

One-Dimensional Diffusion of Li in Rutile*

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The diffusion of interstitial Li in rutile (TiO_2) was measured over a temperature range of 80–360°C, utilizing the optical absorption associated with the Li impurity as a measure of its concentration. Diffusion was found to be strongly anisotropic with diffusion coefficient D perpendicular to the C axis smaller than D parallel by a factor of at least 10^8 up to 550°C. D parallel was accurately described by $D = D_0 e^{-Q/RT}$ with $Q = 0.330 \pm 0.003$ eV and $D_0 = 0.295 \pm 0.028$ cm²/sec (95% confidence limits). Concentrations and solubility of Li in rutile were measured approximately using chemical analysis; a solubility limit of 2.5×10^{19} /cm³ at room temperature was obtained. Lattice distortion and other impurities strongly inhibit Li diffusion. Possible explanations for apparent deviations from Fick's law are suggested, based on the assumption that the optical absorption associated with Li doping is caused by conduction electrons.

I. INTRODUCTION

THE nonmetallic systems in which interstitial diffusion has been studied most extensively are probably Cu^+ and Li^+ in Si and Ge,^{1,2} and to a lesser extent, the same impurities in the III-V compound semiconductors. Obtaining meaningful measurements of the diffusion coefficients for these impurities in Si and Ge has been complicated enormously by the interaction of the impurities with lattice imperfections and other impurities. A fairly complete description of the behavior of interstitials in these materials has apparently been achieved, however, and at least the qualitative aspects of the behavior may be understood on the basis of calculations such as those of Weiser.²

Many of the properties of TiO_2 (rutile) have also been studied rather extensively, but the diffusion of interstitial impurities has received relatively little attention. To the author's knowledge, no previous report of the behavior of interstitial Li in this material has appeared in the literature. A number of studies have been made^{3,4} of interstitial H and Ti in rutile, however, and as will be seen, these problems are apparently very closely related. Understanding of the behavior of interstitial Li in this crystal should aid substantially in the understanding of the behavior of H and Ti interstitials. Li is unique in that it is the only element which has a singly charged ion with a radius substantially less than one Å (0.62 Å), except, of course, for the proton (H^+). Thus, the diffusion of Li in a crystal is of substantial importance in developing a theory of interstitial diffusion. For this reason, and because of the very unusual behavior of Li in rutile, a fairly extensive examination of the diffusion behavior of Li in rutile was undertaken.

The appearance of relatively pure, near-stoichiometric rutile is that of a straw-colored, transparent

crystalline material. A blue coloration is produced when the crystal is heated in a fore-pump vacuum, or in an H atmosphere. This coloration results from optical absorption by conduction electrons, associated with donor levels, introduced into the crystals during the heat treatment.^{3,4} There has been considerable controversy over the identity of these donors; O vacancies,³ Ti interstitials,⁴ and H interstitials⁵ have all been suggested. Ti^{3+} interstitials appear to be the current favorites. An electronic conductivity is associated with this blue coloration; resistivity may be as low as 1 Ω-cm at room temperature. Doping with Li induces a coloration which is apparently indistinguishable from that of an H-reduced or vacuum-reduced specimen, and conductivities of a similar magnitude have been observed to be associated with the coloration. Thus it seems reasonable to assume that the blue coloration is, in this case, also associated with conduction electrons, and that the Li is present in the lattice as Li^+ . Other arguments in favor of this interpretation appear in the detailed discussion to follow.

II. EXPERIMENTAL PROCEDURE

The most striking aspect of the diffusion of Li in rutile is the extreme anisotropy. Over the temperature range measured, the diffusion parallel to the C axis of the crystal was in all cases several orders of magnitude faster than diffusion perpendicular to the C axis. This peculiarity made possible a very simple experimental procedure for measuring diffusion coefficients.

Li concentration was inferred from optical absorption measurements. The average optical density over an area of the specimen 100μ in diameter was measured before and after Li doping, to determine the portion of the optical absorption which was due to Li. All measurements were made at the same point in the specimen. Near-monochromatic light (green lines from a Hg arc lamp) was used for these measurements, to eliminate complications in the analysis of the data due to variations in absorption with wavelength. Measurements

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¹ R. N. Hall and J. H. Racette, *J. Appl. Phys.* **35**, 379 (1964).

² K. Weiser, *Phys. Rev.* **126**, 1427 (1962).

