INTERACTIONS BETWEEN SOLUTES IN GERMANIUM AND SILICON[1]

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I. INTRODUCTION

Up until the early 1930's most chemists and physicists considered the task of explaining the properties of solids and solid solutions too difficult, even though much was known about their structures from x-ray crystal analysis. This was particularly true of insulating and semiconducting solids, although experiments on the electrical properties had already established some important relationships with temperature and composition. Two significant lines of attack, aimed especially at elucidating the electrical and chemical behavior of these solids, were launched at about this time. The one was an extension of the methods of statistical thermodynamics and the law of mass action, both of which had been fruitfully applied to reactions in aqueous solutions and to equilibria involving solids, primarily oxides and sulfides, by Wagner and Schottky and their coworkers (37, 46). The other was the introduction of the energy band model for electrons in solids—in particular insulators and semiconductors—by Wilson (47) and Fowler (5). Since these beginnings a large number of other workers (16, 27, 30, 33, 38, 39), both in chemistry and in physics, have contributed to this rapidly growing branch of science.

It was realized very early by Baedeker (1) and later by Gudden (14) that in order to conduct meaningful experiments on insulators and semiconductors, it was desirable to have available very pure materials, and preferably single crystals. In spite of the early lack of such materials, however, much valuable work

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[1] Paper presented before the Division of Inorganic Chemistry at the 134th Meeting of the American Chemical Society, Chicago, Illinois, September 9, 1958.

was done and the validity of many of the basic theoretical concepts was established. For example, the early work of Wagner (45) showed that the law of mass action has applicability to reactions in solids. Also, the idea that a variety of so-called "defects" in crystalline solids could be treated as if they were chemical species in equilibrium was demonstrated (46). Finally, the important effects of deviations from stoichiometry in compound solids on their electrical properties were pointed out (15). The effects of nonstoichiometry, which will not be discussed here, have more recently been investigated by Verwey, Kröger, Vink, and others in Holland.

The advent of the pure elementary semiconductor crystals, silicon and particularly germanium,[2] in the late 1940's probably more than any other event made possible the quantitative investigation of reactions taking place in semiconductors. It is this topic which will be discussed in this paper; more specifically, mass action equilibria involving atoms, ions, electrons, and holes in these pure single crystals considered as solvents.

II. NATURE OF EQUILIBRIA IN COVALENT SEMICONDUCTOR CRYSTALS

Various kinds of temperature-dependent equilibria exist in pure semiconductor crystals such as silicon and germanium. The most important of these are crystal ionization, solute ionization, ion-pair equilibria, and chemical equilibria.

A. Crystal ionization

This equilibrium arises from the dissociation and recombination of electrons by the covalent-bond system of the solvent crystal, a reaction which may be written (5) as:

$$\text{Valence electron} \rightleftarrows \text{free electron} + \text{free hole} \tag{1}$$

This is similar to the familiar ionic dissociation of solvents like water, and the corresponding mass action expression is

$$np = K_s \tag{2}$$

where n and p are the electron and hole concentrations, K_s is the equilibrium constant for reaction 1, and the concentration of the valence electrons (solvent) has been combined in K_s, since this concentration is essentially constant over a wide temperature range. Actually, the problem is one in statistical mechanics and the above is a simplified view. From thermodynamics the equilibrium constant K_s in equation 2 is

$$K_s = A \exp(-\Delta H_i^0/RT) \tag{3}$$

where A is a factor equal to BT^3, where B is a constant and ΔH_i^0 is the standard heat for equation 1. This simple chemical argument leads immediately to the very useful electron–hole equilibrium equation

$$np = BT^3 \exp(-\Delta E_i/RT) = K_s \tag{4}$$

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[2] These materials were the result of early efforts made during World War II at a number of university and industrial laboratories both in this country and in England. The first large single crystals of germanium were prepared by Teal and Little (42) and of silicon by Teal and Buehler (41). Silicon containing even smaller amounts of impurities (especially of oxygen) was prepared by Keck (24) and independently by Emeis (4).

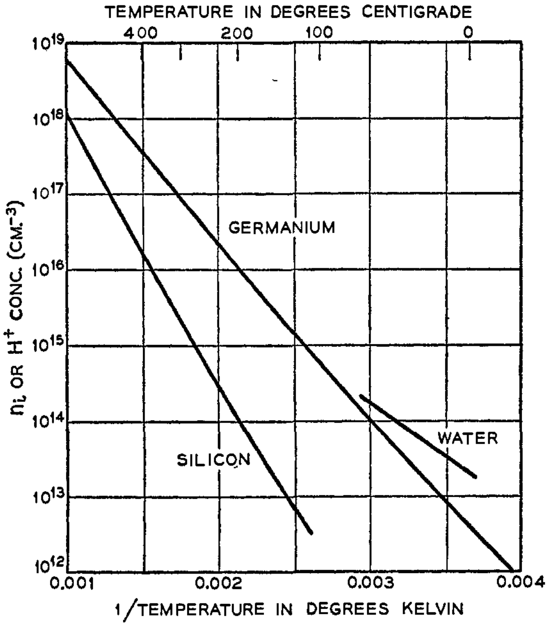

FIG. 1. Crystal ionizations of germanium and silicon compared to the ionization of water, all as functions of the reciprocal of the absolute temperature. The ordinate is the electron concentration (or hole concentration) for the semiconductors and the hydrogen-ion (or hydroxide-ion) concentration for water.

where ΔE_i, the so-called "forbidden gap" energy in calories, has been written for ΔH_i^0, since the pressure and volume are essentially constant. In equation 4 $B = 2.34 \times 10^{31}$ for the special case of "spherical energy surfaces." For silicon B must be multipled by 0.518 and for germanium by 0.089 (3). ΔE_i is 15.2 kcal. for germanium and 24.9 kcal. for silicon at 25°C.

Equation 4 shows that at a fixed temperature the product of the electron concentration by the hole concentration is a constant for the solvent semiconductor. This is true for the pure solvent, in which case $n = p$, as well as for solid solutions, providing the latter are not too concentrated. Values for $\sqrt{K_s} \equiv n_i$ for germanium and silicon are compared to the hydrogen-ion concentration of water in figure 1.

B. *Solute ionization*

In the same manner as for the crystal ionization, relations can be written for donor and acceptor solute ionizations in a crystal.[3]

$$\begin{aligned} D &\rightleftarrows D^+ + n \\ A &\rightleftarrows A^- + p \end{aligned} \tag{5}$$

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[3] A donor solute is one which donates one or more (free) electrons to the crystal and so becomes itself positively charged, such as As^+ and S^{++}. An acceptor solute accepts one or more electrons from the valence bonds of the crystal, thus leaving a corresponding number of holes and becoming negatively charged, for example, Al^- and Zn^{--}.

where D and A, D^+ and A^- stand for unionized and singly ionized donors and acceptors, respectively. As before,

$$\begin{aligned} \frac{n^2}{N_D - n} &= C_d \exp(-\Delta E_d/RT) = K_d \\ \frac{p^2}{N_A - p} &= C_a \exp(-\Delta E_a/RT) = K_a \end{aligned} \tag{6}$$

where N_D and N_A are now the *total* donor and acceptor concentrations expressed in atoms per cubic centimeter, respectively. C_d and C_a are parameters which vary as $T^{3/2}$. Expressions similar to equation 6 can be written when both donors and acceptors are present.

