Diffusion of Li in Si at High T and the Isotope Effect*

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The diffusion rate of Li in Si at high temperatures has been re-investigated using an outdiffusion technique. The resulting D for Li^7 is $(2.21\pm0.07)\times10^{-6}$ cm²/sec at $(800\pm5)°C$ and 2.4×10^{-5} cm²/sec at $(1350\pm5)°C$. If these results are combined with ion drift results, the diffusion constant can be described by $D=(2.5\pm0.2)\times10^{-3}\exp[-(0.655\pm0.01)e/kT]$. The isotopic effect upon the diffusion has been investigated using Li^6 and Li^7. At 800°C, the value for D_{Li^6}/D_{Li^7} is $1.07_5\pm0.02$, in accordance with the expected inverse dependence on the square root of the mass. The ionic charge of the Li and the atomic mechanism for Li diffusion is discussed in the light of these and other results.

I. INTRODUCTION

THE activation energy for Li diffusion is an important parameter in experimental determinations by the junction-ion drift method[1] of the binding energies between Li and acceptors,[2] between Li and oxygen,[3] and indeed between Li and any impurity with which it interacts. Since the activation energies corresponding to these binding energies can be small relative to the activation energy for Li diffusion, a small error in the latter can result in relatively large errors in the binding energies. In addition, the value of D_0, the extrapolated value of the diffusion constant at $1/T=0$, can be significant in distinguishing between possible models for the interstitial diffusion of Li in Si, if a better method for determining the vibrational frequency of the Li⁺ ion can be found. A unique model appears ultimately achievable, for this system is sufficiently simple that it should be possible to understand the nature of the atomic forces which inhibit the diffusion—specifically, whether they are predominantly elastic forces between lattice atoms,[4] polarization forces between the Li⁺ ion and the lattice,[5] or perhaps predominantly Coulomb interactions between the Li⁺ ion and the stationary charge distribution of the lattice.

These considerations have led to a need for a more accurate knowledge of the high-temperature diffusion rate of Li in Si than was previously available,[6,7] as well as a need for careful estimates of possible errors. Of particular significance was the possibility of a systematic error in some of the earlier data which could seriously impair the Li-impurity binding energy determinations.[8]

The outdiffusion method adopted for the high temperature measurements proved to be sufficiently accurate to investigate the effect of the isotopic mass upon the diffusion. The classical model for diffusion in solids[4,5] leads one to expect an inverse dependence of D on the square root of the mass, though correlation effects could change this if vacancies were involved in the diffusion process.[9] This dependence has been experimentally confirmed, even for interstitial diffusants, in suprisingly few cases,[9] while exceptions have been reported in others.[9,10] The relatively large mass ratio between the two stable isotopes of Li makes this diffusant particularly amenable to such an experiment.

II. EXPERIMENT

Choice of Technique

The generally-used techniques based on in-diffusion[5] do not lend themselves to accurate determinations of the Li diffusion constant because of three difficulties: (1) For temperature below roughly 900°C, the Li solubility[11] exceeds the intrinsic carrier concentration,[12] resulting in the presence of an extrinsic region near the surface during the diffusion process. In this extrinsic region, there will be a built-in field which will roughly double the diffusion rate.[13] This violates the boundary condi-

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[1] E. M. Pell, J. Appl. Phys. **31**, 291 (1960).

[2] H. Reiss, C. S. Fuller, and F. J. Morin, Bell System Tech. J. **35**, 535 (1956).

[3] E. M. Pell, *Symposium on Solid-State Physics and Telecommunications, Brussels, 1958* (Academic Press, Inc., New York, 1960), Vol. 1.

[4] C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).

[5] H. Reiss and C. S. Fuller, *Semiconductors* (Reinhold Publishing Company, New York, 1959), Chap. 6.

[6] C. S. Fuller and J. A. Ditzenberger, Phys. Rev. **91**, 193 (1953).

[7] C. S. Fuller and J. C. Severiens, Phys. Rev. **96**, 21 (1954).

[8] The possibility in question could arise from a nonuniformity of the electric field in the samples of reference 7, caused by the

Li-doped region remaining extrinsic at the diffusion temperature. Measurements made subsequent to these early drift measurements indicate that the Li solubility at the 800°C solution temperature used is about 2×10^{19} atoms/cm³ [see E. M. Pell, J. Phys. Chem. Solids **3**, 77 (1957)]; the intrinsic carrier concentration does not reach this value until the temperature is about 900°C [F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954)] which is higher than any of the temperatures used in these early measurements. The excellent agreement between the present results and the earlier measurements indicates, however, that such an error was not present. This can be explained by a probable lack of saturation of the drift samples with Li; ordinary quench techniques often result in a Li concentration at 800° which is a factor of ten or more below the solubility limit (see Pell, *ibid.*). There unfortunately seemed to be no way to eliminate the possibility of such an error in the earlier data, nor to estimate its possible magnitude, without an independent determination.

[9] A. H. Schoen, Phys. Rev. Letters **1**, 138 (1958), and references therein. Also, J. R. Manning, Phys. Rev. **116**, 819 (1960).

