a 30 minute bake at 1200<sup>0</sup> C and again prepared with ohmic contacts. The same three traps were observed, with roughly the same concentrations, though with some added complexity of analysis. The lifetime dropped to 0.1 microsecond as a result of the bake, and a new set of traps at  $E_c - 0.4$  eV was observed. The total trap concentration rose to about  $1.5 \times 10^{15}$  cm<sup>-3</sup>.

A second specimen from this crystal was given a 900<sup>0</sup> C bake. After this treatment the lifetime was 1.5 microsecond, and the three traps listed above (at .32, .36, and .46 eV) were observed in similar concentrations (a total of about  $4 \times 10^{14}$  cm<sup>-3</sup>).

Irradiating this sample with 700 keV electrons to a flux of  $1 \times 10^{15}$  cm<sup>-2</sup> reduced the lifetime to 0.3 microsecond and increased the total trap concentration to  $10^{15}$  cm<sup>-3</sup>. Most of the pre-irradiation traps were unaffected by the bombardment. The radiation-produced traps were approximately at  $E_c - .4$  eV. (The same energy level as the traps produced by the 1200<sup>0</sup> C treatment). At higher irradiation fluxes the lifetime decreased further and the trap concentration increased, but the trap spectrum became so complex that a reliable analysis was impossible.

Some exploratory measurements were made using this sample looking for very long time constant recovery phases, longer than the time between bursts of high-energy electrons from the Van-de-Graaff generator (60 bursts per second). A tungsten lamp was used for this purpose, with an ordinary mechanical switch. The sample voltage was monitored after the illumination was switched off using an X-t recorder. A typical voltage-vs.-time curve is shown in Fig. 9. Two well-separated traps are easily resolved. Their concentrations and energy levels were determined using the single-level theory.

All of these delayed-recovery measurements were made at low sample temperatures (below -100<sup>0</sup> C). As a consequence, following our discussion above of the effect at low temperatures of recombination at the

traps, and following our observations of recombination effects at somewhat higher temperatures, we must regard the trap energy levels observed in these runs as questionable. The trap concentrations are probably reliable, however.

We propose that recombination is dominant at the deep traps seen in the very slow transient recovery at low temperatures. If this is correct, the ratio of slow to fast time constants is not equal to  $(1 + n_t/N_t)^{-1}$  as in the pure trapping case, but the ratio is actually equal to  $p_o v_h \sigma_h$ . Knowing the values of  $p_o$  and  $v_h$  we can determine thus the value of  $\sigma_h$ . For the traps seen in the present sample SG1, our measurements imply a hole capture cross section that is between  $10^{-26}$  and  $10^{-30}$  cm<sup>2</sup>, a range of values that strongly suggests that the traps are multivalent donors.

A summary of the trapping levels which we have seen in all of the samples is shown in Fig. 10. Those levels which are produced by irradiation are shown in dashed lines; the levels which existed before irradiation are shown in solid lines.

## SUMMARY

We have studied theoretically the behavior of samples containing (a) a set of monovalent traps; (b) two sets of monovalent traps; (c) a set of divalent traps. Case (b) is qualitatively different from the other two cases, and by comparison with our experimental results we can conclude that our samples all contained multiple sets of traps. We cannot distinguish between monovalent and divalent traps. The substance of this conclusion is that our observed transient structure is caused by many sets of traps rather than by a small number of multivalent traps. The sets we observe may be either monovalent or multivalent.

We have experimentally studied five different samples of silicon, three n-type and two p-type. All of the samples exhibited evidence of several sets of traps, some existing before irradiation and some produced by electron bombardment. The method of analysis provided some internal consistency checks: the trap concentrations and energy levels did not change with sample temperature, with the exception of the low-temperature effect attributed to the onset of recombination at the traps.

In the p-type sample which we subjected to a high-temperature bake, we produced changes which closely resembled the damage due to electron bombardment: the lifetime was reduced and a set of traps was produced at an energy level which was the same as a set of traps seen after electron irradiation.



In Appendix A we discuss an interesting parallel between our multiple-trapping theory and an annealing study by Damask and Dienes.<sup>(10)</sup> Our quasi-thermal equilibrium assumptions are virtually identical to theirs. The only difference is that in their case they deal with free and trapped lattice defects (vacancies and interstitials) whereas we deal with free and trapped charge carriers. In their annealing study Damask and Dienes confine themselves to the low-concentration case (lattice defect concentration small compared with the concentration of trapping sites). The applicability of our treatment to the general case of annealing where the defect concentration may be comparable to or larger than the concentration of trapping sites should not be overlooked.

We consider a sample of n-type semiconductor having recombination processes which would yield a hole lifetime  $\tau$  if there were no trapping. The semiconductor also contains a group of traps having an energy level  $E_t$ , a concentration  $N_t$  traps per unit volume, and hole- and electron capture cross sections  $\sigma_h$  and  $\sigma_e$ , respectively.

At time  $t = 0$  the excess hole concentration is  $\Delta p_0$  and we assume following Hornbeck and Haynes (6) that a condition of quasi thermal equilibrium exists between the traps and the valence band. Under this condition, the charge populations of the traps and the valence band can be specified in terms of a single quasi-Fermi level  $F_t$ .

Under these assumptions the transient excess hole concentration is governed by the following differential equation:

$$\frac{d}{dt}(\Delta p) = -\frac{a}{\tau} \Delta p \quad (\text{A1})$$

$$a = \frac{(\Delta p - N_t - p_t) + \left[ (\Delta p - N_t - p_t)^2 + 4 p_t \Delta p \right]^{\frac{1}{2}}}{2 \Delta p} \quad (\text{A2})$$

where  $p_t = N_V e^{\frac{E_V - F_t}{kT}}$ ,

and  $a$  is the instantaneous fraction of the excess holes  $\Delta p$  which are free.

Computer solutions of these equations for various trap densities and energy levels were obtained and discussed in (I). We may examine the solutions in two limiting cases: (1)  $\Delta p \gg N_t$  and, (2)  $\Delta p \ll N_t$

In case (1)  $\Delta p \gg N_t$ , the decay of  $\Delta p$  is a pure exponential with a time constant  $\tau$  that is equal to the value of the lifetime in material having the same recombination centers, but no traps.

In case (2)  $\Delta p \ll N_t$ , the decay of  $\Delta p$  is also a pure exponential, with a time constant that is equal to  $\tau \left[ 1 + \frac{N_t}{p_t} \right]$

The transition region between (1) and (2) is quite broad; it may extend over two orders of magnitude of  $\Delta p$ . This circumstance rules out any analysis of the transient conductivity in terms of a simple superposition of pure exponentials.

