

ψ_m is then

$$\langle N_m \rangle = \sum_{N_m} \rho_m(N_m) N_m \\ = \{ \exp \beta [(m | H_1 | n) - \mu] - 1 \}^{-1}. \quad (23)$$

SUMMARY

The approximate variational procedure described herein has enabled us to obtain suitable wave functions for the description of the individual particle states of a system of "weakly" interacting bosons or fermions and to give the distribution of particles in these states. The procedure is not limited to these two cases, which are to be considered merely as illustrative of the general

procedure. An application to ferromagnetism or anti-ferromagnetism can be made and a quantum theory of liquids can be derived along the lines of the classical cell theory as developed by Richardson and Brinkley.¹² In a discussion of helium II, however, one should expect the correlation between different particle states to play an important part, and this requires a modification of the simple assumption of Eq. (11).

One of us (WMM) is indebted to Professor J. A. Wheeler and Professor A. S. Wightman and to L. van Hove for several interesting discussions of this paper.

¹²J. M. Richardson and S. R. Brinkley, Jr., *Phys. Rev.* **87**, 199 (1952); *High Speed Aerodynamics and Jet Propulsion* (Princeton University Press, Princeton, 1953), Vol. I, Sec. F.

Mobility of Impurity Ions in Germanium and Silicon*

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Lithium has been shown to migrate as a singly-charged positive ion in single crystals of both Ge and Si in temperature ranges of 150–600°C and 360–860°C, respectively. The mobility of the Li⁺ in crystalline Ge and Si has been measured as a function of temperature. Through the use of the Einstein relation between diffusion constant and mobility, values of the diffusion constants in cm²/sec of Li⁺ in Ge and Si are obtained as follows: $D = 25 \times 10^{-4} \exp\{(-11\,800)/RT\}$ for Ge and $D = 23 \times 10^{-4} \exp\{(-15\,200)/RT\}$ for Si, in satisfactory agreement with previously published results on the thermal diffusion of Li⁺. A curious reversion of conductivity type of solid solutions of Li in Ge is discussed. Copper has likewise been found to move as a positive ion in germanium in the temperature range 800°–900°C leading to diffusivities in agreement with previously published results.

INTRODUCTION

LITHIUM has already been shown to diffuse rapidly into crystalline germanium and silicon, behaving as a donor element in these semiconductors,¹ and the diffusion constants for these processes have been determined by means of a method involving the measurement of *p-n* junction positions.² An alternative method, capable of greater experimental accuracy, and based on fewer assumptions consists of measuring the mobilities of the Li⁺ ions under an applied electric field. In theory, the diffusivity D can then be determined from the Einstein relationship between diffusion constant and mobility. The sign of the ionic charge (positive in the case of Li as required by its donor properties) can also be ascertained by noting the direction the impurity ion moves in the electric field. The activation energies for diffusion can be obtained in the usual way from the slopes of plots of the logarithm of the diffusion constant

against reciprocal of the absolute temperature. In the present work this method has been applied successfully to Li in solution in Ge and Si.

THEORY

The basic principle of the method (see Fig. 1) is the diffusion of a hemispherical cloud of impurity ions into the semiconductor. We shall refer to such an ion cloud as a "pulse" because of its similarity to the analogous pulses employed in the measurement of electron and hole mobilities by the Haynes-Shockley method.³ The impurity ion pulse is put in at a temperature chosen so as to obtain a relatively high concentration of Li in solution. The location of the diffusion region in the semiconductor is then determined from the location of the *p-n* junction. Thereupon the sample is subjected at a given temperature to a dc electric field for a fixed time after which the pulse, now less concentrated due to thermal diffusion is again located from the new *p-n* junction position. If the net drift motion of the center of the pulse is x , then the mobility is obtained from the relation $\mu = x/Et$; where t is the drift time in seconds and

* A brief report of this work first appeared as a Letter to the Editor, *Phys. Rev.* **92**, 1322 (1953).

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¹ C. S. Fuller and J. A. Ditzenberger, *Phys. Rev.* **91**, 193 (1954).

² Fuller, Theuerer, and van Roosbroeck, *Phys. Rev.* **85**, 678 (1952); C. S. Fuller, *Phys. Rev.* **86**, 136 (1952).

³ J. H. Haynes and W. Shockley, *Phys. Rev.* **81**, 835 (1951). This analogy was first pointed out to the authors by W. Shockley.