[10] D. Lazarus and B. Okkerse, Phys. Rev. **105**, 1677 (1957).

[11] E. M. Pell, reference 8.

[12] F. J. Morin and J. P. Maita, reference 8.

[13] F. X. Hassion, see F. M. Smits, Proc. Inst. Radio Engrs. **46**, 1049 (1958); A. D. Kurtz and C. L. Gravel, J. Appl. Phys. **29**,

tions leading to the usual error function solution[4] and greatly complicates the analysis. (2) For a diffusion temperature in excess of 600°C, it is difficult to prevent precipitation[11] in the region adjacent to the surface when the sample is quenched to room temperature; this makes it difficult to confirm the boundary conditions, especially with regard to the nature of the source.[4] (3) It is difficult to produce planar and hence easily analyzable diffusion geometries because of the strong tendency for Li to diffuse to the surface of the sample, where it can form a tight bond to the oxide.[2] Drift techniques,[7] on the other hand, have another problem, in that the high Li solubility at useful alloying temperatures makes it difficult to ensure that the Li-rich region is intrinsic, and hence has the same field as the rest of the sample at the temperature at which the drift rate is measured.

A procedure which avoids the above problems and which permits a relatively straightforward check of the boundary conditions is to use outdiffusion, coupled with conductivity or Hall measurements to monitor the Li content. In this technique, the first and second of the above three difficulties can be avoided by use of a low solution temperature and a low in-diffusion temperature. Alternatively, they can be avoided by use of a preliminary outdiffusion period; this period is made sufficiently long to bring the maximum Li concentration below the intrinsic carrier concentration at the desired diffusion temperature and also to a sufficiently low value to avoid precipitation problems, which are concentration dependent.[3] The third difficulty is avoided by making use of the tight bond between the Li and the surface oxide in establishing and maintaining the surface boundary condition at effectively zero concentration. It will be shown that with this technique it is a relatively simple matter to check the boundary conditions.

Model for Outdiffusion

The solution of the diffusion equation for outdiffusion from a rectangular bar with the surface concentration maintained at zero, for times sufficiently long that the first mode dominates, is given by[14]

$$N \cong N_0(64/\pi^3) \exp\left[-\pi^2 Dt\left(\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right)\right]$$

$$\times \sin\frac{\pi x}{a} \sin\frac{\pi y}{b} \sin\frac{\pi z}{c}, \quad (1)$$

where N is the concentration in atoms/cm^3, N_0 is the initial concentration at the center of the sample, D is the diffusion constant, t is the outdiffusion time, and $a, b,$ and c are the sample dimensions. The decay is seen

1456 (1958). The same calculation has also been made by J. Bardeen, W. H. Brattain, and W. Shockley [J. Chem. Phys. **14**, 714 (1946)] and by Reiss, Fuller, and Morin (reference 2).

[14] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Clarendon Press, Oxford, 1959), 2nd ed., p. 184.
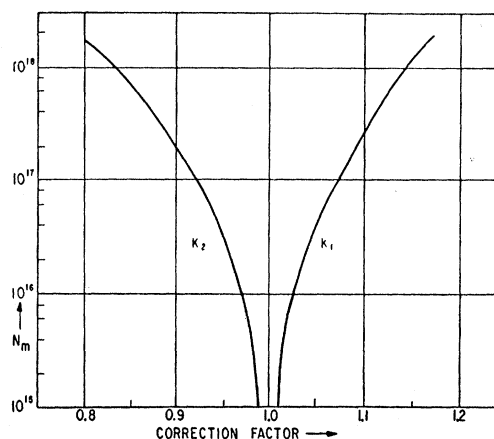

FIG. 1. Correction factor, K, resulting from variation of μ with N.

to be exponential, and therefore the time constant, τ, will give the diffusion constant in accordance with

$$1/D=\pi^2\tau(1/a^2+1/b^2+1/c^2). \quad (2)$$

Since N varies with position in the sample, it is convenient to determine N_m, the maximum concentration at the center of the sample, and plot the logarithm of this as $f(t)$. Since the spatial distribution does not vary after the first mode has become predominant,[14] N_m can be determined either by measuring the total sample conductance or by measuring the effective Hall constant. In the former case, as is shown in the Appendix,

$$N_m = \pi^2 I/4EqabK_1\mu_m, \quad (3)$$

and in the latter case

$$N_m = \pi^2 HI/4V_H \times 10^8 bK_2(\mu_D/\mu_H), \quad (4)$$

where K_1 and K_2 are correction factors (roughly equal to unity) resulting from the dependence of μ on N and are given in Fig. 1, calculated by a graphical integration as outlined in the Appendix. In Eqs. (3) and (4), I is the total sample current in amperes, E is the electric field at the middle of the sample in volts/cm (this is measured by a two-point probe and a vibrating-reed electrometer), q is the electronic charge in coulombs, a is the sample width and b is its thickness in cm, μ_m is the drift mobility corresponding to a carrier concentration N_m, H is the magnetic field in gauss, V_H is the Hall voltage in volts, and μ_D/μ_H is the ratio of drift mobility to Hall mobility.

