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Effect of Pressure on the Interstitial Diffusion of Lithium in Germanium to 45 kbar[†]

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We have measured the diffusion of lithium in germanium to pressures of up to 45 kbar using the p-n-junction-depth method for temperatures between 300 and 550 °C and by the ion-pairing method near room temperature. The data were analyzed assuming a single effective mechanism of diffusion with a temperature- and pressure-dependent activation energy and pre-exponential factor. The activation energy and volume at room temperature and atmospheric pressure are, respectively, $\Delta H = 10.8 \pm 0.3$ kcal/mole and $\Delta V/V_0 = 0.05 \pm 0.03$. The pressure and temperature coefficients of the activation volume are, respectively, $V_0^{-1}\, \partial\Delta V/\partial P = -(2.1 \pm 0.9) \times 10^{-3}$ kbar^{-1} and $V_0^{-1}\partial\Delta V/\partial T = (2.0 \pm 0.3) \times 10^{-4}\, {}^\circ\mathrm{K}^{-1}$. A small but nonzero specific heat of activation was found ($\Delta C_p/R = 0.9 \pm 0.3$) suggesting an increase of about one degree of freedom as the impurity moves from its equilibrium position to the saddle point. The small activation energy in comparison to that for self-diffusion, along with the near-zero activation volume, is indicative of pure interstitial diffusion.

I. INTRODUCTION

Since the advent of the Li-drifted Ge and Si detectors, there has been considerable interest in precise measurements of and the determination of the mechanisms for the diffusion of Li in Ge and Si. The diffusion of Li in Ge has been studied and measured by several different techniques. Fuller and Ditzenberger[1] measured the diffusion of Li in Ge and Si using the p-n-junction-depth method. Later, Fuller and Severiens[2] measured the diffusion of the same couples by applying the Einstein relation to Li$^+$-ion-mobility measurements in an electric field. Their technique was similar to the method of Haynes and Shockley[3] for the measurements of the drift mobility of minority carriers in semiconductors. Reiss, Fuller, and Morin[4] made a rather extensive theoretical study of the ion-pairing technique and then substantiated some of their findings with experimental measurements for the diffusion of Li in Ga-doped Ge. Much later Pratt and Friedman[5] using sectioning techniques in conjunction with conductivity measurements were able to determine impurity concentration profiles and diffusion coefficients for Li in Ge and Si. A good treatment of the various methods that have been used to study diffusion in semiconductors, along with a review of the results of these studies, may be found in a publication by Boltaks.[6]

Nachtrieb and co-workers[7–9] proposed, after making high-pressure self-diffusion measurements on several materials, that diffusion may obey a law of corresponding states along the melting curve and that one may expect the activation energy to scale linearly with the melting temperature. Since high-pressure diffusion measurements had not previously been made on a substance with a negative pressure coefficient of melting, Ge was chosen as an example to check this hypothesis.

High-pressure diffusion measurements were carried out in this investigation for the purpose of obtaining additional data relating to the mechanism of diffusion of Li in Ge. Experimental measurements were made for pressures of up to 45 kbar using the p-n-junction-depth method for temperatures between 300 and 550 °C, and by the ion-pairing method near room temperature.

II. METHOD OF ANALYSIS

The solution of the diffusion equation, appropriate for the p-n-junction-depth method, was shown to be the one-dimensional solution for a semi-infinite medium with a constant impurity source at the boundary. This solution, which is referred to as the complementary error function solution, is given by

$$N(x, t) = N_0 \operatorname{erfc}[x/(4Dt)^{1/2}] , \qquad (1)$$

where N_0 is the constant impurity concentration at the boundary, $N(x, t)$ is the impurity concentration after annealing for a time t at a distance x from the boundary, and D is the diffusion coefficient assumed to depend only on the anneal temperature and pressure. The diffusion coefficient D can be determined from Eq. (1) provided N_0 and at least one other value of $N(x, t)$ are known.

The p-n-junction-depth method consists of diffusing Li, which acts as a donor impurity, into p-type Ge with an acceptor concentration N_a. If $N_a < N_0$, a p-n junction will be formed at a position x_{pn}, where the Li impurity concentration $N(x_{pn}, t)$ equals N_a. Therefore, by measuring the p-n junction depth x_{pn} and knowing the surface concentration N_0 along with the acceptor concentration N_a, one can determine D from Eq. (1). Dunlap[10] made a comparative study of the merits of determining diffusion parameters through measurements of p-n junction depths associated with diffused impurities in germanium as opposed to radioactive tracer techniques. He concluded that the p-n-junction-depth method was at least as reliable as the tracer techniques he employed.

