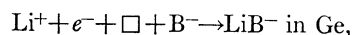
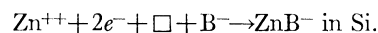


saturation effect corresponding to the B level concentrations. This behavior is observed. However, two facts argue against the levels being donors: (1) their energy depends upon the original acceptor element; (2) calculation of donor and acceptor concentration from carrier concentration curves yields results which do not correspond to the known original acceptor concentration, nor to a donor concentration which would be expected if the new level were associated with substitutional Zn. Hence we conclude that the new levels are probably acceptors and are due to a complex formed between Zn and the original acceptor. We may be dealing with a situation analogous to  $\text{Li}^+ + \text{B}^-$  in germanium<sup>16</sup> where, it is assumed, an ion pair forms and then reacts with a vacancy to form a compound. Thus



<sup>16</sup> Reiss, Fuller, and Pietruszkiewicz, *J. Chem. Phys.* **25**, 650 (1956).

and



The compound shown schematically in Fig. 3(c) would be expected to be an acceptor. The changes in energy level found when Al and Ga are substituted for B seem consistent with the assumption of compound formation. The appearance at different times of two shallow levels when B is used as the acceptor suggests that the situation is even more complicated than has been suspected and that a more careful study must be made of the temperature dependence of equilibria involving substitutional and interstitial Zn, ion pairing, and compound formation.

#### ACKNOWLEDGMENTS

The authors would like to thank J. A. Ditzenberger and J. P. Maita for experimental assistance and N. B. Hannay and Howard Reiss for helpful comments on this work.

## Formation of Ion Pairs and Triplets between Lithium and Zinc in Germanium

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 (Received October 3, 1956)

This paper is a study of ion pairs and triplets formed between zinc and lithium dissolved in single crystal germanium. As in earlier work on ion pairs involving simpler acceptors, the effects of ion complexes on Hall mobility, and impurity energy levels have been investigated. Relaxation-time experiments have also been performed. The theoretical analysis of the results is in complete accord with the idea that zinc provides two energy levels for electrons in the forbidden gap.

### 1. INTRODUCTION

THE formation of ion pairs in germanium and silicon has been discussed in detail in a recent paper.<sup>1</sup> The occurrence of pairs involving the donor lithium and singly charged acceptors such as gallium, aluminum, indium, and boron has been demonstrated experimentally. With the exception of its influence on the diffusivity of lithium, zinc, as an acceptor, was not investigated in any of these experiments. Nevertheless zinc is an especially interesting acceptor since, according to Tyler and Woodbury,<sup>2</sup> it is doubly charged when ionized, possessing energy levels at 0.03 and 0.09 eV above the valence band. This fact is supported by the diffusion data, mentioned above, which show zinc to be orders of magnitude more efficient than the other acceptors in reducing the diffusivity of lithium.

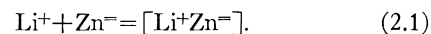
In this article the further investigation of zinc will be described and it will be seen that all measured phe-

nomena associated with ionic interaction are in accord with the existence of two energy levels. Along with pairing, triplet formation is possible when doubly charged ions are involved. This subject will be discussed in the following section.

### 2. TRIPLETS

In another context the problem of triplets has been considered before by Fuoss and Kraus<sup>3</sup> who examined the interaction of two similar singly charged ions with a third singly charged ion of opposite sign. The triplet so constituted bore a net charge. We shall consider the interaction of two singly charged positive lithium ions with one doubly charged negative zinc. Since this triplet is neutral, the phenomena associated with it are quite different from those of the charged triplet.

Two stages of reaction may be distinguished. In the first a charged pair involving one lithium and one zinc is formed:



<sup>1</sup> Reiss, Fuller, and Morin, *Bell System Tech. J.* **35**, 535 (1956).

<sup>2</sup> W. W. Tyler and H. H. Woodbury, *Phys. Rev.* **100**, 1259(A) (1955).

<sup>3</sup> R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.* **55**, 2387 (1933).

In the second stage the pair combines with another lithium to form a neutral triplet:



In the text symbols will be assigned to concentrations as follows:

$$\begin{aligned} D &= \text{concentration of Li}^+, \\ A &= \text{concentration of Zn}^-, \\ P &= \text{concentration of } [\text{Li}^+\text{Zn}^-], \\ T &= \text{concentration of } [(\text{Li}^+)_2\text{Zn}^-], \end{aligned} \quad (2.3)$$

$N_D = D + P + 2T =$  total concentration of lithium,

$N_A = A + P + T =$  total concentration of zinc.

