Self-Diffusion in Germanium*

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An accurate determination of the self-diffusion coefficient in germanium has been obtained. In the temperature range 766–928°C, it is represented by $D = 7.8 \exp(-68\,500/RT)$ cm² sec. The probable errors in the frequency factor and activation energy are ±3.4 cm²/sec and ±0.96 kcal/mol, respectively.

INTRODUCTION

MEASUREMENTS of the diffusion of a number of impurities in germanium have been made in several laboratories.[1] A preliminary value of the self-diffusion coefficient in germanium has been reported[2]; however, in order to understand diffusion processes and their relationship to thermal imperfections, we have undertaken a more accurate determination.

It is interesting to consider the spectrum of activation energies reported for the diffusion of various elements in germanium. The elements appear to separate themselves into two distinct groups, those with activation energies near or less than 1 ev and those with activation energies greater than 2 ev. Among the former one finds lithium (0.5 ev) and copper ($<$0.5 ev)[3] and nickel ($<$1.0 ev).[4] These may be contrasted to the well known substitutional impurities ($\sim$2.5 ev)[1] and to germanium itself (3 ev). Although it is uncertain whether diffusion in germanium takes place by simple interchange, by a ring mechanism, or is associated with thermal defects (vacancies and interstitialities), it seems probable that the members of the first group diffuse interstitially and those of the second by another defect mechanism. The first group is composed of atoms whose positions in the germanium lattice are ill-defined. If, for example, they are located in interstitial positions, they are not bound by the statistics governing the density of intrinsic lattice defects, but find four suitable nearest neighbor sites into which they may jump. Thus, the activation energy for interstitial diffusion would involve only the activation energy of motion of an atom (or ion) from one interstitial position to another. The absence of a term associated with the energy of formation of a defect could account for the observed relatively low activation energies for the diffusion of atoms of this group. Such a mechanism appears to be quite likely in the case of the extremely small lithium ion.[3] The higher activation energy for the diffusion of species of the second group, then, is in part attributable to the energy of formation of a lattice defect and the remainder is associated with the motion of this defect. If our analysis is correct, the self-diffusion coefficient should be related directly to the concentration and diffusion coefficient of the significant thermal imperfection.

EXPERIMENTAL

The basic experimental techniques were described in our previous communication.[2] The measurements were made possible by the use of a precision grinding machine.[5] This technique permits an analysis of the extremely small penetration of radiotracer into both faces of the thin specimens used.

The radioisotope used in the experiment is Ge^{71}, which was obtained from Oak Ridge in the form of GeO_2. Both stable Ge^{70} and Ge^{76} undergo an (n,γ) reaction in the pile. The resulting activities are 11.4-day Ge^{71} which decays by K-capture to stable Ga^{71} and 12-hr Ge^{77} which decays by β emission to As^{77}. The latter isotope is also radioactive, decaying in about two days by β emission to Se^{77}, which undergoes a short-lived isomeric transition.

The plating technique used[2] obviously does not distinguish between the two isotopes of germanium present; moreover, it was found subsequently that As^{77} was plated onto the specimens in sufficient quantity to be detectable at the time of sectioning. This fact was established by a plating experiment in which the bath mixture contained ordinary (non-radioactive) germanium dioxide plus a small quantity of As^{76}, a 27-hr isotope produced by neutron bombardment of an As_2O_3 target at Oak Ridge. It was found that, with the plating conditions reproduced, a considerable amount of radioarsenic was deposited upon test specimens.

The specimens, after preparation and electroplating, were placed upon quartz flats and sealed in Vycor tubes which contained an air atmosphere at about 10^{-5} mm pressure. Annealing was carried out in furnaces which were maintained within ±2°C of the desired temperature. After removal of the specimens from the

[1] W. C. Dunlap, Jr., Phys. Rev. **94**, 1531 (1954); J. A. Burton, Physica **20**, 845 (1954).
[2] Letaw, Slifkin, and Portnoy, Phys. Rev. **93**, 892 (1954).
[3] Fuller, Struthers, Ditzenberger, and Wolfstirn, Phys. Rev. **93**, 1182 (1954); C. S. Fuller and J. C. Severiens, Phys. Rev. **96**, 21 (1954).
[4] F.v.d. Maesen and J. A. Brenkman, Philips Research Rept. **9**, 225 (1954).
[5] Letaw, Slifkin, and Portnoy, Rev. Sci. Instr. **25**, 865 (1954).

furnaces and their tubes, their edges were ground off to a depth several times the expected mean penetration. The specimens were then weighed and sectioned and the residues were assayed.