Ion pairing is the situation in which donor and acceptor ions are bound in pairs by Coulomb forces within the host crystal. An equilibrium equation for this process for Ga acceptors and Li donors is

$$\begin{array}{ccccc} \mathrm{Li(external)} \rightleftharpoons & \mathrm{Li}^+ & + & e^- & \\ & + & & + & \\ & \mathrm{Ga}^- & & e^+ & \\ & \downarrow\uparrow & & \downarrow\uparrow & \\ & \mathrm{Li}^+\mathrm{Ga}^- & & e^+e^- & , \end{array}$$

where $\mathrm{Li}^+\mathrm{Ga}^-$ stands for the ion pair in which the individual ions maintain their polar identity and the binding is ionic. However, because the binding is weak, this interaction is generally limited to temperatures below 300 °C. The ion-pairing method can be visualized by considering a Ge crystal doped with an equal number of mobile positive donor ions of Li, and stationary negative acceptor ions of Ga (compensated). The mean free path of the donors is of the order of an atomic spacing, whereas the distance between the relatively stationary Ga^- acceptors is several hundred lattice spaces. Under these conditions, the pairing rate is diffusion limited. For temperatures and donor concentrations such that the equilibrium pairing probability is high,[4] each positive ion will interact with one and only one negative acceptor ion. In this case the total rate of removal of free ions is proportional to the total number of remaining unpaired ions. This leads to an expression of the form

$$N_f(t) = N_{f0}\, e^{-t/\tau} , \tag{2}$$

where $N_f(t)$ is the number of free Li^+ ions, N_{f0} is the number at $t = 0$, and τ is the relaxation time.

It can be shown[11] that, to first order, the change in sample resistivity due to unpaired ions is proportional to the concentration of ionic scattering centers. This yields

$$\rho(t) - \rho(\infty) = bN_f(t) , \tag{3}$$

where $\rho(t)$ is the resisitivity at time t, $\rho(\infty)$ is the residual resistivity, and b is a constant for a measurement made at constant temperature and pressure. Substitution of Eq. (2) into Eq. (3) yields the result

$$\ln[\rho(t) - \rho(\infty)] = \ln(bN_{f0}) - t/\tau . \tag{4}$$

Therefore, the relaxation time τ may be determined from the time variation of the sample resistivity during pairing. Furthermore, since the pairing mechanism is diffusion limited one would expect the relaxation time to depend on the diffusion coefficient D. Reiss, Fuller, and Morin[12] have shown this relationship to be

$$D = cKkT/4\pi e^2 N_a \tau , \tag{5}$$

where K is the dielectric constant[13] of Ge, k is the Boltzmann constant, e is the electronic charge, T is the absolute temperature, N_a is the concentration of acceptors (also equal to the donor concentration), D is the diffusion coefficient for the mobile Li^+ ions, and c is a factor of order unity which depends on temperature, donor concentration, and the distance of closest approach of the Li^+ and Ga^- ions. The variation in c from unity for our measurements was less than 3% and c was therefore set equal to one. The technique of determining the diffusion coefficient from the resistivity relaxation time is called the ion-pairing method.

By applying the theory of absolute reaction rates[14] and equilibrium thermodynamics, the measured diffusion coefficient for a single mechanism takes the form

$$D_m(P, T) = fa_0^2\, \nu(P, T)\, e^{-\Delta G(P,T)/RT} , \tag{6}$$

where f is the product of a geometric and correlation factor, a_0 is the lattice parameter[15] at the temperature and pressure at which the pertinent measurement leading to the diffusion coefficient is made, $\nu(P, T)$ is the characteristic vibrational frequency of the diffusing ion, p is the pressure, T is the absolute temperature, R is the molar gas constant, and $\Delta G(P, T)$ is the Gibbs free energy of activation for the diffusion mechanism. The explicit dependence of the diffusion coefficient on pressure and temperature was obtained following the analysis of Weyland, Decker, and Vanfleet.[16] This analysis yields a pressure- and temperature-dependent activation energy and pre-exponential factor by expanding $\ln\nu(P, T)$ and $\Delta G(P, T)$ in Taylor's series about $P = 0$, and $T = T_0$. The coefficients in these expansions yield a pre-exponential factor $D_0(0, T_0)$, an activation energy or enthalpy $\Delta H(0, T_0)$, an activation volume ΔV, the pressure and temperature derivatives of the activation volume, and the specific heat of activation ΔC_p. In the evaluation of the diffusion parameters, γ, κ, $\partial\kappa/\partial P$, $\partial\kappa/\partial T$, β, and $\partial\beta/\partial T$ were assumed known and taken equal to 0.7, 1.381×10^{-3} kbar^{-1}, -8.29×10^{-6} kbar^{-2}, 4.12×10^{-7} kbar^{-1}deg^{-1}, 1.125×10^{-4} deg^{-1}, 2.79×10^{-7} deg^{-2}, respectively,[17] where γ is the Grüneisen constant, κ is the isothermal compressibility, and β is the volume coefficient of thermal expansion.

