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THE IMPURITIES LITHIUM AND BORON IN SILICON: ION PAIRING AND GROUND STATE DEGENERACY

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Abstract—The ion pairing reaction $Li^+ + B^- \rightleftarrows LiB$ in silicon was studied by measuring the relaxation time for the approach to equilibrium and impurity concentrations once equilibrium is established. Resistivity and Hall-effect were used as experimental monitors of the degree of association. The equilibrium constant K can be expressed as $K = A \exp(\Delta H/kT)$, with pre-exponential factor $A = 50 \pm 10$ and binding enthalpy $\Delta H = 0.39$ eV. Interpretation of the pre-exponential factor by considering configurational entropy changes and modification of the crystal vibration spectrum resulting from the reaction yields order of magnitude agreement. The results are not sufficiently accurate to draw any conclusions on the occupation of T- or H-sites in the silicon lattice by the interstitial lithium ions. Statistical weight factors for the ground states of the donor lithium and acceptor boron are $g_{Li} = 12.2$ and $g_B = 4.4$, close to the theoretical values 12 and 4 resp.

1. INTRODUCTION

In silicon doped with lithium and boron a pairing reaction between the ionized impurities takes place. This reversible reaction, leading to formation of the neutral associate LiB, is represented by the scheme: $Li^+ + B^- \rightleftarrows LiB$. Association near room temperature is possible by virtue of the high mobility of the lithium ions which occupy interstitial sites in the silicon lattice; the rate of the reaction is diffusion controlled. Most of the binding energy of an impurity pair is accounted for by the electrostatic attraction between the oppositely charged ions. An equilibrium constant K is defined by $K = n_{LiB}/n_{Li^+} \cdot n_{B^-}$, where n_{LiB}, n_{Li^+}, and n_{B^-} are the concentrations of the neutral complexes and of the unpaired ionized donors and acceptors resp. The value of the equilibrium constant depends on the temperature, but is independent of the concentrations of the imperfections. It can be shown, under certain assumptions, that K is described by $K = A \exp(\Delta H/kT)$. In this expression ΔH is the enthalpy change upon formation of a pair, while A is a constant usually called the pre-exponential factor. An experimental determination and theoretical verification of the pre-exponential factor will be subject of this paper.

In the past the equilibrium constant has been determined already by two groups of investigators. Pell[1] observed the rate of decrease of the capacity of reverse-biased lithium diffused p-n junctions. In this way an effective lithium ion drift mobility, proportional to the fraction of unpaired lithium ions, was measured. For these experiments samples containing 1.5×10^{16} or 1.4×10^{17} atoms lithium and boron per cm^3 were used. Taking Pell's data Kröger[2] could calculate the equilibrium constant obtaining the values $A = 19$, and $\Delta H = 0.39$ eV. More recently Spitzer and Waldner[3] carried out an investigation of the ion pairing reaction employing optical techniques. Impurity concentrations were determined by measuring the strength of the absorption associated with local vibrational modes at wave number $\sigma = 644$ cm^{-1} for unpaired B^-, and at $\sigma = 522$, 584, and 681 cm^{-1} for the LiB-complex. In these samples a high amount of impurities, 2.8×10^{19} cm^{-3}, was present. The resulting reaction constant is given by $A = 0.1$, $\Delta H = 0.39$ eV.

Because of the apparent discrepancy in the values reported for the pre-exponential factor A a further investigation seemed worthwhile. Experimental methods different from those used earlier were favored since these provide a more independent check. A first possible method is given by measuring the relaxation time of the ion pairing reaction. In this experiment the pairs are initially dissociated almost completely by subjecting the sample to a high temperature. Subsequently the sample is rapidly cooled to a lower temperature at which the approach of equilibrium is monitored. Because of the reversible nature of the reaction, pairs once formed may dissociate again at a later moment, thereby reducing the net rate of ion pairing. The observed relaxation time therefore is related to the equilibrium constant K of the reaction. Experiments were performed on a highly compensated sample, since for these conditions a mathematical treatment indicates the dependence on K to be strongest. The results, as given in section 2 of this paper, essentially confirm the values reported by Pell[1]–Kröger,[2] although our value for the pre-exponential factor A is slightly higher.

