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DIFFUSION OF SILVER, COBALT AND IRON IN GERMANIUM*

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Abstract—Diffusion of Ag, Co and Fe in Ge are investigated by radiotracer techniques. We found that: (1) In most cases, the concentration varies as $\exp(-x/L)$ rather than the Gaussian or the error function as usually expected from Fick's (second) law. (2) The diffusivities of these elements in Ge are in the range of 10^{-6}–10^{-7} cm²/sec at temperatures around 800°C. The values are higher in low dislocation (less than 10^{3} pits/cm²) than in high dislocation (around 10^{5} pits/cm²) crystals. (3) The solubilities of Ag, Co and Fe in Ge are very low, in the range of 10^{-8}–10^{-9} in atomic fraction. (4) The activation energy of Co diffusion in Ge is about 1 eV, nearly the same as those of Ag, Ni and Fe diffusion as obtained by other workers.

It is suggested that the anomalous diffusion is due to a double stream process which is composed of free species and trapped ones. This trapping mechanism not only leads to a concentration varying approximately as $\exp(-x/L)$ but also offers reasonable explanations for many other experimental facts.

1. INTRODUCTION

FROM STUDIES of diffusion in solids, most of the results can be summarized as follows:

- (a) Diffusion follows Fick's law.
- (b) Diffusion of substitutional solutes can often be interpreted by a vacancy mechanism.
- (c) Diffusion constants for substitutional solutes are usually in the range of 10^{-9}–10^{-14} cm²/sec.
- (d) Diffusion of interstitial solutes, which can hop from one interstice to another, may be much more rapid.

In recent years, work by FULLER(1, 2) VAN DER MAESEN(3) and TWEET(4) on Cu diffusion in Ge gave remarkably different results. They found that:

- (a) Cu diffusion in Ge usually does not follow Fick's law.
- (b) It cannot be interpreted by a vacancy mechanism alone.
- (c) The diffusion constant is about 10^{-5}cm²/sec (700–900°C) which is a million times higher than those of Group III and V elements in Ge.
- (d) Diffusion is structure sensitive.
- (e) The activation energy for diffusion is small.

FULLER has speculated(1) that copper may diffuse at high temperatures as Cu^{+} or Cu^{0}, and assume the role of acceptor only at lower temperatures. FULLER and TWEET found, independently, the importance dislocations had for the diffusion. VAN DER MAESEN and BRENKMAN were led to the concept that both substitutional (Cu_s) and interstitial (Cu_i) atoms are present and are in a temperature dependent equilibrium,

$$Cu_i \rightleftharpoons Cu_s + Q$$

where the "thermochemically denoted Q" has a positive sign. They proved from their experiments that the Cu diffusion was non-Fickian under most conditions and gave the first analytical treatment of the diffusion.

FRANK and TURNBULL(5) then introduced the

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rôle played by vacancies in the mechanism of Cu diffusion in Ge. In crystals of very high dislocation density, as they conceived, vacancies are supplied and maintained in equilibrium by dislocations in the bulk. For Ge crystals relatively free from dislocations (say less than 100 etch pits/cm^2), they proposed a "dissociative mechanism". This mechanism has been used with some success to interpret the data on Cu diffusion and precipitation in Ge.(4, 6)

Besides the above two limiting cases, there is an intermediate one, corresponding to a medium high dislocation density (10^3–10^5 etch pits/cm^2). Since ordinarily Ge crystals have dislocation densities falling in this range, this intermediate case is the one usually observed. In this case, the concentration of vacancies and their generation rate from dislocations in the bulk may not be sufficient to maintain the equilibrium condition of $Cu_2 \rightleftarrows Cu_i + V$. When this occurs, Cu diffusion will not follow Fick's law. This can be seen easily from VAN DER MAESEN'S equations and is clearly shown in the figures of his paper.(3)

Stimulated by the previous work on Cu diffusion, the present author investigated the diffusion of Ag, Co and Fe in Ge. He found that Fick's law was also not followed in most cases of the diffusion studied. The dissociative mechanism which was considered satisfactory for Cu diffusion seems to be inadequate for interpreting our results. We consider that the diffusion of Ag, Co and Fe in Ge is a double stream process, one stream consisting of free species and another of trapped ones. The free species are probably interstitials. The trapped species include substitutionals and those having either loose or tight association with lattice defects (such as dislocations) and impurities. When a species hops from one trap to another trap, this is considered as the "diffusion of trapped species", and forms the slow stream. A species could switch now and then between the slow and the fast streams. This kind of exchange of species is characteristic of a double stream process.

As we shall show in this paper, the trapping mechanism can explain many experimental facts, particularly the exponential characteristic of concentration versus penetration. The trapping mechanism is more general than the dissociative mechanism in two respects: (a) In the dissociative mechanism, only the role of vacancies is considered. In the trapping mechanism, the effect of all kinds of traps including vacancies on diffusion is implied. (b) In the dissociative mechanism, the equilibrium condition: vacancy + interstitial $\rightleftarrows$ substitutional is assumed. In the trapping mechanism, this equilibrium condition is not necessary but is also not excluded. We suggest that other non-Fickian diffusion might also possibly be explained by the trapping mechanism.

2. EXPERIMENTAL

The Ge crystals used were of three grades: (a) high dislocation, HD $\sim 10^5$ pits/cm^2 (b) low dislocation LD $\sim 10^3$ pits/cm^2 (c) dislocation-free, DF < 100 pits/cm^2, supplied by Dr. A. G. TWEET of the General Electric Research Laboratory. All crystals were single crystals with resistivity around 40 ohm-cm.

Samples cut from HD crystals were about 0·6–1 cm long while those cut from LD and DF crystals were about 3 mm thick. The cross-sectional area was about 1·5 cm^2. All samples were ground to mirror polish on one face with a precision grinding machine.(9) They were first cleaned to remove surface contamination by LOGAN'S method(10) and then treated with Complexion III(3) to prevent diffusion from going around the sides and the back. A solution containing a radioactive isotope of the desired element was brushed over one face of the sample and dried in still air.