Corresponding to (2.1), there will be a mass action equilibrium relation

$$P/DA = K_P, \quad (2.4)$$

where  $K_P$  is the equilibrium constant for pairs and may be computed by the methods described in reference 1, provided that wherever  $q^2$  appears in that article it is replaced by  $2q^2$ , the 2 originating in the double charge of the zinc.  $K_P$ , of course, is the symbol referred to as  $\Omega$  in reference 1.

When  $K_P$  is evaluated in this manner it becomes evident that at temperatures below 100°C, where experiments with lithium are conveniently performed, and at reasonable concentrations of zinc, all of the zinc will be at least paired if there are more lithium than zinc atoms present. Therefore, in this paper very little emphasis will be placed on the process (2.1), it being assumed complete in all situations. In future work, however, it may be possible to investigate (2.1) by going to very small values of  $N_A$  and  $N_D$ .

Corresponding to (2.2), we may write

$$T/DP = K_T, \quad (2.5)$$

where  $K_T$  is the equilibrium constant for triplets. We may expect this equilibrium to be affected appreciably by temperature in the range below 100°C and so it will be of paramount interest here. In computing  $K_T$ , two different extreme models may be considered:

(1) In the simplest model the individual ions of the pair are assumed to be so thoroughly polarized that the single positive charge of  $\text{Li}^+$  is cancelled (by superposition) by one of the negative charges of  $\text{Zn}^-$ . All that remains is the point negative charge of the zinc ion. As a result the pair behaves as a single negative ion having the field of a point charge. Under this condition  $K_T$  may be evaluated by the methods of reference 1,  $K_T$  being the  $\Omega$  of that paper. Here it is the triplet which acts the part of the pair, while the pair acts the part of an individual ion.

(2) The other model assumes no polarization to have taken place. Then the pair behaves like an unsymmetrical dipole having a doubly charged negative head and a singly charged positive tail. The evaluation

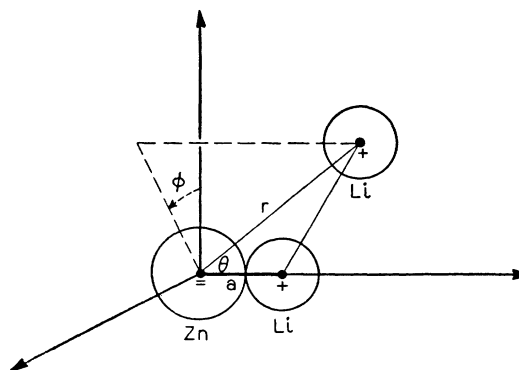


FIG. 1. Construction showing symbols used in calculation for unsymmetrical dipole.

of  $K_T$ , in this case, involves treating the interaction of a lithium ion and this dipole.

These two models will be compared with experiment. It will be recalled that  $K_P$  ( $\Omega$  in reference 1) is computed by the technique of Bjerrum<sup>4</sup> and Fuoss.<sup>5</sup> In this procedure one considers a special system in which  $N_A$  and  $N_D$  are equal ( $N$ ). Furthermore the system is considered to be infinitely dilute so that the amount of pairing is very small. Then  $A$  may be approximated by  $N_A$  and  $D$  by  $N_D$ . Equation (2.4) therefore becomes

$$P/N = NK_P, \quad (2.6)$$

where  $P/N$  is the fraction of donors (or acceptors) paired. This fraction may be computed another way by invoking Boltzmann's distribution law to evaluate the chance that a donor ion will be found in the spherical shell of volume  $4\pi r^2 dr$  located at a distance  $r$  from an acceptor. This chance is

$$4\pi r^2 N e^{-V/kT} dr = g(r) dr, \quad (2.7)$$

where  $V$  is the potential energy of the donor at a distance  $r$  from the acceptor,  $k$  is the Boltzmann constant, and  $T$  the temperature. In the case in question,

$$V = -2q^2/\kappa r, \quad (2.8)$$

i.e., the potential energy of a single positive charge  $q$  in the field of a point double negative charge, in a medium of dielectric constant  $\kappa$ .