In section 3 our second experiment, applied to study the equilibrium conditions of ion pairing, is described. This experiment consisted of measuring the free carrier concentration over a wide temperature range, in both an n-type and a p-type sample, by the Hall-effect. Consideration of carrier statistics by the usual models provides a relationship between carrier concentration, equilibrium impurity concentrations, ionization energy of the majority dopant, and its ground state statistical weight. In the analysis as presented in section 3 it is assumed that the equilibrium constant is already known. This assumption is justified by the agreement between our results given in section 2, our results reported earlier,[4] and those of Pell[1]–Kröger.[2] The equilibrium concentrations of both the unpaired lithium and boron may then be calculated straight-forward. The presentation of the results as chosen for section 3 is such that the numerical values of the ground state degeneracies of lithium and boron are shown clearly. Agreement between these values and those predicted theoretically demonstrates the validity of the analysis and confirms the proper choice of equilibrium constant.

In the final section 4 a discussion is given on the pre-exponential factor A. The changes in configurational entropy upon pairing and changes in the free enthalpy associated with local modes of vibration are considered. Order of magnitude agreement between the theoretical and experimental values for A is achieved. The discrepancies are too large, however, to draw any conclusions about the occupation of T- versus H-type interstitial sites in the silicon lattice by the lithium ions.

2. REACTION KINETICS, EQUILIBRIUM CONSTANT

For the experiments directed at determining the relaxation time of the ion pairing reaction a sample was needed in which the concentrations of boron and lithium were nearly equal, but of a resistivity sufficiently low to enable resistivity measurements at low temperature to be made. These requirements were met by the following sample preparation procedure. Float-zone single-crystal silicon, doped with 1.58×10^{15} boron atoms per cm^3, was taken as the basic material.[5] Lithium was introduced into a slice by diffusion from a lithium-in-oil suspension painted onto a surface, followed by distribution through the sample by applying the lithium ion drift technique.[6–8] A sample uniformly doped with lithium and boron to exactly equal concentrations for most of its volume is then obtained. Subsequently the sample was irradiated by gamma's from a ^{60}Co-source and annealed at 60 °C for a long time causing the loss of some lithium ions by precipitation on irradiation produced defects.[9] A highly compensated p-type sample, in which $n_B - n_{Li} = 4.5 \times 10^{12}\,\text{cm}^{-3}$, was prepared this way. Finally the sample is given a shape suitable for resistivity measurements according to the Van der Pauw method.[10]

The first step in the experimental procedure of determining a relaxation time is heating of the sample to about 50 °C for one hour. After this treatment most of the pairs are dissociated and the free lithium ions are distributed randomly through the crystal. Ion pairing proceeding with time was followed in separate runs at the three temperatures $T = 0$ °C, 9.8 °C, and 19.6 °C, resp. The relaxation process is periodically interrupted by chilling the sample to liquid nitrogen temperature. The resistivity at this temperature is a suitable monitor of the degree of ion pairing at the time of measurement. The resistivity $1/pe\mu_h$ at liquid nitrogen temperature depends on the amount of donors and acceptors present at the particular moment by both the hole concentration p and the hole mobility μ_h. The effect on the mobility, via ionized impurity scattering, was known from previous experiments and could be eliminated. Therefore resistivity measurements sufficed to determine the variation of the hole concentration. From this the time dependence of the free lithium ion concentration is calculated by applying a textbook formula based on carrier statistics, a formula which is also given explicitly in the next section.

Several authors have treated the kinetics of bimolecular reactions.[11–13] In the case of ion pairing reactions, with long range attractive Coulomb forces between the reacting particles present, the introduction of an effective capture radius $R_c = e^2/4\pi\varepsilon kT$ appears useful.[14,15] The capture radius R_c represents the distance at which the electrostatic attractive energy between the ions $e^2/4\pi\varepsilon R_c$ equals the average thermal energy kT. Within this distance the associate is considered to be formed, while outside it the lithium ion is subject only to random diffusional motion. For silicon at the temperature T the capture radius is given by $R_c = 14200 \times 10^{-8}/T$ cm. For a diffusion-limited reaction the appropriate rate expression, assuming uncorrelated recombination, reads:

$$dn_{\mathrm{Li}^+}/dt = dn_{\mathrm{B}^-}/dt = -k_1 n_{\mathrm{Li}^+} n_{\mathrm{B}^-}$$