It is informative to examine the conditions under which quasi-thermal equilibrium may occur. The first requirement is that the hole capture time of the traps, which is given by the expression  $\tau_c = (N_t \sigma_h v_h)^{-1}$  be short compared with  $\tau$ , i. e.,

$$N_t v_h \sigma_h \gg \frac{1}{\tau} \quad (\text{A3})$$

The second requirement is that the thermal emission time  $\tau_E$  which is given by the expression  $\tau_E = (p_t v_h \sigma_h)^{-1}$  must be short compared with the terminal time constant; i. e. ,

$$\tau_E \ll \tau \left[ 1 + \frac{N_t}{P_t} \right] \quad (A4)$$

The latter requirement may be thought of as being equivalent to a multiple-trapping condition, in which the holes are exchanged freely and rapidly between the traps and the valence band before recombination can occur.

Since for all important traps  $N_t \gg P_t$  the second requirement may be rewritten  $\tau_E \ll \tau \frac{N_t}{P_t}$  which reduces to

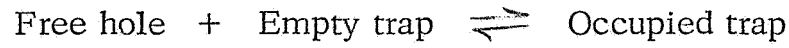
$$N_t v_h \sigma_h \gg \frac{1}{\tau} \quad (A5)$$

i. e. , the two requirements (A3) and (A5) are equivalent.

In practice these two requirements may be somewhat relaxed without invalidating the model. As long as  $N_t \sigma_h v_h$  is not much smaller than  $\tau^{-1}$  the results appear to be valid.

There is an interesting parallel between the present treatment of the transient behavior of excess carriers in a semiconductor and a theoretical study of the annealing of excess lattice vacancies by Damask and Dienes<sup>(10)</sup> The model which they used to describe the annealing kinetics was quite analogous to the carrier-trapping model employed in our calculations. In their model, free vacancies were trapped and untrapped at lattice impurity sites; a competing process caused the annihilation of the vacancies. They calculated the annealing behavior when the concentration of vacancies was small compared with the impurity concentration in the crystal, and obtained solutions which are equivalent to our small signal case in which the decay is

a pure exponential with time constant given by  $\tau (1 + \frac{N_t}{p_t})$ . In fact, we might have derived Eq. (A2) following Dienes and Damask by treating the quasi-equilibrium reaction:



The law of mass action (which is equivalent to our quasi-equilibrium assumption) requires that

$$\frac{a \Delta p [N_t - (1 - a) \Delta p]}{(1 - a) \Delta p} = \text{constant.}$$

If we solve this equation for  $\underline{a}$ , and take  $p_t$  for the value of the constant, we obtain equation (A2) immediately.

## APPENDIX B

### COMPUTER SOLUTIONS OF THE TWO-TRAP PROBLEM

We have carried out computer solutions of equation (10) for the following values of the parameters A, B, C, and D:

<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
0.3	0.03	- 10	200
0.1	0.01	7	100
0.03	0.003	5	50
0.01	0.001	3.33	20
0.003	0.0003	2	10
0.001	0.0001	1.5	7
	0.00003	1	4
	0.00001	0.7	2
		0.5	1
		0.3	0.7
		0.2	0.4
		0.15	0.2
		0.1	0.1
			0.03
			0.01

The values of A were chosen to give a representative selection of separations between the two sets of traps. B was chosen to allow a range of absolute positions of the energy levels of the two traps. Sufficient values of C were selected to allow the concentration of either set of traps to vary up to ten times the concentration of the other set. Sufficient values of D were chosen to allow us to construct, from the computer solutions, a continuous curve giving  $X$  vs. D. Once  $X$  is known for given values of A, B, C, and D, the occupancy fractions of the two sets of traps and the population of the valence band can be computed from the following equations, which follow from equations (5), (6), and (7):

$$(B1) \quad \beta_1 = \frac{x}{D(1+x)}$$

$$(B2) \quad \beta_2 = \frac{ACx}{D(1+Ax)}$$

$$(B3) \quad \alpha = 1 - \beta_1 - \beta_2$$

TABLE I  
Sample #1160

T =	+27°C	-34°C	-62°C	-78°C	-88°C	0°C	-47°C	-75°C
Trap #1							$9 \times 10^{13}$ .29 eV	$1.3 \times 10^{14}$ .25 eV
#2	$1.4 \times 10^{13}$ .37 eV	$2.1 \times 10^{13}$ (.33 eV)	$2.4 \times 10^{13}$ (.32 eV)	$3.4 \times 10^{13}$ (.28 eV)	$4 \times 10^{13}$ .36 eV	$2.4 \times 10^{13}$ .38 eV	$2.9 \times 10^{13}$ (.35 eV)	
#3	$1 \times 10^{12}$ .52 eV					$3.4 \times 10^{12}$ .55 eV		
	←	← $\phi = 0$	←	←	←	←	$\phi = 3.6 \times 10^{14}$	←
							$\frac{\text{electrons}}{\text{cm}^2}$	.7 MeV
			TRAP DENSITIES : $\text{cm}^{-3}$					
			ENERGY LEVELS : eV			FROM VALENCE BAND		

TABLE 2  
Sample 37B

T =	+27°C	-26°C	-64°C	+20°C	-20°C	-62°C		
Trap #1			3.5x10 <sup>14</sup> .21 eV			2x10 <sup>14</sup> .24 eV		
#2		1.8x10 <sup>14</sup> .29 eV	1.7x10 <sup>14</sup> .31 eV		1.1x10 <sup>14</sup> .29 eV	1.1x10 <sup>14</sup> .30 eV		
#3	6.3x10 <sup>13</sup> .34 eV	7x10 <sup>13</sup> .34 eV			7x10 <sup>13</sup> .35 eV	7x10 <sup>13</sup> .34 eV		
#4				6.6x10 <sup>13</sup> .37 eV	4.7x10 <sup>13</sup> .38 eV	4.4x10 <sup>13</sup> .37 eV		
#5					1.9x10 <sup>13</sup> .44 eV			
	← φ = 0 →	← φ = 0 →	← φ = 0 →	← φ = 6x10 <sup>14</sup> →	← φ = 6x10 <sup>14</sup> →	← φ = 6x10 <sup>14</sup> →		.8 MeV
	TRAP DENSITIES : cm <sup>-3</sup>			TRAP DENSITIES : cm <sup>-3</sup>			electrons cm <sup>-2</sup>	
	ENERGY LEVELS : eV			ENERGY LEVELS : eV			FROM VALENCE BAND	