It is evident that by plotting the logarithms of the equilibrium constants, determined as a function of T, against $1/T$, and neglecting the variations of C_a and C_d, the various energies in equations 4 and 6 can be obtained. However, these expressions become quite inaccurate when the ΔE's become less than $\sim 2RT$. When this occurs the Fermi energy must be introduced. Table 1 gives values of ΔE_i, ΔE_d, and ΔE_a for germanium and silicon and some of their dilute solutions.

C. *Ion-pair equilibria*

When the donor or acceptor ions in solid solutions are mobile enough and certain other conditions are met, a pairing of the ions can occur (25). Reiss (36) has pointed out that such pairing in semiconductors should be more pronounced than in aqueous solution and such indeed is the case. The reaction is

$$A^- + D^+ \rightleftarrows P \tag{7}$$

where P stands for the pair. Mass action gives

$$N_P/(N_{A^-})(N_{D^+}) = \Omega_P \tag{8}$$

TABLE 1

Ionization energies in germanium and silicon (25°C.)

Solute	Germanium (ΔE_i = 15.2)		Silicon (ΔE_i = 25.1)	
	ΔE_d	ΔE_a	ΔE_d	ΔE_a
	*kcal.**	*kcal.*	*kcal.*	*kcal.*
P†	0.23		1.02	
As	0.23		1.13	
Sb	0.23		0.90	
Li	0.23		0.76	
Bi	0.23		1.1	
B		0.23		1.04
Al		0.23		1.4
Ga		0.23		1.5
In		0.23		3.7
Tl		0.23		6.0

* To convert kilogram-calories to electron volts multiply by 0.0434.

† Phosphorus, arsenic, antimony, lithium, and bismuth are donors. Boron, aluminum, gallium, indium, and thallium are acceptors. Donor ionization energies are measured from the conduction band; acceptor energies from the valence band. The values are taken from reference 16.

where Ω_P is the pairing constant and N_P, N_{A^-}, and N_{D^+} are concentrations. Following Bjerrum (2) and Fuoss (12, 13), Ω_P may be expressed as:

$$\Omega_P = 4\pi[q^2/KkT]^3Q(\alpha) \tag{9}$$

In this relation

$$\alpha = q^2/KkTa \tag{9a}$$

where a is the distance of closest approach of the ions and K is the dielectric constant. $Q(\alpha)$ is the value of the function which is known when Ω_P is known (17), so that it is possible therefore to derive values of a from determinations of the pairing equilibrium constant. Results of this kind are discussed below.

D. Chemical equilibria

Under this heading allowance is made for reactions which are similar to those of Section II,C but in which the energies involved are much greater and can lead to "chemical" bond formation. As in ordinary chemical reactions, it is the change in free energy which determines whether or not such reactions occur. Since some solutes diffuse very slowly in solids, the reactions may be diffusion controlled and therefore may be kinetically impeded. Examples of this kind are discussed at the end of this paper.

III. SOLUBILITY EQUILIBRIA OF LITHIUM IN SILICON AND GERMANIUM

So far only equilibria within a crystal of a semiconductor, i.e., homogeneous equilibria, have been considered. Determinations of solubility involve also equilibration with an external phase, i.e., heterogeneous equilibria. This section consists of a discussion of such reactions and an examination of the influence upon solubility of (*1*) electron–hole equilibria in the crystal and (*2*) the phenomenon of ion-pairing. The system lithium dissolved in single crystal germanium will be considered for case 2. Lithium is employed because it diffuses interstitially into these crystals, so that equilibration can be rapid and does not require the presence of vacancies (6, 11). The diffusion constants for lithium in silicon and germanium are shown in figure 2.

A. Effect of electron–hole equilibrium

Consider first a simple system such as shown in figure 3, in which a silicon crystal containing the acceptor boron in solid solution is immersed in a melt of tin containing a small percentage of lithium metal. If the concentration of the latter is held fixed, its activity in the melt is fixed and the following equilibrium relationships hold (34):

$$\begin{array}{rc} \text{Li(Sn)} \rightleftarrows \text{Li(Si)} \rightleftarrows \text{Li}^+ + & n \\ & + \\ \text{B(Si)} \rightleftarrows \text{B}^- + & p \\ & \downarrow\uparrow \\ & \text{bond} \end{array} \tag{10}$$

If the activity of the lithium in the external solution is designated as β, N_{D^+}

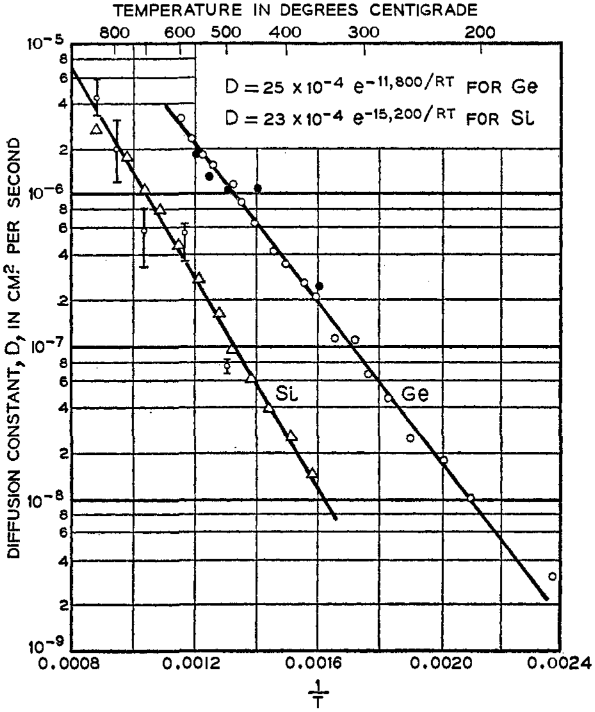

FIG. 2. Plot of diffusion coefficients for lithium in germanium and silicon against the reciprocal of the absolute temperature (11).

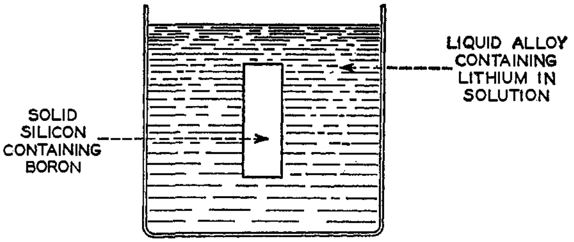

FIG. 3. Equilibration of semiconductor solid with a solution of lithium in melted tin. Lithium diffuses from the liquid bath into the solid rapidly at temperatures above 200°C.

represents the concentration of the ionized lithium in the silicon crystal and N_D represents the total concentration of lithium:

$$(N_D - N_{D^+})/\beta = K_{\text{external}} \tag{11}$$

For the internal equilibria,

$$nN_{D^+}/(N_D - N_{D^+}) = K_d \tag{12}$$

$$pN_{A^-}/(N_A - N_{A^-}) = K_a \tag{13}$$

where N_A and N_{A^-} are the concentrations of the total and the ionized acceptors, respectively.