A resistance furnace was used for annealing. To facilitate quenching, the sample was not sealed in a Vycor tube but put in a molybdenum basket with the painted side facing down on a thin quartz plate. After annealing, the sample was slid onto an aluminum plate which conducts heat away very rapidly.

The remaining procedures are sectioning, weighing and counting as usually done in radiotracer techniques. Before the first sectioning, the edges or sides were ground off for several diffusion lengths around the sample to minimize the effect on counting of possible side diffusion. β-radiation was counted and the counting efficiency was about 20 per cent.

3. RESULTS

(a) *Silver diffusion*

Figs. 1 and 2 show the penetration curves (log C vs. x) of Ag diffusion in high dislocation and dislocation-free crystals of Ge respectively. We see that curves 2 and 3 of Fig. 1 are very good straight lines, i.e. $C = A(t) \exp(-x/L)$ where C is the concentration of the diffusing species. The surface concentrations are roughly proportional to time. Curve 1 shows a structure effect. In Fig. 2, curves (1, 2, 3) have two distinct parts, a sharply falling initial part and a very flat deeper part. The initial part represents possibly a substitutional diffusion

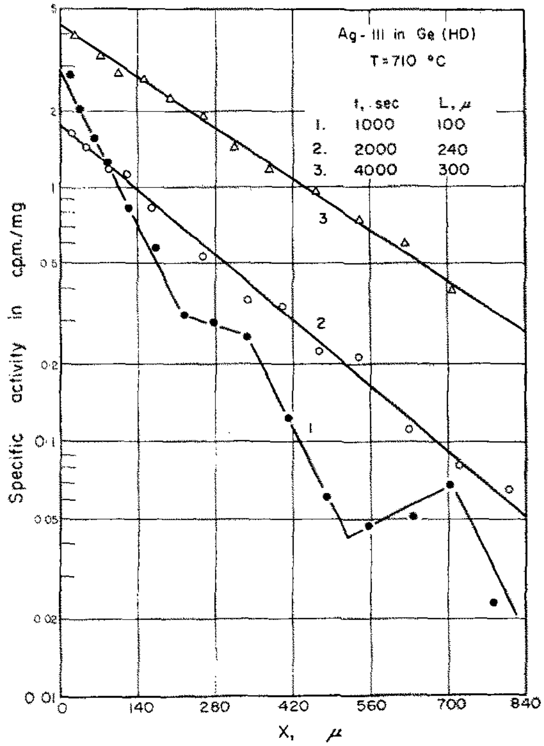

FIG. 1. Penetration curves of Ag diffusion in Ge (high-dislocation, HD).

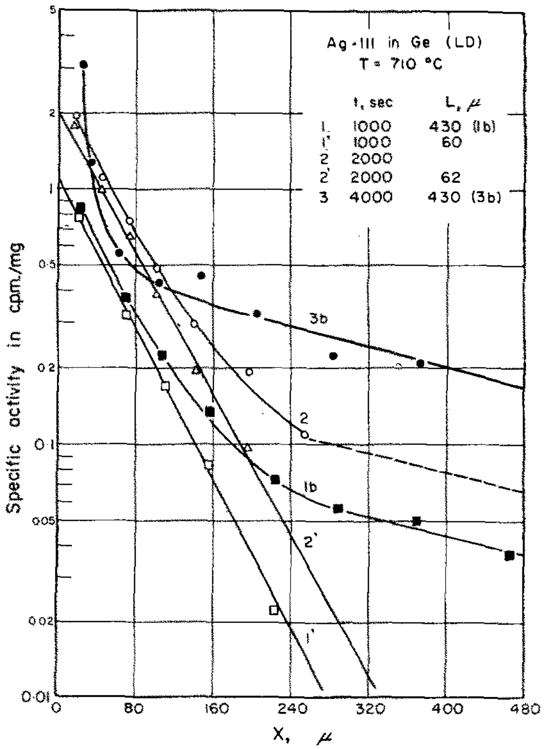

FIG. 2. Penetration curves of Ag diffusion in Ge (dislocation-free, DF).

which is related to the vacancies entering from the surface. However, in the bulk of a dislocation-free crystal, very few vacancies are available and therefore diffusion will be dominated by interstitials. This gives the flat part of the penetration curves.

We shall estimate the "apparent diffusivity" (to be defined in Appendix), which is about what one would obtain if one tried to fit square law penetration. From Fig. 1, for $t = 2000$ sec, $L = 240$ microns,

$$D_a = \frac{2L^2}{t} = \frac{2\times(2{\cdot}4)^2\times10^{-4}}{2000}$$

$$= 5{\cdot}8\times10^{-7}\ \text{cm}^2/\text{cm}.^*$$

For $t = 4000$ sec, $L = 300$ microns, we get $D_a = 2\times9\times10^{-4}/4000 = 4{\cdot}5\times10^{-7}$ cm²/sec. We may take the mean value,

$$D_a = 5\times10^{-7}\ \text{cm}^2/\text{sec}$$

as the diffusivity of Ag in HD Ge at 710°C. BUGAI has obtained D (computed from erfc function,)⁽¹¹⁾

$$D = 4{\cdot}4\times10^{-2}\exp(-23000/RT)$$

At $T = 710°\text{C}$, $D = 3\times10^{-7}$ cm²/sec, which is very close to our value.

In Fig. 2, the lower parts of curves 1 and 3 are very flat with $L = 430$ microns and have features very close to case (i) as described in the Appendix, According to equation (A5), the apparent diffusivity is given by,

$$D_a = \frac{(4{\cdot}3)^2\times10^{-4}}{1000} = 2\times10^{-6}\ \text{cm}^2/\text{sec}.$$

This value may be taken as the interstitial diffusion coefficient of Ag in Ge (at 710°C).