Nineteen successful determinations of the self-diffusion coefficient were obtained. These data are presented in Table I. In Fig. 1, a typical penetration plot is reproduced. Several of the determinations, on the other hand, did not at first appear to be valid because of the presence of curvature in the penetration plots. It was suspected that the curves obtained were the sums of two exponentials; thus, that they could be rectified graphically. The lower asymptote to each curve was extrapolated to zero penetration. Values of specific activity taken from the extrapolations were subtracted from the corresponding experimental specific activities. The resulting normalized specific activities, when plotted against the squares of the penetration

TABLE I. Annealing temperatures and self-diffusion coefficients for germanium.

T (°C)	$1000/T$ (°K^{-1})	D (cm^2 sec^{-1})
927.8	0.8326	2.17×10^{-12}
927.3	0.8330	2.60×10^{-12}
921.8	0.8368	2.94×10^{-12}
918.6	0.8391	2.38×10^{-12}
918.6	0.8391	2.33×10^{-12}
916.2	0.8408	2.33×10^{-12}
898.5	0.8535	1.23×10^{-12}
875.9	0.8702	8.12×10^{-13}
875.9	0.8702	6.65×10^{-13}
863.6	0.8797	5.13×10^{-13}
845.0	0.8943	3.68×10^{-13}
845.0	0.8943	3.51×10^{-13}
842.2	0.8965	3.53×10^{-13}
827.4	0.9086	1.89×10^{-13}
827.4	0.9086	1.73×10^{-13}
813.8	0.9200	1.39×10^{-13}
806.1	0.9265	9.63×10^{-14}
788.6	0.9418	6.54×10^{-14}
766.2	0.9621	3.48×10^{-14}

depths, yielded straight lines characteristic of volume diffusion from a thin source on the surface. Experimental data and the constructions corresponding to this treatment for one case are shown in Fig. 2.

The success of the procedure outlined above suggested that the anomaly could be attributed to the penetration of a radioisotope which diffused more rapidly than germanium. In view of the presence of As[77] in the electroplating bath, it was surmised that this isotope was responsible for the curvature. In addition to confirming that As[77] is electrodeposited upon germanium under the conditions used, two further indications of its presence were found. A specimen after analysis, i.e., after removal of all of the Ge[71] activity and most of the foreign activity, was face-counted and it was found that sufficient activity remained for a half-life determination to be undertaken. This experiment led to a value of about 42 hr for the half-life of the impurity. Although there appears to be some question as to the half-life of As[77], the result obtained is in agreement with
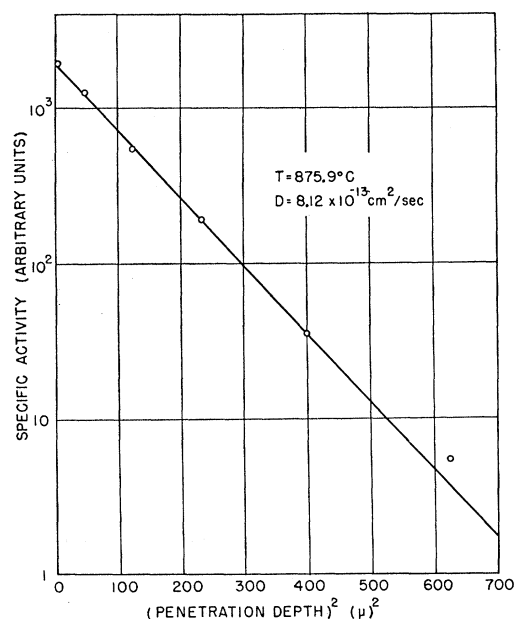