III. EXPERIMENTAL

A. p-n-Junction-Depth Method

Single-crystal germanium, gallium doped to a concentration of 1.8×10^{16} atoms/cm^3, was sliced into wafers approximately 3 mm thick by means of a Laser Technology wire saw. These wafers were lapped to a 600-grit finish using silicon-carbide paper on a plate-glass surface. The wafers were then etched in CP-4, a solution consisting of 40% HF, 40% H_2O_2, and 20% H_2O, for approximately 1 min. This etch removed about 0.003 cm of material from all surfaces. Cylindrical pellets, 0.35 cm in diameter, were then cut from the wafers by means of an Elox electric-discharge machine tool. These pellets were subjected to another etch cycle and stored in polyethylene vials. Lithium dispersed in petrolatum was deposited on one end of each sample pellet just prior to the diffusion anneal. It was applied by heating the germanium to 150 °C on a hotplate and applying small amounts until the melted dispersion just covered the top surface of the pellet. The samples were then quenched to room temperature by placing them on a cool block of aluminum.

The high-pressure diffusion anneals were carried out with the use of a 600-ton-capacity-ram tetrahedral-anvil press as described by Hall.[18] The samples were annealed in a hydrostatic cell[19] contained in a pyrophyllite tetrahedron, 3.2 cm on an edge, using 100 000-cs silicone fluid as the pressure-transmitting medium. After placing a sample in the hydrostatic cell and increasing the pressure, the temperature was then raised to the anneal temperature by passing current through the internally contained thin-walled-inconel-tube furnace. The anneal temperature was monitored by a chromel-alumel thermocouple and was regulated by means of a servo-control system[20] to within ±0.03 °C over the period of the anneal. The small-capacity furnace was heated to the anneal temperature and under control in less than 3 min and the cooling time was less than 15 sec.

Pressure calibration of the hydrostatic cell at elevated temperature involves calibration at room temperature plus a difficult to determine correction due to heating. The room-temperature calibration[16] was made using the well known polymorphic phase transitions, Hg I-I, Bi I-II, and Tl II-III. This calibration was then corrected for heating effects using the measurements of Candland, Decker, and Vanfleet.[21] This correction, although quite uncertain, amounted to 7 kbar for a temperature increase of 500 °C.

The annealed samples were then cleaned, mounted with wax on a steel grinding block, and lapped parallel to the cylindrical axis on wet 600-grit silicon-carbide paper until the ground surface intersected the original plated surface at approximately its center. The ground surface was then further polished with a 5-μ alumina-in-water slurry to a mirror finish. The position of the p-n junction was identified by reverse bias, pulse plating[22] the p-type region with copper. The p-n junction depth was determined as the average distance from the original plated surface to the p-n junction, as measured using a traveling microscope. This distance was typically 0.05 ± 0.002 cm, with the major uncertainty being in the position of the original surface.

B. Ion-Pairing Method

Germanium rods ($6.23\times0.77\times0.75$ mm), gallium doped to a concentration of 1.8×10^{16} atoms/cm^3, were cut from one of the previously prepared wafers. These samples were completely coated with the lithium dispersion in petrolatum and diffusion annealed in argon for $2\frac{1}{2}$ days at 249 °C. This diffusion anneal was for the purpose of compensating the sample. After this anneal the samples were thoroughly cleaned in acetone and distilled water to remove any lithium from the surface. Electrical leads consisting of small tubes of copper foil were fit over the ends of the crystal and indium soldered to the germanium. These leads served as the electrical contacts for the joule heating of the rods and also for the resistivity measurements. The germanium rod, along with a thermocouple, was embedded in polyethylene and inserted in a pyrophyllite tetrahedron.

Measurements of the relaxation time were made by heating the sample to approximately 200 °C to disassociate the ion pairs, and then quenching to the temperature of the press. The change in sample resistivity vs time was measured by maintaining a constant current through the sample and measuring the change in voltage across the sample with a time-base recorder. The relaxation time for ion pairing in our samples at room temperature was almost too short to measure by this method, therefore, the press was cooled to temperatures as low as 18 °C by stacking blocks of dry ice on top of it.

IV. RESULTS

The calculation of the diffusion coefficient using the p-n junction depth method presupposes a knowledge of N_0 from Eq. (1), where N_0 represents the constant concentration of Li impurities externally supplied and dissolved in the Ge at the boundary. The concentration of Li at the boundary is therefore limited by the solid solubility of Li in Ge at the temperature and pressure of the diffusion anneal. In an attempt to determine the effect of pressure on the solubility of Li in Ge, the atmospheric pressure results of Pell[23] and of Reiss and Fuller[24] were fit to a slightly modified equation derived by Thurmond and Struthers[25] which is given by

$$S(P,T)=S_0\,e^{-1.2\,(1-T_{\mathrm{Li}}/T)}\,e^{-7900/T}\,\left(1-e^{-4050\,(1/T-1/T_{\mathrm{Ge}})}\right), \tag{7}$$

where $S(P, T)$ is the temperature- and pressure-dependent solid solubility of Li in Ge, S_0 is a constant equal to 7.31×10^{22} atoms/cm^3, T_{Li}, and T_{Ge} are the pressure-dependent absolute melting temperatures of Li and Ge, respectively. Equation (7), in conjunction with the experimental fusion curves of Li and Ge, predicts a variation of less than 10% in $S(P, T)$ for pressures to 50 kbar in the temperature range of this experiment. A limited experimental study of the solubility indicated that the pressure variation in $S(P, T)$ in the range 0–50 kbar and 300–525 °C was less than the experimental uncertainty. Therefore, N_0 was taken as the empirical solubility of Li in Ge as represented by Eq. (7).