Experimental Procedure

In the outdiffusion experiments, Merck single-crystal floating-zone p-type Si of about 1000 ohm cm resistivity was used. This was cut into bars, typically 0.3 cm$\times$0.3 cm$\times$1.5 cm, which were ground and etched. Li, in the form of a Li-in-oil suspension, was pre-alloyed in He to all four sides of each bar at 650°C by the procedure outlined in reference 3. Each sample was in-diffused for

20 hr at 500°C in argon and quenched by dropping into ethylene glycol.[15] It was then outdiffused in a preliminary experiment, typically for one hour at 800°C in an argon atmosphere without drier, followed by a quench in ethylene glycol. This preliminary outdiffusion schedule of 1 hr at 800°C was also used in the 1350°C outdiffusion experiment for it was felt that a preliminary outdiffusion at 1350°C might introduce precipitation nuclei when quenching to room temperature with the relatively high Li concentration typical of this stage. Soaking for 5 min in HF acid after this preliminary outdiffusion removed oxide layers sufficiently well to permit measurement of E in Eq. (3) with the high-impedance vibrating reed electrometer. Also, the n-p junction resulting from the outdiffusion was sufficiently close to the surface that it did not affect this measurement (there was negligible change in the measured value if the p region were removed with light grinding), though it did affect Hall measurements. After measuring I/E, the main part of the outdiffusion was performed, typically for three hours at 800°C in argon without drier; followed by a quench in ethylene glycol. The p region was removed by light grinding and the Hall constant measured. After a second grind, it was measured again and these two results extrapolated back to the original sample width to obtain the Hall constant used in the calculations (a separate experiment with many successive grinds established that the measured change in Hall constant was linear with the thickness removed by grinding for these small amounts of removal.)

Use of conductivity measurements for the determination of N_m was the method of choice at high N for three reasons: (1) Our Hall apparatus did not give accurate values at high N because of the small Hall voltage; (2) it was determined empirically that accurate conductivity measurements did not require sample grinding at this stage, which would have altered the boundary conditions slightly; accurate Hall measurements, on the other hand, did require such grinding; and (3) there was no reason to feel that the mobility would be anything other than that expected from ionized impurity scattering at high N. Determination of N through Hall measurements was the method of choice at low N, for we were concerned that the mobility might be affected by the possible presence of unknown scattering mechanisms, such as might be caused, for example, by the presence of precipitated particles. These precautions were probably unnecessary, for whenever resistivity and mobility were compared, the results were within experimental error of those found by Morin and Maita.[12]

For determination of N_m it is also necessary to know the drift or conductivity mobility (or the ratio of drift-to-Hall mobility if Hall measurements are used). In these experiments, recent results of Wolfstirn[16] were used at high N, and at low N a value of 1.18 for μ_H/μ_C was used.[12] At high N, an additional correction was determined from Fig. 1 to include the effect of mobility variation with N.

For the Li[6] measurements, a dispersion in mineral oil (with a trace of oleic acid) was prepared by stirring the AEC isotope with a high-speed stainless steel and Pyrex blender at 235°C in argon. The resulting dispersion was satisfactory for the present prupose, although it was inferior to the commercial Li[7] product (the particle size was larger and the dispersion more dilute; also, it was not as easily preserved). In the measurement of D_{Li^6}/D_{Li^7}, two samples, one alloyed with Li[6] and the other with Li[7], were outdiffused simultaneously while positioned adjacently in the furnace.

Check of Boundary Conditions

For the procedure which has been outlined to be valid, it is necessary that the Li distribution vary as $\sin(\pi x/d)$ across any cross section, d, during the duration of the outdiffusion. If it can be shown that the distribution is sinusoidal at the end of the outdiffusion, and additionally that the decay is exponential with a single time constant during the measured period of outdiffusion,
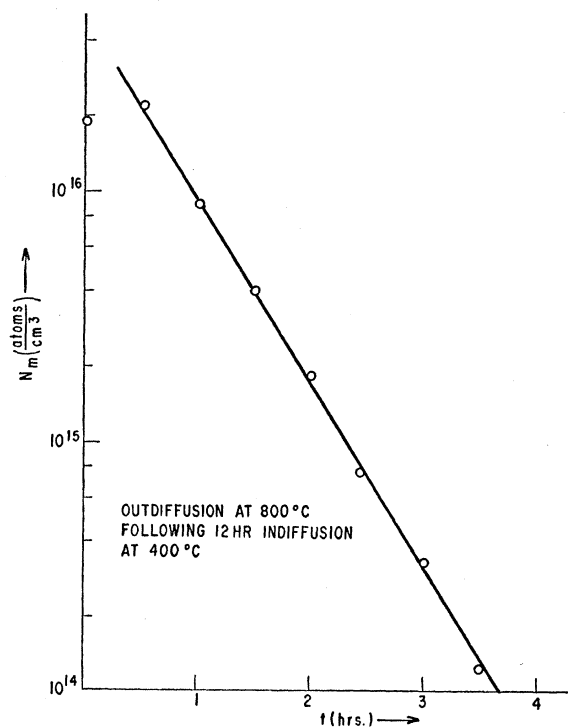

FIG. 2. Exponential decay of N_m.