FIG. 1. Typical penetration plot. Mean penetration $[\sqrt{(Dt)}]$ approximately 10μ.

published data.[6] Furthermore, a conventional semi-logarithmic plot of the diffusion coefficients estimated from the extrapolated asymptotes versus the reciprocal of the absolute temperature yielded an activation energy which, while statistically uncertain, was in excellent agreement with Dunlap's value for the diffusion of arsenic in germanium.[1] It may be mentioned parenthetically that the solid state diffusion technique is applicable to the separation of small quantities of radioisotopes of different elements for the purpose of half-life determination when the half-lives are similar.
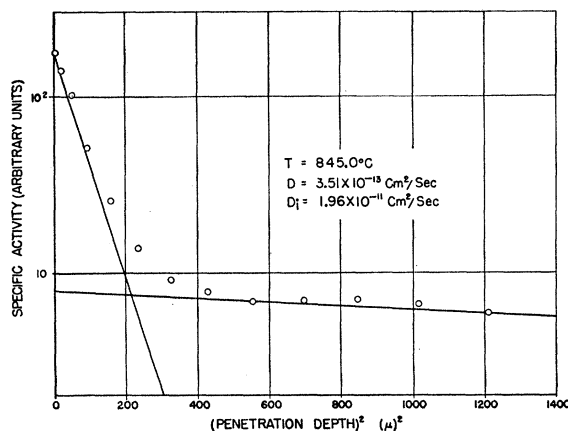

FIG. 2. Penetration plot showing both radioarsenic and radio-germanium diffusion. The extrapolated lower asymptote corresponds to the aresenic penetration and the difference line to germanium penetration.

[6] H. J. Watters and J. F. Fagan, Jr., Phys. Rev. 92, 1248 (1953); Nuclear Data, National Bureau of Standards Circular 499 (U. S. Government Printing Office, Washington, D. C., 1950).
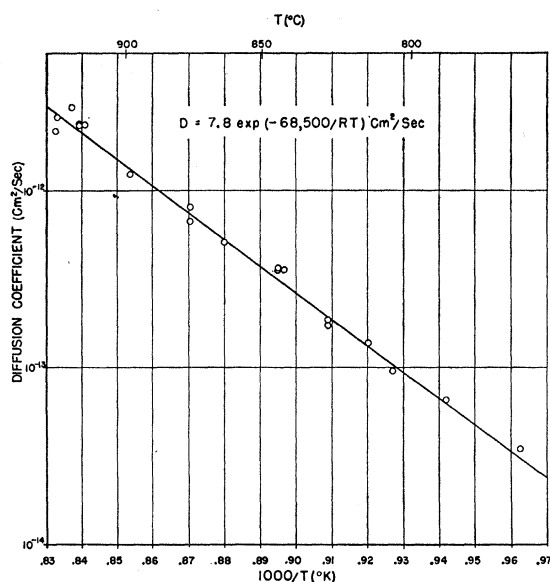
FIG. 3. Temperature dependence of germanium self-diffusion.

The data of Table I are plotted in Fig. 3. In the temperature range 766–928°C, the self-diffusion coefficient in germanium is represented by

$$D = 7.8 \exp(-68\,500/RT) \text{ cm}^2/\text{sec}.$$

The probable errors in frequency factor and activation energy, computed by the method of Birge,[7] were ±3.4 cm²/sec and ±0.96 kcal/mole, respectively.

DISCUSSION

The energy of formation of thermally introduced acceptors has been determined several times.[8] Probably the best of these is that of Mayburg and Rotondi as amended by Mayburg. The acceptor density as a function of temperature was found to be given by $N_A = 3 \times 10^{23} \exp(-46\,300/RT)$ cm^{-3}. Mayburg characterized these defects as vacancy-interstitial pairs. The identification of these acceptors as Frenkel defects has not been established conclusively. Among the points difficult to interpret are the annealing curves observed at temperatures greater than 516°C. If Frenkel defects were responsible for thermal conversion, one would expect a second-order process to govern the annealing rate. Although the data in this temperature range appear to be approximately rectified by a second-order treatment, certainly more than one rate constant is required for an accurate description of the process. At lower temperatures, the annealing process

was found to be extremely complicated. It was proposed that interstitials diffuse much more rapidly than vacancies in the temperature range below 516°C.

