DIFFUSION OF GERMANIUM IN COPPER

A thesis submitted by

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All the work in this thesis has been done by me except
where otherwise indicated.

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ABSTRACT

The impurity diffusion coefficient of germanium in single crystal copper has been measured at fourteen temperatures in the range 652-1014°C. The distribution of the radioactive Ge^{68} through the copper crystals was mainly determined by the surface decrease method with the sectioning technique used as a check on several samples. The results show that the diffusion coefficients can be described by the equation

$$D_{\text{Ge} \rightarrow \text{Cu}} = 0.238^{+0.099}_{-0.070} \exp - \frac{43\,700 \pm 779}{RT} \text{ cm}^2/\text{sec}$$

where R is the gas constant in cal/mole and T is the absolute temperature.

The difference between the activation energy for germanium diffusion and self-diffusion in copper is in good agreement with the theories of Lazarus and Le Claire.

Chapter 1

INTRODUCTION

A large amount of experimental data has accumulated concerning the diffusion of impurities in metals. Several theories have been proposed to explain the experimental results^{1,2,3}, the most successful of which has been the Lazarus¹ and the Le Claire² theory which applies particularly to impurity diffusion in the noble metals, copper, silver and gold. The best agreement with the theory is for the diffusing elements which lie in the same row and to the right side of the solvent metal in the periodic table. In the case of copper, values of the impurity diffusion coefficients for Zn, Ga and As have been published^{4,5} but no data exists for germanium. In this work germanium was diffused in copper to complete the results and to offer another check on the Le Claire theory.

In recent years, the availability of high purity high specific activity radioisotopes has greatly aided the study of both self-diffusion and impurity diffusion in metals. The use of high quality detection equipment along with the radioisotopes allows greater sensitivity and accuracy in the measurement of diffusion coefficients. Since only a thin layer of radioactive material need be placed on the surface of the solvent metal, the large concentration gradients through the solvent are eliminated. The small concentration of solute atoms allows the interactions between the solute atoms themselves to be

neglected. These diffusion studies yield more accurate results than the earlier methods involving chemical analysis and are thus contributing to a greater understanding of the process of diffusion.

It is found experimentally that the activation energy for impurity atoms diffusing into monovalent metals is considerably different from the activation energy for self-diffusion. These results are explained by three types of effects: the effects arising from the valence of impurity atoms, the effects arising from the difference in size between the impurity and solvent atoms and the effects arising from the correlation between the motions of impurity and solvent atoms.

The diffusion of tracer impurities into noble metals is found experimentally to follow the Arrhenius relation

$$D_2 = A_2 \exp(-Q_2/RT) \quad (1)$$

where the subscript 2 refers to the property of impurity diffusion, D_2 is the diffusion coefficient, A_2 is the frequency factor and Q_2 is the activation energy, R is the gas constant in cal/mole deg., and T is the absolute temperature. The impurity diffusion coefficient differs from the self-diffusion coefficient which is given by the relation

$$D_0 = A_0 \exp(-Q_0/RT) \quad (2)$$

where the subscript 0 refers to the property of self-diffusion. The difference between D_2 and D_0 is related to changes in both the A 's and the Q 's. The same factors which influence A_2 and Q_2 also influence

A_0 and Q_0 . Lazarus and Le Claire have determined a difference in activation energies

$$\Delta Q = Q_2 - Q_0 \quad (3)$$

and use this quantity to compare the theoretical difference ΔQ_{th} and the experimental difference ΔQ_{expt} . Experimental observations show that impurities diffuse in a solvent at a different rate than the self-diffusion of the solvent and, in particular, the diffusion rate for impurities which lie to the right of the solvent in the periodic table is larger than the self-diffusion rate. Lazarus¹ suggests this result is due to an electrostatic interaction between the vacancies in the solvent and the impurity atoms of the solute. Later Le Claire² improved the Lazarus theory by incorporating into it a correlation correction factor and also a more exact solution to the Thomas-Fermi equation. Swalin³ has suggested a theory which showed a relation between the activation energy for impurity diffusion and the relative sizes of the solute and solvent atoms. However, experiments show that the diffusion of impurities into the noble metals is in better agreement with the Lazarus-Le Claire theory than with that of Swalin.

Much of the previous work with copper^{4,5,6,7,8,9} has employed the sectioning technique for the determination of the diffusion coefficients. The basic technique used in this work was the surface decrease method.¹⁰ Linnenbom, Tetenbaum and Cheek¹¹ were quite successful in using this method to measure the diffusion coefficients for iron diffusing in copper. A precision lathe was acquired near the completion of the work and several specimens were sectioned to check the results of the surface decrease method.

Chapter 2

THEORY

2.1 Diffusion Equations

Diffusion in metals is described by the expression

$$J = -D \partial c / \partial x \quad (4)$$

where $\partial c / \partial x$ is the change in concentration of solute with penetration distance x of the solute into the solvent, J is the flux of material across a unit area per unit time, and D is a proportionality constant which is called the diffusion coefficient. The minus sign appears because the concentration of solute is greatest at the surface of the sample and decreases as the penetration distance increases. This equation is called Fick's first law.

By using a continuity equation

$$\nabla \cdot \vec{J} = -(\partial c / \partial t) \quad (5)$$

equation (4) can be easily transformed to a more solvable form known as Fick's second law,

$$(\partial c / \partial t) = \nabla \cdot D \nabla c \quad (6)$$

If D is independent of penetration distance, that is, the concentration gradients in the solvent are very small, equation (6) can be rewritten as

$$(\partial c / \partial t) = D \nabla^2 c \quad (7)$$

It is the usual procedure to place the solute on the surface of the sample and let it diffuse in the x -direction through the sample. This

simplification allows equation (7) to be rewritten as

$$(\partial c / \partial t) = D(\partial^2 c / \partial x^2) \quad . \quad (8)$$

For this work a thin layer of tracer solute, less than 0.1 micron thickness, was plated on the surface of a relatively thick sample, that is, thickness much greater than the penetration depth of the tracer. Thus the diffusion could be considered to take place from an infinitely thin film into a semi-infinite medium, and a solution of equation (8) under these conditions is

$$C = \frac{C_0}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4 D t}\right) \quad (9)$$

where C_0 is the initial concentration of the solute, t is the annealing time of the sample and C is the concentration of the solute at the penetration distance x .