The ordinates in curves 1′ and 2′ of Fig. 2 represent the difference between the concentrations on the initial part of curves 1 and 2 and the straight line extrapolation (not shown) toward the surface from the deeper part of these curves. They (1′ and

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* Curves 1 and 2 have features very similar to case (iv), i.e. $A(t) = ct$ and $L = k\sqrt{t}$, in Appendix, hence formula (A1) is used for D_a.

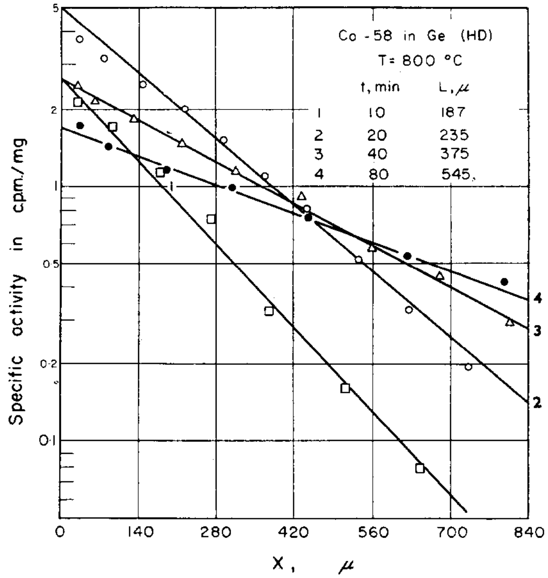

FIG. 3. Penetration curves of Co diffusion in Ge (HD, 800°C), log C vs. x.

2′) may be taken as the concentrations of substitutionals penetrating by vacancy diffusion from the surface. From them, we get,

$$D_a = \frac{36\times10^{-6}}{1000} = 3{\cdot}6\times10^{-8}\ \text{cm}^2/\text{sec}.$$

(Note: Curves 1′ and 2′ of Fig. 2 have the features of case (i) in Appendix. Hence formula (A5) is used here).

(b) *Cobalt diffusion*

Since Co^{58} has a half-life of 72 days and is claimed as "carrier-free", it is better suited for the study of fast diffusion. We have done much work on Co^{58} diffusion in crystals of Ge for different annealing times at three temperatures (750, 800 and 850°C). From Figs. 3–7, we get:

(a) In HD crystals, all penetration curves (log C vs. x) are straight lines (Figs. 3 and 6). The curves in Fig. 4 use the same data as used in Fig. 3 but are plotted as log C vs. x^2. It is very evident that they do not fit either gaussian or erfc function.

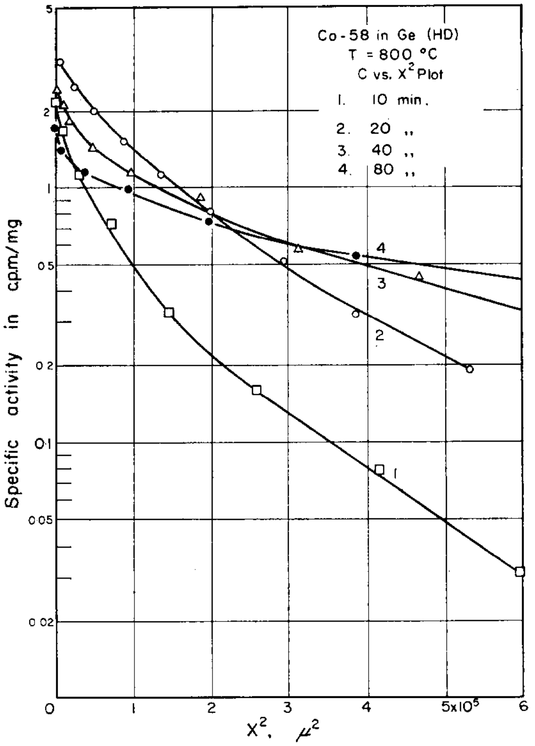

FIG. 4. Penetration curves of Co diffusion in Ge (HD,. 800°C), log C vs. x^2.

(b) In LD (CBS Hytron) crystals at 800°C, the penetration curves (Fig. 5) are straight lines with x^2. At 852°C, the penetration curves in LD crystals are straight lines with x (Fig. 7).

(c) By comparing Fig. 3 with Fig. 5 and comparing Fig. 6 with Fig. 7, we can see that the apparent solubility in HD crystals is much higher than that in LD crystal (the comparison between Figs. 6 and 7 is particularly striking) while the diffusivity in the latter is about 2–3 times that in the former.

From the penetration curves, we calculated the apparent diffusivity, D_a of cobalt in Ge to be 10^{-6}–10^{-7} cm²/sec in the range of 750–850°C. We obtain (Fig. 8),

$$D_a = 4{\cdot}4\times10^{-3}\exp(-20000/RT)$$

for Co diffusion in HD crystals of Ge, and

$$D_a = 0{\cdot}16\exp(-25800/RT)$$

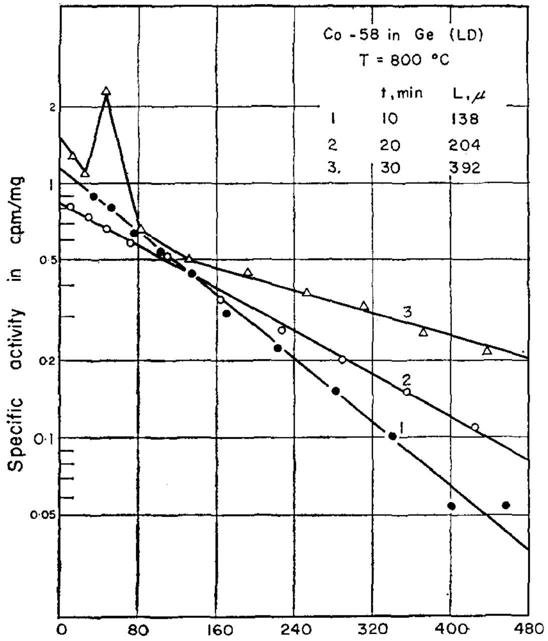

FIG. 5. Penetration curves of Co diffusion in Ge (low-dislocation, LD, 800°C).