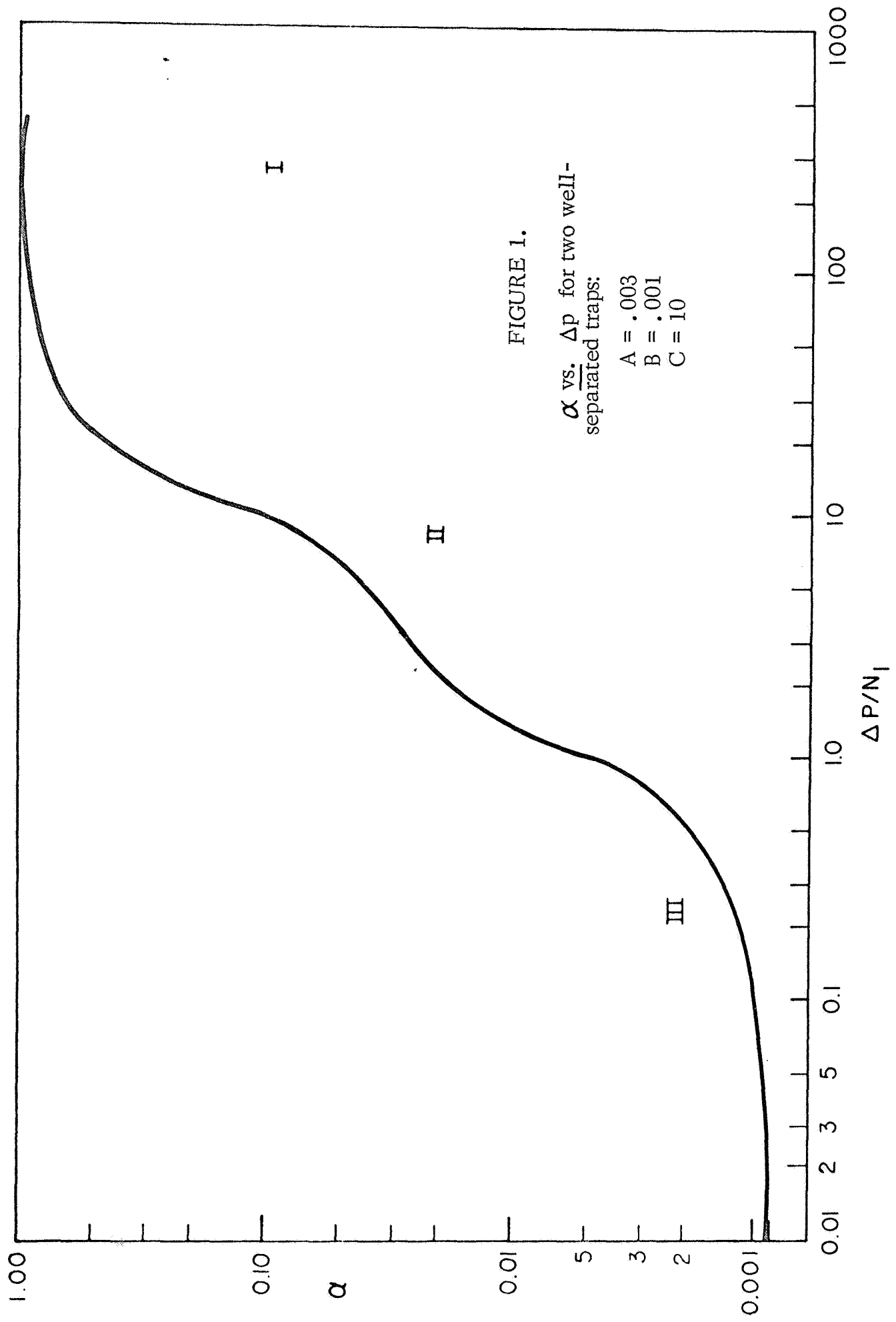
TABLE 4  
Sample 852

T =	-30°C	-40°C	-90°C	+26°C	-22°C	-56°C			
Trap #1	$3.5 \times 10^{13}$ .29 eV	$2.6 \times 10^{13}$ .30 eV	$2.5 \times 10^{13}$			$1.8 \times 10^{13}$ .30 eV			
#2					$1.4 \times 10^{13}$ .34 eV	$6 \times 10^{12}$ .34 eV			
#3	$1.8 \times 10^{12}$ .48 eV			$1.8 \times 10^{12}$ .50 eV	$1.0 \times 10^{12}$ .46 eV	$6 \times 10^{11}$ .44 eV			
	←	$\phi = 0$	→	←	$\phi = 1.3 \times 10^5$	→			
					$\frac{\text{electrons}}{\text{cm}^2}$	.8 MeV			
					TRAP DENSITIES : $\text{cm}^{-3}$				
					ENERGY LEVELS : eV	FROM CONDUCTION BAND			

TABLE 5  
Samples SG1, SG2, SG3, SG4

T = Trap #1	← 1 →		← 2 →		← 2I →		← 3 →		← 4 →		← 4I →		← 4 →		← 4I →		4I <sub>2</sub>						
	+30°C	0°C	-21°C	-81°C	-8°C	-42°C	-63°C	0°C	-25°C	-13°C	-50°C	-47°C	-38°C	-68°C	-62°C	-68°C		-103°	-110°	-110°	-108°	-85°	
						3x10 <sup>14</sup> .26 eV	6x10 <sup>14</sup> .27 eV						4x10 <sup>14</sup> .27 eV	2.4x10 <sup>14</sup> .33 eV	6x10 <sup>14</sup> .30 eV	4x10 <sup>14</sup> .29 eV	7x10 <sup>14</sup> (.28 eV)	1x10 <sup>14</sup> (.23 eV)	1x10 <sup>14</sup> (.23 eV)	2x10 <sup>14</sup> (.26 eV)	3.6x10 <sup>14</sup> (.25 eV)		
#2			1.5x10 <sup>14</sup> .32 eV	1.10 <sup>14</sup> (.28 eV)		M	M				1.7x10 <sup>14</sup> .32 eV				3x10 <sup>14</sup> .39 eV	2.4x10 <sup>14</sup> .35 eV	1x10 <sup>14</sup> (.30 eV)	1.3x10 <sup>14</sup> (.26 eV)	1x10 <sup>14</sup> (.32 eV)	2x10 <sup>14</sup> (.34 eV)			
#3		6x10 <sup>13</sup> .36 eV	6x10 <sup>13</sup> .38 eV	1.5x10 <sup>14</sup> (.32 eV)	5x10 <sup>13</sup> .36 eV	1.5x10 <sup>14</sup> .37 eV	3.6x10 <sup>14</sup> (.35 eV)		1.2x10 <sup>14</sup> .36 eV	2x10 <sup>14</sup> .37 eV	3x10 <sup>14</sup> .35 eV	1.7x10 <sup>14</sup> .36 eV	2x10 <sup>14</sup> .36 eV										
#4										2.3x10 <sup>14</sup> .41 eV	3x10 <sup>14</sup>									1x10 <sup>15</sup> (.39 eV)			
#5	2.5x10 <sup>13</sup> .46 eV	3x10 <sup>13</sup> .46 eV	3x10 <sup>13</sup> .46 eV		4x10 <sup>13</sup> .44 eV		5x10 <sup>13</sup> .45 eV										1.1x10 <sup>14</sup> .45 eV			1.4x10 <sup>14</sup> .46 eV	2x10 <sup>14</sup> .46 eV	3.6x10 <sup>14</sup> .44 eV	
#6																						6.5x10 <sup>13</sup> .52 eV	