To substantiate that the proper boundary conditions had been imposed for the solution of the diffusion equation, a series of p-n junction depths were measured for different anneal times while maintaining the temperature and pressure constant. It can be seen that if Eq. (1) represents the correct form for the concentration profile for the diffusion of Li in Ge for these measurements, the p-n junction depth must be proportional to the square root of the corresponding anneal time since all other parameters in Eq. (1) are constant. The results of these measurements, which were made at 377 °C and atmospheric pressure, are shown in Fig. 1. A similar plot was made for these data, using the assumption of a δ-function source, and no correlation was found.

Figure 2 shows a typical curve for the resistivity change due to ion-pairing in a Li-compensated Ga-doped-Ge sample immediately after quenching from 200 to 22.1 °C at 14.4 kbar. It should be noted that the curves, of which Fig. 2 is typical, show some curvature as opposed to the theoretical result of Eq. (4). This curvature is probably due to a slight decrease in temperature during the measurement and yields an uncertainty in the measured diffusion coefficient of about ±35%.

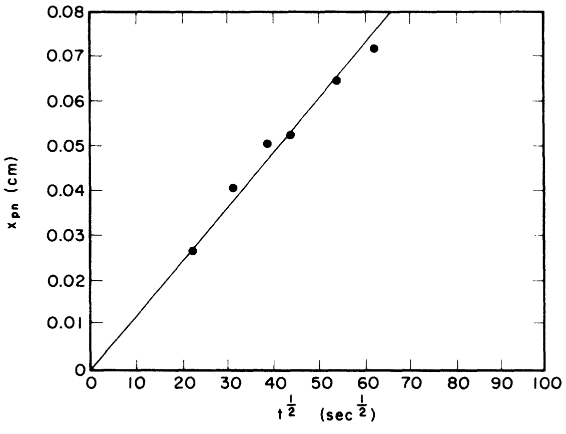

FIG. 1. Variation of the p-n-junction depth with the square root of the anneal time for the diffusion of Li in Ge at atmospheric pressure and 377 °C.

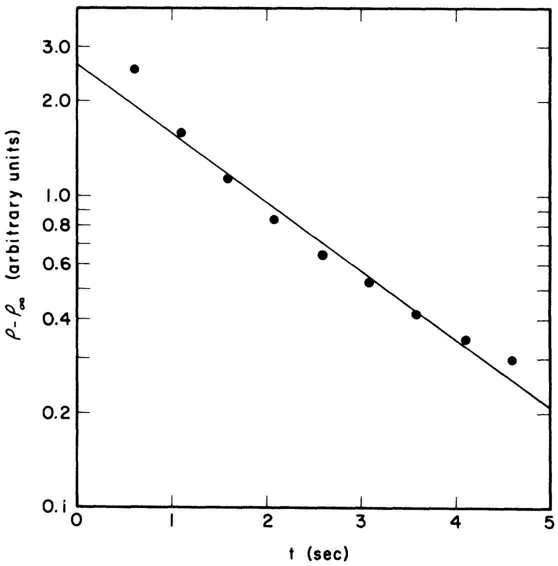

FIG. 2. Typical variation of the resistivity change with time as the result of ion pairing, measured at 22.1 °C and 14.4 kbar after quenching from 200 °C.

The measured diffusion from the ion-pairing and p-n-junction methods can not be compared directly because the diffusion coefficients from the ion-pairing experiment were measured at the anneal temperature and pressure, whereas the p-n-junction-depth measurements were made at ambient after the high-pressure anneal. Therefore, the diffusion constants from the ion-pairing experiments were corrected by the ratio $a_0^2(0, T_0)/a_0^2(P, T)$ so as to correspond to the p-n-junction-depth measurements. The measured diffusion coefficients from the p-n-junction-depth method along with the corrected ion-pairing measurements were then fit by a least-squares technique to Eq. (6) using the method of Weyland *et al.*[16] The calculations yielded the diffusion parameters D_0, ΔH, $\Delta V/V_0$, $V_0^{-1}\,\partial\Delta V/\partial P$, $V_0^{-1}\,\partial\Delta V/\partial T$, and $\Delta C_p/R$, all at $T = T_0 = 25$ °C and $P = 0$. These values along with values for $D_0(P, T)$, $\Delta H(P, T)$, and $\Delta V(P, T)/V_0$ at selected pressures and temperatures are given in Table I along with an uncertainty for each.

The isobaric variations of $\log_{10}D$ with reciprocal temperature are shown in Fig. 3. The data points for pressures of 1 bar and 35 kbar show the typical scatter in the data compared with the best fit curves of Eq. (6).

Figure 4 gives $\log_{10}D$ vs P along selected isotherms. These curves come directly from the computer fit of Eq. (6) with the relative scatter in the measurements being similar to that in Fig. 3.

TABLE I. Measured parameters for the diffusion of Li in Ge.