Combining the above equations with equation 2 and the relation stating electrical neutrality, namely,

$$N_{D^+} + p = N_{A^-} + n \tag{14}$$

one obtains the final equation for the solubility of lithium in acceptor-doped silicon. This solubility is essentially N_{D^+}, because the lithium is almost completely ionized:

$$N_D \sim N_{D^+} = R + [R^2 + (N^0_{D^+})^2]^{1/2} \tag{15}$$

where

$$R = N_{A^-}/1 + [(1 + 2K_s^{1/2}/N^0_{D^+})^2]^{1/2}$$

In equation 15 $N^0_{D^+}$ is the solubility of lithium in *pure* silicon, i.e., in silicon containing no other added solutes, and K_s is the intrinsic ionization constant of the silicon crystal (equation 2). $N^0_{D^+}$ must be obtained from measurements on the pure semiconductor crystal using the proper external phase; then equation 15 enables the calculation of the solubility for any concentration, N_{A^-}, of acceptor ions. Temperature enters the equation through K_s (equation 2). The solubilities of lithium in *undoped* germanium and silicon have been determined (10, 29, 31, 32, 35, 36). The results are shown in figure 4. The values for silicon were determined by electrical conductivity and chemical analysis. Those for germanium were calculated from equation 15 and conductivity determinations on doped germanium in which N_A was known, as well as by chemical analysis.

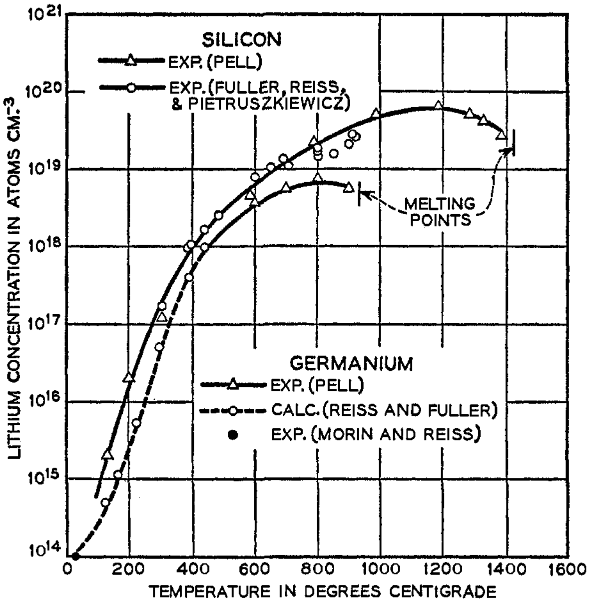

FIG. 4. Solubilities of lithium in undoped germanium and silicon. The results have been compiled from references 10, 29, 31, 32, 34, 35, and 36. The external phase is a lithium-germanium or lithium-silicon alloy in equilibrium with the semiconductor phases at each temperature.

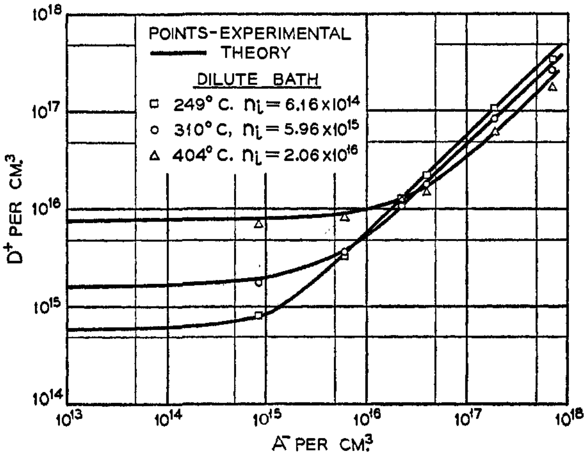

FIG. 5. Solubility of lithium in silicon, N_D, as a function of boron concentration, N_A. Full lines are calculated from equation 15. The external phase was tin containing 0.18 per cent lithium.

Although not shown on figure 4, the solubility must, in both germanium and silicon, drop to zero at the melting points, as required by thermodynamics.

The striking agreement of equation 15 with experiment for silicon doped with boron in varying amounts is shown in figure 5, in which curves for several temperatures are shown. These results leave no doubt about the effect of the interactions of the kind shown in equations 10 on the solubility of lithium. In fact, similar experiments using germanium crystals containing gallium show that interactions occur at gallium concentrations as low as 10^{14} gallium atoms per cubic centimeter, and solubility may be increased as much as 10^5 times by increasing the acceptor concentration. In a manner similar to that given above, it can be shown that a solute donor will *decrease* the solubility of lithium. This effect also has been found experimentally, although quantitative results are lacking.

B. Effect of ion-pairing equilibrium

Reiss (36) predicted that the formation of ion-pairs between Li^+ and acceptors like B^- or Ga^- (the reality of which will be shown subsequently in this review) should produce changes in the solubility of lithium in germanium and silicon superimposed upon the electron–hole effect discussed in Section III,A. Since both the formation of ion-pairs (Section IV) and the crystal ionization are highly dependent on temperature, their combined effects can be rather complicated. However, from the mass action equations and the neutrality relation it is possible to solve this problem quite simply. This has been done (35) for germanium crystals doped with gallium by adding the additional pairing equilibrium,

$$\mathrm{Li}^+ + \mathrm{Ga}^- \rightleftarrows [\mathrm{Li}^+\mathrm{Ga}^-] \tag{16}$$

to the reactions given in equations 10, where Ga^- now replaces B^-, and Ge replaces Si. The result for the total lithium concentration, N_D, in solution is

$$N_D = N_{D^+}\left[1 + \frac{\Omega_P N_A}{1 + \Omega_P N_{D^+}}\right] \tag{17}$$

In equation 17 the pairing constant, Ω_P, must be calculated from the distance of closest approach (Section IV), and N_{D^+} must also be known before N_D can be calculated. Now N_{D^+} depends on the combined constants, $(K_{ext}K_d)$, from equations 11 and 12, and on $N^0_{D^+}$, the solubility of lithium in the undoped crystal, which may be regarded as known. The solution for N_D must be carried out numerically. When this is done (35) the curves in figure 6 are obtained. These are to be compared with the experimental results given for two different concentrations of gallium. Also shown on the figure for the lower gallium concentration is the theoretical curve to be expected if no ion-pairing were present.