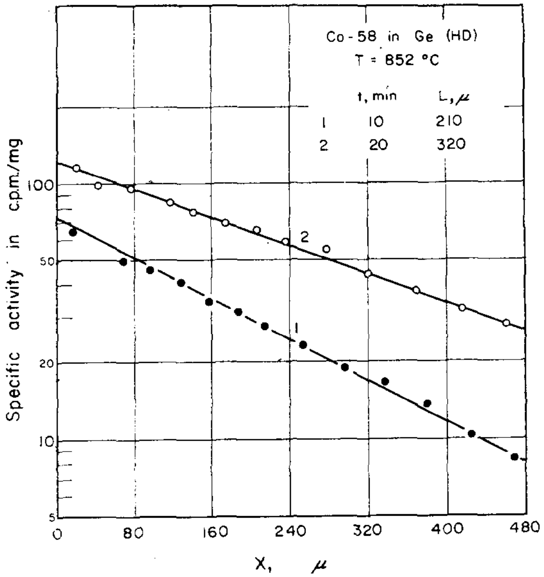

FIG. 6. Penetration curves of Co diffusion in Ge (HD, 852°C).

for Co diffusion in LD crystals of Ge (CBS Hytron). The values of activation energy are very interesting. For Ni diffusion in Ge,(12)

$$D_{\mathrm{Ni}} = 0{\cdot}8 \exp(-21000/RT)$$

From BUGAI's measurements on Fe and Ag diffusion in Ge,(11,13)

$$D_{\mathrm{Fe}} = 0{\cdot}13 \exp(-25000/RT)$$

$$D_{\mathrm{Ag}} = 4{\cdot}4 \times 10^{-2} \exp(-23000/RT)$$

All these activation energies are around 1 eV. This suggests that their diffusion mechanisms may be nearly the same.

(c) *Iron diffusion*

From our data (Figs. 9 and 10), we observed that,

(i) The points are more scattered than those shown in other figures for Ag and Co diffusion in Ge.

(ii) Some of the penetration curves are good straight lines, i.e. C varying as $\exp(-x/L)$. None of the curves has a shape like $\exp(-ax^2)$.

(iii) The maximum concentration is about 2×10^{13} atoms/cm^2 which is the same value as obtained by TYLER(14).

(iv) By comparing Fig. 9 (HD case) with Fig. 10 (LD case), we see no difference in maximum concentration and diffusion lengths. The diffusivity estimated from the diffusion lengths is about $(2{\cdot}3 \pm 0{\cdot}7) \times 10^{-7}$ cm^2/sec at 800°C.

The very low solubility of Fe in Ge and its strong chemical activity impose extreme difficulties in experimentation. Though the tracer measurement appears as one of the best, the results can be widely different in experiments by different workers because of many uncontrolled factors, such as the impurity contents of the tracer and in the crystal. For example, BUGAI obtained the solubility (S) and

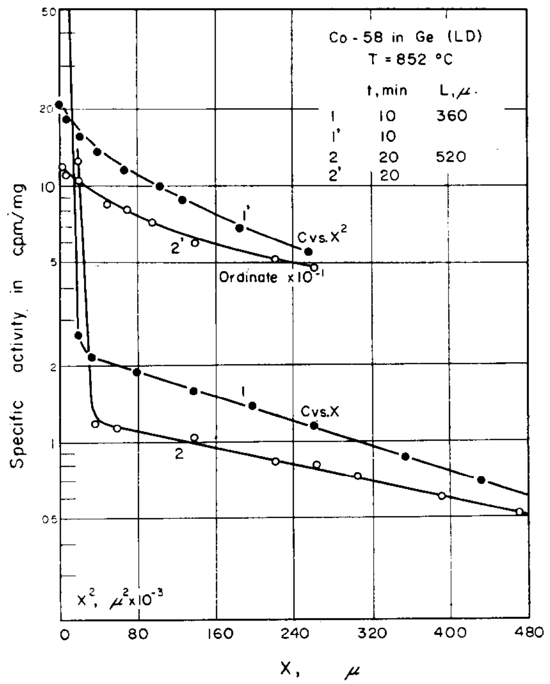

FIG. 7. Penetration curves of Co diffusion in Ge (LD, 852°C).

the diffusivity of Fe in Ge at 800°C as,⁽¹³⁾

$S = 10^{15}$ atoms/cm^2 = 50 times TYLER's value.⁽¹⁴⁾

$D = (1{\cdot}6 \pm 0{\cdot}6)\times 10^{-6}$ cm^2/sec = 6 times our value.

4. DIFFUSION MECHANISM

If a diffusion process is composed of two streams with different diffusivities and if there is an exchange of flow between them, then by the principle of continuity, we have (for one dimension),

$$\frac{\partial N_1}{\partial t} = D_1\frac{\partial^2 N_1}{\partial x^2} - K_1N_1 + K_2N_2 \tag{1}$$

$$\frac{\partial N_2}{\partial t} = D_2\frac{\partial^2 N_2}{\partial x^2} - K_2N_2 + K_1N_1 \tag{2}$$

These equations were first used by VAN DER MAESEN in dealing with Cu diffusion in Ge.⁽⁸⁾ Now, we can see that unless $K_1N_1 = K_2N_2$, Fick's law will not be followed.

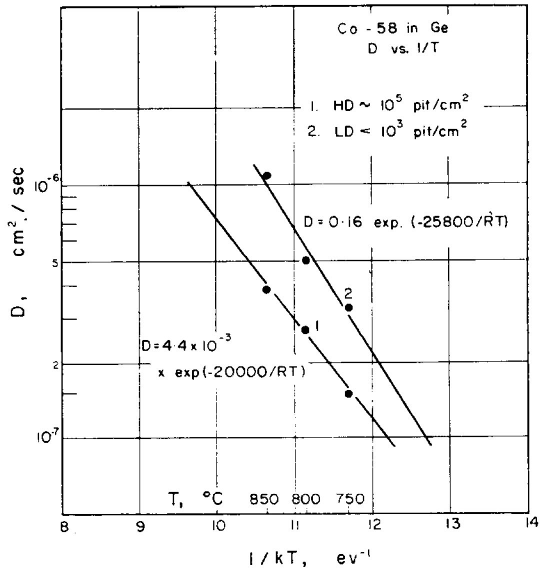

FIG. 8. Diffusivity vs. temperature of Co in Ge (HD).