TRAP DENSITIES : cm<sup>-3</sup>  
ENERGY LEVELS : eV FROM CONDUCTION BAND  
M = Masked by adjacent levels



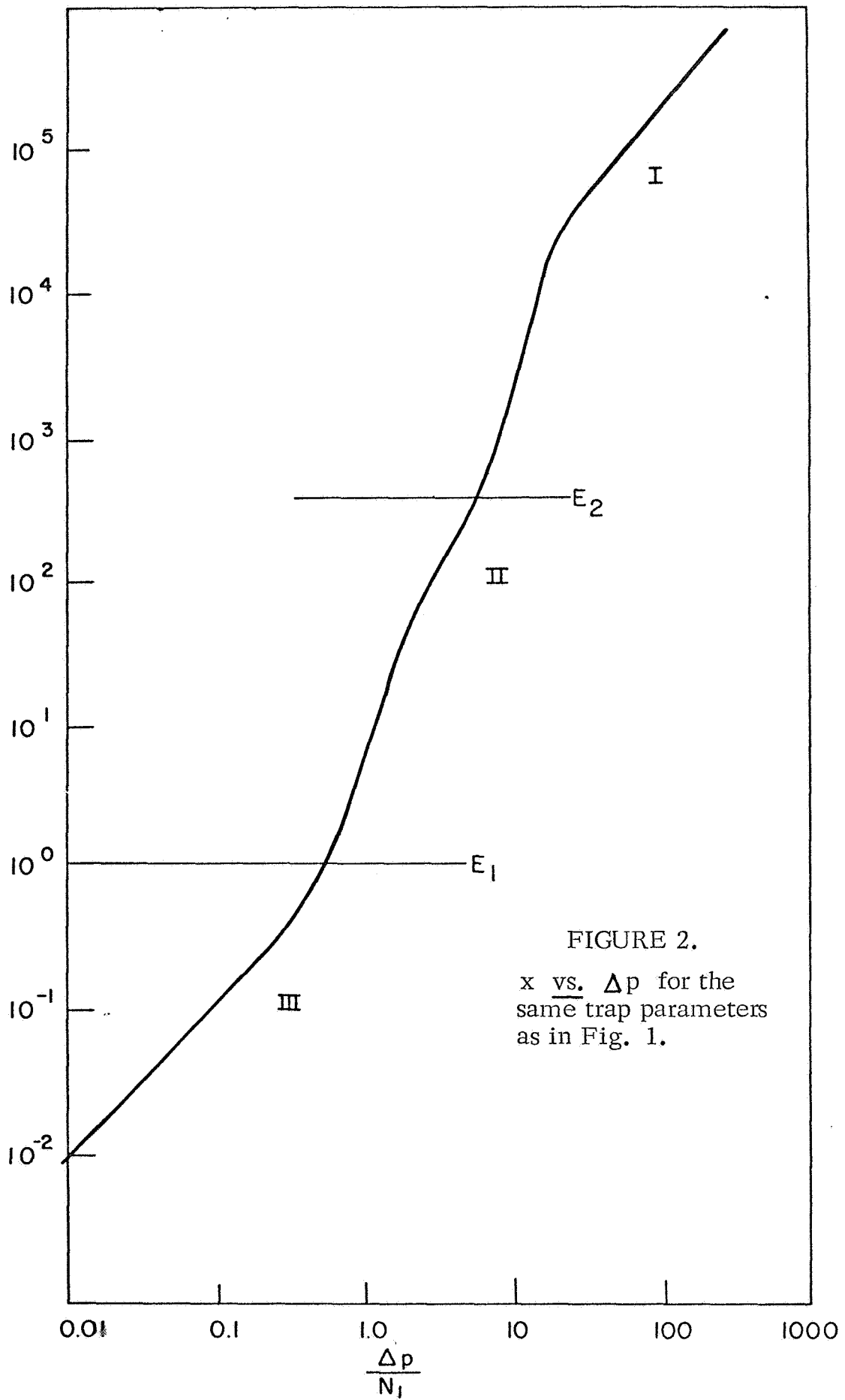


FIGURE 2.  
 $x$  vs.  $\Delta p$  for the  
 same trap parameters  
 as in Fig. 1.