2.2 Surface Decrease Method

The surface decrease method of determining diffusion coefficients requires measurement of the tracer radiation emitted from the plated surface of the solvent sample before and after the diffusion anneal. The activity measured after the anneal is reduced due to absorption of the radiation by the solvent material through which the tracer has diffused. If the radiation absorption is described by an exponential equation of the form $I = I_0 \exp(-\mu x)$ (I is the intensity of the radiation after passing through material of thickness x , I_0 is the initial intensity

of the radiation and μ is the linear absorption coefficient), then the ratio of the two activities may be simply related to the diffusion coefficient.

Consider a small section of the sample between x and $x+dx$. Assuming that the radiation from the tracer is exponentially absorbed, the contribution to the total activity from this small section is

$$dB = \frac{KC_0}{\sqrt{\pi Dt}} \left(\exp - \frac{x^2}{4Dt} \exp - \mu x \right) dx \quad (10)$$

where K is a constant which depends on the counting efficiency. The total activity B over the whole sample may be found by integrating equation (10) to give

$$B = \frac{KC_0}{\sqrt{\pi Dt}} \int_0^\infty \exp - \frac{x^2}{4Dt} \exp - \mu x \, dx \quad (11)$$

By changing the variable to

$$\xi = \frac{x}{2\sqrt{Dt}} + \mu\sqrt{Dt} \quad (12)$$

equation (11) becomes

$$B = KC_0 \exp(\mu^2 Dt) [1 - \operatorname{erf} \mu\sqrt{Dt}] \quad (13)$$

Before the sample is annealed the activity is just $B_0 = KC_0$. Taking a ratio of the activity after annealing to the activity before annealing gives the result

$$(B/B_0) = \exp(\mu^2 Dt) [1 - \operatorname{erf} \mu\sqrt{Dt}] \quad (14)$$

A general graph is made by plotting calculated values of B/B_0 for

various assumed values of $\mu^2 Dt$ as shown in figure 1. For the experimentally determined ratio B/B_0 , the corresponding $\mu^2 Dt$ can be read off the graph. Knowing μ and t , D may be calculated.

This method is applicable to measuring small diffusion coefficients in the range 10^{-9} to 10^{-12} cm^2/sec , if the radiation is strongly absorbed by the solvent. If the radiation is weakly absorbed, e.g., strong gammas, then the method is of no use. The largest experimental problem is to measure the absorption coefficient accurately.

2.3 Lazarus-Le Claire Model for Impurity Diffusion

There are several possible mechanisms by which a solute atom may diffuse into a solvent lattice. These mechanisms are the vacancy mechanism, the interstitial mechanism and the exchange mechanism. The vacancy and interstitial mechanisms have been found experimentally to play important roles for diffusion in metals and alloys, while the exchange mechanism has not yet been found experimentally. There is strong evidence to support the argument that a solute atom diffuses in a face-centered cubic lattice metal by the vacancy mechanism, and Lazarus assumes this mechanism in his model of impurity diffusion.

It is desired to obtain expressions for A_0 and Q_0 (equation 2) since this will give a better understanding of the diffusion process. Since atoms diffuse through a metal lattice by jumping in all directions and in no particular pattern, random walk theory may be used to determine

Figure 1 Theoretical Curve for $\frac{B}{B_0}$ versus $u^2 Dt$

the rate of jumping and the distance travelled by the diffusing atoms. The derivation of the expression for A_0 given by Zener¹² and Le Claire¹³ begins with the fundamental equation for the three-dimensional random walk problem

$$D = \left(\frac{1}{6}\right) \sum_i \Gamma_i \delta \ell_i^2 \quad (15)$$

where D is the diffusion coefficient, Γ_i is the rate at which the diffusing atom makes a jump of type i and $\delta \ell_i$ is the corresponding jump distance. In f.c.c. lattice metals all the Γ_i jump rates may be considered to be equal so that equation (15) becomes

$$D = \left(\frac{1}{6}\right) \Gamma \sum_i \delta \ell_i^2 \quad (16)$$

Wert and Zener¹⁴ have derived theoretically, using statistical mechanics, the expression

$$\Gamma = \nu \cdot \exp - \frac{G}{RT} \quad (17)$$

where ν is the vibration frequency of the impurity atom in an equilibrium position and is of the order of the Debye frequency. G , the total isothermal work required for a jump of a solute atom from one lattice site to a neighbouring vacancy, is given by

$$G = G_f + G_m \quad (18)$$

where G_f and G_m are respectively the isothermal work required to form a vacancy in a particular lattice site and the isothermal work necessary to move the solute atom from a position of equilibrium to the saddle point position. Equation (18) can be rewritten in terms of enthalpy and entropy as

$$G = H_f - TS_f + H_m - TS_m \quad (19)$$

where H_f and H_m are the enthalpy of formation and the enthalpy of movement of the vacancy and S_f and S_m are the entropy of formation and the entropy of movement of the vacancy. Substituting equation (19) into equation (17) gives

$$\Gamma = \nu \exp \frac{S_f + S_m}{R} \exp - \frac{(H_f + H_m)}{RT} \quad (20)$$

Combining equation (20) with equation (16) yields

$$D = \gamma a^2 \nu \exp \frac{S_f + S_m}{R} \exp - \frac{(H_f + H_m)}{RT} \quad (21)$$

where a is the lattice parameter and γ is defined by the equation

$$\frac{1}{6} \sum_i \delta \ell_i^2 = \gamma a^2 \quad (22)$$

The coefficient γ is determined by the geometry of the atomic jumps and for an f.c.c. lattice equals unity.