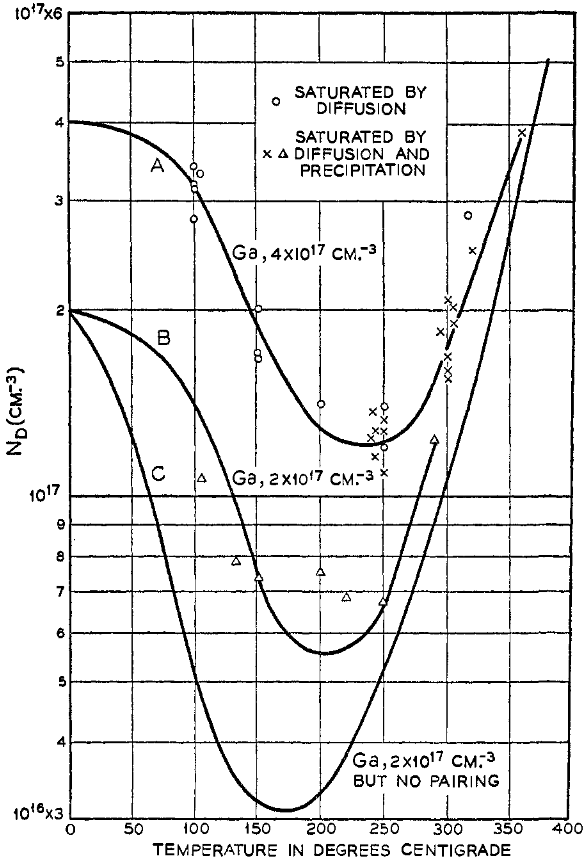

FIG. 6. Effect of ion-pairing on the solubility of lithium in germanium containing gallium from an external lithium-germanium alloy phase. Curve A shows the experimental curve for 4 × 10^{17} atoms of gallium per cubic centimeter. Curve B shows theory (full line) and experiment (triangles) for 2 × 10^{17} atoms of gallium per cubic centimeter. Curve C shows theory for 2 × 10^{17} atoms of gallium (curve B) *not* taking account of ion-pairing.

It is seen that the effect of the pairing is to increase the solubility over that expected on the basis of the electron–hole effect alone. Both effects are seen to be small at higher temperatures, where the solubility of lithium in the undoped crystal becomes large. Effects of the kind just described for germanium do not occur in silicon, because the electron–hole effect for silicon is much larger. This in turn arises because K_s for silicon is considerably smaller than for germanium. (K_s is 5.76×10^{26} cm.$^{-6}$ for germanium at 300°K. and 2.25×10^{20} cm.$^{-6}$ for silicon at 300°K.) Thus, the effect of the electron–hole equilibrium in silicon is still large at temperatures where the ion-pairing effect has become small.

Of particular interest are the solubility results when doubly charged acceptors like Zn^{--} are present as the nonmobile ion. In this case, triplets as well as pairs are formed (29) and the binding energy of the pair is greatly increased by the double charge. Figure 7 shows the curves predicted for this case based on values of Ω_P and Ω_T for the pair and triplet, respectively, from reference 29. Although the experimental results scatter rather widely because of difficulties in attaining equilibrium, they confirm the expectation of a greater effect on solubility by the Zn^{--} ion as compared to the Ga^- ion. A curve for the latter, taken from figure 6 and reproduced in figure 7, shows this comparison.

The above results on solubility are one aspect of the effects of interactions taking place between electrons and solvent and solutes in semiconductor crystals.

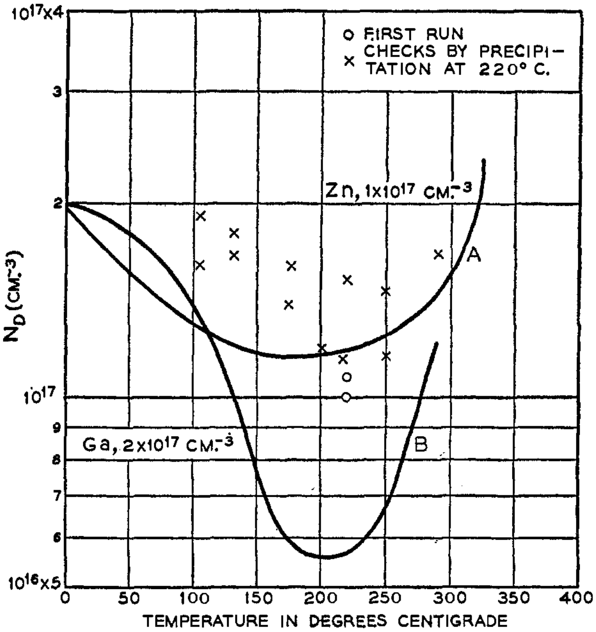

FIG. 7. Effect of doubly charged Zn^{--} on the solubility of lithium in germanium from an external germanium–lithium alloy phase. Curve A shows theory (full line) for 1.0×10^{17} atoms of zinc per cubic centimeter. Points marked O are those shown by crosses at 100°C., which were reëquilibrated at 220°C. Curve B shows the theoretical curve for 2×10^{17} Ga^- ions per cubic centimeter, including ion-pairing for comparison.

They are, however, not as striking as those now to be discussed, which provide direct and quantitative evidence for solute–solute interactions.

IV. ION-PAIR EQUILIBRIA

A. Ion-pairing and carrier mobility

Equation 8 may be written in terms of the *total* donor and acceptor concentrations as follows:

$$\Omega_P = N_P/(N_A - N_P)(N_D - N_P) \tag{18}$$

If Ω_P can be determined, it is possible to obtain the value of the function $Q(\alpha)$ from equation 9. From the value of $Q(\alpha)$ and Ω_P, α itself is deducible from the pair distribution functions (2, 12, 13) and is available in published tables (17, 36). From α, the distance of closest approach of the ions is obtained from equation 9a.

In the experiments to be described, the ratio of the concentration of pairs, N_P, to the concentration of mobile donors, N_D, which ratio is the fraction of the donor atoms which are paired, is often the quantity determined:

$$N_P/N_D \equiv \theta \tag{19}$$

Reiss (36) has shown that in terms of θ, $Q(\alpha)$, and therefore α and a, is given by

$$Q(\alpha) = \frac{1}{4\pi}\left(\frac{KkT}{q^2}\right)^3 \frac{\theta}{(N_A - \theta N_D)(1 - \theta)} \tag{20}$$

Consequently all one needs is to determine the temperature where θ has a given value, in order to get the "distances of closest approach" of the ions. This is done uniquely by means of Hall mobility measurements as follows:

Hall mobility, μ_H, is determined by measuring the so-called "Hall constant," R, and the electrical conductivity, σ, of a small specimen of germanium or silicon containing both the fixed acceptor and mobile lithium ions. The measurement involves simply the determination of a voltage in the presence of a known magnetic field and is discussed in standard texts (39). The relation is

$$\mu_H = R\sigma \text{ cm.}^2\text{/volt second} \tag{21}$$

Now the Hall mobility of electrons (and holes) is greatly dependent (in the appropriate temperature range) on the concentration and nature of the charged solute atoms in the conducting crystal. When Li^+ and Ga^- ions are separately present the scattering effect on the mobility is very much greater than when the charges are effectively shielded, as they are in the pair $[Li^+Ga^-]$, for example. Furthermore, since the effect of the charge goes up as its square, doubly charged ions become very effective in reducing the carrier (electron or hole) mobility.