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[15] This indiffusion period is insufficient to produce a uniform concentration through these samples. It is estimated that the concentration at the center is about 80% of that at the surface. The preliminary one hour outdiffusion is sufficient to allow the higher modes resulting from this initial nonuniformity to decay,[14] as indicated from the checks of the boundary conditions to be discussed presently and also from independent experiments which gave the same result for D for wide variations in indiffusion procedure, ranging from $\frac{1}{2}$ hr at 800°C to 16 hr at 400°C and from 5 hr to 24 hr at 500°C.

[16] K. Wolfstirn, J. Phys. Chem. Solids (to be published).

these boundary conditions will have been demonstrated. The possibility of any departure from the sinusoidal distribution is here excluded because it would lead to contributions by higher modes and hence a change in the time constant.

The exponential decay was confirmed by measuring the sample conductance many times during a single outdiffusion. The resulting N_m vs t is exhibited in Fig. 2, and it is seen that after the first half-hour the data can indeed be represented by a single time constant. Because of the initial presence of higher modes, it is not surprising that the initial point does not lie on a linear extrapolation of the other data, but it would be expected to be above such a line rather than below it. The reason for the observed behavior has not been analyzed in detail; it may result from the dependence of mobility on carrier concentration, which would cause the initial somewhat-irregular carrier distribution resulting from nonuniform alloying (see next section) to give a higher sample resistance than would be given by the same carriers distributed more regularly. The relaxation toward a smoother distribution during the first half hour could then have a greater effect on the resistance than Li loss. Regardless what the true reason is, the fact that the first point is low means that the position of the second point on the line may be fortuitous; nevertheless, it is reproducibly so, so that it would seem to be conservatively safe to use a point measured a half hour later, at a total time of one hour, as descriptive of the decay of the fundamental mode. This empirical argument based on the data is confirmed by the theoretical model[14] which for the data of Fig. 2 gives a time constant of only about four minutes for the next higher mode.

Although the experiment just described is useful for confirming the boundary conditions, the procedure used does not lead to maximum accuracy in measuring the diffusion constant beacuse of small changes in the sample dimensions resulting from the necessity of grinding off the p region at each of the later steps to permit conductivity measurements; for this reason, only two points were measured for each sample in determining D.

The sinusoidal distribution is implicit from the model and the observations that the decay is a simple exponential and that an n-p junction is formed near the surface. The first observation indicates that only one mode is present and the second that this mode has a value of essentially zero at the surface.

The sinusoidal distribution has also been confirmed explicitly along the long axis of the sample by cutting the sample in half and measuring the total resistance of one half as a function of the length of Si removed from the original sample-end by grinding. For a sinusoidal distribution of Li such that $N = N_m \cos\pi x/L$, where the origin is taken at the center of the sample and L is the original sample length, it can be easily shown that the resistance of the half-sample should vary as $\log\tan(\pi/4 + \pi d/2L)$, where d is the length of the half-sample after each grinding. That the resistance does vary in this

manner is illustrated by Fig. 3, thus confirming the sinusoidal Li distribution along this axis, and by inference along the others.

Although the preceding confirms the boundary conditions for the samples used in this investigation, a similar procedure when used with twisted samples (1° and 5°) indicated that in such samples these boundary conditions were not obeyed. These samples outdiffused initially at roughly the same rate as the others (indicating that diffusion through dislocation-pipes was not significant), but the rate of carrier loss increased with time and even occurred with the sample merely standing at room temperature. This resulted, we believe, from a secondary loss of Li by precipitation internally. It indicates that the present test of boundary conditions is capable of detecting such anomalous conditions.

Sample Uniformity

Since a given amount of Li if distributed nonuniformly will lead to a higher sample resistivity than if uniformly distributed,[17] this nonuniformity arising, for example, from faulty alloying, and since such nonuniformity is more likely near the beginning of the outdiffusion, it is possible from this cause to obtain a low value for D. The present samples were not completely uniform; resistivity measurements on different sides of even the good samples varied by as much as 3% (which leads to a much smaller error in D because the outdiffusion was carried out over 3 decades in N_m). Such results were particularly apparent in the measurement of D_{Li^6}/D_{Li^7} because of the lack of a good Li^6 dispersion. For example, if the Li^6 were added in the form of small pellets of Li alloyed to the Si, abnormally low values of D_{Li^6}/D_{Li^7} were obtained (as low as 1.00), presumably because of a decrease in the measured D of Li^6 resulting from the
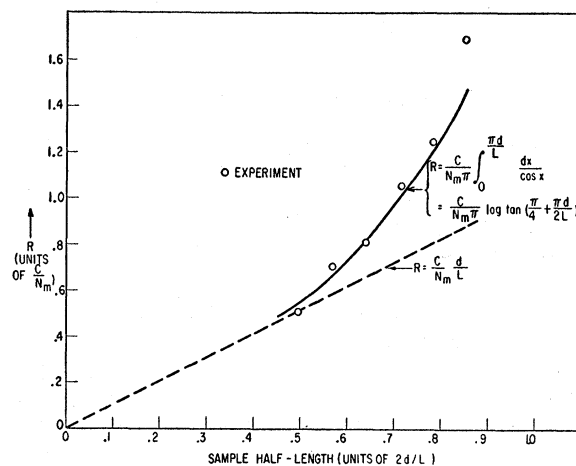

FIG. 3. Resistance vs half-sample length to establish shape of Li concentration profile.