³ F. A. Grant, *Rev. Mod. Phys.* **31**, 646 (1959).

⁴ J. H. Becker and W. R. Hosler, *J. Phys. Soc. Japan* **18**, Suppl. II, 152 (1963).

⁵ A. Von Hippel, J. Kalnajs, and W. B. Westphal, *Phys. Chem. Solids* **23**, 779 (1962).

were taken using a Reichert metallograph for the optical system, with appropriate precautions taken to eliminate the effects of scattered or reflected light.

Diffusion coefficients were measured using an out-diffusion technique. A uniform concentration of Li impurity was first established through the length of the specimen, by heating a specimen which had one end coated with LiOH, to approximately 450° for 10–20 h in a fore-pump vacuum. Li doping may also be accomplished by placing Li metal in contact with the crystal and heating in vacuum to a temperature somewhat less than this (200–300°C); more uniform impurity distributions were readily obtained using LiOH, however. Some doping was also obtained with several Li salts. A detailed investigation of this aspect of the problem was not undertaken. It seems likely that the Li is introduced into the crystal from the LiOH coating only after reduction of the Li by hydrocarbon contaminants in the system. In any event, since a uniform distribution of Li is maintained through the specimen at all times during the doping process, it is clear that a surface reaction of some sort is rate-limiting. This is not true when metallic Li is the doping agent, in which case the indiffusion proceeds at a much faster rate.

After doping, the concentration of Li in the specimen was measured as described above. Out-diffusion of the Li was accomplished by heating the specimen in one of several baths, depending on the temperature at which measurements were being made. Distilled water was found to serve adequately below the boiling point of water. A $\text{KNO}_3\text{-NaNO}_2$ bath was used between 150 and 300°C. KNO_3 alone was used above 300°C. All three of these baths appeared to establish the appropriate boundary condition at the surface of the crystal (zero concentration of Li at the surface). Subsequent to the out-diffusion portion of the cycle, optical density was again measured at the preselected location in the specimen. Temperature of the out-diffusion bath was controlled to $\pm 1^\circ\text{C}$.

The condition of the surface of the specimen was found to be of extreme importance in obtaining meaningful results. In all cases, an undamaged fracture surface was used for both in-diffusion and out-diffusion. Surface damage produced by abrasion with silicon-carbide paper was found to reduce diffusion through this layer below measurable values over the temperature range investigated. This behavior was utilized to simplify the experimental procedure somewhat, in that only one end of the specimen was left "open," while the other end was "sealed" by abrading with 600-grit silicon-carbide paper. This resulted in substantial simplification of experimental procedure, as well as increased sensitivity of measurement, as will be seen in the next section. The crystalline defects responsible for this inhibition of diffusion resulting from surface abrasion apparently become mobile at approximately 500°C, since the effect was found to "anneal out" to at least some extent after heat treatment at 500°C or

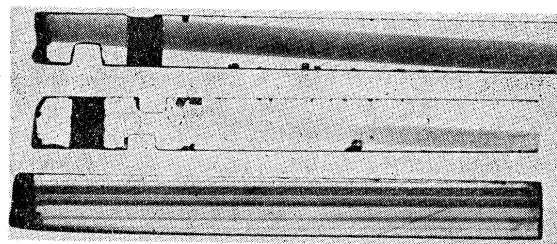


FIG. 1. Li-doped rutile single crystals.

more. It seems likely that strains associated with a plastically deformed surface layer are responsible for this inhibition of diffusion, since other tests involving specimens macroscopically deformed at elevated temperatures indicated that the diffusion coefficient is reduced by about a factor of 10 in regions which have been deformed 1%.

Specimens were cut from single crystal boules (obtained from Linde Company), approximately $2 \times 2 \times 20$ mm. with the specimen axis roughly parallel to the crystalline C axis. Opposite faces of each specimen were polished sufficiently to permit microscopic examination of the interior of the specimen. Typical specimens are shown in Fig. 1. The top specimen is one in which a fairly uniform Li concentration has been obtained, by applying LiOH to the end with the "collimating" slots. The second specimen has undergone the full out-diffusion cycle. The bottom specimen was doped with metallic Li.