An alternative model to explain thermal conversion has been proposed by one of us.[9] In this case, Schottky defects are identified as thermal acceptors. The annealing process takes place by the formation of divacancies and clusters of higher order. This model appears to account well for the annealing data obtained by Mayburg.

Here, we have assumed that the defect responsible for thermal conversion is also associated with diffusion. For this reason, we assume, in keeping with the model described above, that the vacancy mechanism is involved in germanium self-diffusion. Other mechanisms such as simple interchange or ring rotation have been invoked.[10] A consideration of the directional nature of the covalent bond in this material indicates that an extremely high activation energy must be associated with either of those mechanisms in such a lattice. It seems reasonable to discard both the simple interchange and ring rotation mechanisms in this case.

Continuing for the moment to assume that the defect responsible for thermal conversion is also active in self-diffusion, we may calculate the diffusion coefficient of this defect. The diffusion coefficient of the defect, D_V, is just the self-diffusion coefficient divided by the fraction of lattice sites occupied by the defects. The density of lattice sites is $8/a^3$, where a is the lattice parameter. Using the defect density determined by Mayburg and Rotondi, we find that the desired fraction is $6.6 \exp(-46\,300/RT)$ defect per lattice site and that $D_V = 1.2 \exp(-22\,200/RT)$ cm²/sec. Under the assumption that the thermal defect is a Frenkel defect[8] and that the Schottky defect had been ruled out, Mayburg pointed out that during the time elapsing in a quenching operation, the Frenkel defects would annihilate by recombination if either vacancies or interstitials diffused at the rate D_V.[10] Thus, despite objections such as those raised above, he proposed a ring mechanism for self-diffusion in germanium. One can very simply avoid these difficulties by assuming that thermal defects are vacancies and can thereby develop a theory which is in agreement with diffusion data and also accounts for the annealing process in germanium.[9]

One is not by any means justified in applying deductions based on the properties of metals to germanium; however, the use of Zener's theory of the frequency factor[11] in the present case is of heuristic value. One cannot at this time estimate clearly the validity of

[7] R. T. Birge, Phys. Rev. 40, 207 (1932).

[8] See for example: C. Goldberg, Phys. Rev. 88, 920 (1952); L. Esaki, Phys. Rev. 89, 1026 (1953); R. A. Logan, Phys. Rev. 91, 757 (1953); S. Mayburg and L. Rotondi, Phys. Rev. 91, 1015 (1953); S. Mayburg, Phys. Rev. 95, 38 (1954). Effects reported by some of the earlier investigators are definitely attributable to copper. We do not consider copper to be a "thermal acceptor" nor do we classify conversion caused by copper as "thermal conversion."

[9] H. Letaw, Jr. (to be published).

[10] S. Mayburg, Phys. Rev. 98, 1134 (1955).

[11] C. Zener, J. Appl. Phys. 22, 372 (1951). Later work by G. H. Vineyard and G. J. Dienes [Phys. Rev. 93, 265 (1954)] and Huntington, Shirn, and Wajda [Phys. Rev. 99, 1085 (1955)] have placed the calculation of entropies of lattice defects upon a much firmer ground than heretofore. These theories have not been applied at this time to the diamond lattice.