The first term of equation (21)

$$\gamma a^2 \nu \exp \frac{S_f + S_m}{R}$$

is the expression for A_0 while the activation energy Q_0 is the sum of H_f and H_m as found in the second term. Le Claire¹⁵ points out that in most normal self-diffusion measurements in metals, A_0 lies in the range 0.05 to 5.0 cm²/sec. To obtain this range of values, S_f and S_m must be positive. Huntington, Shirn and Wajda¹⁶ have made a direct theoretical calculation of S_f and S_m for self-diffusion in a metal and have shown that it is approximately R .

No account has been taken in this derivation of the correlation effect. In self-diffusion each succeeding jump of the vacancy is uncorrelated with the previous jump. When a vacancy jumps from one site to another, all the surrounding neighbouring atoms look the same to the vacancy. The next jump of the vacancy will be in any direction that the vacancy wishes to go. For impurity diffusion, the succeeding jumps of the vacancy after the first impurity-vacancy exchange are correlated. After the first impurity-vacancy exchange, the vacancy sees one atom which is different from the other neighbouring atoms. The vacancy will tend to re-exchange with this impurity on its next jump. A correlation factor f must be incorporated into the equation for the diffusion coefficient to take account of these correlated jumps. Le Claire and Lidiard¹⁷ give a very good approximation to f for impurity diffusion with the expression

$$f_2 = (w_1 + \frac{7}{2} w_3) / (w_1 + w_2 + \frac{7}{2} w_3) \quad (23)$$

where w_2 is the vacancy-impurity atom exchange frequency, and w_1 and w_3 are the exchange frequencies of the vacancy with the solvent atoms which are respectively the nearest and non-nearest neighbours of the solute atom. These exchange frequencies are related to the annealing temperature by the following expressions:

$$\begin{aligned} w_1 &= \nu_1 \exp - H_1/RT \\ w_2 &= \nu_2 \exp - H_2/RT \\ w_3 &= \nu_3 \exp - H_3/RT \end{aligned} \quad (24)$$

where H_1 , H_2 and H_3 are the activation energies for the respective jumps and ν_1 , ν_2 and ν_3 are the vibration frequencies of the respective jumps.

The equation for the self-diffusion coefficient then is

$$D_0 = a^2 f_0 \nu_0 \exp \frac{S_{f0} + S_{m0}}{R} \exp - \frac{(H_{f0} + H_{m0})}{RT} \quad (25)$$

where f_0 , the self-diffusion correlation factor, is independent of temperature. From equation (23) the value of f_0 is 9/11 since in self-diffusion $w_1 = w_2 = w_3$. The self-diffusion activation energy is

$$Q_0 = H_{f0} + H_{m0} \quad (26)$$

A similar expression for impurity diffusion is

$$D_2 = a^2 f_2 \nu_2 \exp \frac{S_{f2} + S_{m2}}{R} \exp - \frac{(H_{f2} + H_{m2})}{RT} \quad (27)$$

where f_2 is the correlation factor for impurity diffusion. The activation energy for impurity diffusion is affected by the correlation factor since the latter is dependent on the temperature. The slope of the curve $\ln D_2$ against $1/T$ is the activation energy Q_2 and is given by

$$Q_2 = -R \frac{\partial \ln D_2}{\partial (1/T)} = H_{f2} + H_{m2} - R \frac{\partial \ln f_2}{\partial (1/T)} \quad (28)$$

The difference in activation energies $\Delta Q = Q_2 - Q_0$ is given by

$$\Delta Q = \Delta H_2 + \Delta E - R \frac{\partial \ln f_2}{\partial (1/T)} \quad (29)$$

where $\Delta H_2 = H_{m2} - H_{m0}$ and $\Delta E = H_{f2} - H_{f0}$. Equation (29) can be rewritten as

$$\Delta Q = \Delta H_2 + \Delta E - C \quad (30)$$

where C is called the correlation correction factor. Since ΔE is the difference in energy of formation of vacancies in the solvent, the vacancies will be repelled from the impurities when ΔE is positive, and attracted to the impurities when ΔE is negative. The binding energy of the vacancy and impurity is thus $-\Delta E$.

Le Claire² shows that the correlation correction factor may have a considerable effect upon the value of ΔQ . The expression given for C is

$$C = (A_2/A_0) f_0 \exp \frac{C}{RT} \cdot \left\{ \frac{(\Delta H_2 - \Delta H_1) \exp^{-[(\Delta H_1 + \Delta H_2)/RT]} + \frac{7}{2}(\Delta H_2 - \Delta H_3) \exp^{-[(\Delta H_3 + \Delta H_2)/RT]}}{\left(e^{-(\Delta H_1/RT)} + \frac{7}{2} e^{-(\Delta H_3/RT)} \right)^2} \right\} \quad (31)$$

where $\Delta H_1 = H_1 - H_{m0}$ and $\Delta H_3 = H_3 - H_{m0}$.