Measurements of optical density before and after the out-diffusion cycle were normally made only at a preselected location near the sealed end of the specimen; however, data on optical density over the full length of the specimen were also taken in several cases. It was subsequently possible to relate the impurity density indicated by optical absorption to impurity concentration determined from chemical measurements. For this purpose, specimens were prepared as described above, impurity-induced optical density measured, then the specimens were boiled in distilled water for ten to fifty hours, after which the optical density was again measured. It was then possible to determine the amount of Li removed from the specimen by titration of the water bath.

III. ANALYSIS OF DATA

The one-dimensional character of the Li diffusion in rutile permits a particularly simple mathematical description of the system. For a specimen of length L , in which a uniform concentration of Li impurity exists at $t=0$, and in which the concentration of Li at each end of the specimen is maintained at 0, the solution to Fick's equation is

$$C(x,t) = C(x,0) \left[1.27 e^{-(\pi/L)^2 D t} \sin(\pi x/L) + 0.42 e^{-9(\pi/L)^2 D t} \sin(3\pi x/L) + \dots \right], \quad (1)$$

where $C(x,t)$ is the Li concentration as a function of time and position, and D is the usual diffusion coefficient. When $C(L/2,t)$ is less than $0.8 C(x,0)$, all but the first term of Eq. (1) are negligible, and the equation may be solved explicitly for D . This is in marked contrast to the usual diffusion experiment, where numerical solution on a computer is normally required. A specimen of length $L/2$, with one end "sealed," is entirely equivalent to the specimen described by Eq. (1). The boundary condition appropriate to the "sealed" end is, of course,

$$\partial C/\partial x|_{x=L/2}=0.$$

The simplest assumptions regarding the relationship between optical density \mathfrak{D} and C are that Lambert's law is obeyed

$$I=I_0e^{-\alpha d}, \tag{2}$$

(where I is light intensity, and d is thickness of the doped material), and that α is proportional to $C(x,t)$, leading to the relationship

$$C=(K/d)\log(I_0/I)=K\mathfrak{D}/d. \tag{3}$$

\mathfrak{D} is normally defined as $\log_{10}(I_0/I)$, and it is implicit in this definition that I_0 is the incident intensity less reflections and absorption due to the undoped crystal.

Assuming that the out-diffusion has proceeded far enough that the second term on the right of Eq. (1) is negligible compared to the first term, this equation may

be solved for D to give

$$D=\frac{1}{(\pi/L)^2t}\ln\left[\frac{1.27\mathfrak{D}(L/2,0)}{\mathfrak{D}(L/2,t)}\right]. \tag{4}$$

If, on the other hand, Eq. (3) were replaced by

$$C(x,t)=K\mathfrak{D}/d+C_0 \quad (C(x,t)\geq C_0), \tag{5}$$

where C_0 is a numerical constant, the solution for D would then be written

$$D=\frac{1}{(\pi/L)^2L}\ln\frac{1.27[\mathfrak{D}(L/2,0)+dC_0/K]}{\mathfrak{D}(L/2,t)+dC_0/K}. \tag{6}$$

The significance of these expressions is discussed below.

Measurement of the apparent diffusion coefficient over different portions of the out-diffusion cycle [calculated by assuming the validity of Eq. (3)] indicated a systematic variation of D with concentration (Fig. 2). The value of D , calculated in this way, was highly reproducible for a given temperature and concentration, for each specimen. With one exception (specimen 14-2 which is discussed below), the dependence of D on concentration did not change with temperature; large differences in the concentration dependence of D were found between specimens, however. Such behavior could result from an actual concentration dependence of diffusion coefficients, or equally well from failure of the assumption that the absorption coefficient is proportional to impurity concentration [Eq. (3)]. The complexity of the behavior of D as a function of C in different specimens seems to rule out identification of a single factor as accounting for the departure of the diffusion coefficient from ideal behavior. For this reason, the simple expedient of assuming a linear relationship between diffusion coefficient and concentration for each specimen was assumed, to permit analysis of the data for determination of diffusion activation energy. Since the range of concentrations over which it was possible to obtain accurate data was rather narrow (approximately a factor of 4), it is felt that this expedient is not likely to have introduced any serious error in the value of activation energy obtained. Thus the data were analyzed by assuming a dependence of D on C and T as follows:

$$D(C,T)=D_0(1+\beta C)e^{-Q/KT}, \tag{7}$$

where Q is the activation energy and K is Boltzmann's constant. A least-squares technique was then used to obtain the best value of D_0 , β , and Q for each specimen. The values of D_0 obtained in this way are probably not particularly significant since they involve extrapolation of the data to zero concentration, which was well outside the range of observation. For this reason, the values of D_0 quoted in later sections of this paper are those corresponding to concentrations of $5\times 10^{18}/\text{cm}^3$, which was approximately the middle of the range of concentrations studied.