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[17] This is true even if the nonuniformity occurs entirely across the direction of current flow because of the effect of the variation of mobility with concentration.
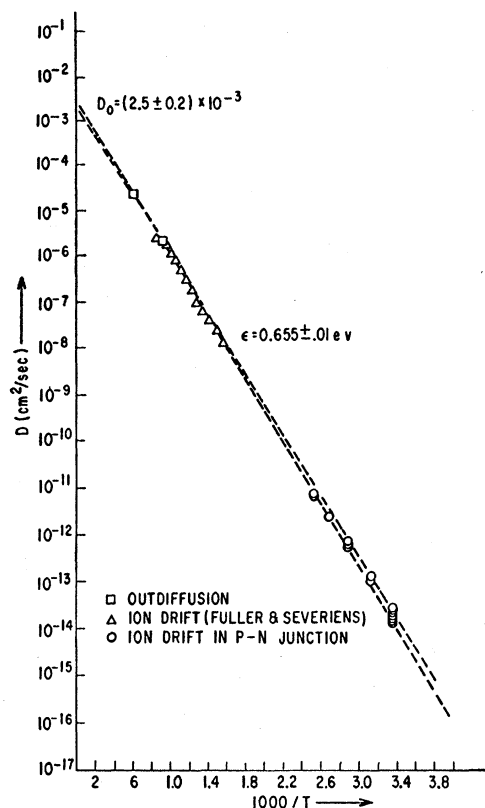
FIG. 4. Diffusion constant for Li and Si.

For each sample, the experimental slope of $\ln N_m$ vs t gave D in accordance with Eq. (2). A correction arising from boron compensation proved to be negligible. A slight correction (0.3%) for Hall-probe displacement from the midpoint of the sample was also included.

The resulting value for D of Li^7 at $(800\pm5)°C$, based on seven trials, is $(2.21\pm0.07)\times10^{-6}$ cm^2/sec, where the error is the calculated mean probable (random) error. Possible additional systematic errors have already been discussed; they are felt to be small. (An earlier experiment, based on five trials, under conditions felt to yield somewhat larger systematic errors, gave $(2.17\pm0.05)\times10^{-6}$ cm^2/sec.)

The value for D of Li^7 at $(1350\pm5)°C$, based on two trials and hence without an error index, is 2.4×10^{-5} cm^2/sec. The value of the diffusion constant at $1/T=0$, based on the present results and room temperature ion drift results[18] is $(2.5\pm0.2)\times10^{-3}$ cm^2/sec and the activation energy from these same results is 0.655 ± 0.01 ev.

These results are summarized graphically in Fig. 4, which also includes the data of reference 18. Any subsequent changes in the accepted values for drift mobility at high N, or for μ_H/μ_D at low N, will alter these values. For these particular experiments, a 10% decrease in μ_D for n-type Si in the region of $N=10^{18}$ atoms/cm³, or a 10% decrease in μ_H/μ_D in the region of $N=10^{15}$ atoms/cm³, will increase these values of D by 1.4%; the correction is proportional to the logarithm of the change in μ.

The value for D_{Li^6}/D_{Li^7} (at 800°C), based on seven trials, is $1.07_5\pm0.02$. Any remaining systematic error resulting from a relatively greater initial nonuniformity in the Li^6 samples would tend to make the correct answer larger. The smaller relative error in this value compared to that in the value for D_{Li^7} is explained by the fact that this value represents a ratio of rates in simultaneously diffused samples; it is therefore not sensitive to the errors in temperature and diffusion times which affect D_{Li^7}. It is also not affected by moderate changes in μ_D or μ_H/μ_D. The inverse ratio of the square root of the mass is 1.080.

The magnitude of the diffusion coefficient measured at 800°C is identical to that obtained by Fuller and Severiens.[7] The D measured at 1350°C is consistent with the activation energy measured by Fuller and Severiens, and it falls on an extrapolation of a line between the 800° results and room temperature ion drift results,[18] indicating that the same mechanism of diffusion is operative to near the melting point.

The measured isotope effect is consistent with the expected inverse dependence on the square root of the mass.

IV. IONIC CHARGE OF INTERSTITIAL Li

If one believes that the drift data of Fuller and Severiens[7] were not affected by the possible presence of a

excessive initial nonuniformity. Low values were also obtained after our locally-produced Li^6 dispersion stood too long on the shelf. The reproducibility of the results when using fresh Li^6 constitutes good evidence that uniformity in this case was adequate. If an error remains, it is likely that the correct ratio of D_{Li^6}/D_{Li^7} is somewhat greater than that reported here.