It follows that if the carrier mobility is determined as a function of T in two acceptor-doped specimens, one containing lithium and the other not, they should exhibit the same mobility when the number of scattering charges is the same in each. Consider two specimens of germanium containing the same concentration of acceptor, N_A. Introduce a lithium concentration, N_D, into one of them. When the temperature is such as to give equal mobilities in the two cases,

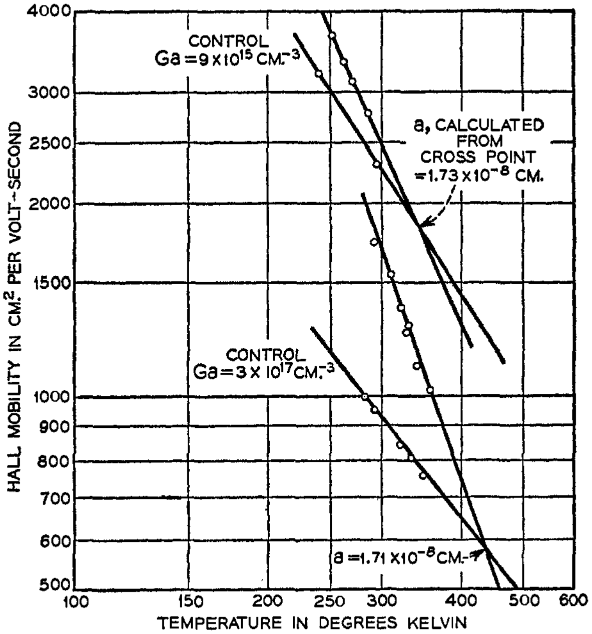

FIG. 8. Plots of Hall mobilities against absolute temperature for two different gallium dopings in germanium. The values of a, the distance of closest approach of the ions, are obtained from the intersection point of the specimens with and without lithium in each case.

$$N_A = N_A + N_D - 2N_P \quad \text{or} \quad N_P/N_D = \theta = 0.5 \tag{22}$$

These are the quantities needed in equation 20 to provide a.

Figure 8 shows the results of measurements of Hall mobility in germanium containing known concentrations of gallium and lithium. These concentrations are readily determined from Hall and conductivity measurements. The cross-over points give the temperature for $\theta = 0.5$ and hence, a, for [Ga$^-$Li$^+$]. The agreement ($a = 1.72$ A.) for the two runs shown is excellent.

Values of a for all of Group III acceptors in germanium containing lithium are shown in table 2 (36). The agreement between the last two columns is satis-

TABLE 2

Distance of closest approach of lithium-acceptor pairs in germanium

Li$^+$ radius = 0.60 A.

Acceptor	Tetrahedral Radius	Sum of Tetrahedral Radius and Lithium-ion Radius	Distance of Closest Approach
	A.	*A.*	*A.*
B	0.88	1.48	2.16
Al	1.26	1.86	1.68
Ga	1.26	1.86	1.72
In	1.44	2.04	1.83
Ge	1.26		

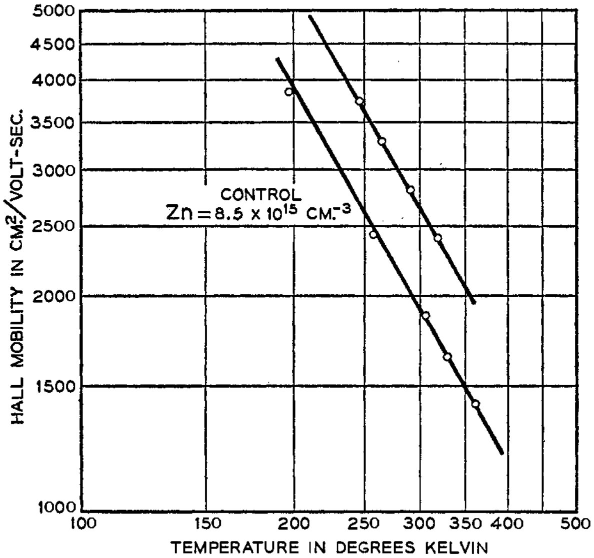

FIG. 9. Plot similar to figure 8 for germanium containing zinc. No intersection of the curves occurs because of the high degree of stability of the [Zn^{-} $^{-}Li^{+}$] pairs (curve B) compared to the control (curve A).

factory except for *B*. The poor agreement in this case is believed to be due to lattice strain.

Figure 9 shows data similar to those in figure 8, but for germanium containing Zn^{--}. In this case the triplet [$(Li^{+})_2Zn^{--}$] is essentially dissociated and the higher mobility of the specimen containing lithium, compared to the one containing only zinc, attests to the fact that [$Li^{+}Zn^{--}$] pairs exist in the former. The fact that the two curves are nearly parallel conforms to the stability expected from such pairs. There is some difficulty in calculating a distance of closest approach for a doubly ionized atom in that two assumptions are possible regarding the charge distribution. Depending on whether a point charge model or an unsymmetrical dipole model is adopted (29), an *a* of 2.76 A. or one of 3.50 A. can be calculated.

Further convincing evidence of the presence of [$Li^{+}Zn^{-}$] is provided by determinations of the variation of the free carrier concentration as a function of the temperature for specimens of germanium containing both zinc and lithium. These results (29) are shown in figure 10. The curve for the specimen containing only zinc (marked "control" on figure 10) shows the two slopes corresponding to the double ionization of zinc at the high temperatures (43). On the other hand, the curve for the lithium-containing specimen shows only one ionization corresponding to a ΔE_i of only 231 cal. (0.0095 e.v.) compared to 660 cal. (0.0286 e.v.) for the first electron from the zinc. This is precisely the result expected, since a singly ionized acceptor in germanium has approximately this value. From measurements of this kind Morin and Reiss (29) have been able to de-

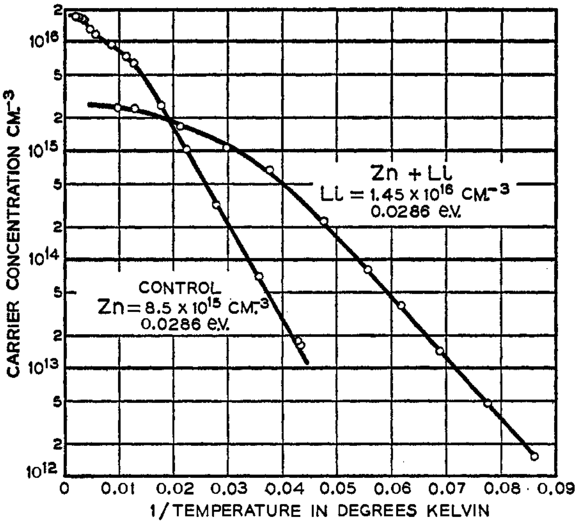

FIG. 10. Carrier concentration versus $1/T$ for specimens of zinc-doped germanium with and without the addition of lithium. The two slopes corresponding to the two zinc ionizations are shown by the control. The lithium-containing specimen shows an energy typical of a simple acceptor, thus confirming the presence of $[Zn^{-}{}^{-}Li^{+}]$.

termine the complete distribution into Li^{+}, $[Li^{+}Zn^{-}{}^{-}]$, and $[(Li^{+})_2Zn^{-}{}^{-}]$ species for specimens prepared in various ways.

B. Ion-pair relaxation

Since the ion-pairing reaction (equation 7) is very dependent upon temperature, information on the kinetics of the reaction should be obtainable from an investigation of the change of mobility with time when the temperature is rapidly changed in such a way as to "quench in" nonequilibrium concentrations of pairs. Reiss (36) has calculated the fraction of $[Li^{+}Ga^{-}]$ pairs in germanium (figure 11) as a function of temperature and concentration, assuming equal initial concentrations of lithium and gallium. From these results it is evident that, in a specimen containing 10^{17} atoms of each kind per cubic centimeter, about 95 per cent of the atoms will be paired at room temperature, whereas only about 10 per cent will remain paired at 500°K. Since the reaction is dependent on the diffusion of the lithium ions to the fixed ions of the acceptor, one might expect to determine the diffusion coefficient for lithium from a study of the pairing kinetics. It turns out, in fact, that this pairing relaxation method is by far the most precise method for determining this constant.