To calculate ΔQ , the terms ΔH_2 , ΔE and C are determined and substituted into equation (30). Lazarus¹ assumes that a metal containing a solute differs from a pure metal only by the electrostatic interaction between the vacancy and the screened effective charge difference between the solute and solvent ion cores. This interaction is calculated using the Thomas-Fermi approximation. The free electron model of a pure metal assumes that all the positive ion cores are smeared out to give a uniform positive charge density equal to the negative charge density. When an impurity atom is added, the positive charge density is increased

by a factor Ze , where Z is the number of electrons in the solute atom in excess of those in the solvent atom. The excess charge Ze is assumed to be concentrated at a point in the center of the impurity atom. When Z is positive, the point charge attracts electrons and when Z is negative, the point charge attracts holes. This attraction or repulsion of electrons has the effect of screening out the point charge at large distances. The electrostatic potential due to the point charge is the solution of the Thomas-Fermi equation. The first term of the series solution to the Thomas-Fermi equation^{18,19,20} is

$$V(r) = +\alpha \frac{Ze}{r} \exp(-qr) \quad (32)$$

where α is a constant dependent on Z , r is the distance from the point charge and q is the screening parameter given by

$$q^2 = \frac{4me^2}{\hbar^2} \left(\frac{3n_0}{\pi} \right)^{\frac{1}{3}} \quad (33)$$

where m , e and n_0 are respectively, the mass, charge and number per unit volume of electrons.

To calculate ΔE , a vacancy is regarded as being an impurity of zero ionic charge. When a vacancy and an impurity are nearest neighbours, there is an interaction between them whose energy is given by

$$\Delta E = - \frac{Ze^2}{a} \alpha \exp(-qa) \quad (34)$$

where a is the nearest neighbour distance.

To calculate ΔH_2 , ΔH_1 and ΔH_3 , the positions of the vacancy

at the saddle point of the jump are considered. In determining ΔH_2 , the vacancy at the saddle point is regarded as two point charges, each of charge $-\frac{1}{2}e$, situated at the centroid of the hemisphere on each side of the impurity. Huntington²¹ has calculated the redistribution of charge of the vacancy about the impurity. The result obtained for ΔH_2 is

$$\Delta H_2 = -[2Z\frac{1}{2}e^2/(11/16)a]\alpha \exp -[q(11/16)a] + (Ze^2/a)\alpha \exp -(qa) , \quad (35)$$

In the case of ΔH_1 , the vacancy exchanges with a nearest neighbour solvent atom. At the saddle point of the jump, the solvent atom is between two sites each of which is a nearest neighbour to the impurity. The distance from the $\frac{1}{2}e$ point charge positions of the half-vacancies to the center of the impurity is 1.106a. The expression for ΔH_1 is

$$\Delta H_1 = -(Ze^2/1.106a)\alpha \exp -(1.106qa) - \Delta E . \quad (36)$$

An expression may be obtained for ΔH_3 by a similar method of considering the positions of the half-vacancies with respect to the impurity during a vacancy non-nearest neighbour solvent atom exchange.

Le Claire² has calculated the values of ΔH_1 , ΔH_2 , ΔH_3 and ΔE , listed in Table 1, for impurities diffusing in copper. It is seen that both ΔH_2 and ΔE become more negative for the positive Z impurities, which indicates that as Z increases it is easier for a vacancy to form next to the impurity and to exchange positions with the impurity. Thus

the diffusion rate increases as Z becomes more positive. Table 2 shows the values of C and ΔQ_{th} for Zn, Ga and As, as determined by Le Claire using the experimental values of A_2 and A_0 , $f_0 = 9/11$ and RT equal to 2 Kcal/mole which corresponds to a temperature of 807°C . The effect of C upon the comparison of ΔQ_{th} and ΔQ_{expt} is also seen in Table 2. The column $\Delta H_2 + \Delta E$, in effect, is ΔQ_{th} if the correlation correction factor is neglected. The results of the present work including values for C and ΔQ_{th} are also shown in Table 2.

Table 1

(All energies in units - Kcal/mole)

	Z	-3	-2	-1	+1	+2	+3	+4
	α	2.34	1.85	1.40	0.77	0.67	0.60	0.55
<u>Cu</u>	ΔH_1	---	---	-0.80	+0.44	+0.77	+1.03	+1.26
$q = 1.81 \text{ \AA}^{-1}$	ΔH_2	+46.56	+24.54	+9.28	-5.11	-8.89	-11.94	-14.59
	ΔH_3	---	---	-0.45	+0.18	+0.28	+0.34	+0.37
	ΔE	---	+4.76	+1.80	-0.99	-1.72	-2.32	-2.83

Table 2

(All energies in units - Kcal/mole)

<u>Impurities in Cu</u>				$A_0 = 0.62$	$Q_0 = 49.56$	ref 25	
Z	A_2	C(RT=2)	$\Delta H_2 + \Delta E$	ΔQ_{th}	ΔQ_{expt}		
Zn	+1	0.34	-2.35	-6.10	-3.75	-3.96	4
Ga	+2	0.55	-6.36	-10.61	-4.25	-3.66	5
Ge	+3	0.24	-8.00	-14.26	-6.26	-5.86	present work
As	+4	0.12	-9.36	-17.42	-8.06	-7.56	5

Chapter 3

EXPERIMENTAL

3.1 Materials

The copper single crystals used in this experiment were in the form of discs, $\frac{3}{4}$ inch in diameter and 5 millimeters thick. The manufacturers, Monocrystals Company of Cleveland, Ohio, U.S.A., specified a purity of 99.999%. The copper samples were spark planed flat and smooth on one surface using a Servomet spark planing machine. Immediately before plating the samples were cleaned by lightly etching with dilute nitric acid and then washed in acetone and distilled water.

The radioactive tracer was one millicurie of carrier free germanium-68 obtained through the Australian Atomic Energy Commission at Lucas Heights, N.S.W., from Nuclear Science and Engineering Company of Pittsburg, Pennsylvania, U.S.A. The radiochemical purity of the tracer was 99%. The isotope was received in the form of GeF_6 dissolved in five millilitres of 0.5 N HCl and 0.2 N HF.