(P, T) (kbar, °K)	D_0 (10^{-4} cm^2/sec)	ΔH (kcal/mole)	$\frac{\Delta V}{V_0}$	$\frac{1}{V_0}\frac{\partial \Delta V}{\partial P}$ (10^{-3}/kbar)	$\frac{1}{V_0}\frac{\partial \Delta V}{\partial T}$ (10^{-4}/°K)	$\frac{\Delta C_p}{R}$
(0, 298)	7.3 ± 2.8	10.8 ± 0.3	0.047 ± 0.029	−2.1 ± 0.9	2.0 ± 0.3	0.91 ± 0.29
(0, 600)	17.8 ± 2.8	11.6 ± 0.3	0.107 ± 0.029			
(0, 800)	31.9 ± 2.8	12.4 ± 0.3	0.146 ± 0.029			
(50, 298)	1.5 ± 2.8	9.7 ± 0.3	−0.058 ± 0.029			
(50, 600)	3.7 ± 2.8	10.6 ± 0.3	0.001 ± 0.029			
(50, 800)	6.7 ± 2.8	11.4 ± 0.3	0.040 ± 0.029			
(0, · · ·)[a]	13.0	10.7 ± 1.0				
(0, · · ·)[b]	25.0	11.8				
(0, · · ·)[c]	91.0 ± 4.6	13.1 ± 0.4				

[a] Fuller and Ditzenberger (temperature range 625–1125 °K), Ref. 1.
[b] Fuller and Severiens (temperature range 425–875 °K), Ref. 2.
[c] Pratt and Friedman (temperature range 575–675 °K), Ref. 5.

The pressure- and temperature-dependent activation energy for the diffusion of Li in Ge is displayed in Fig. 5. Finally, using the melting temperature T_m of germanium vs pressure measured by Vaidya, Akella, and Kennedy,[26] we have plotted $\log_{10}D$ vs T_m/T in Fig. 6.

V. DISCUSSION AND CONCLUSION

The experimental measurements were analyzed assuming a single mechanism of diffusion characterized by a pressure- and temperature-dependent activation energy and pre-exponential factor, following the analysis of Weyland *et al.*[16] This analysis, which considers all of the data simultaneously,

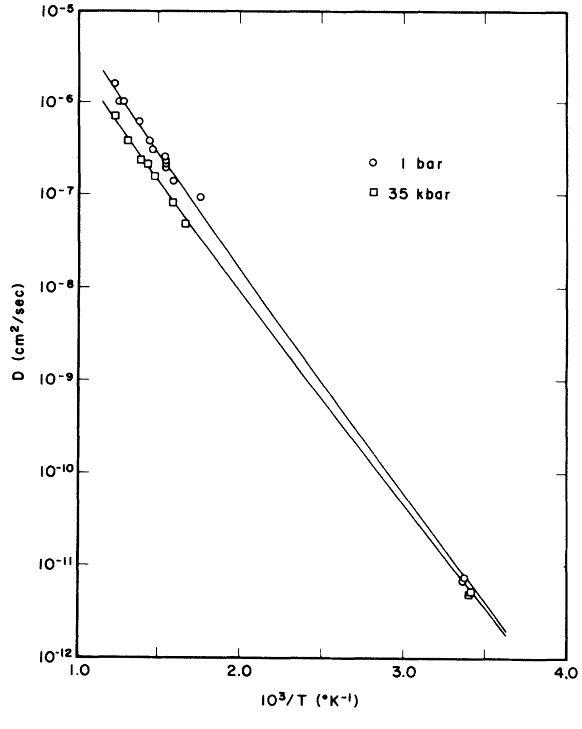

FIG. 3. Variation of the diffusion coefficient D with reciprocal temperature along selected isobars. Solid lines are the best-fit curves of Eq. (6) to all of the data.

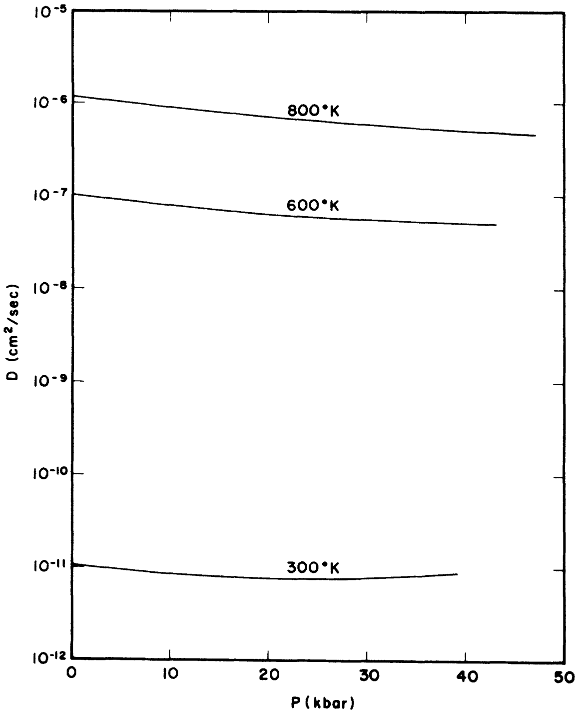

FIG. 4. Variation of the diffusion coefficients D with pressure along selected isotherms. Data points are not shown on the graph because no measurements were made isothermally. However it should be noted that the measured diffusion coefficients differed from those calculated from Eq. (6) by no more than ±20%. Solid lines represent the best-fit curves of Eq. (6) to all of the data.