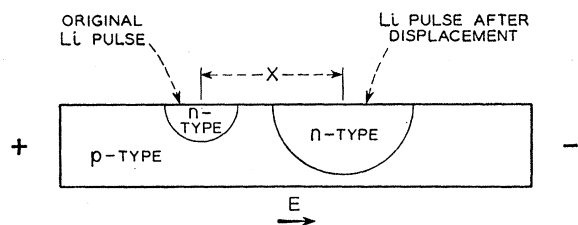


FIG. 1. Sketch of *p*-type semiconductor bar showing original pulse (small circle) and pulse after migration for a time, t , in field E .

E the field in volts/cm. The diffusion constant is then obtained from the Einstein relationship giving $D = (kT/q)(x/Et)$; where k is Boltzmann's constant, T the absolute temperature, and q the ionic charge. Since the quantities T , x , E , and t can all be measured to within a few percent, this method provides an accurate means of determining D . The method, if taken in conjunction with the thermal diffusion measurements,² can also serve to prove that these ions do obey the Einstein relation, at least to within the experimental error of both methods.

A difficulty in the method arises from the fact that thermal diffusion makes the pulses less concentrated and therefore their location becomes less precise for longer times. Large fields are therefore desirable so as to move the center of the pulses for appreciable distances (20 mils is sufficient for a measurement to within 5 percent) before they have spread out so much thermally as to cause inaccuracies in location. Solubility considerations likewise put a lower temperature limit on the method. These considerations apply particularly to copper in Ge for which the maximum solubility is about $4 \times 10^{16} \text{ cm}^{-3}$ and the diffusivity is high ($3 \times 10^{-5} \text{ cm}^2/\text{sec}$) in the temperature range investigated ($800^\circ\text{--}900^\circ\text{C}$).

EXPERIMENTAL TECHNIQUE WITH LITHIUM

Single crystals⁴ of Ge and Si (*p* type, since Li is a donor) were cut into bars 0.7 in. \times 0.1 in. \times 0.06 in. by means of a diamond saw. The samples were then dry-ground and small cubes [approx 15 mils (0.038 cm) on a side] of metallic Li were placed near the midpoint of the bars, one cube of Li per bar. The bars, with the metallic Li on them, were then heated for about 30 seconds in a tubular furnace in a helium atmosphere at a temperature of $800^\circ\text{C} \pm 10^\circ\text{C}$. At this temperature most of the Li fuses into the semiconductor to form a Li-rich alloy while some of the Li (about 10^{18} atoms per cm^3) diffuses into the lattice to give a hemispherical diffusion region. After this short heating period the samples were quenched on a large steel block. The surface was thereupon reground and etched to remove surface contaminants. The etching process completely removed the Li-rich alloy region, leaving a pit of about 5–10 mils (0.0125–0.0250 cm) deep and about 20 mils (0.050 cm)

⁴ G. K. Teal and J. B. Little, Phys. Rev. **78**, 637 (1951); G. K. Teal and E. Buehler, Phys. Rev. **81**, 637 (1951).

in diameter. Concentric with this pit there remained the hemispherical diffusion region into which the Li had diffused and which was thereby converted from *p*-type to *n*-type. The *p*-*n* boundary, which is a circle on the surface concentric with the pit, was then made visible by the deposition of barium titanate under reverse voltages of about 40 volts.⁵ The diameter of the diffusion pulses thus prepared varied from 35 mils (0.089 cm) to 55 mils (0.140 cm). The ends of the bars were finally plated so as to provide good electrical contact for the electrodes.

The specimen was then placed in a series circuit consisting of storage batteries and current limiting slide wire resistors. It was supported (as shown in Fig. 2) between two steel cooling rods, electrically insulated therefrom by thin mica separators. Electrical contact was made through pressure contacts on the plated end areas. An ammeter was placed in the circuit and currents ranging from 0.3 to 10 amp were passed through the specimen, the current serving to heat up the specimen as well as to provide the electric field. The electric field acting on the ions was determined by measuring the voltage across two tungsten probes, 1.0 cm apart, which could be brought in pressure contact with the sample. Knowing the current and voltage across the sample, the resistivity, and in turn the temperature, can be found. Data of Morin were used for this purpose.⁶ The drift times during which the samples were exposed to the field varied from 5 minutes to 5 hours, depending on the temperatures at which the runs were made. After exposing the pulse to the field for a definite time, the sample was cooled down to room temperature as quickly as possible. This required about