A plot of  $g(r)$  versus  $r$  exhibits a minimum (if the 2 is omitted in 2.8) at

$$r = b = q^2/\kappa kT, \quad (2.9)$$

and all ions contained within the sphere of radius  $b$  constructed about their negative partners are said to be paired (see reference 1). The fraction paired is therefore obtained by integrating (2.7),

$$\frac{P}{N} = \int_a^b g(r) dr, \quad (2.10)$$

<sup>4</sup> N. Bjerrum, Kgl. Danske Videnskab. Selskab, mat.-fys. Medd. 7, No. 9, (1926).

<sup>5</sup> R. M. Fuoss, Trans. Faraday Soc. 30, 967 (1934).

TABLE I. Radial distribution function for a positive ion in the fields of an unsymmetrical dipole (column 2) and a single point charge (column 3).

$\xi$	$G(\xi)/\pi N\gamma^2$	$g(\xi)/\pi N\gamma^2$
0.050	$2.03 \times 10^{10}$	$4.85 \times 10^6$
0.055	$1.04 \times 10^9$	$2.48 \times 10^6$
0.070	$6.32 \times 10^6$	$3.12 \times 10^4$
0.080	$5.25 \times 10^4$	$6.87 \times 10^3$
0.090	$1.59 \times 10^4$	$2.16 \times 10^3$
0.100	$1.28 \times 10^3$	$8.81 \times 10^2$
0.50	7.55	7.39
0.70	8.21	8.17
1.00	10.9	10.9

where  $a$  is the distance between the two ions when they are as close to one another as they can be. Equating the right members of (2.6) and (2.10) gives

$$K_P = \frac{1}{N} \int_a^b g(r) dr \tag{2.11}$$

a quantity independent of  $N$  because  $g(r)$  depends linearly on  $N$ . If the negative ion is singly charged (as in reference 1 or in model 1 for  $K_T$ ), the factor 2 is left out of (2.8).

When the negative ion is an unsymmetrical dipole, then  $V$  for the second lithium ion is

$$V = -\frac{q^2}{\kappa} \left\{ \frac{2}{r} - \frac{1}{(a^2+r^2-2ar \cos\theta)^{\frac{1}{2}}} \right\}, \tag{2.12}$$

where  $r$  and  $\theta$  are coordinates in the spherical coordinate system in Fig. 1 in which the center of the zinc ion is shown at the origin.

With an unsymmetrical dipole the problem loses its spherical symmetry. Nevertheless it is possible to write the counterpart of  $g(r)$  in (2.7) by integrating over the angle variables after  $V$  has been taken as (2.12). Before doing this, it is convenient to introduce the quantity

$$\gamma = q^2/\kappa kT \tag{2.13}$$

and the transformation

$$\xi = r/\gamma. \tag{2.14}$$

We also define

$$\alpha = a/\gamma. \tag{2.15}$$

Assuming  $V$  in (2.7) to be given not by (2.8) but by the corresponding expression for a singly charged negative ion, i.e., by  $-q^2/\kappa r$  (because in employing model 1 for  $K_T$  we use (2.7) under these conditions), we arrive at the result

$$g(\xi) = 4\pi\gamma^2 N \xi^2 e^{1/\xi} \tag{2.16}$$

and for (2.11) written for  $K_T$  instead of  $K_P$ ,

$$K_T = \frac{\gamma}{N} \int_a^{\frac{1}{\gamma}} g(\xi) d\xi. \tag{2.17}$$

For the case of the unsymmetrical dipole we may write  $G(\xi)$  for the counterpart of  $g(\xi)$  where the angle variables have been integrated away. We find by straightforward integration [using as an alternative for  $\theta$  the coordinate  $(a^2+r^2-2ar \cos\theta)^{\frac{1}{2}}$ ] that

$$G(\xi) = \frac{2\pi N\gamma^2 \xi}{\alpha} e^{2/\xi} \left\{ \frac{(\xi+\alpha)(\xi+\alpha-1)e^{-1/(\xi+\alpha)}}{2} - \frac{(\xi-\alpha)(\xi-\alpha-1)e^{-1/(\xi-\alpha)}}{2} - \frac{1}{2} \right. \\ \left. \times \left[ \text{Ei}\left(-\frac{1}{(\xi+\alpha)}\right) - \text{Ei}\left(-\frac{1}{(\xi-\alpha)}\right) \right] \right\}, \tag{2.18}$$

where Ei stands for the exponential integral, tables<sup>6</sup> of which are available.