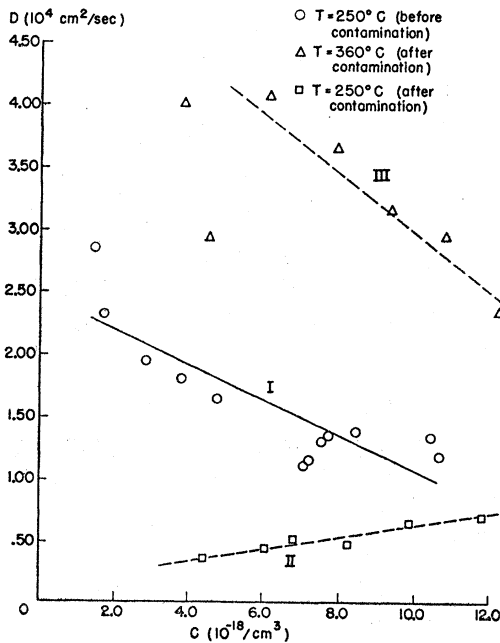


FIG. 2. Diffusion coefficient versus apparent concentration of Li, specimen No. 14-2.

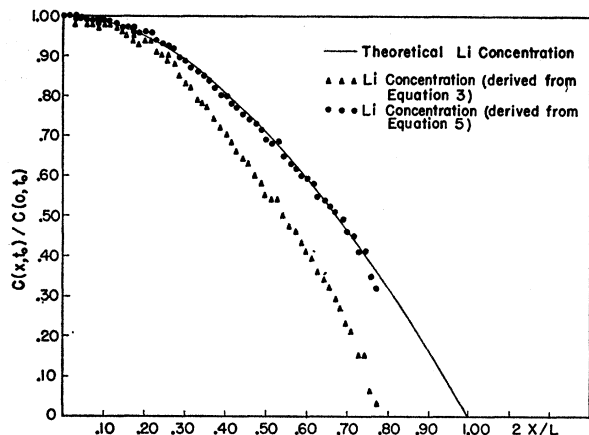


FIG. 3. Li concentration at various positions in crystal, after partial out-diffusion.

The assumption of Eq. (7) was merely an expedient to permit analysis of the data. No physical significance should be attached to the form of the equation. Both positive and negative values of β were observed. Some of the mechanisms which might give rise to departure from the behavior predicted by Eqs. (3) and (4) are discussed in later sections.

IV. EXPERIMENTAL RESULTS

Li Concentration and Optical Density

In addition to comparison of values of D over different portions of the out-diffusion cycle as discussed above and illustrated in Fig. 2, the validity of Eqs. (1) and (3) may also be tested by comparing apparent concentration [as derived from Eq. (3)] with that predicted by Eq. (1) at different positions along the impurity column after partial out-diffusion. Results of such a comparison are indicated in Fig. 3. The behavior indicated by Fig. 3 was fairly typical of most specimens tested, although the departure from ideal behavior was more complex in some cases, and specimens cut from near the center of the boule generally showed a somewhat smaller departure. The triangles represent experimental points plotted in accordance with Eq. (3), while the circles represent the same data plotted according to Eq. (5), with the constant C_0 treated as an experimentally determined parameter. The solid line is a plot of Eq. (1). The second specimen in Fig. 1 demonstrates this behavior; there is no optically detectable Li within several mm of the "open" end.

If the diffusion coefficient varies along the length of the specimen, departures from Eq. (1) are certainly to be expected; however, behavior such as that indicated in Fig. 3 cannot be explained on this basis, as this would require an infinite diffusion coefficient over the last 20% of specimen length. Behavior such as would be expected from variation of D_0 at different locations in the specimen was also observed in some cases, but it is readily

seen that this type of behavior would not interfere with the accurate determination of diffusion activation energy since the measured diffusion coefficient represents an average over the length of the specimen, and it is this average which is measured as a function of temperature.