Temperature Determination

The Li was outdiffused in a quartz tube furnace of 1-in. diameter with a heater winding extending about 4 in. along its outer surface. The temperature was measured before each run with an annealed Pt-Pt 10% Rh thermocouple (0.010 in. for 800°C data and 0.020 in. for 1350°C data) welded to a dummy sample consisting of an Aquadag-coated Pt box. This dummy sample was placed in the normal position of the Si sample, within a quartz crucible inside the furnace tube. Motion of the dummy sample by an amount felt to be large compared to errors in positioning the Si sample resulted in a maximum temperature change of 3°C. In an early set of experiments, whose results were within the experimental error of the final values, the thermocouple was also checked against the melting point of gold. We estimate that the temperature measurements were accurate to $\pm5°C$.
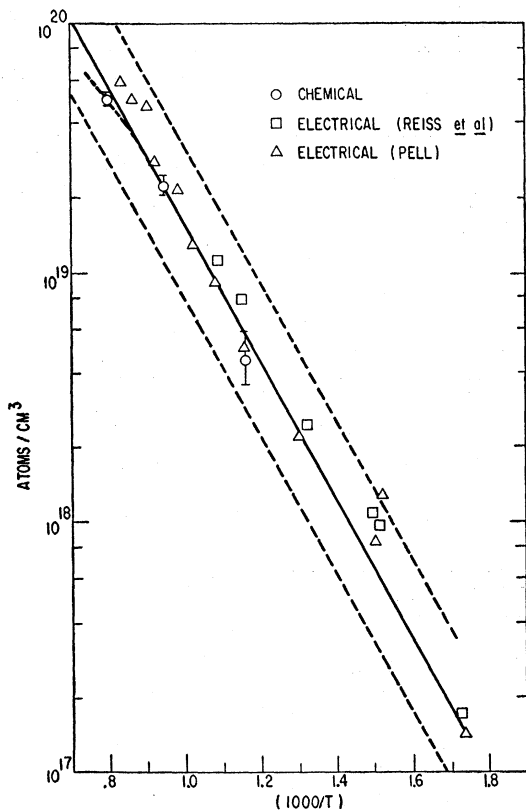
[18] E. M. Pell, Bull. Am. Phys. Soc. 4, 320 (1959).

FIG. 5. Comparison of chemical and electrical solubilities of Li in Si.

nonuniform electric field as mentioned earlier, then the agreement between the present diffusion data and their drift data through the Einstein relation would, upon the assumption that the Li is interstitial,[9] lead directly to the conclusion that the Li is present as a singly charged positive ion.

The same conclusion can be reached from solubility data. In Fig. 5, chemical solubility data using flame analysis[11] (which is not sensitive to the ionic charge) are compared with electrical data[2,19] based on the assumption that the Li is present as Li^{+}. The agreement is well within a factor of two, as indicated by the dotted lines. Note that although the possibility that the Li is present as Li^{++} can probably be discounted because of the high ionization energy for the second electron (and additionally because a deep level has never been reported for Li in Ge or Si), the possibility of its being present as Li$_2$[+] cannot as easily be discounted without evidence such as presented in Fig. 5.

V. ATOMIC MECHANISM OF Li[+] DIFFUSION

The present experiment yields an accurate value for D_0, the diffusion constant at $1/T = 0$, and it is of interest to compare this with the Wert-Zener model for inter-

stitial diffusion.[5] This model assumes that the activation energy for diffusion arises from elastic forces between lattice atoms[20] and that the interstitial diffusant jumps from the center of one hollow region in the lattice to the center of the next hollow region. The parameter of greatest uncertainty in the model is the vibrational frequency of the Li^{+} ion in its potential well, and we accordingly treat this as the unknown. The diffusion results, in conjunction with the above assumptions and the Wert-Zener relation between D_0 and v, yield $v_{\exp} = (4.50$ to $5.35) \times 10^{12}$/sec, using the value -4.4×10^{-5}/°C for $d\mu/\mu dT$,[21] where μ is the shear modulus. This value for v can be compared with a theoretical approximation made by Wert and Zener in which v is related to the activation energy for diffusion and to the jump distance; this approximation yields $v = (9.0$ to $9.1) \times 10^{12}$/sec. If the potential well were somewhat more flat-bottomed than given by their sinusoidal approximation, the theoretical value would be decreased and could reasonably be made equal to the experimental.