Like  $g(\xi)$ ,  $G(\xi)$  has a minimum when plotted *versus*  $\xi$ . In fact the minimum occurs at about the same place (at  $\xi = \frac{1}{2}$ ) as does that for  $g(\xi)$ . Calling this minimum  $\xi_m$ , we have

$$K_T = \frac{\gamma}{N} \int_a^{\xi_m} G(\xi) d\xi \tag{2.19}$$

for the triplet constant based on the nonpolarized model. In (2.19) no account is taken of the fact that the lithium ion in the dipole prevents the second lithium from occupying its position. A negligible error is committed by this simplification. The integrand  $G(\xi)$  is integrated over the angle coordinates and, since it is based on the Coulomb repulsive potential operating between these ions, the contribution to  $G(\xi)$  in the range of angle integration in which the ions overlap is very small.

Table I lists values of  $G(\xi)/\pi N\gamma^2$  and  $g(\xi)/\pi N\gamma^2$  as functions of  $\xi$ , for the case  $T=300^\circ\text{K}$ ,  $\kappa=16$ ,  $a=1.7 \times 10^{-8}$  cm, values typical for acceptors in germanium. It is seen that  $G(\xi)$ , at  $\xi=0.05$  ( $a=1.7 \times 10^{-8}$  cm) is much larger than  $g(\xi)$  but becomes equal to the latter at large distances. This is to be expected since at great distances the field of the unsymmetrical dipole becomes undistinguishable from that of a singly charged negative ion. When one uses (2.17) and (2.19), the values of  $K_T$  for model 1 and model 2 can be computed for the case to which Table I refers ( $T=300^\circ\text{K}$ ,  $\kappa=16$ ,  $a=1.7 \times 10^{-8}$  cm). Calling these  $K_T^{(1)}$  and  $K_T^{(2)}$ , respectively, we obtain

Model 1 (polarization):

$$K_T^{(1)} = 1.6 \times 10^{-15} \text{ cm}^3, \tag{2.20}$$

Model 2 (unsymmetrical dipole):

$$K_T^{(2)} \approx 10^{-11} \text{ cm}^3.$$

These two values differ by about four orders of magni-

<sup>6</sup> Tables of Sine, Cosine, and Exponential Integrals (WPA and National Bureau of Standards, Washington, D. C., 1940).

tude. Unfortunately the only parameter which is not known independently is  $a$ , the distance of closest approach. It is true that  $K_T$  is very sensitive to  $a$ , but this means that  $a$  is not sensitive to  $K_T$ . As it will appear later, the values of  $a$  determined from the experimental data on the basis of the two models are not different enough to allow a real decision to be made between the two. On the other hand, this means that it doesn't matter which of the two models we use to describe the triplet process.

### 3. EXPERIMENTS

The specimens employed in our investigations were adjacent sections of a single crystal of germanium grown from a melt doped with zinc. Lithium was diffused into one of these in such a manner that conversion from  $p$  to  $n$  type was avoided. The details of such techniques are presented in reference 1.

As mentioned earlier we shall be concerned mainly with reaction (2.2), reaction (2.1) being complete below 100°C. As in reference 1 experiments on carrier mobility, relaxation times, and variation of energy levels have been performed. These will be discussed in order.

#### A. Carrier Mobility

Hall mobilities were measured on two bridges. One was a control cut from a germanium crystal containing zinc at the atom concentration  $8.5 \times 10^{15} \text{ cm}^{-3}$ . The other was cut from the same crystal but lithium had been diffused into it to the concentration  $1.45 \times 10^{16} \text{ cm}^{-3}$ . Since each zinc contributes two holes the specimen remained  $p$  type, i.e.,  $1.45 \times 10^{16} < 2(8.5 \times 10^{15})$ .

Figure 2 shows plots of the logarithm of Hall mobility for these samples versus the logarithm of temperature. Curve  $A$  is for the control and  $B$  for the lithium doped specimen. As anticipated, curve  $B$  lies above  $A$ , indicating the removal of charged impurity scatterers due to the formation of pairs and triplets. The increase in mobility due to pair formation alone should be very considerable since, even though the pairs remain charged, single charges are considerably less efficient scatterers than the double charges.