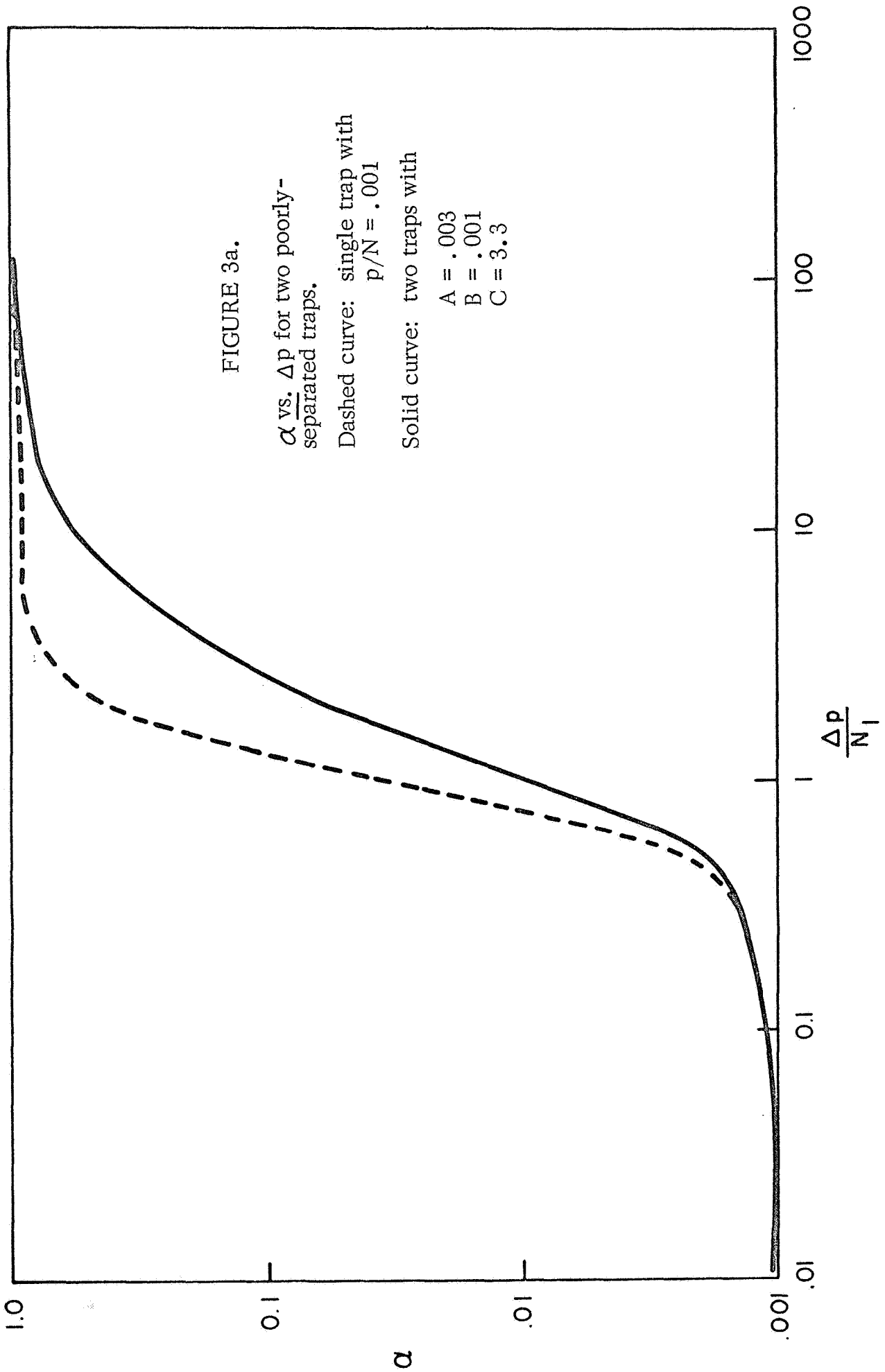


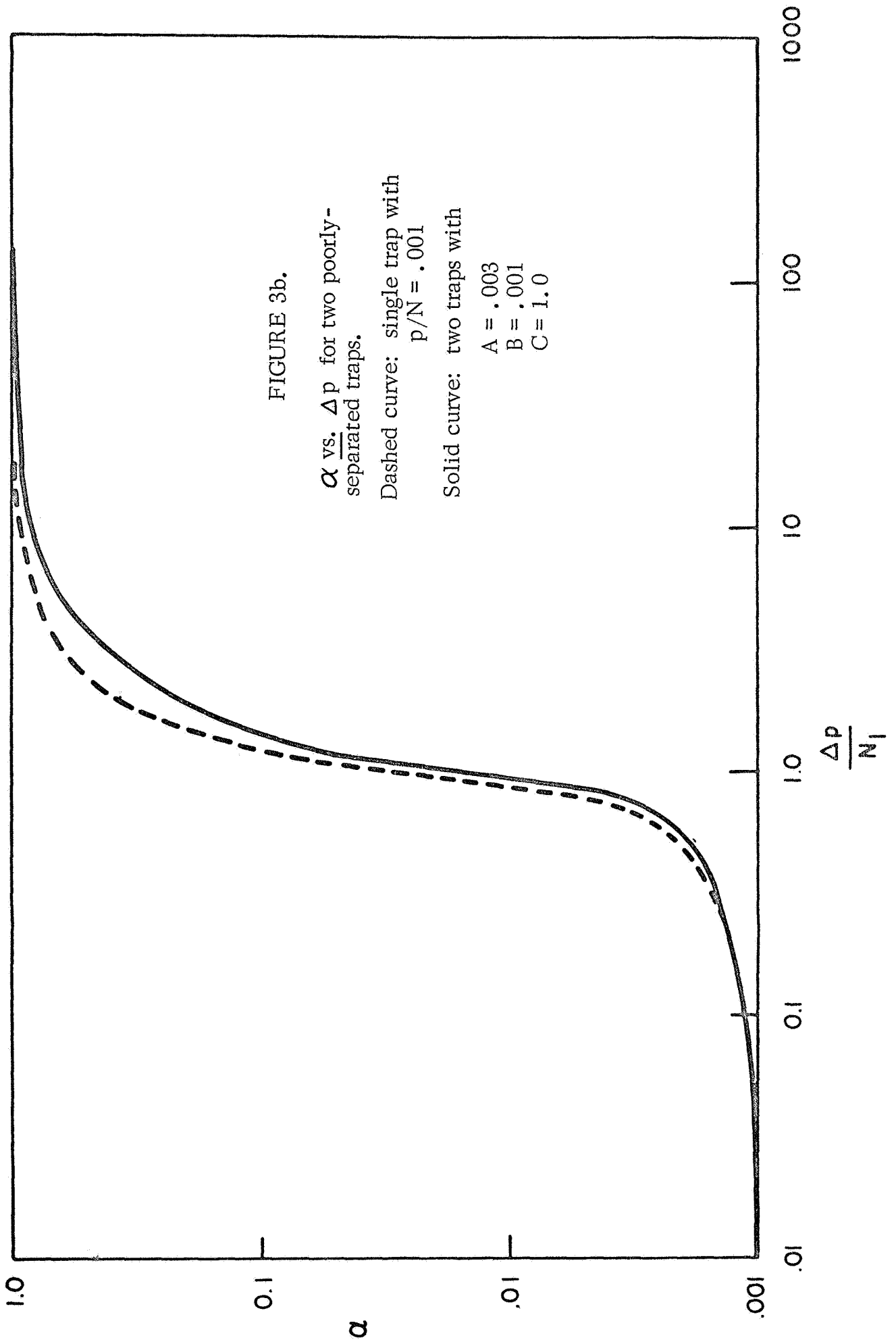
FIGURE 3a.