It does not seem likely, however, that the diffusion rate of Li in Si is determined by a need to elastically displace lattice atoms. The small size of the Li^{+} ion (1.20 A diameter[22]), coupled with the large diameter of the interstitial site in Si (2.35 A) and the large hexagonal-tunnel diameter (2.07 A), would appear to cause little hindrance through electron shell overlap to the motion of the ion through the lattice. The same inference can be drawn from the observation that copper diffuses more rapidly than lithium through Si (at 900°C, D is 5×10^{-5} cm^2/sec for Cu[23] and 4×10^{-6} cm^2/sec for Li^{+}; a crude radioactive outdiffusion experiment at 500°C permitted an estimate of 0.35 ev or less for the activation energy for Cu diffusion, which is about half that of Li^{+}). Similar results are observed in Ge.[7,24] There is evidence that Cu in Si diffuses as Cu^{+} at high temperatures.[25] Since Cu^{+} is larger than Li^{+} (1.92 A diam for Cu^{+},[22] it is not reasonable that the smaller ion should diffuse more slowly if elastic forces determine the rate. Neither of these arguments constitutes conclusive proof; but we shall nevertheless assume, as a working hypothesis for the remainder of this discussion, that elastic forces are not important.

If the diffusion of the Li^{+} ion is not determined by elastic forces, then it is very likely determined by elec-

[19] H. Reiss, C. S. Fuller, and A. J. Pietruszkiewciz, J. Chem. Phys. 25, 650 (1956).

[20] In this model, repulsive overlap forces between diffusant and lattice atoms requires a displacement of the lattice atoms to permit the diffusant to pass through. This appears to be a good assumption in the cases of close-packed metal lattices; it is open to question in the case of the diamond lattice. The displacement of lattice atoms results in an entropy term in the expression for D which is a function of the elastic shear modulus of the lattice.

[21] H. J. McSkimin, J. Appl. Phys. 24, 988 (1953). Use of these data accounts for the slight difference between the above values and those of J. N. Hobstetter, in Progress in Metal Physics (Pergamon Press, New York, 1957), Vol. 7.

[22] L. Pauling, Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1942).

[23] J. D. Struthers, J. Appl. Phys. 27, 1560 (1956).

[24] A. G. Tweet, J. Appl. Phys. 30, 2002 (1959).

[25] C. J. Gallagher, J. Phys. Chem. Solids 3, 82 (1957).

trical forces arising from the ionic character of Li$^+$. Such forces could arise either through the polarization of the Si by the Li$^+$ (the polarizability of the Li$^+$ can be neglected[26]) or through the interaction of the Li$^+$ with the periodic electrostatic potential which must exist in the lattice quite apart from any possible polarization. Weak inferences may be drawn from several experiments which suggest that the latter possibility is the more probable. It does not seem worthwhile to do more than enumerate these experiments and suggest the arguments: (1) Li$^+$ diffuses more easily in the more polarizable Ge lattice than in Si; the Ge-Si size ratio appears insufficient to account for this on a polarization model; (2) the more polarizable[26] Mn^{++} is found, by spin resonance,[27] to be symmetrically located at an interstitial site in Si, though it is amply small to be displaced in the [111] direction if polarization is significant (Ni$^+$, comparable in size, is displaced, though probably for other reasons[27]); (3) the Li$^+$—B$^-$ distance in both Ge[2] and Si[28] is found to be anomalously large; if polarization forces were predominant, one feels that the atoms would be especially likely to approach each other as closely as possible, the added Coulomb force of the B$^-$ serving to further ensure this.

If polarization were important, one would expect a displacement of the Li$^+$ ion in a [111] direction from the center of the interstitial site toward a nearest-neighbor Si atom. If the electrostatic crystal potential were the predominent influence, one would expect the Li$^+$ ion to seek out a position of symmetry with respect to the Si atoms and their associated valence electrons. The most likely location would seem to be at an interstitial site. Although the positive Li$^+$ ion in this position would be in only quasi-stable equilibrium with respect to the positive Si cores, it would be in stable equilibrium with respect to the negative space charge cloud of valence electrons because of the restoring force produced by the integral of the negative space charge left behind in any small displacement.

Since Li$^+$ has no unpaired electrons, spin resonance is not a possible tool for further elucidating its position. In principle, the value for D_0 and ν, with the Wert-Zener theory, can distinguish between some possibilities because of the dependence of these parameters on jump distance and jump directions, but for this approach to be practical one needs a better value for ν than is provided by the model. (We have looked for an absorption peak in the 40–50 μ region of the infrared, at temperatures down to that of liquid N$_2$, which might be associated with the Li$^+$ vibration. These experiments have not been unsuccessful. An acute problem is the high free-carrier absorption from the donor electrons of Li$^+$.) In the spirit of the calculation at the beginning of this section, the ν_{exp}, based on the Wert-Zener model with our experimental D_0 but without displacement of lattice atoms and hence without the entropy term, becomes (6.25 to 7.55)$\times 10^{12}$/sec for the Li$^+$ ion located at an interstitial site. This is somewhat closer to the previously discussed theoretical ν of (9.0 to 9.1)$\times 10^{12}$/sec, but this cannot be considered significant in view of the uncertainties in the theoretical approximations for ν.