Light transmitted through the doped material was found to be partially polarized. The polarization with E parallel to the C axis was preferentially absorbed, particularly at the longer wavelengths. An intensity ratio of 3:4 for $E_{\parallel}:E_{\perp}$ at an optical density of 1 was typical.

Chemical measurement of Li concentration, as previously described, was made on 3 specimens. The specimens were all cut from the region near the center of a single TiO_2 boule. Values of the constant K in Eqs. (3) and (5) obtained from these measurements were as follows: $1.3 \times 10^{18}/\text{cm}^2$, $1.2 \times 10^{18}/\text{cm}^2$ and $1.4 \times 10^{18}/\text{cm}^2$. The Li concentration at which the measurements were made was in the range of $10^{19}/\text{cm}^3$. Similar measurements on a control specimen, which had not been Li-doped, gave an upper bound of $4 \times 10^{16}/\text{cm}^3$. The accuracy of the determination of K is probably not better than 20 to 30%, but the rather low upper bound on Li impurity concentration in the control specimen argues against any large systematic errors in the determination.

From these measurements, it is possible to make a rough estimate of the solubility limit of Li in rutile at room temperature. Solubility apparently decreases rapidly with temperature in the range near room temperature, as precipitates which were observed to form on or near dislocations and grain boundaries, dissolved quite readily as the temperature was increased a few degrees. The precipitation of Li near lattice imperfections in rutile is discussed in detail elsewhere.⁶ From observations of the minimum concentration at which precipitates were observed to form, the solubility at room temperature is estimated to be approximately $2.5 \times 10^{19}/\text{cm}^3$. This corresponds to a concentration of approximately 800 ppm of Ti.

Li Diffusion

Results of the diffusion measurements described above are shown for one specimen (No. 14-4) in Fig. 4. Values of the diffusion parameters, D_0 and Q , are indicated in Table I, with 95% confidence limits. These

TABLE I. Lithium diffusion parameters.

Specimen No.	D_0 (cm^2/sec)	Q (eV)	Number of measurements
14-2	0.28 ± 0.06	0.335 ± 0.007	22
14-4	0.295 ± 0.028	0.330 ± 0.003	22

⁶ O. W. Johnson, J. Appl. Phys. (to be published).

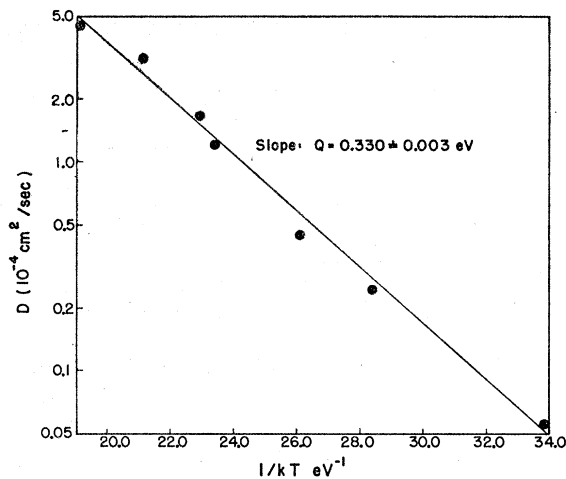


FIG. 4. Diffusion coefficient versus $1/KT$ for specimen No. 14-4.

are the two specimens for which most extensive data were available. These specimens were cut from a region near the center of the same boule from which the specimens used in concentration determinations were cut. Less extensive measurements on several other specimens gave results which were consistent with those indicated in Table I, except that generally lower values of D_0 were obtained for specimens further from the axis of the boule.

Several attempts were made to obtain corresponding data for diffusion perpendicular to the C axis. The most sensitive of these measurements was one in which a narrow streak of Li was diffused into the crystal, after which both ends were heavily abraded with silicon-carbide paper. The width of the doped region was approximately 10μ . The specimen was then heated in vacuum to a temperature of 550°C for 1 h. Longer treatments than this were not possible using this technique, due to the "annealing out" of the surface damage which prevented out-diffusion of the Li through the ends of the specimen. There was no detectable spreading of the Li after this heat treatment. Order-of-magnitude calculations give an upper bound for the diffusion coefficient perpendicular to the C axis under these circumstances of about 10^{-12} cm²/sec. This is in contrast to an extrapolated value, from the data in Table I for diffusion parallel to the C axis, of 2.7×10^{-3} cm²/sec for a temperature of 550°C . Thus, at this temperature, D perpendicular appears to be at least 10^8 smaller than D parallel to the C axis.