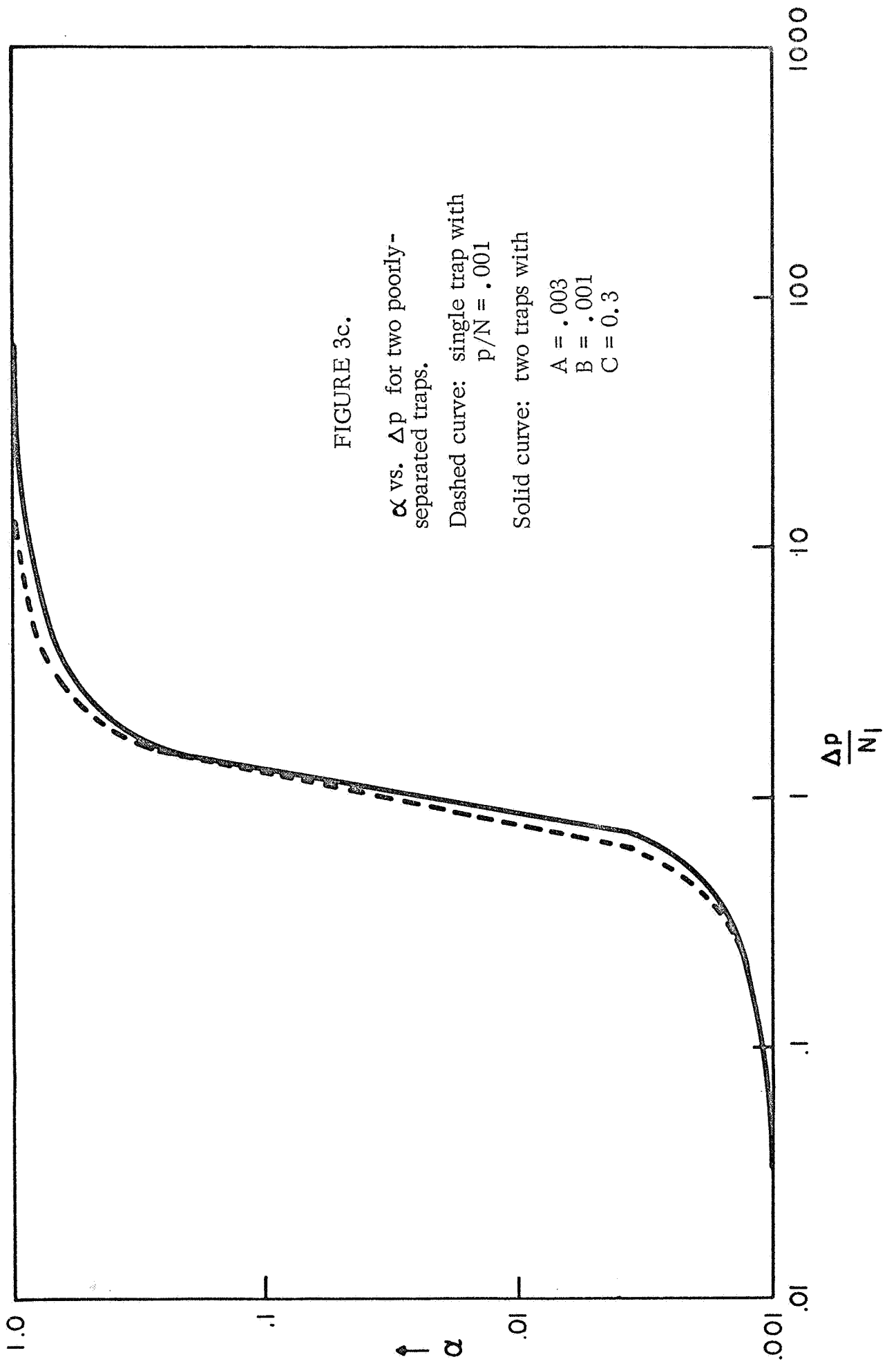
$\alpha$  vs.  $\Delta p$  for two poorly-separated traps.