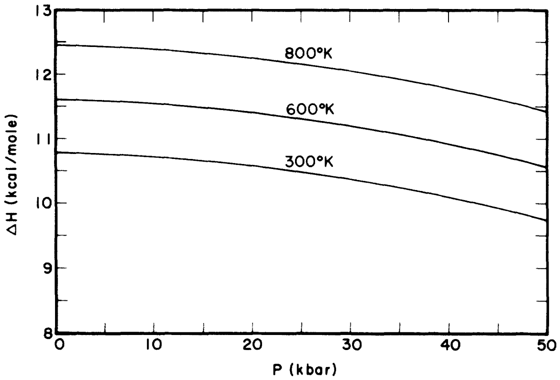

FIG. 5. Variation of the activation energy ΔH with pressure along selected isotherms. The uncertainty in these curves is the same as that shown in Table I and amounts to ±0.3 kcal/mole.

tends to smooth the scatter in the individual diffusion measurements and selects a best set of least-squares-fit parameters from the data. This is equivalent to making more measurements along a given isotherm or isobar in order to improve one's statistics. Thus one can obtain meaningful numbers for previously unmeasured and/or uncertain diffusion parameters such as ΔV, $\partial\Delta V/\partial P$, $\partial\Delta V/\partial T$, and ΔC_p. One finds, in fact, the fit of the data, as determined by the χ^2 test, is significantly worsened by taking the diffusion parameters outside of the range given for them in Table I. There may, however, be systematic errors resulting from the nonideal geometry of the high-pressure cell along with errors resulting from temperature and pressure calibration.

First consider the temperature uncertainty that may result from temperature gradients in the relatively short annealing furnace and the effect of pressure on the thermocouple emf. To get a feeling as to how a small error in temperature would change our results, we analyzed our data using the thermocouple emf correction of Getting and Kennedy[27] and compared the results with those when using the emf correction of Hanneman, Strong, and Bundy.[28] The difference in the two thermocouple emf pressure corrections amounted to as much as 5 °C, however, the effect on the diffusion parameters were well within the quoted uncertainties as given in Table I.

What was thought to be a more serious problem comes from the uncertainty in the pressure calibration. The calibration at room temperature is probably good to no more than ±2 kbar and to that we must add the rather large uncertainty in the hard-to-determine calibration correction due to heating of the high-pressure cell. The correction due to heating amounted to as much as 7 kbar and could conceivably be uncertain by as much as 50%. The data were analysed using a "worst-possible" pressure correction with the parameters again falling well within the uncertainties of Table I.

The nonzero value of ΔC_p is the "fly in the ointment" which results in the nonlinear Arrhenius curves of Fig. 3 along with the temperature dependence of ΔH as shown in Fig. 5. One is therefore reluctant to allow a nonzero value of ΔC_p in view of the long tradition of linear Arrhenius curves involving single-mechanism interactions. However, analysis of the data, when holding $\Delta C_p = 0$, results in an increase in χ^2 of about 25% which is indicative of a rather high statistical probability that ΔC_p is nonzero and positive. It should be noted that although our statistical uncertainty in ΔC_p includes an uncertainty due to both pressure and temperature one can not rule out the possibility that ΔC_p is nonphysical and results from some systematic error.

The comparison of our measured diffusion coefficients with those of Fuller and co-workers,[1,2] although being lower by about 20%, fall within the experimental uncertainty of the measurements. The differences in D_0 and ΔH can be attributed to the

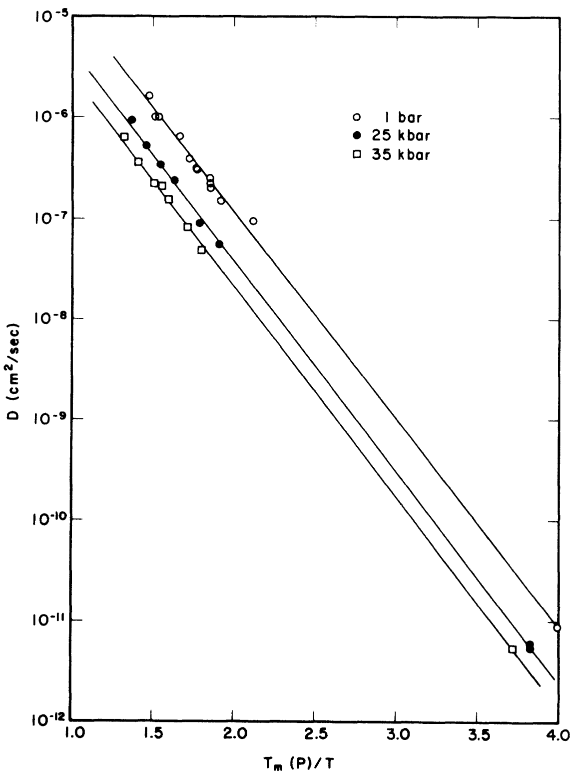

FIG. 6. Variation of the diffusion coefficients D with reciprocal of the reduced temperature along selected isobars.

method of analysis and the experimental uncertainties. Pratt and Friedman's[5] diffusion coefficients along with D_0 and ΔH are high in comparison to the other experimental measurements. This discrepancy probably results from the method of data analysis and the small temperature interval and number of measurements.