This expression is valid for a random initial distribution of the reacting particles, as is the case in our experiment. Apart from an initial transient the rate constant k_1 is time independent and is given by $k_1 = 4\pi R_c D_{\mathrm{Li}}$. The significance of the initial transient is negligible in the present experiment where highly diluted samples were used, as is indicated by the parameter $\frac{4}{3}\pi R_c^3 n_{\mathrm{Li}} \simeq 8 \times 10^{-4} \ll 1$. Because of the low impurity concentrations also the screening of the ions by the carriers may be neglected. During relaxation at the temperatures mentioned above the impurities lithium and boron are completely ionized; the Fermi level is near the middle of the gap. Therefore the concentrations of the unpaired and ionized impurities, n_{Li^+} and n_{B^-}, are equal to the total concentrations of unpaired impurities, either ionized or neutral, n_{Li} and n_{B}. Total amounts of lithium and boron in the crystal, irrespective of their presence as unpaired impurities or as constituent of an LiB-complex are denoted by $n_{\mathrm{Li,tot}}$ and $n_{\mathrm{B,tot}}$, resp. The known diffusion coefficient of lithium in silicon is designated by the symbol D_{Li}.[16] To account for the reversibility of the ion pairing process a term $+ k_2 n_{\mathrm{LiB}}$ is added to the reaction rate expression. For similar reasons as advanced above k_2 is also considered to be constant. The differential equation by which the relaxation rate is described then reads:

$$dn_{\mathrm{Li}}/dt = -k_1 n_{\mathrm{Li}} n_{\mathrm{B}} + k_2 n_{\mathrm{LiB}}$$

Integration of this equation for our special case of equal lithium and boron concentration yields as solution for the lithium concentration at the time t:

$$n_{\mathrm{Li}}(t) = \{\alpha + \beta \exp(-t/\tau)\}/\{\gamma + \delta \exp(-t/\tau)\} \quad (1)$$

with

$$\begin{aligned}
\alpha &= \{2n_{\mathrm{Li}}(0) + D + K^{-1}\}\{D - K^{-1}\} \\
\beta &= \{2n_{\mathrm{Li}}(0) - D + K^{-1}\}\{D + K^{-1}\} \\
\gamma &= 2\{2n_{\mathrm{Li}}(0) + D + K^{-1}\} \\
\delta &= -2\{2n_{\mathrm{Li}}(0) - D + K^{-1}\} \\
D &= (4n_{\mathrm{Li,tot}}K^{-1} + K^{-2})^{1/2} \\
K &= k_1/k_2 \\
\tau &= (k_1 D)^{-1}
\end{aligned}$$

On substituting for k_1, R_c, and D one obtains for the relaxation time τ:

$$\tau = \varepsilon kT/e^2(4n_{\mathrm{Li,tot}} + K^{-1})K^{-1/2}D_{\mathrm{Li}} \quad (2)$$

By this formula the explicit dependence of the relaxation time τ on the equilibrium constant K is demonstrated. Under the conditions of our experiment the approximation $K^{-1} \ll 4n_{\mathrm{Li,tot}}$ is valid and the formula for τ can be simplified to:

$$\tau = \varepsilon kT/2e^2 n_{\mathrm{Li,tot}}^{1/2} K^{-1/2} D_{\mathrm{Li}}$$

Thus the temperature dependence of τ/T is governed by the activation energy of $D_{\mathrm{Li}}^{-1}K^{+1/2}$. This is to be contrasted to the usual case where only the temperature dependence of D_{Li} is involved.

To analyse the experimental data the formulas derived above were applied. For purposes of illustration one better writes the expression (1) as:

$$\exp(-t/\tau) = -\{\alpha - \gamma n_{\mathrm{Li}}(t)\}/\{\beta - \delta n_{\mathrm{Li}}(t)\} \quad (3)$$

Figure 1 shows that on plotting the variation of $n_{\mathrm{Li}}(t)$ versus time using the right hand side expression of equation (3) one obtains straight lines. Their slopes are indicative for the relaxation times,