This isotope was chosen for its relatively long half-life of 280 days. It decays to gallium-68 by electron capture.²² The gallium-68 decays to zinc-68 with a half-life of 68 minutes. This decay proceeds 87% of the time by positron emission and 13% of the time by electron capture. The positron emission produces annihilation gammas of energy 0.51 Mev. Low energy x-rays characteristic of gallium and zinc are also produced by the electron capture process.

3.2 Plating Process

Several authors^{23,24} have reported only very limited success in the deposition of pure germanium metal by electrolysis. Fink and Dokras,²⁴ however, found that good deposits of the alloy, Cu_3Ge , could be obtained from an alkaline plating solution containing both germanium and copper. This plating process was therefore used in the present work, since the plating of the alloy containing copper should not affect the validity of diffusion experiments in a copper lattice.

The plating solution was made up of three milligrams of cuprous cyanide and three grams of potassium hydroxide dissolved in thirty millilitres of distilled water. A second solution was made with seven milligrams of stable germanium dioxide and one gram of potassium hydroxide dissolved in thirty millilitres of distilled water. The two solutions were then mixed to provide a 1.2 N KOH plating bath of total volume sixty millilitres. The method of dissolving the cuprous cyanide and the germanium dioxide separately was adopted since the cuprous cyanide would not always dissolve properly in the 1.2 N solution, while this normality appeared to be near optimum for the plating process. Preliminary trials showed that the bath consistently produced bright, adherent deposits of the copper germanium alloy, and that the addition of 5 millilitres of 0.5 N HCl and 0.2 N HF (to simulate the tracer solution) did not affect its plating characteristics. However, when the final plating bath was prepared containing the actual Ge-68 tracer,

the deposits obtained were usually a dull grey colour, possibly due to additional impurities in the tracer solution. Measurements showed, nevertheless, that the radioactive Ge-68 was plating out of the solution with reasonable efficiency.

The electroplating apparatus is shown in figure 2. The anode consisted of a platinum wire, the cathode being the copper sample to be plated. Best results were obtained with the cathode rotating at several hundred rpm. The plating was done with a constant current of fifty milliamperes for periods ranging from three to twenty minutes depending upon the amount of tracer and copper remaining in the solution. The thickness of the alloy deposits on the surface of the samples was assumed to be proportional to the activity of the tracer material. A standard sample was given a sufficiently large deposit so that the alloy thickness could be found by weight measurements before and after plating. The alloy thickness on the samples was then found by comparing their activities with the activity on the standard sample. The thickness of the alloy deposits was found to range from 200 to 500 angstroms.

3.3 Positron Counting

The radiations emitted following the decay of Ge-68 are of three main types: x-rays of energy about 9 kev, annihilation gammas of energy 0.51 Mev and the positron spectrum with maximum energy 1.89 Mev. Of these, the positron radiation is the only one suitable for use with the surface decrease method. The very low absorption

Figure 2. Plating Apparatus

coefficient of the annihilation gammas and the difficulties involved in detection of the low energy x-rays precluded the use of either of these radiations.

Since positrons are not normally exponentially absorbed, a special counting setup was designed in which near exponential absorption was attained. A block diagram of the positron detection system is shown in figure 3. A thin plastic scintillator, 0.5 millimeter thick, was used to discriminate against detection of the 0.51 Mev gamma radiation. The photomultiplier was operated at 1000 volts and the discriminator of the amplifier was adjusted so that all pulses above 6 volts would register on the scaler. The absorption of the positron radiation from the diffused tracer material was simulated by placing copper absorbing foils immediately adjacent to the plated surface of the sample. It was found that the positron counting rate actually increased as the foils were added until at a thickness of about 160 mgm/cm^2 the counting rate reached a maximum. Additional absorbing foils then produced an essentially exponential decrease in counting rate, from which an absorption coefficient could be measured. The range of exponential absorption was about 0.015 inch, followed by an upward curvature due to the small but finite ability of the equipment to detect the 0.51 Mev gamma radiation. The sample holder (figure 3) was therefore designed to include a window of brass foil of thickness 0.008 inch (180 mgm/cm^2) so that the positron measurements were well within the range of the exponential absorption. The absorption curves

Figure 3. Sample Holder for Positron Counting

were obtained by measuring the positron counting rate, as five copper foils with the thicknesses shown in Table 3 were placed consecutively between the plated surface of the copper sample and the brass window of the holder. The total thickness of the five foils was about 0.015 inch, i.e., approximately equal to the range over which the exponential absorption was observed. Only negligible error resulted from this limited range which was about four times the value of $\sqrt{Dt}$ used in the experiments. All points on the absorption curves contained 10^5 counts except where the count rate was less than 100 per second when 3×10^4 counts were taken. Suitable precautions were observed to maintain identical counting geometry at all times. Counting rates were corrected for decay of the tracer and variations in the electronic equipment by comparison with the standard germanium plated copper sample.

Table 3

<u>Foil</u>	<u>Thickness</u> (mgm/cm ²)
1	66.215
2	64.648
3	66.029
4	67.570
5	67.756

An absorption curve was determined for each sample, both before and after the diffusion anneal. The measurements were made

at least twelve hours after the plating process and the anneal to allow the gallium-68 and the germanium-68 to come to equilibrium. Figure 4 shows the absorption curves obtained for one of the samples. It is seen that the curve before anneal is straight throughout the five foils, whereas the curve after anneal is straight through only the first three foils, due to the penetration of the tracer into the copper sample.

The slope of the upper curve in figure 4 gives the mass absorption coefficient of the copper foils. This value must be multiplied by the density of the copper diffusion samples to give the linear absorption coefficient required for the surface decrease method. The densities were determined by measuring the sample dimensions with a travelling microscope and the sample weights on a Mettler microbalance.