In contrast to similar plots for singly charged acceptors in reference 1, curves  $A$  and  $B$  exhibit no tendency to intersect—at least at the temperatures involved in the graph. This tends to confirm (along with the diffusion data in reference 1 and the Hall data of Tyler and Woodbury) the idea that zinc is doubly charged. In the temperature range investigated, all the triplets may have dissociated leaving pairs and isolated lithium ions. But the pairs, already bearing a negative charge, will not dissociate until much higher temperatures are reached, say 600 or 700°K. Curves  $A$  and  $B$  can meet only after some fraction of the pairs have dissociated. The failure of the curves to cross in Fig. 1 indicates that the pairs do remain associated in the

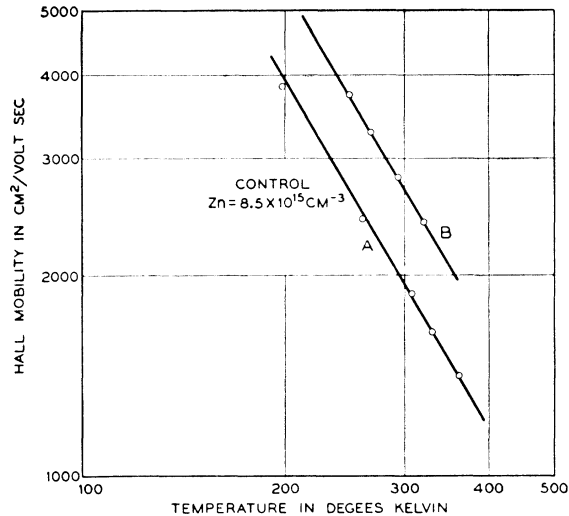


FIG. 2. Temperature dependence of carrier mobility in sample  $A$  containing only zinc and in sample  $B$  containing zinc-lithium pairs and triplets.

neighborhood of room temperature, a fact which is easily explained by the assumption that zinc is doubly charged so that the pair is not easily dissociable.

#### B. Relaxation

The lithium-doped bridge involved in subsection  $A$  was studied for relaxation (see reference 1). To dissociate triplets it was heated to 350°K. This state was partially quenched into the specimen by plunging it into liquid nitrogen. The bridge was then warmed to dry-ice temperature, 196°K, where the relaxation time was measured by following its electrical conductivity,  $\sigma$ , as a function of time. Let  $\sigma_\infty$  be the conductivity at infinite time when pairing equilibrium characteristic of 196°K has been established. According to arguments presented in reference 1,

$$\ln(\sigma_\infty - \sigma) = \ln \varphi + (t/\tau), \quad (3.1)$$

where  $\varphi$  is a constant,  $t$  is time, and  $\tau$  is the relaxation time given by

$$\tau = \kappa k T / 4\pi q^2 (N_D - N_A) D_0, \quad (3.2)$$

where  $D_0$  is the diffusivity of lithium at the temperature in question.  $N_D - N_A$  is the residual concentration of lithium, available for forming triplets after pairing has been completed. From subsection  $A$ ,  $N_D = 1.45 \times 10^{16} \text{ cm}^{-3}$ ,  $N_A = 8.5 \times 10^{15} \text{ cm}^{-3}$ .  $D_0$  can be obtained by extrapolation (see reference 1) of the data of Fuller and Severiens<sup>7</sup> to 196°K where the value  $10^{-16} \text{ cm}^2/\text{sec}$  is obtained. In this way, (3.2) predicts

$$\tau = 2.5 \times 10^5 \text{ sec}. \quad (3.3)$$

The plot of the experimental  $\ln(\sigma_\infty - \sigma)$  versus time yielded a good straight line, from the reciprocal of

<sup>7</sup> C. S. Fuller and J. C. Severiens, Phys. Rev. **95**, 21 (1954).