The small activation energy of 10.8 kcal/mole, compared to 68.5 kcal/mole for self-diffusion,[29] along with the small activation volume of 0.05 atomic volumes are both indicative of a purely interstitial mechanism.

Nachtrieb and co-workers,[7-9] on the basis of diffusion measurements to pressures of about 10 kbar, postulated a law of corresponding states for diffusion along the melting curve of the form

$$D(P, T) = D_0 e^{-bT_m(P)/T} , \tag{8}$$

where D_0 and b are constants independent of temperature and pressure, and $T_m(P)$ is the pressure-dependent melting temperature of the alloy. Nachtrieb along with Rapoport[30] have interpreted this relation to imply a proportionality between the pressure-dependent activation energy and the melting temperature. However, the validity of the Nachtrieb relation must depend on both the ratio $b' = \Delta H(P, T)/T_m(P)$ and on $D_0(P, T)$, through the frequency factor $\nu(P, T)$ and the entropy of activation

$$\Delta S(P, T) = \Delta S(0, T_0) - \frac{P\partial\Delta V}{\partial T} + \frac{\Delta C_p(T - T_0)}{T_0} + \cdots . \tag{9}$$

If the activation energy scales along the melting curve and is independent of temperature then b' is independent of pressure and the Nachtrieb relation would supposedly be satisfied. For the diffusion of Li in Ge one finds that the ratio b' varies by less than 5% for pressures to 50 kbar, however, $D_0(P, T)$ increases by a factor of 4, due primarily to the pressure dependence of $\Delta S(P, T)$ from Eq. (9). Thus we have the interesting result that, within the experimental uncertainty, the activation energy decreases proportionately with the negative melting curve of Ge as postulated, but that the Nachtrieb relation is not satisfied as a result of the large decrease in the entropy of activation with pressure. For the diffusion of Ag and Au in Pb one has a fortuitous situation in which b' increases by about 20% for pressures to 50 kbar, causing D to decrease, whereas, $D_0(P, T)$ increases by about the same amount, thus satisfying Eq. (8). For Cu in Pb, both b' and $D_0(P, T)$ produce an increase in the diffusion coefficient with pressure and Eq. (8) is not satisfied.

The theories of D_0 of Wert and Zener[31] and, more recently, of Weiser[32] are based on a temperature-independent activation energy at atmospheric pressure. Since the temperature dependence of $\Delta H(P, T)$ and $D_0(P, T)$ in our analysis comes primarily through ΔC_p, for comparison purposes, the data were analyzed for ΔC_p equal to zero. The results of the analysis gave 16.0×10^{-4} cm^2/sec and 11.4 kcal/mole for $D_0(0, T_0)$ and $\Delta H(0, T_0)$, respectively. The pressure dependence of $\Delta H(P, T)$ was the same as shown in Fig. 5 and was independent of temperature. The corresponding Arrhenius curves of Fig. 3 also become linear while the activation volume along with its pressure and temperature derivatives were virtually unaffected, falling well within the range shown in Table I. The values of D_0 for the hexagonal interstitial equilibrium sites as calculated from the Wert and Zener, and Weiser theories are 21.8×10^{-4} and 13.3×10^{-4} cm^2/sec, respectively. The fact that our measured effective value of D_0, for $\Delta C_p = 0$, falls midway between the values calculated from the Wert and Zener, and the Weiser theories does not allow one to differentiate between the theoretical formulations. It should be noted, however, that we used $\frac{1}{4}\sqrt{2}\,a_0$ for the distance between the hexagonal equilibrium sites as opposed to the path length of $\frac{1}{4}\sqrt{3}\,a_0$ used by Weiser. The values of D_0 from both theories increase by a factor of 2.45 if the tetrahedral interstices are the equilibrium sites. These results support Weiser's conclusion that the equilibrium sites for the diffusion of Li in Ge are the hexagonal interstices.