One of the two specimens on which data are quoted above (No. 14-2), was accidentally heated to a temperature of 1100°C in a fore-pump vacuum for a period of nearly one hour. Since this treatment resulted in some coloration due to the so-called vacuum-reduction,³ a similar heat treatment in air was necessary to restore the crystal to approximate stoichiometry. Subsequent to this, Li diffusion measurements were again made on

the specimen, with the results indicated by Curves II and III of Fig. 2. Curve I represents data taken before the high-temperature heat treatment of the specimen, at a diffusion temperature of 250°C . Curve II was taken at the same temperature, subsequent to heating at 1100°C . Curve III was taken, after heating to 360°C , at 360°C . Comparison of I and II shows that the value of the diffusion coefficient obtained at relatively high concentrations has not changed substantially, although the low-concentration behavior is markedly altered. No Li diffusion data were taken on this specimen above 250°C prior to the high-temperature heat treatment; however, extrapolation from lower temperatures predicts a diffusion coefficient at 360°C quite close to that indicated by III, at least at concentrations above $5 \times 10^{18}/\text{cm}^3$. It should be noted that the data at 360°C indicate a dependence of diffusion coefficient on concentration quite similar to that observed prior to the accidental heat treatment, although there has been a marked change in behavior at 250°C . A possible explanation for this behavior is suggested in the next section.

V. DISCUSSION AND CONCLUSIONS

On the basis of the data presented above, it seems likely that the optical absorption associated with Li in rutile results from conduction electrons, as is the case in the previously studied vacuum-reduced and H-reduced material. Li apparently exists in the lattice as a positive, singly charged, interstitial ion. An absorption mechanism involving conduction electrons appears to be the only explanation which would account for the similarity in both optical absorption and electronic conductivity observed in the Li-doped material and in the reduced material. This mechanism also suggests a means of accounting for the observed polarization of light transmitted through a Li-doped specimen. It has been observed³ that the electron mobility in slightly reduced rutile is strongly anisotropic, being much greater in the C -axis direction. Thus, it seems reasonable to expect that some polarization of transmitted light would occur. Furthermore, the conduction-electron hypothesis also suggests a plausible explanation for the behavior indicated in Fig. 3. It seems likely that some of the impurities that are known to be present in this material (such as Fe) may act as electron traps, with an acceptor level below the conduction band. Various lattice defects are also known to behave in this manner in other semiconductors. If such traps occur in rutile, at a level of an electron volt or so below the conduction band, and if the optical absorption is indeed due to the free carriers donated by Li, then essentially no optical absorption from conduction electrons would be observed until the traps are completely filled. Thus the constant C_0 in Eq. (5) would represent the concentration of such electron acceptors. The behavior indicated in Fig. 3 was found to some extent in all specimens

examined, but was most marked for specimens cut from regions near the original surface of the parent boule. Typical values of the constant C_0 , evaluated from chemical measurements described above, were of the order of 3×10^{18} per cm^3 , or approximately 100 ppm. This is in the range (somewhat higher) of the known impurity concentration. It was previously found⁷ that crystals obtained from the same supplier had a higher concentration of impurity near the original surface than at the center of the boule.

The fit obtained to the theoretical curve in Fig. 3 was somewhat better than was obtained in most cases, as most specimens showed some deviations from the theoretical curve even after allowing for acceptor impurities. Most of the deviations, however, could be explained on the basis of a slowing of diffusion due to grain boundaries, or other impurity effects, discussed below.

The discussion above also suggests an explanation for the observed discrepancy⁴ between the temperature at which a specimen may be reduced in vacuum, and in an H_2 atmosphere (approximately 900 and 600°C, respectively). On the basis of the observations described in this paper, it seems likely that H diffuses interstitially in a manner similar to that observed for Li. Von Hippel *et al.*⁵ have reported evidence, from infrared absorption measurements, for rapid diffusion of H into rutile at 800°C. Thus it seems likely that in these three systems with superficially similar characteristics, three different impurity species are responsible for the free carriers; in vacuum-reduced material, Ti interstitials (or possibly O^{-2} vacancies) behave as donors; in H-reduced material, H atoms act as donors; and in the Li-doped material, the Li is a donor impurity.