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APPENDIX. CALCULATION OF N_m FROM CONDUCTIVITY OR HALL CONSTANT

I. N_m from conductivity: For a rectangular bar of width a and thickness b,

$$I/E = q \int_0^b \int_0^a \mu N \, dx \, dy, \qquad (1A)$$

where I is the total current, E is the electric field, q is the electronic charge, μ is the mobility, and N is the carrier concentration. If N varies with position in accordance with Eq. (1) of the text, this becomes

$$I/E = q N_m \int_0^b \int_0^a \mu \sin(\pi x/a) \sin(\pi y/b) dx \, dy$$

$$= (2q N_m b/\pi) \int_0^a \mu \sin(\pi x/a) dx. \qquad (2A)$$

With the substitution $u = \pi x/a$, there results

$$I/E = (4q N_m \mu_m ab/\pi^2)\left(1 + \int_0^{\pi/2} \frac{\Delta\mu}{\mu_m} \sin u \, du \right), \qquad (3A)$$

where μ_m is the drift mobility corresponding to carrier concentration N_m and $\Delta\mu$ is the increase in μ at positions of lower N. The remaining integral can be evaluated graphically as a function of μ_m (or of N_m) for a particular semiconductor, and this has been done in Fig. 1 for n-type silicon, using the mobilities given in reference 16. Thus, the second term of Eq. (3A), defined by K_1, becomes

$$K_1 = 1 + \int_0^{\pi/2} \frac{\Delta\mu}{\mu_m} \sin u \, du. \qquad (4A)$$

II. N_m from Hall Constant: For the same bar,

$$V_H \times 10^8 = \int_0^a E_H \, dx = H E_L q_a \int_0^a \mu_H \, dx, \qquad (5A)$$

[26] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).
[27] H. H. Woodbury and G. W. Ludwig, Phys. Rev. **117**, 102 (1960); and Bull. Am. Phys. Soc. **5**, 158 (1960).
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where V_H is the Hall voltage, E_H is the Hall field, H is the magnetic field in gauss and E_L is the longitudinal field. E_L can be written as the product of I and the gradient of the resistance in the z direction. The latter, in turn, is given by

$$1\bigg/\left(q\int_0^b\int_0^a \mu_D N dx dy\right),$$

so that

$$V_H\times 10^8=HI\int_0^a \mu_H dx\bigg/\int_0^b\int_0^a \mu_D N dx dy. \quad (6A)$$

Substituting, as before, the value for N given by Eq. (1) of the text, integrating over y, and making the additional substitution $u=\pi x/a$, one can obtain

$$V_H\times 10^8=\pi^2 HI/4N_m bK_2(\mu_D/\mu_N), \quad (7A)$$

where

$$K_2=\left(1+\int_0^{\pi/2}\frac{\Delta\mu}{\mu_m}\sin u\, du\right)\bigg/\left(1+2/\pi\int_0^{\pi/2}\frac{\Delta\mu}{\mu_m}du\right),$$

the μ's in this expression being drift mobilities. As before, K_2 has been evaluated graphically for n-type Si and the results are given in Fig. 1.

Phonon Scattering in KCl-KBr Solid Solutions at Low Temperatures*

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The scattering of phonons by point defects at liquid helium temperatures has been studied. Single crystals of KCl-KBr solid solutions were employed, since it is known that the Cl⁻ and Br⁻ ions are randomly distributed in the anion lattice sites. A 1 mole percent addition of KBr reduced the conductivity of KCl by a factor of three. For all the crystals measured, including pure KCl and pure KBr, the thermal conductivity showed a maximum at the same temperature (5°K). Hence, point defects reduce the conductivity on both the high- and low-temperature sides of the maximum. For the mixed crystals the thermal conductivity was found to be related to the absolute temperature by the empirical formula $K=K_0 e^{-0.099T}$ for the temperature interval 6°K to 16°K.

INTRODUCTION

KLEMENS' theory of phonon scattering by crystal imperfections at low temperatures[1–4] has stimulated a great deal of experimental work but has not been well verified—especially in the case of high concentrations of imperfections. Klemens calculated an additive thermal resistance due to point defects and dislocations, and these predictions were tested experimentally by Slack,[5] Williams,[6,7] Toxen,[8,9] Sproull, Moss, and Weinstock,[10] Pohl,[11] and others. Pohl[11] could not fit his data

on LiF containing F centers using Klemens' theory. Sproull et al.[10] found that dislocation scattering is much more significant than Klemens' theory predicts. Although Slack[5] obtained agreement within a factor of two for low concentrations of Ca⁺⁺ in KCl, Williams[6] and Toxen[8,9] found that the Klemens formula did not give the right concentration dependence when extended to the range of up to 50% "impurity" (KCl-KBr and Ge-Si solid solutions, respectively).

Another theoretical treatment of low-temperature thermal conductivity has been given recently by Callaway.[12] Curves generated by his theory are in good agreement with the experimental data of Geballe and Hull[13] on isotopically-enriched and normal germanium, where the effect of isotopes on thermal conductivity is clearly shown but is substantially less than predicted by Klemens. Although the Callaway formulation is approximate, it proved successful in interpreting this critical experiment and has prompted this examination of Williams' data on KCl-KBr mixed crystals. The present discussion, then, is an account of the experimental procedures and results. An analysis of the data using the Callaway formulation will follow as a separate paper.

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