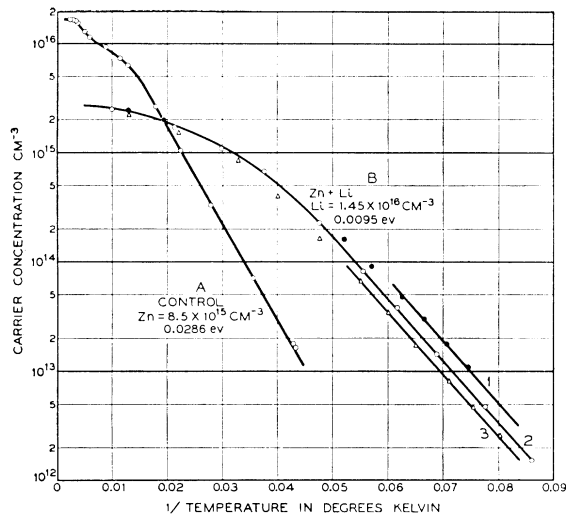


FIG. 3. Dependence of carrier concentration on reciprocal temperature. Curve for sample *A* indicates the presence of the two electronic levels associated with zinc. Curves for sample *B* show disappearance of zinc levels and appearance of new level associated with zinc-lithium pairs. Situations (1), (2), and (3), respectively, indicate decreasing concentrations of triplets.

whose slope we obtain

$$\tau = 2.6 \times 10^5 \text{ sec} \quad (3.4)$$

in excellent agreement with the predicted value (3.3).<sup>8</sup>

### C. Variation of Energy Levels and Measurement of $K_T$

Analysis of Hall effect data in reference 1 revealed the loss of energy levels from the forbidden gap as a result of ion pairing. In the present case a similar phenomenon is expected, but with an interesting difference. We expect triplet formation to remove the  $\text{Li}^+$  level and both  $\text{Zn}^-$  levels. However, pair formation should remove only one zinc level since the pair retains a single negative charge. This energy level should resemble that of an ordinary singly charged acceptor in germanium, for according to the hydrogen-like model the hole in its ground state is very far from the center of negative charge and should not be able to distinguish the charged pair from a simple ion. On this basis we expect the pair level to be about 0.01 eV above the valence band, a value typical of acceptors in germanium.<sup>9</sup>

From Hall data, not only is it possible to measure the position of the pair energy level, but also we can determine the concentrations  $N_A$ ,  $N_D$ ,  $D$ ,  $P$ , and  $T$  corresponding to the equilibrium at any temperature where the relaxation time is long enough to permit quenching of the specimen before changes can occur.

<sup>8</sup> This tends to prove we are dealing with the kinetics of triplet formation, rather than pair formation. In the latter case the negative ion would be doubly charged and  $\tau$  would have had one-half the value in (3.3).

<sup>9</sup> T. H. Geballe and F. J. Morin, Phys. Rev. **95**, 1085 (1954).

These data, in turn, permit the evaluation of  $K_T$ , and through the latter, of  $a$ , the distance of closest approach.

Figure 3 shows Hall effect results (logarithm of carrier concentration *versus* the reciprocal of temperature) for the control sample, and for the lithium-doped specimen used in subsection *A*. The presence of the two zinc acceptor levels is evident in curve *A* for the control. The straight-line portion of the curve indicates the shallow level to be located at 0.0286 eV above the valence band. The second hump, at high temperatures, occurs as the deep acceptor level ionizes. At high temperatures, when both levels are completely ionized, carrier concentration becomes constant at  $1.7 \times 10^{16} \text{ cm}^{-3}$ . Therefore the specimens contain  $8.5 \times 10^{15} \text{ cm}^{-3}$  zinc atoms, i.e.,

$$N_A = 8.5 \times 10^{15} \text{ cm}^{-3}. \quad (3.5)$$

Curves *B* for the lithium-doped specimen shows only one hump, indicating, as expected, only one energy level (associated with the pair) at 0.0095 eV above the valence band. This value is in excellent agreement with the value typical of singly charged acceptors in germanium. Upon complete ionization of this level, the carrier concentration is  $2.5 \times 10^{15} \text{ cm}^{-3}$ . Hence

$$2N_A - N_D = 2.5 \times 10^{15} \text{ cm}^{-3}, \quad (3.6)$$

or, using (3.5),

$$N_D = 1.45 \times 10^{16} \text{ cm}^{-3}. \quad (3.7)$$

Three different carrier concentration curves have been measured corresponding to three different proportions of pair and triplet formation quenched into the bridge to which curves *B* of Fig. 3 applies. These proportions were obtained by:

(1) Allowing the sample to relax into equilibrium at 205°K, followed by rapid cooling to quench the equilibrium characteristic of 205°K into the specimen. This was possible because of the large relaxation time characteristic of 205°K.