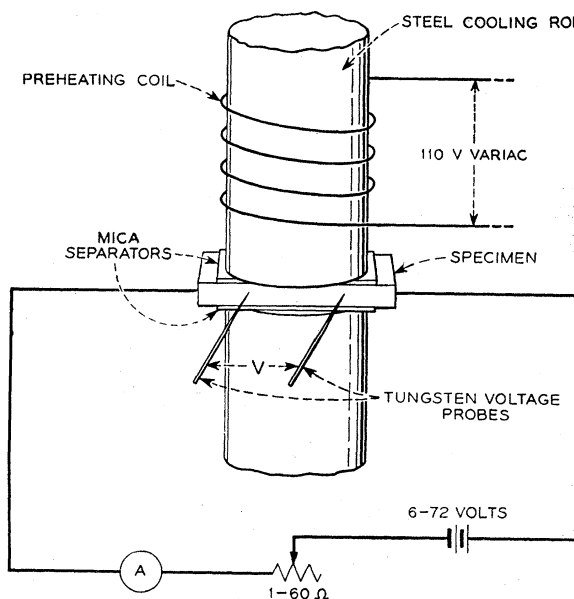


FIG. 2. Experimental arrangement.

⁵ G. L. Pearson, U. S. Patent No. 2,669,692, February 16, 1954.

⁶ F. J. Morin (private communication).

40 seconds. The surface was re-cleaned and the p - n boundaries brought out again by means of barium titanate. The circular trace of the displaced pulse was then located optically under a microscope, and the drift distance measured by means of a micrometer eyepiece. The drift distances ranged from 3 to 20 mils (0.0076 to 0.0508 cm). All the necessary information is thus available to determine the ion mobilities.

It has been found as was expected from its donor properties² that Li moves as a positive, singly-charged ion in Ge and Si. The diffusion constant as a function of temperature was calculated and the results are shown in Table I and plotted in Fig. 3. For comparison, this plot also shows the thermal diffusion measurements.² Good agreement obtains between the two methods, showing that the Einstein relation is valid for these ions in the concentration and temperature ranges investigated. The curves can best be described by the equations:

$$D = 25 \times 10^{-4} \exp(-11\,800/RT) \text{ for Ge;}$$

$$D = 23 \times 10^{-4} \exp(-15\,200/RT) \text{ for Si.}$$

The activation energies are therefore 11 800 and 15 200 cal/mole for Ge and Si, respectively.

TABLE I. Tabulation of experimental data.

$T(^{\circ}\text{C})$	$E(\frac{\text{volts}}{\text{cm}})$	$t(\text{sec})$	Germanium			$D(\frac{\text{cm}^2}{\text{sec} \times 10^7})$
			$x(\text{cm})$	$\mu(\frac{\text{cm}^2}{\text{volt sec} \times 10^6})$		
150	6.00	1500	0.0076	0.085	0.031	
174	9.00	8400	0.0153	0.201	0.078	
203	5.45	13 200	0.0178	0.248	0.102	
227	6.15	1000	0.0263	0.430	0.183	
254	4.27	1000	0.0238	0.560	0.255	
274	4.00	9000	0.0330	0.97	0.458	
295	3.70	7200	0.0312	1.36	0.667	
313	3.25	7200	0.0500	2.17	1.10	
334	2.52	3800	0.0216	2.23	1.17	
358	2.26	6300	0.0558	3.92	2.14	
373	2.56	4620	0.0554	4.68	2.61	
400	2.06	4500	0.0554	5.98	3.48	
418	2.22	3600	0.0576	7.22	4.31	
451	1.60	3000	0.0432	10.0	6.50	
460	2.20	600	0.0140	10.6	6.70	
473	1.65	2760	0.0605	13.3	8.56	
491	1.33	2400	0.0522	16.3	11.4	
524	1.71	1500	0.0578	22.6	15.5	
554	1.50	1680	0.0623	24.6	17.6	
574	1.49	900	0.0432	32.2	23.6	
600	1.24	600	0.0320	43.0	32.4	
			Silicon			
360	12.0	4500	0.0139	0.258	0.147	
390	13.0	4200	0.0246	0.452	0.258	
422	11.3	3600	0.0274	0.675	0.405	
460	8.15	4200	0.0381	1.11	0.70	
494	7.55	3600	0.0444	1.64	1.08	
527	5.95	3000	0.0464	2.61	1.80	
564	6.23	2040	0.0554	4.36	3.15	
620	5.20	1500	0.0515	6.60	5.10	
670	4.21	1200	0.0556	11.0	8.95	
707	4.75	660	0.0436	14.0	11.8	
780	3.68	360	0.0305	23.0	20.9	
877	3.40	300	0.0368	36.0	27.3	