3.4 Gamma Counting

A small fraction of the plated tracer material is usually lost by evaporation during the diffusion anneals, and this fraction does not participate in the diffusion process. If no allowance were made for this loss, the value of B used in equation (14) would be too small. The fraction lost during each anneal was determined by measuring the intensity of the 0.51 Mev gamma radiation from each sample before and after the anneal. Since the gamma radiation has a very small absorption coefficient in copper, the two measurements should

Figure 4. Absorption Curves

the same dimensions as the sample. The silica plate and the two copper discs were bound together with thin copper wire so that only minimum error was involved in measuring the temperature of the diffusion samples. The sample assembly was sealed inside a quartz tube with the thermocouple leads extending through the brass plug of the tube as shown in figure 5b. The quartz tube was evacuated to about 5×10^{-5} torr using an Edwards rotary-diffusion pump unit and industrial grade argon gas was admitted to the tube to raise the pressure to about one-half an atmosphere. Inside the furnace about five inches of the sample end of the quartz tube was placed inside a refractory steel cylinder so that the temperature gradients around the sample were reduced. The temperature of the electrical resistance furnace (see figure 5a) was controlled with a Phillips strip chart recorder. A Speedomax strip chart recorder monitored the temperature of the sample from the thermocouple tied to the sample, while more accurate measurements were made periodically on a Leeds and Northrup millivolt potentiometer type 8686.

Fourteen diffusion anneals were made in the temperature range 652°C to 1014°C . The temperature was controlled to $\pm 2^{\circ}\text{C}$ of the mean temperature during the diffusion anneal.

The diffusion time required for each temperature was estimated by assuming that the values of A_2 and Q_2 for the Cu-Ge system would be about equal to the average of the corresponding published values for the Cu-Ga and the Cu-As systems. The aim in each diffusion anneal was to obtain a $\sqrt{Dt}$ value of about 10^{-2} cm., this value being a useful

Figure 5A. Furnace System

Figure 5B. Diffusion Tube

compromise between obtaining sufficient accuracy from the surface decrease method and excessively long diffusion times.

3.6 Sectioning Method

A Swiss made precision Schaublin lathe was acquired near the completion of the work. The lathe was used to section several samples to check the validity of the surface decrease method.

The diffused samples were waxed to a brass holder which was held in the lathe chuck. The sample was aligned with its front plated face parallel to the motion of the cutting tool using a dial gauge which was graduated to 0.0001 inch. A perspex chip catcher was constructed to fit over the sample holder with the opposite end open to allow the cutting tool and the dial gauge to enter. Several trial cuts were made to determine the proper positioning and shape of the cutting tool and also to verify the effectiveness of the chip catcher. The chips were transferred from the chip catcher to small pre-weighed glass bottles of uniform size which were then reweighed. The thickness of the cut was determined from the cross-section of the cut face, the weight of the chips and the density of the copper samples. The thickness determined by weight and the thickness determined by the dial gauge were always within the experimental error of the two methods.

The samples were reduced in diameter by about 0.035 to 0.040 inch to eliminate any edge effects. Each of the fifteen cuts off the face of the sample was approximately 0.001 inch thick.

The chips were dissolved in five millilitres of dilute nitric acid to maintain a uniform counting geometry in the well type NaI (Tl) scintillation crystal. The scaling was done using an RIDL unit which contained the high voltage supply, the amplifier and the scaler. Typically, 10^5 counts were taken of the 0.51 Mev gammas for each section.

Chapter 4

RESULTS

4.1 Absorption Coefficient

The absorption curve for each of the fourteen samples before annealing was analysed by a least squares method to give the mass absorption coefficient of the copper absorbing foils. The fourteen values were averaged to give an average mass absorption coefficient of $7.699 \pm 0.271 \text{ cm}^2/\text{gm}$. The average density of the copper samples was $8.979 \pm 0.045 \text{ gm/cm}^3$, giving an average linear absorption coefficient of $69.128 \pm 2.091 \text{ cm}^{-1}$. The errors in each case are the standard deviations.

4.2 Diffusion Coefficients from the Surface Decrease Method

The value of B/B_0 (equation 14) was found by calculating the ratio of the positron counting rate of each sample before and after annealing. The counting rates were, in fact, those used to plot the absorption curves of each anneal. The ratio was calculated with, respectively, 0, 1, 2 and 3 copper absorbing foils in the sample holder to obtain an average value of B/B_0 for each run. This procedure was used since the sample holder already included a certain amount of absorbing material (0.008 inch brass) and there appeared little justification in not using all the points on the post anneal absorption curves which fell within the range of the exponential

absorption (figure 4). In addition, the four values of B/B_0 for each run were always equal within the range of experimental errors on the individual counting rates. All of the previously explained corrections were made on each counting rate.

The approximate value of $\mu^2 Dt$ was read off figure 1 and a more exact value obtained by solution of equation (14). The known values of μ and t were then used to calculate D for each run. Table 4 shows the results obtained for each of the fourteen samples.

4.3 Diffusion Coefficients from the Sectioning Method

Three samples were sectioned and their diffusion coefficients determined. The specific activity of each section was plotted on a log scale against the penetration distance squared to obtain the penetration profiles shown in figure 6. According to equation (9), the curves should be straight lines with slopes equal to $-1/4Dt$.