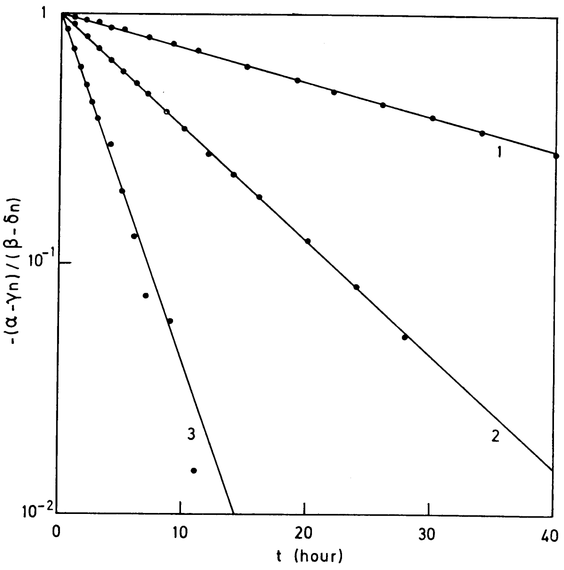

FIG. 1. Illustration of the analysis of the ion pairing kinetics. Points (●) are calculated by the right hand side expression of equation (3), while straight lines represent the function exp $(-t/\tau)$. Labeling of the curves corresponds to the experiments performed at 0.0 °C (1), 9.8 °C (2) and 19.6 °C (3).

TABLE I

Summary of the data obtained by measuring the relaxation time τ of the ion pairing reaction. For the calculation of pre-exponential factor A the impurity concentrations and equilibrium constant K^{-1} were expressed as lattice site fraction.

T (°C)	τ (hour)	K^{-1} (10^{14} cm^{-3})	A
0.0	32.5	0.65	49
9.8	9.6	1.15	49
19.6	3.0	2.09	46

for which, by least squares fitting, the values given in table I are found. Using equation (2) the equilibrium constant K is then calculated. Since for the evaluation of the right hand side of equation (3) knowledge of K is already required, Pell's value was chosen as a first approximation. For consistency a rapidly convergent series of calculations has to be performed. Results for the pre-exponential factor A, calculated by assuming $\Delta H = 0.39$ eV, are slightly higher than those of Pell[1]-Kröger,[2] but are felt to be essentially in agreement. To avoid confusion it must be emphasized here that only for the calculation of A the impurity concentrations were expressed as fraction of the number of silicon lattice sites $n_{\mathrm{Si}} = 5.00 \times 10^{22}\ \mathrm{cm}^{-3}$. For the temperature dependence of τ/T the data lead to an activation energy of 0.86 eV. Comparing this value to 0.85 eV, which is the sum of the activation energies 0.655 eV for D_{Li}^{-1} and 0.195 eV for $K^{1/2}$, one concludes that agreement in this respect is excellent.

3. EQUILIBRIUM IMPURITY CONCENTRATIONS, GROUND STATE DEGENERACY

For the study of the ion pairing reaction in equilibrium conditions a lower resistivity p-type and a similar n-type sample were prepared. Again the basic material was float-zone single-crystal silicon,[5] p-type from boron doping to the level of about 1.5×10^{15} atoms/cm^3. The samples, slices with a typical thickness of 0.3 mm, are uniformly doped with lithium by immersion in a bath of liquid tin, containing 1.5 at.% lithium, for several hours at elevated temperature. In this way the n-type sample is counterdoped by indiffusion of $n_{\mathrm{Li,tot}} = 6.2 \times 10^{15}$ lithium atoms per cm^3, while in the sample remaining p-type only 1.0×10^{15} lithium atoms per cm^3 are introduced.

To establish equilibrium of the ion pairing reaction the sample is kept at a predetermined temperature for more than seven time constants of the reaction. Then the sample is cooled rapidly in liquid nitrogen to freeze in equilibrium concentrations of the unpaired and the associated impurities. The variation of carrier concentration in the temperature range $25\ \mathrm{K} < T < 300\ \mathrm{K}$ was measured by the Hall-effect, using a magnetic field of 1.21 MA/m (15.2 kOe). For these measurements the method described by Van der Pauw was adopted.[10] To reduce the effects of finite contact size the samples were given a shape resembling a four-leafed clover. Carrier concentrations n or p are calculated from the Hall coefficient R_{H} by the relations $R_{\mathrm{H}} = -r_{\mathrm{e}}/ne$, or $R_{\mathrm{H}} = r_{\mathrm{h}}/pe$. Not doing justice to a tremendous amount of theoretical work[17] the Hall factors r_{e} and r_{h} were determined empirically by the following considerations. At $T = 300\mathrm{K}$ r_{e} was set equal to 1.25, and $r_{\mathrm{h}} = 0.85$, to bring the results of resistivity and Hall-effect measurements into mutual agreement.[18] To make carrier concentrations constant above $T = 250$ K, r_{e} and r_{h} are given a temperature dependence proportional to $T^{0.2}$ and $T^{-0.2}$ resp.[19] At low temperatures, where high field conditions will be realized ($\mu H > 1$), the Hall-factors are made to approach 1 according to theory. Series of measurements were performed after equilibrium was established at several temperatures between 0 and 100 °C. For example for the p-type sample the temperatures chosen were 48.9, 72.8, 96.4, 24.4, 0.0, and 48.9 °C, in this order. The final run, done to check the reversibility of the reaction and the reproducibility of the experiment, very satisfactorily confirmed the results of the first run.