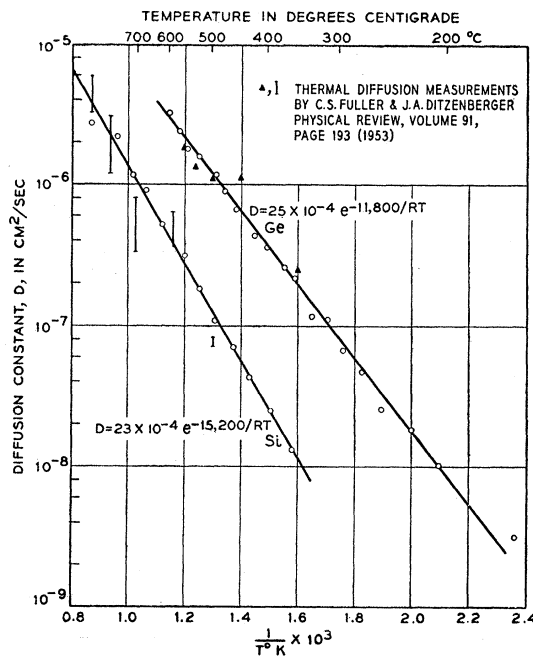


FIG. 3. Plots of diffusivity against reciprocal of absolute temperature for Li in Ge and Si.

REVERSION PHENOMENON SHOWN BY LITHIUM IN Ge

A curious effect, which incidentally permits a graphic demonstration of the drift, was observed for the case of Li in Ge. This is illustrated in Fig. 4. After the pulse had been exposed to the electric field, it was found that the barium titanate would bring out not only the displaced diffusion area, but also an image of the original spot, i.e., the original pulse position. Upon probing this region with a tungsten point and examining the characteristic rectification curves on an oscilloscope, it was found that this original spot had returned to p type, the same type as the body of the Ge specimen, whereas the area into which the Li had been moved under the action of the electric field was n type. This phenomenon was observed over the entire temperature range and is shown for two cases in the photograph of Fig. 5. These show the small original circle which has reconverted to p type after exposure to the field, inside of (A) or partially inside of (B) a larger n type pulse after it has been moved. The rest of the sample is of course still p type.

The following is offered as an explanation of the above observations: Upon quenching rapidly from the temperature (800°C), at which the original pulse is produced, the Li remains, at room temperature, in a supersaturated state. However, upon re-heating in the mobility apparatus, the temperature rise is of necessity slower (several minutes). It is believed that precipitation of some of the Li occurs throughout the original region during this stage. Upon reaching the experimental temperature, all of the Li, except for some residual nucleation centers, is again in solution, the field is then applied for a fixed time

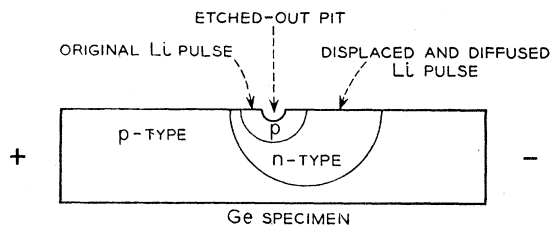


FIG. 4. Ge specimen after exposure to dc field, showing displaced diffused pulse (large circle) and original pulse (small circle) where reversion to the original *p*-type conductivity occurs.

and the specimen again cooled to room temperature in about 40 sec. During this cooling the ion cloud remains in solution except where nuclei from the original precipitation still persist, i.e., in the original pulse where crystallization occurs rapidly on the residual nuclei. The almost complete loss of dissolved Li from this region thus returns it again to *p* type.

No such behavior as described above was observed for silicon. This we attribute to the fact that Li does not precipitate readily from Si in the temperature range (room temperature up to about 100°C) in which it precipitates rapidly from Ge. Thus, the warming-up period in the mobility apparatus does not precipitate enough Li to leave nucleation centers and no reversion to the original conductivity type takes place. In the silicon experiments, therefore, care was taken to preserve the original etched-out pit (Fig. 4) so that determination of the drift distance x could be determined.