One of the physical interpretations for a double-stream process is a trapping mechanism suggested by Prof. BARDEEN. We may conceive the double stream process as made of a running stream and a trapped stream. The running stream of free species probably interstitials, maintains a quasi-steady flow. During the course of diffusion, some of them may fall into traps. They will be held forever by deep traps but will be released in a short time from shallow traps. As long as the trapping rate is greater than the release rate, the concentration of the trapped species will build up with time. Because of the releasing action, the diffusion length of the running and the trapped streams will increase slowly with time. In the following, we shall give a simple mathematical treatment.

Let N_1, N_2 = concentrations of free and trapped species.

D_1, D_2 = diffusivities of free and trapped species.

K_1 = probability of each free species being trapped per unit time.

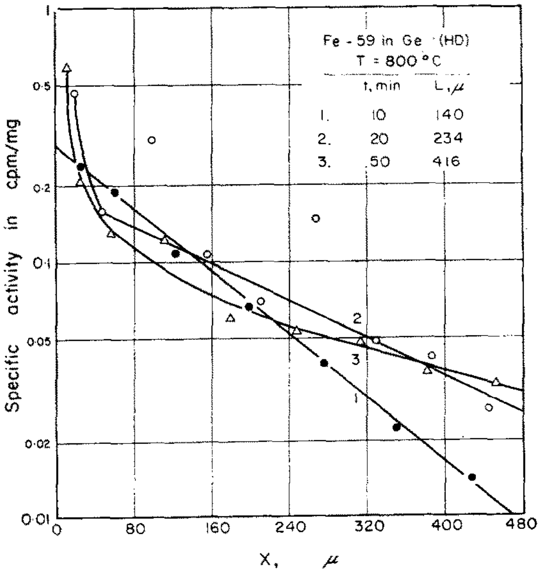

FIG. 9. Penetration curves of Fe diffusion in Ge (HD).

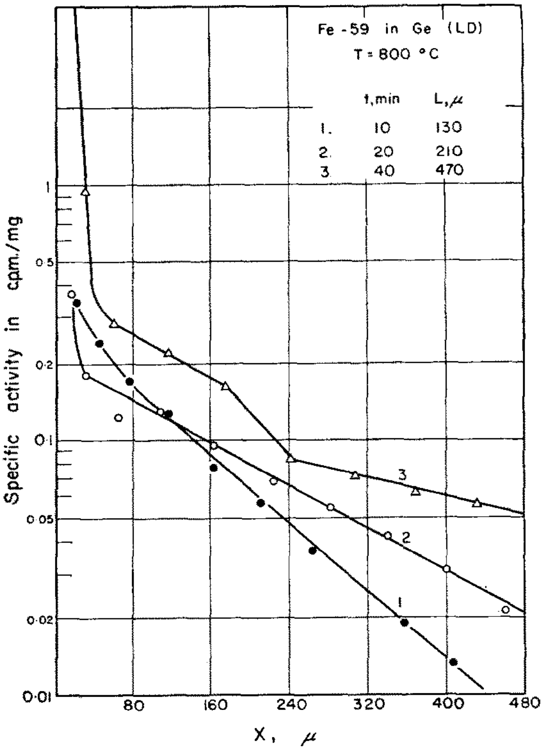

FIG. 10. Penetration curves of Fe diffusion in Ge (LD).

K_2 = probability of each trapped species being released per unit time.

We assume that,

$$K_1 > K_2$$

For simplicity of mathematical treatment, we take

$$D_2 = 0$$

We further assume that the stream of free species maintains a quasi-steady flow,

$$\frac{\partial N_1}{\partial t} = 0$$

The physical significance of $\partial N_1/\partial t = 0$ is as follows. We may consider N_1 to consist mostly of interstitials. As it is generally believed that the interstitials have very low solubility but rather great mobility, N_1 will reach its saturation value within a very short time after diffusion starts. Then, since the concentration is limited by the solubility, N_1 cannot grow with time. Shortly after the start of the diffusion, the process thus consists of the influx of the free species and trapping of them in the bulk at about the same rate.

(a) Dead trapping, $K_2 = 0$

The equations for N_1 and N_2 are:

$$\frac{\partial N_1}{\partial t} = 0 = D_1 \frac{\partial^2 N_1}{\partial x^2} - K_1 N_1 \tag{3}$$

$$\frac{\partial N_2}{\partial t} = K_1 N_1 \tag{4}$$

The solutions are:

$$N_1 = N_0 \exp(-x/L) \tag{5}$$

$$N_2 = K_1 N_0 t \exp(-x/L) \tag{6}$$

where

$$L = \sqrt{(D_1/K_1)} \tag{7}$$

We have to understand that K_1, the trapping probability is proportional to the concentration of the unoccupied traps. When the number of traps,

N_T is great, K_1 may be taken as a constant, and so also is the diffusion length L. If N_T is small, K_1 may decrease with time (because the number of unoccupied traps may decrease) and L will increase accordingly. When all traps are filled, equations (3) and (4) are no longer valid. Instead, we shall have,

$$\frac{\partial N_1}{\partial t} = D_1 \frac{\partial^2 N_1}{\partial x^2}$$

$$N_2 = N_T$$

The total concentration will be,

$$N_t = \frac{N_0}{2\sqrt{(\pi D_1 t)}} \exp(-x^2/4D_1 t) + N_T \qquad (8)$$

The resultant curve (N_t) will thus look like a gaussian when N_T is small (for example, in LD crystals), but will approach the $\exp(-ax)$ shape as N_T becomes greater.