Because measurements need only be made at constant temperature, it is possible to determine the pairing relaxation time, τ, from electrical conductivity changes alone. This follows from the fact that the formation of pairs changes the carrier mobility but not the carrier concentration. When the pairing reaction is first order, as it is here (36), it can be shown that

$$\log (\sigma_\infty - \sigma_t) = \log \phi + t/\tau \qquad (23)$$

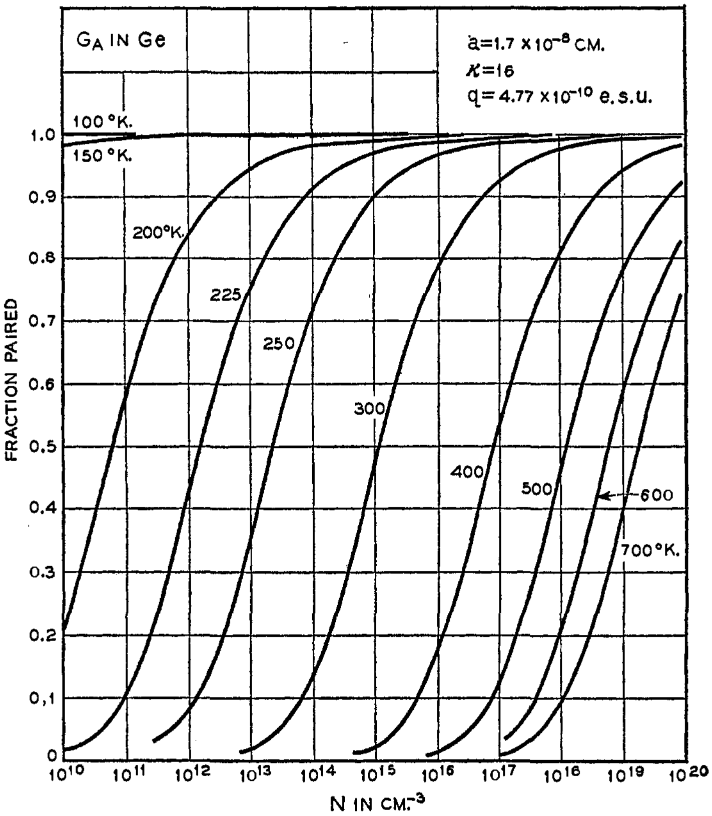

FIG. 11. Fraction of ions paired versus concentration of the ions (considered equal) for various temperatures (after Reiss (36)). $a = 1.7 \times 10^{-8}$ cm. and $K = 16$.

where σ_∞ and σ_t are the electrical conductivities at "infinite" time and time t, respectively, and ϕ represents a constant. The relaxation time, τ, is simply obtained from the slope of the plot of log $(\sigma_\infty - \sigma_t)$ against time. Figure 12 is an example of such a plot for gallium and lithium in germanium. In turn, D, the diffusion constant of lithium, is obtained from

$$\tau = KkT/4\pi q^2ND \tag{24}$$

where N is equal to the original concentrations (atoms per cubic centimeter) of the lithium and acceptor ion taken as equal.

The method in practice is as follows: A specimen of germanium or silicon containing a known concentration of one of the acceptors is saturated with lithium by heating in contact with the alloyed metal or a solution of lithium in tin in an inert atmosphere. When the conditions are chosen properly, an amount of lithium very nearly equal to the acceptor concentration present can be introduced. This point is readily determined by conductivity measurements which measure the degree of "compensation" achieved. Once the lithium has been introduced, the crystal is ready for the relaxation measurement. First it is

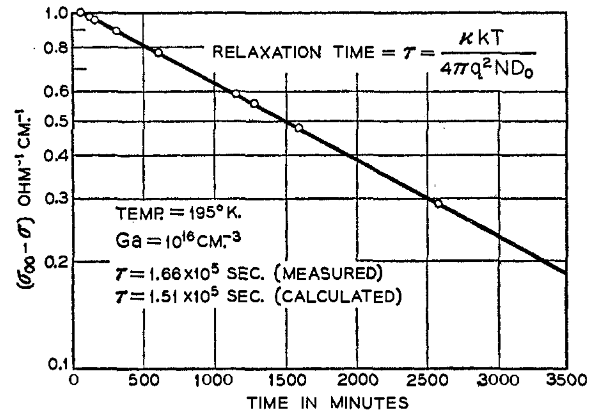

FIG. 12. Plot of log ($\sigma_\infty - \sigma_t$) against time for germanium containing [Ga$^-$Li$^+$] pairs. The first-order kinetics of pair formation is evident.

warmed sufficiently above room temperature to assure complete or nearly complete dissociation of the pairs. It is then suddenly cooled by plunging the specimen into liquid nitrogen to quench in the unpaired state. Finally, the change in conductivity is measured as a function of time at a temperature chosen to give an easily measurable reaction (diffusion) rate. The experiment shown in figure 12 was conducted at the temperature of dry ice and illustrates the very good agreement with the first-order reaction kinetics derived from the theory.

Relaxation times for lithium pairs have been determined in the above manner for gallium-, boron-, and zinc-doped germanium (29, 36) and for boron-doped silicon (28). It is interesting that τ is found to be independent of the nature of the acceptor (whether gallium or boron)—in other words independent of a, the distance of closest approach, as the theory demands. Of most interest are the values for D which are calculable from τ (equation 24). The results for germanium are in excellent agreement with those of reference 11. A remarkable result has been obtained by Maita (28) for the diffusion of lithium in silicon. This is shown in figure 13, in which the results of two measurements of D, one at 273.2°K. and one at 300.4°K., are indicated. The agreement with the results obtained at higher temperatures (and also shown in figure 2) is good evidence of the validity of the relaxation method.

In closing this section on ion-pair formation, it should be pointed out that phenomena in solid solutions other than those discussed can also furnish valuable information. Some of these are discussed in reference 36 and include diffusion in the presence of ion-pairs as well as the effect of the pairing reaction on the ionizations of the component atoms. The mobility aspect of ion-pairing has been emphasized here, primarily because of its uniqueness and in order not to prolong the treatment unduly.