(2) Cooling the sample slowly. In this manner the system had time to relax into equilibrium during part of the cooling process. Again so a nonequilibrium state (depending on the cooling rate) was quenched into the specimen.

(3) Plunging the sample into liquid nitrogen after it had been heated to 350°K. In this manner some chance nonequilibrium state was quenched into the specimen. The curves belonging to the different procedures are identified by the numbers (1), (2), or (3). All three curves have the same low-temperature slope indicating that the same energy level (0.0095 eV) is involved, but curve (1) lies above (2) and (2) lies above (3). In all cases complete ionization showed  $2N_A - N_D$  to be  $2.5 \times 10^{15} \text{ cm}^{-3}$  as in (3.6). This is to be expected since the state of pairing or triplet formation has no effect on carrier concentration when ionization is complete.

The relative heights of the curves are in complete accord with theory. Thus, as before, suppose that all

zinc ions are bound at least in pairs. Then, corresponding to each zinc there can at the most be one acceptor level left in the forbidden gap. In fact, since  $A=0$ , the number of these levels must be

$$P = N_A - T. \quad (3.8)$$

Procedure (1) permits the formation of the greatest number of triplets so that according to (3.8)  $P$ , the number of acceptor states remaining, will be smallest in (1). The statistics of the freezing out of holes on these states then demands (since there are fewer states available for freezing) that the carrier concentration be higher than for cases where  $P$  is larger. Thus curve (1) is the highest in Fig. 3. Procedures (2) and (3) as would be expected permit the formation of smaller concentrations of triplets in their respective order. Hence by (3.8) they leave larger concentrations of states in the same order. Thus curves (2) and (3) are progressively lower. These curves can be analyzed, by using statistics,<sup>10</sup> to give the values of  $D$ ,  $P$ , and  $T$  associated with them. The results of this analysis are listed in Table II.

The last column  $T/(T+D)$  is the fraction of lithium left after pairing has been completed, which is bound in triplets. It is analogous to the fraction of donor paired in reference 1. As expected, this fraction decreases in the order of procedure number. Of course, the sum  $D+P+2T$ , which according to (2.3) must be  $N_D$ , is  $1.45 \times 10^{16} \text{ cm}^{-3}$  for all three procedures.

Procedure (1) presumably yields equilibrium values of  $D$ ,  $P$ , and  $T$ , corresponding to 205°K. Substituting these into (2.5) yields

$$K_T = 1.39 \times 10^{-15} \text{ cm}^3. \quad (3.9)$$

<sup>10</sup> W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), Chap. 16.

TABLE II. Concentration of uncombined lithium  $D$ , of pairs  $P$ , of triplets  $T$ , and fraction  $T/(T+D)$  of lithium not in pairs which is bound in triplets for (1) equilibrium conditions at 205°K, (2) slow cooling from room temperature, and (3) quenching from 350°K.

Procedure	$D(\text{cm}^{-3})$	$P(\text{cm}^{-3})$	$T(\text{cm}^{-3})$	$T/(T+D)$
1	$3.52 \times 10^{15}$	$1.02 \times 10^{15}$	$4.98 \times 10^{15}$	0.83
2	$4.07 \times 10^{15}$	$1.57 \times 10^{15}$	$4.43 \times 10^{15}$	0.74
3	$4.50 \times 10^{15}$	$2.00 \times 10^{15}$	$4.00 \times 10^{15}$	0.66

Using model 1, the polarized model, we can apply the method of reference 1 to compute a distance of closest approach. The result is

$$a = 2.76 \text{ \AA}. \quad (3.10)$$

If model 2 is used, since  $K_T$  according to it is larger than the value obtained using model 1, it is necessary to employ a value of a larger than 2.76 Å to arrive at the value of  $K_T$  given by (3.9). A rough estimate of the required  $a$  yields

$$a \approx 3.5 \text{ \AA}. \quad (3.11)$$

This value is not different enough from that given in (3.10) to merit a decision between the two models. Probably, the real state of affairs lies between the extremes represented by the models, i.e., the ions are partially polarized.

It is noteworthy, however, that both  $a$  values are much larger than the values given in reference 1 where the negative ions were simple acceptors. In the present case the negative ion is a charged pair and  $a$  would be expected to be larger than for a simple acceptor.

The authors wish to thank J. P. Maita for assistance with the measurements and H. Guggenheim for preparation of the samples.