For the analysis of the Hall-effect data the usual models to deal with carrier statistics are applied. For the n-type case the distribution of electrons between conduction band states, the majority lithium donor levels, and the compensating boron acceptor levels is considered. On this model the following relation can be shown to hold:

$$n(n + n_{\mathrm{B}})/(n_{\mathrm{Li}} - n_{\mathrm{B}} - n)T^{3/2} = (n_{\mathrm{c}}/g_{\mathrm{Li}}T^{3/2})\exp(-E_{\mathrm{Li}}/kT) \quad (4)$$

A similar expression for the p-type case may of course be written down.[20] It is assumed in the present analysis that the reaction constant K is known and defined by $A = 50$, $\Delta H = 0.39$ eV. Then the equilibrium concentrations n_{Li} and n_{B} are known and therefore also the left hand side of equation (4) at all temperatures. A logarithmic

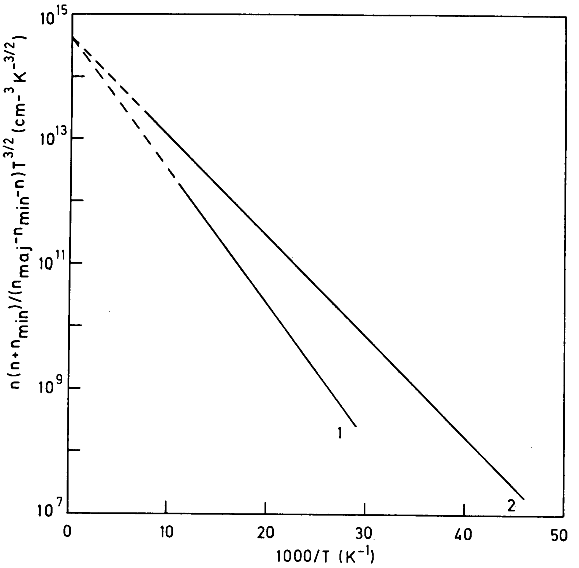

FIG. 2. Illustration of the analysis of the Hall-effect data using equation (4). Lines are drawn over the temperature region where measurements were made, and represent each a collection of about 150 points, which deviate from the line by an average of only 9%. Dashed portions of the lines are extrapolations. Curve 1: p-type sample; curve 2: n-type sample. n = electron or hole concentration; n_{maj} = majority dopant concentration; n_{min} = minority dopant concentration.

plot of this quantity versus $1/T$ yields a straight line as is shown in Figure 2 for both the n- and p-type case. Substitution of $m_e^* = 0.33\ m_e$ and $m_h^* = 0.55\ m_e$ for the effective masses of electrons and holes resp. the effective density of states in the conduction and valence bands[21] are found to be $n_c = 12\ (2\pi m_e^*\ kT/h^2)^{3/2} = 5.4 \times 10^{15}\ T^{3/2}\ \text{cm}^{-3}$, and $n_v = 2\ (2\pi m_h^* kT/h^2)^{3/2} = 1.95 \times 10^{15}\ T^{3/2}\ \text{cm}^{-3}$. Then the right hand side expression of equation (4) has only to be solved for the two unknown parameters impurity ionization energy E_{Li} and ground state degeneracy g_{Li}. These quantities, illustrated in Figure 2 by the slope of the straight lines and their intersection with the $(1000/T = 0)$-axis, are determined by least squares fitting of the theoretical expression to the experimental data. The results are $E_{\text{Li}} = 31 \times 10^{-3}$ eV, $E_B = 43 \times 10^{-3}$ eV, $g_{\text{Li}} = 12.2$ and $g_B = 4.4$. The impurity ionization energies are close to the usual values.[21] In addition, the ionization energy for lithium agrees quite well with the value $E = 29 \times 10^{-3}$ eV calculated on the basis of the effective mass theory, thereby indicating that the lithium donor is an example for which this theory is particularly valid.[22,23] Lending support to this conclusion the statistical weight of the donor lithium $g_{\text{Li}} = 12.2$ agrees very well with the value $g = 12$ of the Kohn-Luttinger model, neglecting any splitting between the ground state levels.[24] If the splitting Δ between the $(E + T_1)$- and A_1-states of the lithium ground state has to be taken into account, then the so-called inverted level scheme,[25] with the corresponding statistical weight $g = 10 + 2\exp(-\Delta/kT)$, is favored by our experimental result for g_{Li}. For the acceptor boron the theoretical $g = 4$ is understood as a twofold degeneracy arising from spin multiplied by the twofold orbital degeneracy of the valence band at its top at $\mathbf{k} = 0$. The experimental value $g_B = 4.4$ is close to 4. From this consistency we conclude that a correct choice for the equilibrium constant K was made.