The nonzero positive value for the specific heat of activation of 1.8 cal/mole °K does not seem unreasonable in terms of the principle of equipartition of energy and the Dulong-Petit law. As discussed by Weiser,[32] there are two types of interstices in the diamond lattice. The tetrahedral (T sites) interstitials have four nearest neighbors at a distance of $0.433a_0$, and the hexagonal (H sites) interstitials have six-nearest neighbors at a distance of $0.415a_0$. Experimental and theoretical evidence suggests that, for the diffusion of Li in Ge, the equilibrium sites for the Li impurity are the H sites with T sites at the saddle points. Associated with each H site there are two T-site saddle points or two directions of escape from equilibrium. However, at the T-site saddle points there are four adjacent H-site equilibrium points and hence four directions of motion toward equilibrium. This suggests that there may be an additional degree of freedom available as the diffusing Li atom moves from its equilibrium position to the saddle point with an associated increase in the specific heat of the order of 2 cal/mole °K. This hypothesis could be verified if sufficiently accurate measurements for the diffusion of Ag or Au in Ge could be made. In this case ΔC_p would be negative since Ag and Au take the T sites as their equilibrium position and the argument would be reversed.

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

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

[3] J. R. Haynes and W. Shockley, Phys. Rev. 81, 835 (1951).

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

[5] B. Pratt and F. Friedman, J. Appl. Phys. 37, 1893 (1966).

[6] B. I. Boltaks, *Diffusion in Semiconductors* (Academic, New York, 1963).

[7] N. H. Nachtrieb, J. A. Weil, and A. W. Lawson, J. Chem. Phys. 20, 1189 (1952).

[8] N. H. Nachtrieb, H. A. Resing, and S. A. Rice, J. Chem. Phys. 31, 135 (1959).

[9] N. H. Nachtrieb, and A. W. Lawson, J. Chem. Phys. 23, 1193 (1955).

[10] W. C. Dunlap, Jr., Phys. Rev. 94, 1531 (1954).

[11] R. Kubo and T. Nagamiya, *Solid State Physics* (McGraw-Hill, New York, 1969), p. 359.

[12] Reference 4, p. 622.

[13] M. Cardona, W. Paul, and H. Brooks, J. Phys. Chem. Solids 8, 204 (1959).

[14] A. E. Stern and H. Eyring, J. Phys. Chem. 44, 955 (1940).

[15] R. N. Jeffery and D. Lazarus, J. Appl. Phys. 41, 3186 (1970).

[16] J. A. Weyland, D. L. Decker, and H. B. Vanfleet, Phys. Rev. B 4, 4225 (1971).

[17] O. L. Anderson, J. Phys. Chem. Solids 27, 547 (1966).

[18] H. T. Hall, Rev. Sci. Instr. 29, 267 (1958).

[19] H. R. Curtin, D. L. Decker, and H. B. Vanfleet, Phys. Rev. 139, A1552 (1965).

[20] D. L. Decker, Rev. Sci. Instr. 39, 602 (1968).

[21] C. T. Candland, D. L. Decker, and H. B. Vanfleet, Phys. Rev. B 5, 2085 (1972).

[22] R. Glang, J. Electrochem. Soc. 107, 356 (1960).

[23] E. M. Pell, J. Phys. Chem. Solids, 3, 74 (1957).

[24] H. Reiss and C. S. Fuller, J. Phys. Chem. Solids 4, 58 (1958).

[25] C. D. Thurmond and J. D. Struthers, J. Phys. Chem. 57, 831 (1953).

[26] S. N. Vaidya, J. Akella, and G. C. Kennedy, J. Phys. Chem. Solids 30, 1411 (1968).

[27] I. C. Getting and G. C. Kennedy, J. Appl. Phys. 41, 4552 (1970).

[28] R. E. Hanneman, H. M. Strong, and F. P. Bundy, in *Accurate Characterization of the High Pressure Environment*, edited by E. C. Lloyd (National Bureau of Standards, Washington, D.C., 1971).

[29] H. Portnoy, Jr., W. M. Letaw, and L. Slifkin, Bull. Am. Phys. Soc. 30, 13 (1955).

[30] E. Rapoport, J. Chem. Phys. 44, 3581 (1966).

[31] C. A. Wert and C. Zener, Phys. Rev. 76, 1169 (1949).

[32] K. Weiser, Phys. Rev. 126, 1427 (1962).

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Trends in the Nearest-Neighbor Distance: Elements and Binary Compounds

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Trends relating nearest-neighbor distance (d) in elemental materials and A^NB^{8-N} compounds to atomic number (Z), valence (z), and principal quantum number (n) of the outermost filled electron shell are reported. These trends can be described by simple functional relationships which are typically accurate to within a few percent. For elements, these relations are $dZ^{1/3}/n \cong$ constant for fixed z, and $d^{1/n}Z \cong \frac{4}{3}(Z-z+12)$ for fixed n. An analysis of the results based on a Fermi-Thomas model for the core electrons and a free-electron model for the valence electrons is given. The trend observed for the A^NB^{8-N} compounds is that $d\bar{Z}^{1/3}/\bar{n} \cong$ constant for a fixed cation species. This relation is used to construct a modified Mooser-Pearson plot which yields a complete separation of zinc-blende, wurtzite, and rocksalt structures.

I. INTRODUCTION

Crystal structure is perhaps the most fundamental property of a material and at the same time one of the most difficult to understand theoretically. Two rather different approaches have historically been used to discuss crystal structure: (i) the analysis of structural trends in terms of some scaling parameter such as ionicity; and (ii) the detailed computation of the lowest-energy structure