(b) Shallow trapping, $K_2 \neq 0$

The equations for N_1 and N_2 are:

$$\frac{\partial N_1}{\partial t} = 0 = D_1 \frac{\partial^2 N_1}{\partial x^2} - K_1 N_1 + K_2 N_2 \qquad (9)$$

$$\frac{\partial N_2}{\partial t} = K_1 N_1 - K_2 N_2 \qquad (10)$$

The approximate solutions are obtained as follows. Using the assumption $\partial N_1/\partial t = 0$, i.e. N_1 independent of t, we obtain from (10),

$$N_2 = \frac{K_1}{K_2} N_1 [1 - \exp(-K_2 t)] \qquad (11)$$

Substituting this into (9), we get,

$$N_1 = N_0 \exp(-x/L) \qquad (12)$$

where

$$L = (D_1/K_1)^{1/2} \exp(K_2 t/2) \qquad (13)$$

From (11) and (12), we get,

$$N_2 = \frac{K_1}{K_2} N_0 [1 - \exp(-K_2 t)] \exp(-x/L) \qquad (14)$$

A more exact solution for N_2 may be obtained by plugging (12) into (10) but the integration involved is somewhat difficult.

The total concentration is,

$$N_t = N_1 + N_2 = N_0 \times \\ \times \exp(-x/L) \left[1 + \frac{K_1}{K_2}[1 - \exp(-K_2 t]\right] \qquad (15)$$

With two sets of values of L and t, K_1 and K_2 can be calculated from (13). For example, using data from Fig. 1 and $D_1 = 2 \times 10^{-6}$ cm^2/sec, we obtain,

$$K_1 = 5 \times 10^{-3}\ \text{sec}^{-1}, \qquad K_2 = 2 \times 10^{-4}\ \text{sec}^{-1}$$

Then $K_1/K_2 > 20$ which justifies the trapping mechanism.

Since the solutions for N_1 and N_2 are first-order approximations, they cannot exactly satisfy the original differential equations. Obviously, N_1 given by (12) is not consistent with $\partial N_1/\partial t = 0$. However, if

$$\frac{\partial N_1}{\partial t} \ll D_1 \frac{\partial^2 N_1}{\partial x^2} \qquad (A)$$

our solution may be considered a good approximation. With the substitution of N_1 from (12), the above inequality becomes

$$\frac{x}{L} \cdot \frac{d}{dt}(\ln L) \ll D_1/L^2 \qquad (B)$$

Since the distance of interest is $x \sim 2L$, using (13), we have from (B),

$$K_2 \ll D_1/L^2 \qquad (C)$$

With the above numerical values substituted (L = 240 microns from Fig. 1), we see that (C) is satisfied. If one inserts (12) and (14) into (10), one would find the error in per cent to be,

$$\Delta = \frac{x}{2L}\left(\frac{K_1}{D_1} L^2 - 1\right) \qquad (D)$$

At $x = 2L$,

$$\Delta_{2L} = \frac{K_1}{D_1} L^2 - 1 \qquad (E)$$

This is very sensitive with regard to the numerical value of L. For example, when $K_1 = 5 \times 10^{-3}$ sec^{-1}, $D_1 = 2 \times 10^{-6}$ cm^2/sec, and $L = 2{\cdot}4 \times 10^{-2}$ cm, one gets

$$\Delta_{2L} = 45 \text{ per cent}$$

However, if $L = 2{\cdot}1\times10^{-2}$ cm, $\Delta_{2L} = 10$ per cent. Thus, it would be difficult to judge the approximate solutions simply on the basis of (D). However, the form of the solutions is in qualitative agreement with the general shape of the experimental curves

After a sufficient length of time,

$$N_t = N_0\left(1+\frac{K_1}{K_2}\right)\exp(-x/L) = N_0'\exp(-x/L) \tag{16}$$

where N_0' is the surface concentration. If the source material is exhausted after this time, N_0' will be determined by the following condition,

$$C = \int_0^\infty N_t\,dx = N_0'L$$

$$N_0' = C/L \tag{17}$$

or the surface concentration will decrease with time.

5. DISCUSSION

For diffusion by the "dissociative mechanism", Frank and Turnbull obtained,

$$D_s = D_vC_v/(C_v+C_s) \simeq D_{\text{Ge}}/C_s', \quad \text{if } C_v \ll C_s$$

where C_v, C_s are the concentrations of vacancies and substitutionals; C_s', the saturation solubility of substitutional Cu atoms, and D_v, D_s and D_{Ge}, the diffusivities of vacancy, substitutional and Ge atoms. An estimate of D_s from this formula is in good agreement with the experimental result by Tweet of Cu diffusion near the surface of a high perfection crystal of Ge.(4) In our experiments, we have used a high perfection crystal supplied by Tweet for Ag diffusion in Ge and obtained data as shown in Fig. 2. In Section 3, we have calculated D_a near the surface of the crystal based on Fig. 2 as

$$D_a = 3{\cdot}6\times10^{-8}\ \text{cm}^2/\text{sec}$$

Using Frank and Turnbull's formula and the values of D_{Ge} and C_s' at $T = 710°\text{C}$, for Ag in Ge,

$$D_{\text{Ge}} = 6\times10^{-15}\ \text{cm}^2/\text{sec}$$

$$C_s' = 10^{14}/4{\cdot}5\times10^{22} = 2\times10^{-9}$$

we would have

$$D_s = 6\times10^{-15}/2\times10^{-9} = 3\times10^{-6}\ \text{cm}^2/\text{sec}.$$