V. CHEMICAL REACTIONS INVOLVING OXYGEN IN SILICON

Because reactions between solutes in solid solutions can only occur through a diffusing together of the reactants, such processes can be very slow. Furthermore,

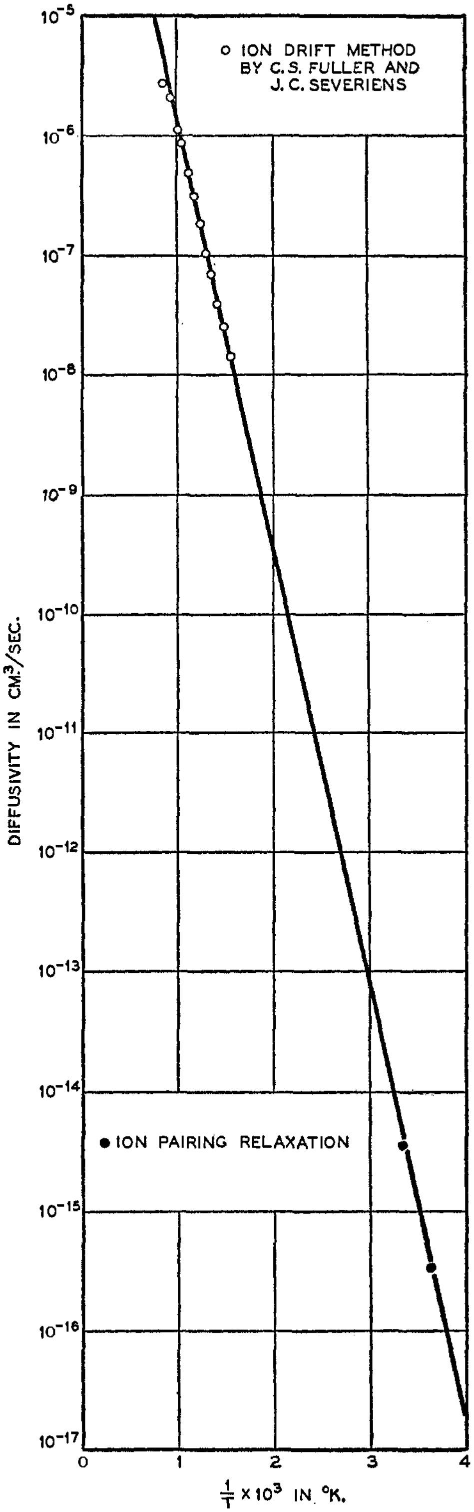

FIG. 13. Determination of the diffusion constant for lithium in silicon by means of the ion-pair relaxation method provides the two points shown by the filled circles. The agreement with the results obtained by other methods is shown. (After J. P. Maita (28).)

if diffusion is increased by raising the temperature, thermal dissociation of the products of the reaction may occur. There are, however, some reactions where the rates of reaction and the binding energies are sufficiently high to lead to products which are capable of measurement. One of the earliest such reactions was found through investigation of zinc sulfide phosphors, where evidence was obtained of Ag^+ replacing the Zn^{++} ions and Cl^- replacing the S^{--} ions (26). Recently, however, reactions which involve the formation of donors in silicon by (*a*) the interaction of dissolved oxygen atoms (7, 9, 20, 22, 23, 24), (*b*) the reaction of oxygen atoms with lithium (32), and (*c*) the reaction of oxygen with acceptor atoms (8) like aluminum have been reported. Although the precise nature of these reactions is still in doubt, sufficient is known to make a brief discussion of them of interest.

A. Oxygen–silicon interactions

The evidence for the interaction of oxygen atoms with silicon, resulting ultimately in the precipitation of silica in silicon crystals, derives principally from investigations of the infrared absorption properties of oxygen–silicon solid solutions which have been subjected to various heat treatments (18, 20). These data, together with electrical measurements (9), have permitted a qualitative idea of the nature of the processes taking place to be pieced together. The picture is as follows: When silicon containing dissolved oxygen is rapidly cooled from the melt, the oxygen is held in the crystal in the supersaturated state and is believed to be randomly dispersed (18) as Si—O—Si units covalently bonded to the silicon diamond lattice. The exact crystallographic position of the oxygen is not known, but a substitutional position seems favored (40). When such a solution is heated, oxygen atoms (possibly associated with vacancies) migrate together and react to form a donor. Four such oxygens are believed to unite in quick succession to form stable tetrahedral SiO_4 units which possess donor-like properties (20, 21). Further reactions lead to larger aggregates which are elec-

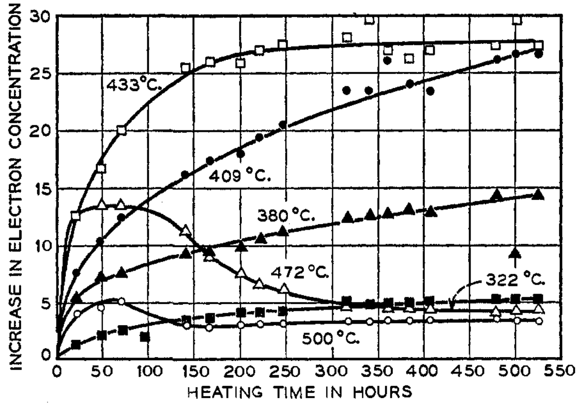

FIG. 14. Increase in electron concentration as a function of heating time for a silicon crystal containing approximately 10^{18} atoms of oxygen per cubic centimeter. Curves for a series of temperatures are shown.

trically neutral or to donors or acceptors which are only weakly ionized at room temperature. Data on the kinetics of the formation and disappearance of the donors have been shown to provide a good prediction of the observed electrical changes (21). Typical changes for a silicon crystal containing approximately 10^{18} atoms of oxygen per cubic centimeter are shown for several temperatures in figure 14. Furthermore, the recent finding of specific infrared absorption spectra corresponding to successive oxygen additions to form such an SiO_4 unit lend further evidence to the validity of this model for the reaction (19).

B. Reaction of lithium with oxygen

The fact that lithium is able to react with other solutes in semiconducting crystals has already been pointed out. However, a stronger type of interaction between lithium and oxygen in silicon has been investigated by Pell (32), who finds that when lithium is introduced into silicon containing dissolved oxygen at high temperatures (~600°C.), the reaction

$$\mathrm{Li}^+ + \mathrm{O} \rightleftarrows \mathrm{LiO}^+ \qquad (25)$$

occurs. At this temperature the formation of LiO^+ (a donor) is believed essentially complete in an excess of lithium. However, at lower temperatures the reaction

$$\mathrm{Li\ (dissolved)} \rightleftarrows \mathrm{Li\ (precipitated)} \qquad (26)$$

causes the LiO^+ to decompose with the formation of Li^+ and O. By identifying $[LiO^+]$ with the final donor concentration reached upon precipitation in crystals having high oxygen concentration, and by assuming the equilibrium constant, K, to have the same temperature dependence as $[Li^+]$, the equilibrium constant for reaction 25 was determined:

$$K = 8 \times 10^{23} \exp(-12{,}000/RT) \qquad (27)$$

The heat of reaction is then the known heat of solution of lithium, i.e., 12 kcal or 0.52 e.v. The preëxponential factor in equation 27 also is reasonable in view of the 5×10^{22} interstitial sites per cubic centimer in silicon, the number of oxygen sites per cubic centimeter being the concentration of oxygen.

Pell is able to show that the above reaction can satisfactorily account for the observed kinetics of the precipitation of lithium from silicon containing oxygen.