4. THE PRE-EXPONENTIAL FACTOR A

To derive an expression for the reaction constant K we start from the thermodynamic condition that for a process occurring at a given temperature and pressure the free enthalpy (or Gibbs function) G is a minimum in equilibrium. From this condition it follows that for small departures from equilibrium the change in free enthalpy $\Delta G = \Delta(H - TS)$ is zero. First we consider the configurational entropy changes ΔS_{conf} associated with the reaction. Separating this term one may write: $T\Delta S_{\text{conf}} = \Delta G$, where now ΔG represents the change of free enthalpy upon association of one impurity pair arising from any other origin. e.g. Coulomb interaction or lattice vibrations. From the statistical interpretation of entropy it is known that ΔS_{conf} equals Δ (k ln P) when P is the number of distinguishable ways the system can be realized in a particular state. For the present case it is easily shown that

$$\Delta(k \ln P) = k \ln\left(\frac{n_{\text{LiB}}}{Zn_{\text{Si}}} \Big/ \frac{n_{\text{Li}}}{n_i} \cdot \frac{n_B}{n_{\text{Si}}}\right)$$

Combining these equations we obtain:

$$K = n_{\text{LiB}}/n_{\text{Li}}n_B = (Z/n_i)\exp(\Delta G/kT)$$

The symbols n_{Si} and n_i represent the density of lattice and interstitial sites resp., while Z is the number of sites at which a lithium ion is bound to a substitutional boron ion. So, the pre-exponential factor Z/n_i is simply the ratio of the number Z of sites available for a bound lithium ion to the number n_i of sites available for an unpaired one.

By adopting the usage of expressing impurity concentrations as fraction of the number of sites they may occupy the factor n_i is eliminated from the pre-exponential factor. The formula for K then reads $K = Z \exp(\Delta G/kT)$, and the pre-exponential factor A equals Z.

Two types of interstitial sites present in the silicon lattice must be considered. The first of these, the T-sites, are found on positions given by the coordinates $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the equivalent ones. The sites are named T-sites after the tetrahedral symmetry of the surrounding lattice. Their concentration equals that of the silicon lattice positions, $n_{i,T} = n_{Si} = 5.00 \times 10^{22}\ \mathrm{cm}^{-3}$. The second type of sites, the H-sites, are found in the centers of the nearly hexagonal rings occurring in the silicon lattice. The coordinates for H-sites are $(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$, and all others equivalent by symmetry. The concentration is twice as high as that for T-sites, i.e. $n_{i,H} = 1.00 \times 10^{23}\ \mathrm{cm}^{-3}$. Whether the lithium ions occupy the T-sites or the H-sites has been the subject of much discussion. Calculations made by Weiser[26] indicate the H-sites as the more stable interstitial position for the lithium ion. The response of the optical excitation spectra to uniaxial stress is explained in all details assuming the T-site symmetry, as shown by Aggarwal *et al.*[25] Nara and Morita[27] however pointed out that the inverted level scheme of the lithium ground state is consistent only with the H-site symmetry $\bar{3}$ m. From their EPR studies Watkins and Ham[28] conclude that the lithium ion definitely occupies a position close to the T-site. As Table II shows the number of binding sites in the shell nearest to a substitutional boron leads to pre-exponential factors $A = Z_{1,T} = 4$ and $A = Z_{1,H} = 12$ for the T- and H-type sites resp. The experimental finding $A = 50$ is closest to the latter value. It must be remembered however that the data were analysed by expressing concentrations as fractions of silicon lattice sites $n_{Si} = n_{i,T}$, assuming tacitly that the T-sites are occupied. If the H-sites are to be preferred then, because of their higher density, the lithium concentrations are halved, raising the experimental result for the pre-exponential factor to $A = 100$. So the apparent difference is reduced by a factor two, making it too small to draw any reliable conclusions on the occupation of the T- or H-sites from the results of the present experiment. We will continue assuming the T-sites to be occupied.