Other mechanisms might be considered which could lead to a departure from the predictions of Eqs. (1) and (3), in addition to the electron-trap mechanism discussed in the paragraphs above. With a relatively large concentration of other impurities, mostly substitutional, it is reasonable to expect some effects due to ion pairing or other impurity interactions. Ion pairing, between the Li^+ and some impurity introduced into the specimen during the accidental heat treatment at 1100°C with a concentration of approximately $5 \times 10^{18}/\text{cm}^3$, could account for the departure from "normal" behavior exhibited at 250°C by specimen No. 14-2, described previously. The inhibition of Li^+ diffusion due to ion pairing would, in this case, exhibit a saturation effect when the Li concentration exceeded that of the newly introduced impurity. Furthermore, if the binding energy between this unknown contaminant and the Li ion were such that, at 250°C, most pairs were bound, and at 360°C the majority were not bound, the return to "normal" behavior at 360°C would be explained. The high-temperature heat treatment occurred in a Vycor tube in the presence of LiOH

and hydrocarbons, etc., from the vacuum pump oil; thus, contamination of the specimen is not unlikely.

Several other ways in which an apparent concentration dependence of D can occur have been observed. The validity of the equations used to calculate D depends critically on obtaining an initial uniform concentration of Li through the specimen. Optical density was measured over approximately a 100μ region, and variations of impurity concentration through this region would give rise to an apparent concentration dependence. Also, voids of sizes up to 15 or 20μ have been observed in some specimens. Voids anywhere along the impurity column intercepted by the region of observation would also cause spurious results. Finally, accidental Li doping in a layer parallel to (below or above) that in which measurements are taken would also cause erroneous results. All of these factors caused difficulty in the early stages of the experiment. However, the data quoted above were taken after considerable experience had been gained, and reasonable precautions were taken to avoid these pitfalls.

It is gratifying to observe, that in spite of the obvious complexity of the behavior of Li in rutile, highly reproducible and significant data may still be obtained. It seems likely that the activation energy observed, 0.330 eV, is characteristic of the rutile crystal, and is not likely to change significantly when more perfect crystals are available. The values obtained for D_0 , however, probably are somewhat lower than those characteristic of a pure crystal.

Weiser² has proposed a "model" to account for the behavior of interstitial impurities in Ge and Si. It appears likely that similar, though somewhat more complicated, calculations would account for the behavior of Li in rutile. The extreme sensitivity of Li diffusion to lattice strain might be explained qualitatively as follows: In Weiser's formulation of the interstitial diffusion problem in Ge and Si, the energy of an impurity ion at any point in the lattice is divided into positive and negative parts. The negative part results primarily from the electronic polarization of the lattice, due to the charge on the impurity; the positive term is predominantly due to overlap of the electron clouds of the Li^+ and the host atoms. (The situation is complicated somewhat by electrostatic (monopole) forces in a crystal such as TiO_2 with partially ionic character, but inclusion of these forces probably would not change the major conclusions.) The attractive forces are quite long range in nature, while the repulsive forces can be approximated fairly well by a Born-Mayer potential, which is very short range. The activation energy for diffusion is given by the difference between the total energy at the equilibrium position and that at the saddle point between two equilibrium positions. Because of the difference in the effective range of these forces, a minimum in the diffusion activation energy generally

⁷ N. E. Farb, O. W. Johnson, and P. Gibbs (to be published).

will occur, for an impurity radius such that the attractive and repulsive potentials are of comparable magnitude. Such a minimum apparently occurs in Ge for ions with a radius of approximately 1 Å, which corresponds rather closely to that of Cu (0.96 Å). The activation energy for the diffusion of Cu in Ge is 0.33 eV or less.¹ The diffusion activation energy for Li, which has a considerably smaller ionic radius (0.62 Å) is approximately 0.5 eV. The situation may be qualitatively similar in rutile with the minimum activation energy occurring at a somewhat smaller ionic radius. If the ionic radius of Li corresponds roughly to such a

minimum in rutile, any lattice strain would be likely to increase the diffusion activation energy. This also would account for failure to detect diffusion of Na⁺ (ionic radius 0.97 Å). Also, the difference in saddle-point configuration due to the anisotropy of rutile explains, at least qualitatively, the observed difference in diffusion rates parallel and perpendicular to the C axis.