C. Reaction of oxygen with acceptor solutes

When silicon crystals containing both oxygen and an acceptor element in solution are heated to temperatures of about 450 to 700°C., reactions occur between the two solutes which lead to products having donor-like properties (8). The oxygen–silicon reactions discussed in Section V,A also take place simultaneously. However, in the presence of an excess of acceptor, the main reaction is with the acceptor. Donor impurities do not appear to react. These reactions may be written

$$p + \mathrm{A}^- + x\mathrm{O} \rightleftarrows \mathrm{AO}_x^+ + n \qquad (28)$$

where A^- stands for a boron, aluminum, gallium, or indium ion and p and n for the hole or electron, respectively. For boron, gallium, and indium it is found that reaction 28 is always less than half complete, i.e., silicon crystals in which the reaction occurs never turn n-type unless insufficient acceptor is present to compensate the donors discussed in Section V,A. However, when aluminum is the acceptor the reaction, in an excess of oxygen, appears to go essentially to completion, all or nearly all of the aluminum being transformed into the donor complex. The latter is quite stable, as shown by the fact that temperatures above about 1000°C. are required to decompose it. At 1300°C. and above, rapid decomposition into aluminum and oxygen takes place, leading to crystals of the original electrical properties. At temperatures of 700–800°C., aggregative reactions leading to neutral complexes appear to occur, analogous to those between oxygen and silicon alone. Attempts to establish equilibria for reaction 28 have been only partially successful and confirm that other reactions occur.

The boron–oxygen donor-like complex shows an unusual behavior with temperature (gallium also exhibits a similar behavior). When the temperature exceeds about 500°C. the donors disappear in precisely the same manner (first-order kinetics) as do the donors formed from oxygen and silicon alone (9). Silicon crystals containing aluminum and oxygen do not show this decrease, suggesting that the donor-like compounds in this case possibly do not react further at temperatures of 500–600°C.

Figure 15 (lower curve) shows a plot of the log of first-order rate constant divided by T against reciprocal temperature for silicon crystals containing 10^{18}

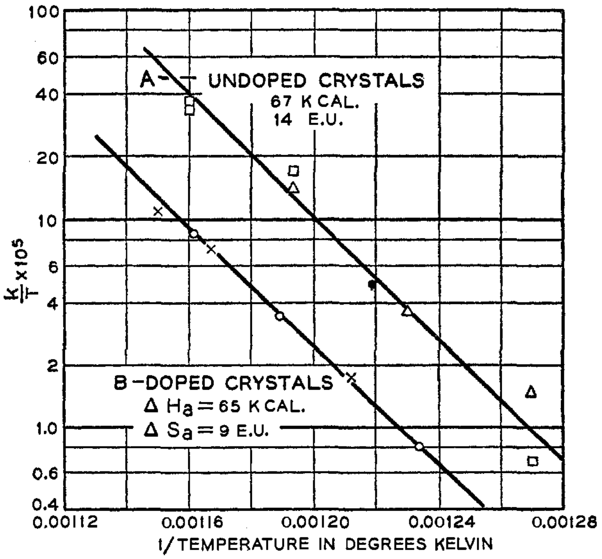

FIG. 15. Plot of logarithm of first-order reaction constant k, divided by T, against $1/T$ for (A) silicon containing $\sim 10^{18}$ atoms of oxygen per cubic centimeter and (B) silicon containing $\sim 10^{18}$ atoms of oxygen and 1×10^{18} atoms of boron per cubic centimeter. The reaction is one leading to the disappearance of the heat-treatment donors.

atoms of boron per cubic centimeter as doping impurity and approximately 10^{18} atoms of oxygen per cubic centimeter. The equation of the straight line is given by

$$k = RT/Nh \exp(9.2/R) - \exp(65{,}000/RT) \tag{29}$$

The activation energy is about the same as for silicon crystals containing only oxygen (upper curve). The difference in rates between the doped and undoped crystals is believed to be due to the fact that the lower curve (doped) was determined at the reaction temperatures, whereas the upper curve (undoped) was determined by quenching to room temperature. This in turn suggests that several products, some of which are unionized at room temperature, may form.

In the case of boron at 470°C. a maximum of $2\text{–}3 \times 10^{17}$ electrons per cubic centimeter are produced in the presence of $\sim 10^{18}$ atoms of oxygen per cubic centimeter. This is shown by curves of figure 16 for crystals containing 1.3×10^{18} and 5.2×10^{18} atoms of boron per cubic centimeter. For aluminum (figure 16) the maximum concentration of electrons is greater ($\sim 6 \times 10^{17}$ per cubic centi-

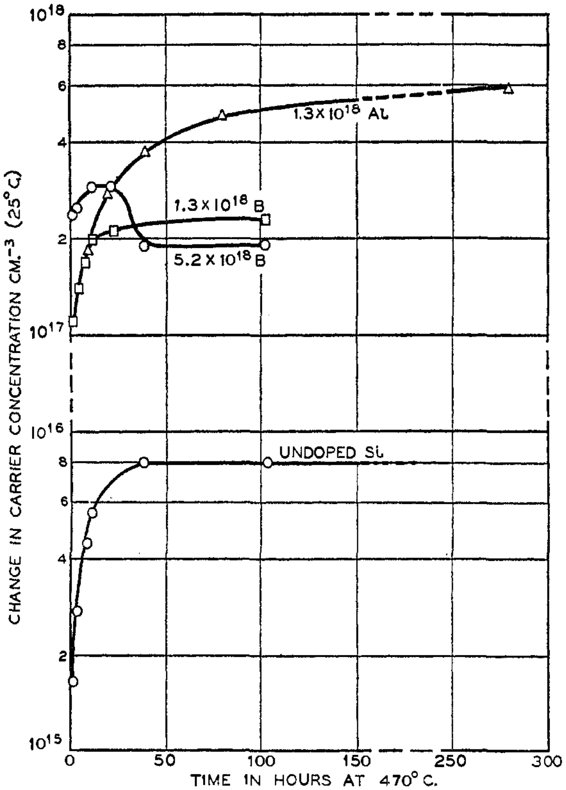

FIG. 16. Change in carrier concentration (25°C.) as a function of time for $\sim 10^{18}$ atoms of oxygen per cubic centimeter and (*a*) 5.2×10^{18} atoms of boron per cubic centimeter, (*b*) 1.3×10^{18} atoms of boron per cubic centimeter, (*c*) 1.3×10^{18} atoms of aluminum per cubic centimeter, and (*d*) no added impurities. Heating was at 470°C. for the times indicated.

meter), suggesting that perhaps the reaction *terminates* at AlO_3 or AlO_4. More precise determinations of oxygen content will be required before more definite conclusions can be reached.

The reactions between acceptors and oxygen are still, as is evident from the above brief discussion, poorly understood. The differences between aluminum and the other acceptors appear to be related to the greater bond energies of aluminum–oxygen as compared to the others (and to silicon–oxygen), but so far no quantitative treatment is possible. Also to be explained is the strange behavior of the boron and gallium donor complexes which disappear at temperatures above 500°C. only to reappear in a slower reaction above this temperature. To unravel the mechanisms through which the different neutral and charged molecules form and to establish their identities will require much further work. However, these reactions have considerable value in elucidating the steps by means of which precipitations are initiated and in demonstrating the occurrence of compounds which are able to behave as donors (and possibly as acceptors also) in semiconductors.

The above work demonstrates that with sensitive measuring tools such as infrared spectroscopy, electrical conductivity, and the Hall effect provide, one may expect to learn considerably more in the future about solid-state reactions occurring in semiconducting crystals.

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