Zener's assumption that the entire activation energy is included in the elastic strain energy associated with the jump of an atom from one site to the next. Because of the relative openness of the germanium lattice, one might surmise that elastic terms are actually less important than the contribution from the breaking of covalent bonds. We may, however, compare the value given by his theory to that obtained experimentally and thereby estimate the applicability of the theory to the present case. With these reservations, we may compute the frequency factor for self-diffusion in germanium by use of the expression

$$D_0 = \gamma a^2 \nu \, \exp(\Delta S/R) \text{ cm}^2/\text{sec},$$

where γ is determined by the geometry of the lattice and equals $\frac{1}{8}$, a is the lattice parameter (5.66 A),[12] ν is the (Debye) vibration frequency, and ΔS is the entropy of activation. The latter quantity may be estimated from Zener's relationship, $\Delta S = -\lambda H d(\mu/\mu_0)/dT$, λ being a numerical coefficient less than, but of the order of, unity, H the activation energy for self-diffusion, μ a suitable elastic modulus, and T the absolute temperature. The data of Fine[13] and of Baker, Slifkin, and Marx[14] on the elastic moduli of germanium and the specific heat data of Keesom and Pearlman[15] permit the computation of the theoretical entropy of activation and the pre-exponential part of the frequency factor, respectively. Assuming λ to be unity, the former is 9.0 cal/mole-deg and the latter, 3.0×10^{-3} cm²/sec. One arrives at the calculated frequency factor, 0.27 cm²/sec. The experimentally determined value of this quantity is 7.8 ± 3.4 cm²/sec. If it is assumed that an additional contribution to the entropy of activation arises from effects not accounted for in this treatment, then the experimental value may be fitted by adjusting the value of the entropy to 16 cal/mole-deg. Since large errors in the pre-exponential part of the frequency factor are unlikely, this may be termed the experimental entropy of activation.

Fuller and Severiens[3] found that the frequency factor in the case of diffusion of lithium ion in germanium is 2.5×10^{-3} cm²/sec. Although the agreement of this number and the pre-exponential part of the frequency factor calculated above is quite likely fortuitous, it leads to the conclusion that the motion of that small ion in the germanium lattice involves an entropy of activation which is essentially zero (under the assumption that ν for interstitial lithium is of the same order as that value used above). This may be taken as evidence that that ion diffuses by an interstitial mechanism. On the other hand, the frequency factors associated with the diffusion of the common substitutional impurities and self-diffusion in germanium are

of the order of ten. The fact that these are at least two thousand times greater than the calculated pre-exponential part of the frequency factor is a strong indication that a relatively large entropy of activation is involved in the diffusion of atoms of these elements.

If we assume that thermal acceptors are vacancies, then the energy of formation of a vacancy is about 2 ev.[8] Since the activation energy for self-diffusion should be the sum of the energy of vacancy formation and the activation energy for vacancy motion, we can estimate the activation energy for the motion of a vacancy to be about 1 ev. It would be impossible, of course, for lithium, copper, or nickel to diffuse by the vacancy mechanism if this estimate is correct in view of the fact that the activation energies in these three cases are less than one electron volt.

Taking the acceptor density as a function of temperature determined by Mayburg and Rotondi[8] as the density of vacancies in the lattice, we are then able to compute the entropy of formation of a vacancy, ΔS_f. The pre-exponential factor in their expression is just $N_s \exp(\Delta S_f/R)$, where N_s is the density of sites in germanium. From this expression, we find that the entropy of formation of vacancies in germanium is 4 cal/mole-deg. Since the activation entropy for self-diffusion is the sum of the entropy of formation of a vacancy and the entropy of activation for the motion of a vacancy, we obtain the latter by subtraction. The entropy of motion of a vacancy in germanium is estimated to be 12 cal/mole-deg.

The evidence presented here leads one to conclude that diffusion in germanium can occur by either interstitial or vacancy mechanisms but that self-diffusion probably occurs by the latter process. Data obtained in investigations of thermal conversion as well as studies of impurity diffusion appear to be consistent with these conclusions. Such mechanisms as simple interchange or ring diffusion are considered to be unlikely because of the nature of the germanium lattice. The simplicity and applicability of the concept has encouraged us to assume throughout that the defect responsible for thermal conversion is probably associated with self-diffusion in germanium.

ACKNOWLEDGMENTS

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[13] M. E. Fine, J. Appl. Phys. 24, 338 (1953).
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[15] P. H. Keesom and N. Pearlman, Phys. Rev. 91, 1347 (1953).