It is seen that the lowest temperature profile has an upward curvature at the lower end. This is attributed to edge contamination since the diameter of that sample was only reduced by about 0.010 inch, instead of 0.040 inch as on the other two samples. The low temperature profile was drawn by ignoring the curvature and sighting the best line, while the remaining two were drawn after analysing the sectioning data by the least squares method. The diffusion coefficients obtained from this analysis are also shown in

Table 4

DIFFUSION OF GERMANIUM-68 IN COPPER

Temperature (°C)	Time (sec)	D _{absorp} (cm ² /sec)	D _{section} (cm ² /sec)
1014.4	1.353×10^4	9.048×10^{-9}	
979.7	1.547	5.205	
961.8	2.435	4.783	
932.1	3.343	2.734	2.864×10^{-9}
905.1	4.435	2.181	
881.3	6.963	1.049	
853.5	1.076×10^5	9.165×10^{-10}	
829.9	1.727	5.075	
803.4	2.707	2.901	3.233×10^{-10}
779.7	4.430	2.690×10^{-11}	
775.7	7.710	1.186×10^{-10}	
728.4	1.302×10^6	6.991×10^{-11}	
701.7	2.326	3.941	3.649×10^{-11}
652.6	6.584	6.293×10^{-12}

Figure 6. Penetration Profiles for the Diffusion of Ge In Cu.

Table 4 for comparison with the values obtained from the surface decrease method.

4.4 Determination of A_2 and Q_2

The diffusion coefficients obtained from the surface decrease method were plotted on a log scale against the inverse absolute temperature to obtain the Arrhenius plot shown in figure 7. The Arrhenius relation (equation 1) allows the determination of both the frequency factor A_2 and the Activation energy Q_2 from this plot.

The two samples diffused at the temperatures 779.7 and 652.6 gave anomalous results for D_2 . No adequate explanation can be given for these results but it may be significant that in both cases there was an abnormally large loss of tracer material during the diffusion anneal. A least squares analysis was made on the remaining twelve values of D_2 to determine the line of best fit which is given by the expression

$$D_2 = 0.238^{+0.099}_{-0.070} \exp - \frac{43\,700 \pm 779}{RT} \text{ cm}^2/\text{sec} \quad (37)$$

where the errors given are the standard errors arising out of the least squares treatment.

Figure 7 also shows Mercer's²⁵ result for the self-diffusion of copper.

Figure 7. Temperature dependence of Ge diffusion in Cu. Self diffusion in Cu is also shown.

Chapter 5

DISCUSSION

5.1 Discussion of Errors

The surface decrease method was chosen over the sectioning method for measuring the diffusion coefficients because a precision lathe was not available when the work was begun. The principle difficulty with the absorption technique is the determination of the absorption coefficient of the copper. Zhukhovitsky²⁶ and Smith, Jaumot and Arné²⁷ compare the methods of determining diffusion coefficients using radioactive tracers and give some of the errors associated with each method.

In deriving the basic equation for the surface decrease method, equation (14), D was assumed to be independent of penetration distance. This assumption is good since only a thin layer of radioactive tracer is plated on the surface of the sample thus reducing the concentration gradient through the solvent. However, the diffusion coefficient also varies with the annealing temperature. As the sample warms up, the diffusion coefficient takes a series of values until the final annealing temperature is reached. A correction for these intermediate values of D has been made by Lai²⁸ using the equation

$$t_{\text{corr}} = \frac{\int_0^{t_1} \exp[-Q/RT(t)] dt}{\exp(-Q/RT_1)} + (t_2 - t_1) \quad (38)$$

where t_1 is the time when the annealing temperature is reached, t_2 is the time at the end of the anneal, T_1 is the annealing temperature, Q is an estimated activation energy and t_{corr} is the corrected time of annealing to give the true diffusion coefficient. By plotting $\exp(-Q/RT(t))/\exp(-Q/RT_1)$ against time, an equivalent time at the annealing temperature can be found which corresponds to the warm up period. The error involved in determining the total annealing time will, in general, be significant only for the shorter anneals. In the shortest anneal of about three hours forty five minutes, there was an approximate error of ± 5 minutes in the correction term which gives an error in the total time of about $\pm 2\%$. For the next five runs the total times ranged from four hours eighteen minutes to nineteen hours twenty minutes as shown in Table 4, and the error in the total times ranged from $\pm 1.9\%$ to $\pm 0.4\%$. Below $\pm 0.4\%$ the errors were neglected in the determination of D . This same method can also be used for the cooling off time correction. However, in this work the cooling off time was negligible compared to the warm up time.

The ratio of the corrected positron count rate of the samples after anneal to the positron count rate of the samples before anneal is B/B_0 . Each corrected value of B/B_0 was determined from eight separate counting measurements: positron count rates on the sample and the standard both before and after anneal and gamma measurements on the sample and the standard before and after anneal. The error in B/B_0 is the statistical error involved in the number of counts taken

in each measurement. Since 10^5 counts were taken for all measurements except where the count rate was less than 100 per second when 3×10^4 counts were taken, the error in B/B_0 ranged from about $\pm 2.5\%$ to $\pm 3.6\%$. Four values of B/B_0 were determined from the first four points on the absorption curves for each of the fourteen samples. The average of the four values for each sample was then used to determine $\mu^2 Dt$ from equation (14). In all cases the standard deviation of the four values was less than $\pm 2.5\%$. The resulting error associated with the values of $\mu^2 Dt$ was about $\pm 10\%$, since a small error in B/B_0 gives a larger error in $\mu^2 Dt$ as seen in figure 1. The absorption coefficient used was the average of the fourteen values found from the absorption curves. The standard deviation of the values of μ was $\pm 3\%$ or $\pm 6\%$ in μ^2 . The error bars shown on the values of D plotted in figure 7 are about $\pm 16\%$ and are the result of the errors in counting, absorption coefficient and time of anneal, as discussed above.

The values of D determined at the temperatures 779.7 and 652.6 were not used in finding the equation of the Arrhenius plot. Figure 7 shows these two results were sufficiently anomalous that it seemed justified to ignore them in the calculation of A_2 and Q_2 . No positive explanation can be given for the results in these two cases but it is most likely related to the large loss of tracer material which occurred for these samples. However, it should be noted that the sample annealed at 905.1°C also suffered a large loss of tracer but gave a result which appeared normal.