A final comment might be made regarding a peculiar wiggly appearance of the diffused and migrated pulses when made visible with barium titanate. One of these is evident in Fig. 5(A). We are uncertain as to the cause of these fluctuations in pulse radius. One explanation is that they correspond to resistivity variations in the specimens. There is some evidence against this, however, and in support of structural variations in the single crystal lattice. Further work will be required to establish this point.

MOBILITY OF COPPER IN Ge

Experiments similar to those described above have also been performed using copper particles instead of Li to produce *p*-type^{7,8} pulses in *n*-type Ge. Because of the small solubility of copper in Ge, (approximately 10^{16} cm⁻³) the precise location of the copper pulses after migration presents considerable difficulty. In addition, the danger of contamination and the high diffusivity of copper in Ge (3×10^{-5} cm²/sec)⁷ require that short times (about 45 to 60 seconds) be employed. This

⁷ C. S. Fuller and J. D. Struthers, *Phys. Rev.* **87**, 526 (1952).

⁸ Fuller, Struthers, Ditzenberger, and Wolfstirn, *Phys. Rev.* **93**, 1182 (1954).

greatly reduces the precision. Successful experiments have however, been performed at 800°C and 900°C which show that copper moves as a positively charged ion in Ge at these temperatures. The drift distances were 0.011 and 0.020 cm for fields of 1.0 and 1.3 volts/cm, respectively. The calculated diffusivities are 2.4×10^{-5} and 3.0×10^{-5} cm²/sec in satisfactory agreement with previously reported thermal measurements of 2.8×10^{-5} cm²/sec. One test at 700°C showed no essential motion. However, the solubility at this temperature is just at the detection limit. Large boundary fluctuations also exist. Because of these and other inaccuracies we are unable to be entirely certain whether the ion is singly or doubly charged, although the above figures for the diffusivities are based on the assumption of a single positive charge.

The above finding that copper behaves as a positive ion in Ge at temperatures of 800°–900°C is interesting in view of the reported acceptor properties of copper.⁷ It suggests the possibility that the ionization of copper is

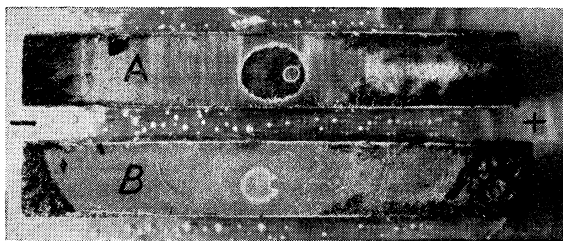


FIG. 5. Two Ge bars showing original pulses (small circles) and drifted pulses (large circles). (A) Shows original pulse within the drifted one. (B) Shows the drifted pulse partially separated. In each case the negative electrode is to the left. The pulses were made visible by means of barium titanate deposition.

dependent upon temperature in such a way that it acts as a negative ion at room temperatures and as a positive ion at the higher temperatures of these experiments. The single result at 700°C in which no motion was observed, lends some further support to this hypothesis, since it might be expected that intermediate temperatures might favor neutrality of the copper.

It has not been possible to investigate the behavior of copper in silicon by this method inasmuch as its acceptor properties in silicon are too feeble to allow the *p*-*n* junction method to be employed. In addition, J. D. Struthers has found copper to precipitate readily in silicon.

ACKNOWLEDGMENT

The authors wish to thank J. A. Ditzenberger for help with the measurements and E. Buehler and E. Kolb for supplying single crystals of germanium and silicon. Mr. F. G. Foster kindly provided the photograph in Fig. 5.

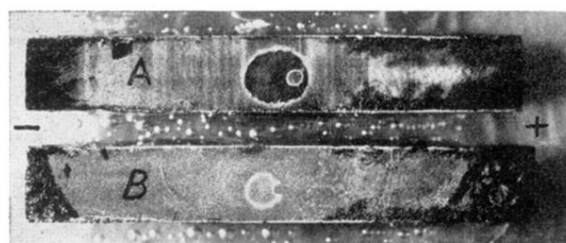


FIG. 5. Two Ge bars showing original pulses (small circles) and drifted pulses (large circles). (A) Shows original pulse within the drifted one. (B) Shows the drifted pulse partially separated. In each case the negative electrode is to the left. The pulses were made visible by means of barium titanate deposition.