This value is higher by two orders of magnitude than the experimental value D_a, $3{\cdot}6\times10^{-8}$ (the difference between this D_a and the erfc function extrapolated D is about a factor of 2–3, the latter is usually the smaller one). This would suggest that the diffusion of Ag in Ge is by a mechanism other than the dissociative one. We should realize that the dissociative mechanism occurs if: (1) the interstitial and the vacancy diffuse independently after dissociations and (2) $D_i > D_v$. At very high diffusivities, the interstitials will quickly attain the equilibrium concentration. Under these conditions, the formula for D_s,

$$D_s = D_vC_v/(C_v+C_s)$$

is valid. In the case of Ag diffusion in Ge, we first note that the Ag atoms are much larger than the Ge atoms. Because of the strain interaction between a large interstitial and a vacancy, their diffusion immediately after dissociation would not be entirely "independent". Secondly, D_i of Ag in Ge as obtained above is about 2×10^{-6} cm²/sec. At 700°C, $D_v = 6\times10^{-5}$ cm²/sec. Hence $D_i < D_v$. At much lower diffusivities, the Ag interstitials may not reach the equilibrium concentration in a short diffusion time. All these conditions do not favor the dissociative mechanism and hence the above formula for D_s is no longer valid for the case of Ag in Ge. Thus a lower value of D_s of the Ag substitutionals in Ge than that calculated from Frank and Turnbull's formula is to be expected. When the interstitial and vacancy concentrations do not reach equilibrium and vacancies enter as a third kind of diffusion species having reactions with both substitutionals and interstitials, the situation is difficult to deal with theoretically. This case is worthy of further investigation.

For diffusion of Ag and Co in Ge, we observed that the apparent concentration* is greater in high dislocation than in low dislocation crystals. Most of

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* Throughout this paper, the "concentration" usually means the observed concentration which is not necessarily the *equilibrium* concentration.

the data show strikingly the exponential characteristic of concentration vs. penetration distance. All these findings can be interpreted by the trapping mechanism. The concentration measured is the sum of the free species (probably interstitials) and the trapped species. The higher trap density as in the case of HD crystals, would result in (a) a higher concentration of trapped species and (b) a higher trapping rate which will reduce the diffusion length and hence the apparent diffusivity of the composite stream. We have shown in Section 4 that if the trapping rate is greater than the release rate, the concentration will follow a simple $\exp(-x/L)$ law. However, Fick's law will be followed if (a) $K_1N_1 = K_2N_2$ or (b) all traps are filled. This could occur in LD crystals because of low trap density. The case of Fig. 5 may be due to either of these two conditions.

Another interesting conclusion from our study is that in HD crystals, the surface concentration is proportional to time up to a certain time limit. This fact is shown in Fig. 1 (curves 2 and 3), Fig. 3 (curves 1 and 2), and Fig. 6. The rise with time of the surface concentration is predicted by our theory (Section 4). It appears that our theory of trapping mechanism is able to account for many experimental facts and so may be taken as a sound basis in dealing with this type of diffusion.

The limited supply after a certain time as shown by the drop of surface concentration (Figs. 3 and 9) may be due to either or both of the following causes: (a) formation of oxide on the surface. This is quite possible because cobalt and iron are easily oxidized. (b) formation of an alloying layer.

The characteristics of iron diffusion in Ge as described in Section 3 deserve further discussion. To interpret the data, we conceive that "vacancies" may not be a determining factor in Fe diffusion. Instead, some other kind of traps, possibly oxygen may play an important role. If the role of vacancies becomes insignificant, it would be expected that the dislocation density would have little effect on concentration and diffusivity. Furthermore, the concentration of Fe substitutionals (trapped by vacancies) would be small, an important factor contributing to the very low solubility. The impurity traps may have higher concentration than the equilibrium concentration of vacancy and may produce pockets in the crystal. The high rate of trapping, if it can occur, would give the non-Fickian diffusion.

The following table shows us the present status of diffusion of various elements in Ge. It is very interesting to note from Table 1 that most properties of Class B solutes are midway between those of Class A and Class C solutes. The solubilities of

Table 1. *Diffusion in* Ge

Class	A	B	C
Elements	Li Cu Ni*	Ag Co Fe	Au, Zn & Group III IV, V elements
(1) Bond with Ge atoms	very weak	weak	strong
(2) Activation energy for diffusion	$<\frac{1}{2}$ eV	~ 1 eV	>2 eV
(3) D† (800°C) in cm²/sec.	10^{-4}–10^{-5}	10^{-6}–10^{-7}	10^{-9}–10^{-13}
(4) Maximum solubility (atomic fraction)	10^{-4}–10^{-7}	10^{-8}–10^{-9}	1–10^{-3}
(5) Diffusion process	interstitial and others	double stream	substitutional
(6) Diffusion mechanism	interstitial, dissociative and others	trapping	vacancy mechanism and others
(7) Fick's law	mostly no	mostly no	yes

* Ni may be considered as an element between class A and B. Its activation energy for diffusion in Ge is 0·9 eV.

† Diffusivity is usually measured in ordinary Ge crystals (10^4–10^6 pits/cm²). D's for Cu, Ni, Ag, Co and Fe are "apparent" rather than "true".

Class B elements in Ge are the lowest perhaps because they are not good substitutionals due to weak bonding and also not good interstitials due to large atomic size.

6. CONCLUSIONS

From experiments of Ag, Co and Fe diffusion in Ge, we have found:

(a) The concentration often varies approximately as $\exp(-x/L)$, where the diffusion length L increases with time.
(b) In high dislocation crystals, the concentration near the surface increases with time up to a certain time limit.
(c) In some cases, the penetration curves show great irregularities.
(d) The apparent diffusivities of these elements in Ge are very great, in the range of 10^{-6}–10^{-7} cm^2/sec at temperatures around 800°C.
(e) The apparent diffusivities are usually higher in low-dislocation (less than 10^3 pits/cm^2) crystal than in high-dislocation (10^5 pits/cm^2) crystals.
(f) The solubilities are very small in Ge. They are in the range of 10^{-8}–10^{-9} in atomic fraction (700–850°C).
(g) For cobalt diffusion in Ge, the activation energy is about 1 eV which is nearly the same as the value for Ag, and Ni and Fe in Ge obtained by other workers.