Dashed curve: single trap with  $p/N = .001$

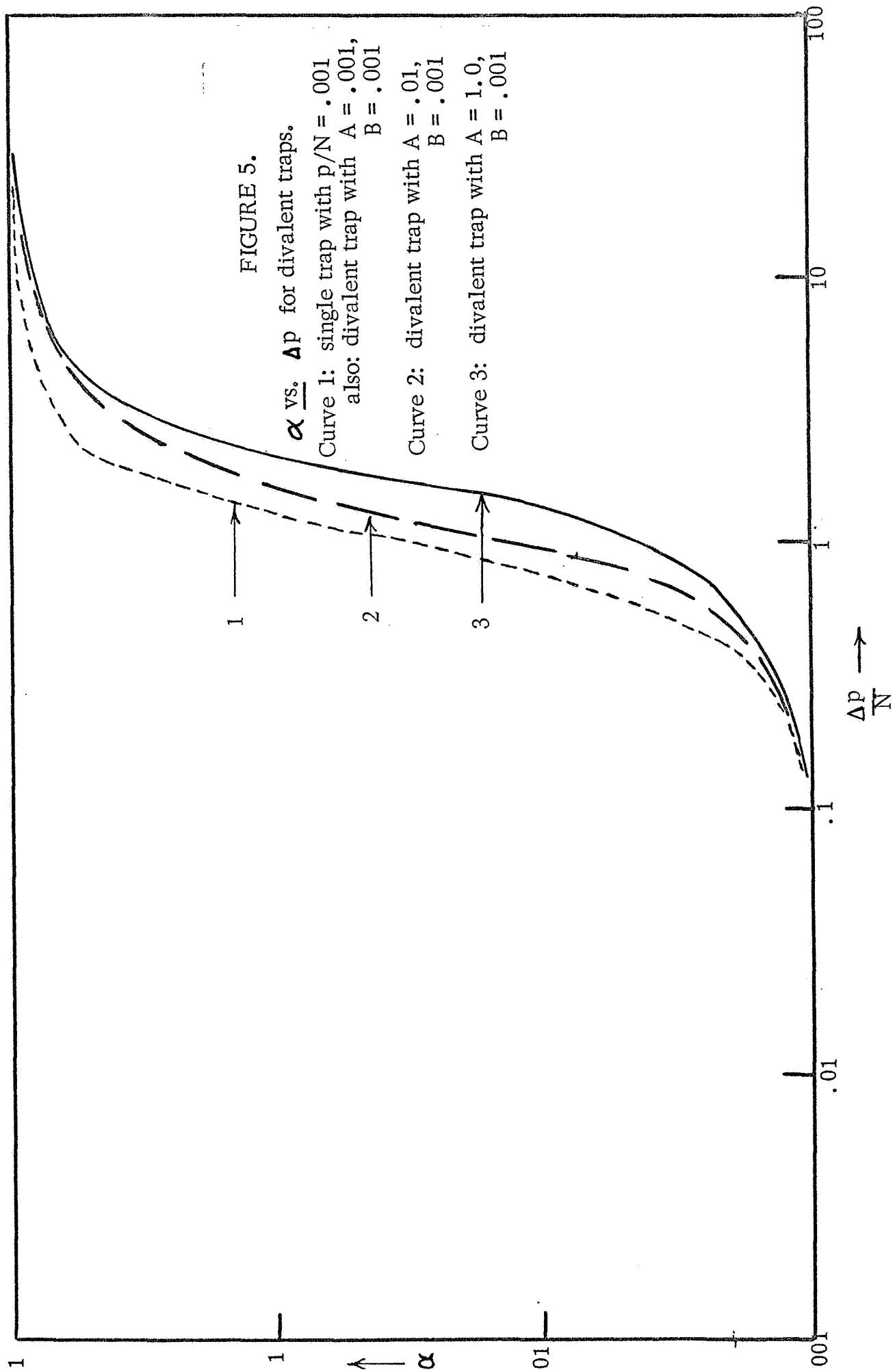
Solid curve: two traps with

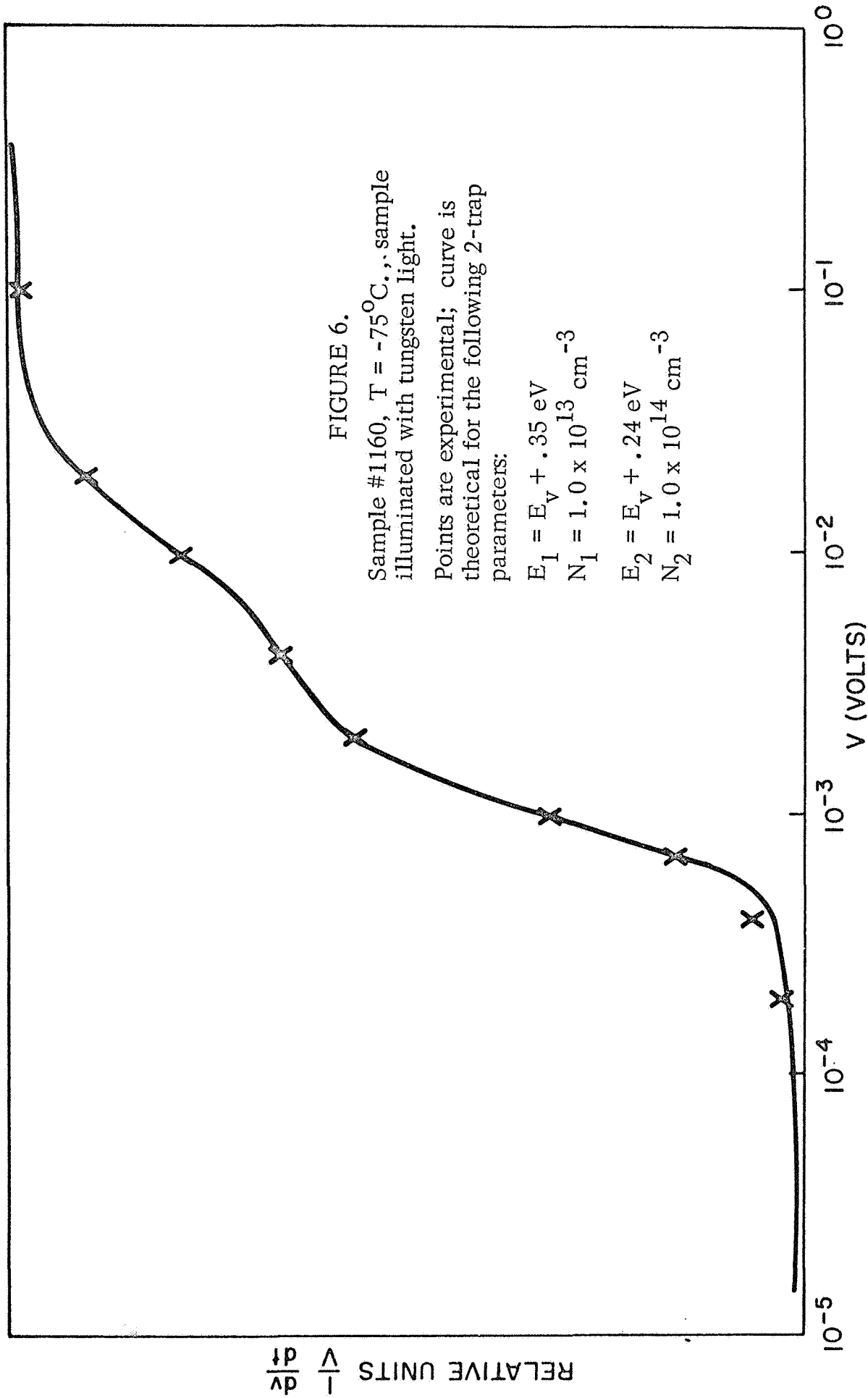
- A = .003
- B = .001
- C = 3.3



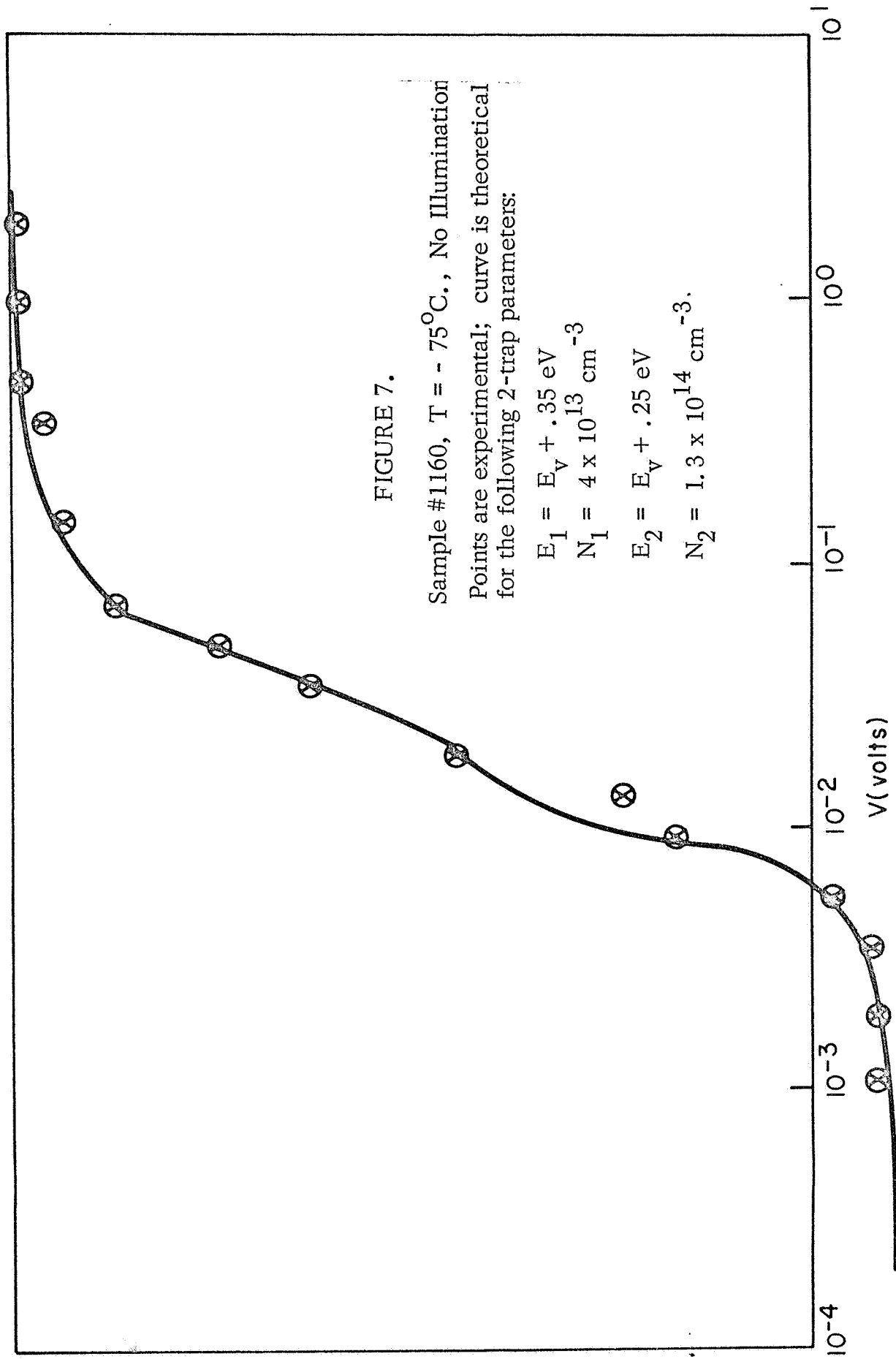








$$\frac{I dv}{V dt}$$



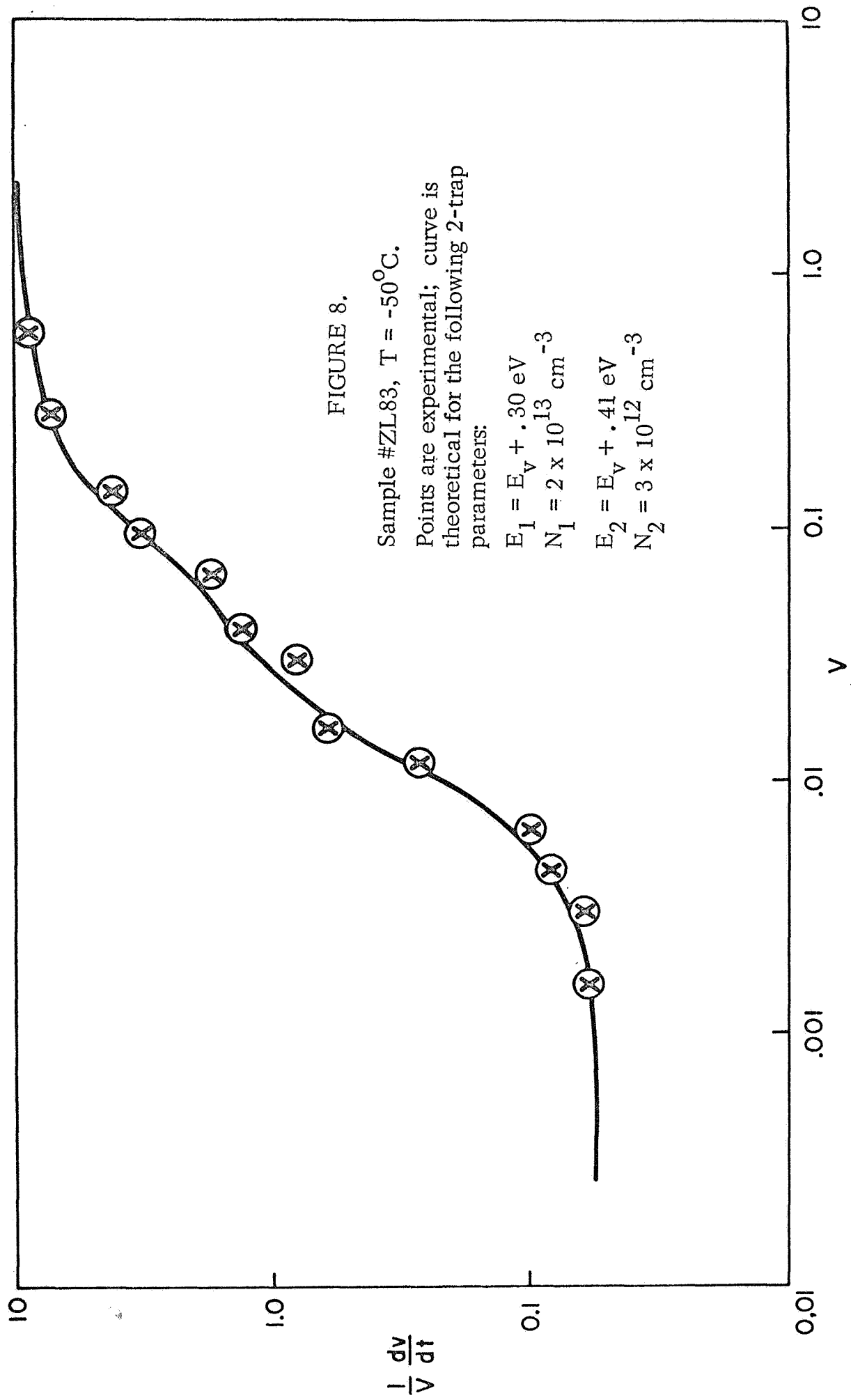


FIGURE 8.

Sample #ZL83,  $T = -50^{\circ}\text{C}$ .

Points are experimental; curve is theoretical for the following 2-trap parameters:

$$E_1 = E_v + .30 \text{ eV}$$

$$N_1 = 2 \times 10^{13} \text{ cm}^{-3}$$

$$E_2 = E_v + .41 \text{ eV}$$

$$N_2 = 3 \times 10^{12} \text{ cm}^{-3}$$