The ease with which diffusion activation energy can be measured in this material and the extreme mathematical simplicity of the data analysis suggests that this system may be a very useful one for purposes of comparison with theory as it is developed.

Electrons in Bi-Sb Alloys

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Galvanomagnetic and thermoelectric measurements have been performed on doped and undoped Bi₈₅Sb₁₅-alloy single crystals. The thermal gap, obtained from the temperature variation of resistivity on high-purity *n*- and *p*-type samples, is 0.024 ± 0.003 eV, a significantly larger value than the previously measured maximum gap (0.014 eV) for this system. Hall data on Te-doped samples indicate that two Te atoms must be added to the crystal to add one additional free electron. Transport properties have been analyzed for Te-doped samples at 20 °K, using a multivalley conduction band. The magnitudes of the Seebeck and Hall coefficients indicate that most of the electrons must reside in three (not six) bismuth-like tilted ellipsoids. However, the lack of agreement between experiment and calculations based on the three-ellipsoid model for the ratio $\rho_{33,11}:\rho_{33,33}$ suggests the possible existence of a small number of electrons in an additional electron ellipsoid along the trigonal axis.

INTRODUCTION

THE thermoelectric and thermomagnetic properties of Bi-Sb alloys have recently received considerable attention.¹ However, little has been done in characterizing the basic band structure and transport properties of these alloys, nor have they been used extensively to understand the basic properties of bismuth.^{2,3} By performing transport measurements on doped and undoped Bi₈₅Sb₁₅ alloys, our purpose was to ascertain (1) the value of the thermal gap, (2) the number of Te atoms required to produce one additional free electron, (3) the valley multiplicity of the conduction band, and (4) the electron mobility tensor components. Conclusions based on resistivity, Hall and Seebeck coefficient data were checked against magneto-resistance data.

¹ G. E. Smith and R. Wolfe, *J. Appl. Phys.* **33**, 841 (1962); R. Wolfe and G. E. Smith, *Appl. Phys. Letters* **1**, 5 (1962); R. Wolfe, *Semicond. Prod.* **6**, 23 (1963); C. F. Gallo, B. S. Chandrasekhar, and P. H. Sutter, *J. Appl. Phys.* **34**, 144 (1963); S. R. Hawkins, J. H. Harshman, and G. M. Enslow, *Bull. Am. Phys. Soc.* **7**, 621 (1962).

² H. Jones, *Proc. Roy. Soc. (London)* **A147**, 396 (1934); D. Shoenberg and M. Z. Uddin, *ibid.* **A156**, 687 (1936); N. Thompson, *ibid.* **A155**, 111 (1936); **A164**, 24 (1937); V. Heine, *Proc. Phys. Soc. (London)* **A69**, 513 (1956).

³ A. L. Jain, *Phys. Rev.* **114**, 1518 (1959).

BACKGROUND—BISMUTH

The semimetallic properties of bismuth are caused by slightly overlapping electron-hole bands. The conventional model is represented by a single-hole band on the trigonal axis with a density of states effective mass of 0.16 m_0 , overlapping three- or six-electron ellipsoids located on the binary axes, but tilted slightly out of the basal plane. Many other more complicated models have been proposed because a vast and somewhat confusing amount of information has been published on the band structure and electrical properties of bismuth. However, there now appears to be relatively consistent agreement on the values for the effective masses of electrons on the Fermi surface. Further verification concerning the exact number of equivalent electron constant energy surfaces has been impeded by recent and often contradictory observations relating to the total electron concentration and the magnitude of the direct optical-band gap between the electron-band minimum and the valence band. The present situation is summarized in Table I where α_1 , α_2 , and α_3 are the eigenvalues of the reciprocal effective mass tensor; $\langle m \rangle / m_0 = (\alpha_1 \alpha_2 \alpha_3)^{-1/3}$ is the density of states effective mass for a parabolic band, E is the Fermi energy, E_0 is

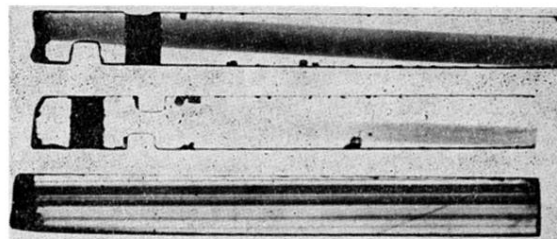


FIG. 1. Li-doped rutile single crystals.