In theory, we have shown that a double stream diffusion process would in general not follow Fick's law because of non-equilibrium exchange of streams. The trapping mechanism, a possible interpretation of a double-stream process, not only leads to a concentration varying approximately as $\exp(-x/L)$ but also is able to explain many other experimental facts.

In conclusion, we can say that our experimental results, the theory of double-stream process and its physical interpretations (trapping mechanism) show very good accord. Combining these results with the knowledge of Cu and Ni diffusion in Ge obtained elsewhere, we can further conclude that diffusion of most Group I and transition elements in Ge (700–850°C) has the following characteristics.

(a) Non-Fickian diffusion in many cases.
(b) High diffusion rate.
(c) Very low solubility.
(d) Low activation energy.
(e) Subject to structure and impurity effects.

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APPENDIX

The concept and definition of apparent diffusivity

Throughout this paper, we use "apparent diffusivity" rather than "true diffusivity". This concept may be bewildering and therefore could cause misunderstanding even to those workers who have had long experience in this field. The author should mention that to his knowledge, this concept was originally introduced by VAN DER MAESEN in connection with Cu diffusion in Ge.(3) Later, FULLER, FRANK and TURNBULL used the adjective "apparent" rather liberally for the diffusivity of Cu in Ge.(2, 5) This concept is followed in this paper because none better is available.

The "apparent diffusivity" is defined by the following equation,

$$J(x_1)-J(W) = -D_a\left(\frac{\partial N}{\partial t}\right)_{x_1} -J(W) = \int_{x_1}^{\overline{W}} \frac{\partial N}{\partial t}\,dx \tag{A1}$$

This is just the integration of Fick's second law between x_1 and W (the thickness of the sample). If W is very great in comparison with the diffusion length, which is practically true for most experimental cases, then we can take $J(W) \approx J(\infty) = 0$. Since x_1 can be any point in the sample, there is no need for its subscript. With these simplifications, we get,

$$D_a = -\int_{x}^{\overline{W}} \frac{\partial N}{\partial t}\,dx \Big/ \left(\frac{\partial N}{\partial x}\right)_x \tag{A2}$$

We now consider (A2) as the "generalized definition" of diffusivity no matter how $N(x,t)$ is obtained and whether or not Fick's law is obeyed. When diffusion follows Fick's law, D from (A2) will be automatically the true diffusivity. However, if Fick's law is not followed, we still can determine D according to (A2) if $N(x,t)$ and only $N(x,t)$ can be found by some means (from experimental or from other theoretical derivation). In this case, D in (A2) is called the "apparent diffusivity".

In our study, we found both from experiment and from theory

$$N(x, t) \cong A(t)\exp(-x/L) \tag{A3}$$

where $A(t)$ is the surface concentration, and L the diffusion length. Then based on (A2), the apparent diffusivity, for $W \gg L$, will be given by,

$$D_a = \frac{L}{A}(A'L + AL') + L'x \tag{A4}$$

where the prime (′) stands for differentiation with respect to time. Let us consider the following special cases:

(i) $A = ct$, $L =$ const.,

$$D_a = L^2/t \qquad (c = \text{const.}) \tag{A5}$$

(ii) $A =$ const., $L = k\sqrt{t}$,

$$D_a = \frac{L}{2t}(L+x) = \frac{k^2}{2} + \frac{kx}{2\sqrt{t}} = a + b\lambda \tag{A6}$$

(iii) $AL =$ const., $L = k\sqrt{t}$,

$$D_a = \frac{1}{2t}Lx = \frac{kx}{2\sqrt{t}} = \frac{k}{2}\lambda \tag{A7}$$

(iv) $A = ct$, $L = kt$,

$$D_a = \frac{3L^2}{2t} + \frac{Lx}{2t} = \frac{3}{2}k^2 + \frac{kx}{2t} = 3a + b \tag{A8}$$

From (A5) to (A8), we note that: (a) D_a is not a constant but a function of x and t. (b) In cases (ii)–(iv), D_a is linear with $\lambda(= x/\sqrt{t})$. These two results may surprise some workers in this field. Fig. 11 taken from VAN DER MAESEN's data(3) should serve as a good example to justify our statement.

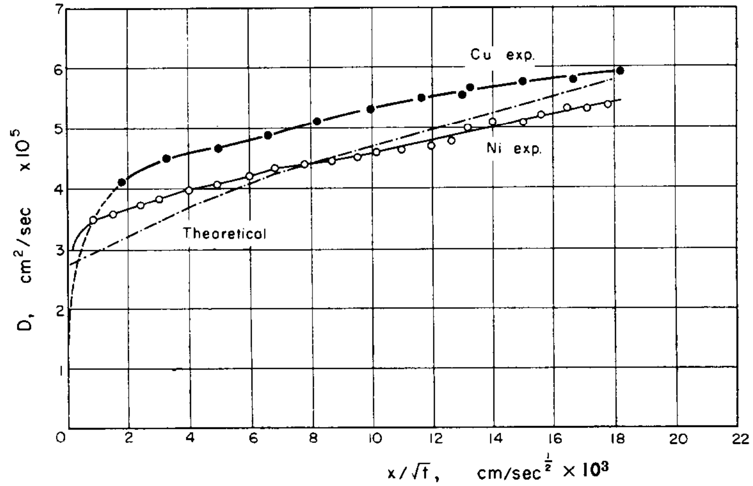

FIG. 11. Diffusivities of Cu and Ni in Ge (After VAN DER MAESEN(3)).

If we define D_a at $x = L$ as the "nominal Fick diffusivity", D_{an}, then in cases (i) and (ii),

$$D_{an} = L^2/t \tag{A9}$$

In case (iii),

$$D_{an} = L^2/2t \tag{A10}$$

In case (iv),

$$D_{an} = 2L^2/t \tag{A11}$$

Which of formulas (A9)–(A11) should be used depends on which ideal case as set in (A5)–(A8) is nearest to the actual situation. This can be judged without great error simply by examining the penetration curves. This is our basis for obtaining the apparent diffusivity throughout this paper.

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