TABLE II

Summary of the various interstitial sites with reference to a substitutional lattice point. Number Z_j, distances r_j and binding enthalpy ΔH_j for T- and H-sites in the near shells j.

	j	Z_j	r_j (10^{-8} cm)	ΔH_j (eV)
T-sites	1	4	2.35	0.520
	2	6	2.72	0.450
	3	12	4.50	0.272
	4	8	4.70	0.260
H-sites	1	12	2.25	0.542
	2	16	3.53	0.347
	3	12	4.45	0.274
	4	36	5.21	0.234

A major contribution to the change of free enthalpy ΔG arises from the electrostatic attractive forces between the ions. Neglecting differences between binding energy ΔU and binding enthalpy $\Delta H = \Delta(U + pV)$ the latter quantities are calculated using $\Delta H_j = e^2/4\pi\varepsilon r_j$. Results for the sites in the various shells are given in the last column of Table II. The temperature dependence of r_j and ΔH_j via thermal expansion is small and can safely be neglected. Other contributions to the binding enthalpy, from repulsive forces, polarization effects, etc., are probably also temperature independent. This assumption is supported by the fact that the diffusion activation energy of lithium in silicon, interpreted as the energy difference between T- and H-sites, is constant over a very wide temperature region.[26,16,29] No terms representing entropy of formation have therefore to be included.[30]

Since also appreciable binding exists for lithium positions in shells other than the closest one, these have to be considered as well. A generalized expression for K applicable to this case reads

$$K = \sum_j K_j = \sum_j Z_j \exp(\Delta H_j/kT)$$

Over the narrow temperature region where we performed all our measurements, between 0 and 100 °C, we may approximate by a single term: $K = Z_{\mathrm{eff}} \exp(\Delta H_{\mathrm{eff}}/kT)$. Inserting the values from table II one obtains as a best fit $A = Z_{\mathrm{eff}} = 6$ for the T-sites.

The next contribution to ΔG which must be considered results from the change in the crystal vibration spectrum due to the reaction. The free enthalpy associated with a simple harmonic oscillator of frequency ν is given by:[30]

$$G = \tfrac{1}{2}h\nu + kT \ln\{1 - \exp(-h\nu/kT)\}$$

All the impurities we are concerned with, either the unpaired or the associated ones, have masses which are lower than that of the host silicon atoms. They therefore give rise to local modes of vibration outside the frequency spectrum of the perfect lattice. The frequencies of these modes are known for the greater part.[31] For example a substitutional ^{11}B-atom has one triply degenerate mode[32] at wavenumber $\sigma = 620\ \mathrm{cm}^{-1}$. The vibrations of the interstitial lithium ions have been considered by Bellomonte and Pryce.[33,34] The most abundant type of associate $^{7}\mathrm{Li}^{11}\mathrm{B}$ has three optically active modes at the different frequencies given by $\sigma =$ 522,564 and $655\ \mathrm{cm}^{-1}$. This change in localized mode frequencies upon pairing represents the most radical change of the vibration spectrum. For all these frequencies the corresponding temperature $hc\sigma/k$ is far above all temperatures at which ion pairing was investigated. Therefore the usual high temperature approximation[2,30,35] is not applicable to the present case; instead the opposite condition $kT \ll h\nu$ is comparatively well satisfied. It leads to

$$G \simeq \tfrac{1}{2}h\nu - kT\exp(-h\nu/kT)$$

or even

$$G \simeq \tfrac{1}{2}h\nu$$

The change in free enthalpy $\Delta G \simeq \Delta(\tfrac{1}{2}h\nu)$ is not dependent on temperature and may be viewed as a contribution to the binding enthalpy ΔH. There is no significant effect on the pre-exponential factor. For the extreme frequencies mentioned above, $\sigma = 620\ \mathrm{cm}^{-1}$ for ^{11}B and $\sigma = 522\ \mathrm{cm}^{-1}$ for $^{7}\mathrm{Li}^{11}\mathrm{B}$, the resulting change in binding enthalpy $\Delta H = \Delta(\tfrac{1}{2}h\nu) = 6 \times 10^{-3}$ eV represents only a minor correction to the main term.

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