The diffusion coefficients obtained from the sectioning method included an error of about $\pm 11\%$. This figure is a standard error arising from the least squares analysis of the penetration profiles shown in figure 6 and is due to chip collection, weighing and counting.

The straight penetration profiles of figure 6 show a Gaussian distribution of the tracer in the sample, which indicates that the thin film solution of Fick's law (equation 9) and also the assumption of D being independent of penetration distance were applicable. The good agreement between the diffusion coefficients obtained from the two methods (Table 4) indicates the general validity of the surface decrease method.

5.2 Comparison of Results with the Lazarus-Le Claire Theory

The Lazarus theory predicts that germanium ($Z = +3$) diffuses in copper more rapidly than the self-diffusion of copper. Figure 7 shows that this is indeed the case. Figure 8 shows the experimental activation energies for Cu, Zn, Ga, Ge, and As diffusing in copper, plotted against the positive excess valence Z . As predicted by the Lazarus-Le Claire theory, the activation energies decrease linearly as Z increases, the main discrepancy being the value for zinc. Also in figure 8 is the curve of $Q_0 + \Delta H_2 + \Delta E$ (from Table 2) plotted against positive excess valence. The difference between this latter curve and the experimental activation energies is the correlation correction

Figure 8. Variation of Activation Energy with Positive Excess Valence

factor of the Le Claire theory. It is seen that this difference increases as Z increases and hence makes a significant contribution to the activation energies.

Table 5 shows the percent difference between the values of ΔQ_{th} and ΔQ_{expt} given in Table 2.

Table 5

Z		% difference between ΔQ_{th} and ΔQ_{expt}
Zn	+1	-5
Ga	+2	+16
Ge	+3	+7
As	+4	$+6\frac{1}{2}$

It is seen that the results of the present work with germanium are in as good agreement with the Le Claire theory as the previous work with the other impurities.

5.3 Correlation Factors

Le Claire² uses the expression

$$f_2 = 1 - (A_2/A_0) f_0 \exp(C/RT) \exp(-\Delta H_2/RT) \left[\exp(-\Delta H_1/RT) + \frac{7}{2} \exp(-\Delta H_3/RT) \right]^{-1} \quad (39)$$

to give an estimate of the impurity correlation factor f_2 . This relation is obtained by equating the empirical ratios of D_2/D_0 obtained from the Arrhenius equations (1) and (2) to the theoretical ratio from equations (25) and (27). This gives an expression for the ratio v_2/v_0 which when combined with equations (23) and (24) gives the above value of f_2 . The derivation also assumes, following Manning,²⁹ that the ratios v_1/v_0 and v_3/v_0 are both equal to unity since these frequencies all refer to the same atomic species.

Values of C , ΔH_1 , ΔH_2 , ΔH_3 and the experimental A_2 found in Tables 1 and 2 were substituted into equation (39). The result for germanium is $f_2 = 0.36$. This result is in good agreement with the values given by Le Claire for the other impurities, e.g., 0.55 for Zn, 0.27 for Ga and 0.37 for As. Since $f_0 = 9/11$ for self-diffusion, impurities which diffuse faster than the self-diffusion rate should have values of f_2 less than $9/11$ as is the case.

5.4 Conclusion

The results obtained from these experiments have been shown to be in good agreement with the Lazarus-Le Claire theory, and thus offer more evidence that impurity diffusion in f.c.c. lattice metals proceeds by the vacancy mechanism.

It would be interesting to continue the sectioning technique on the remaining samples and especially on the two samples for which

the surface decrease method gave anomalous results. The extension of this work to lower temperatures would also be useful, particularly to investigate the effects of dislocations in the copper crystals.

REFERENCES

1. D. Lazarus, Phys. Rev. 93, 973 (1954)
2. A.D. Le Claire, Phil. Mag. 7, 141 (1962)
3. R.A. Swalin, Acta Met. 5, 443 (1957)
4. J. Hino, C.T. Tomizuka and C.Wert, Acta Met. 5, 41 (1957)
5. C.T. Tomizuka, to be published. Quoted from Lazarus, Solid State Physics, 10 (1960)
6. A. Kuper, H. Letaw Jr., L. Slifkin, E. Sonder and C. Tomizuka, Phys. Rev. 96, 1224 (1954)
7. T. Hirone, N. Kunitomi, M. Sakamoto and H. Yamaki, J. Phys. Soc. Japan 13, 838 (1958)
8. M.C. Inman and L.W. Barr, Acta Met. 8, 112 (1960)
9. C.E. Mackliet, Phys. Rev. 109, 1964 (1958)
10. J. Steigman, W. Shockley and F.C. Nix, Phys. Rev. 56, 13 (1929)
11. V. Linnenbom, M. Tetenbaum and C. Cheek, J. Appl. Phys. 26, 932 (1955)
12. C. Zener, J. Appl. Phys. 22, 372 (1951)
13. A.D. Le Claire, Acta Met. 1, 438 (1953)
14. C. Wert and C. Zener, Phys. Rev. 76, 1169 (1949)
15. A.D. Le Claire, "Diffusion in Body-Centered Cubic Metals", The American Society for Metals, Metals Park, Ohio, U.S.A., Chap.1 (1965)
16. H.B. Huntington, G.A. Shirn and E.S. Wajda, Phys. Rev. 99, 1085 (1955)
17. A.D. Le Claire and A.B. Lidiard, Phil. Mag. 1, 518 (1956)
18. L.C.R. Alfred and N.H. March, Phys. Rev. 103, 877 (1956)

19. H. Fujiwara, J. Phys. Soc. Japan 10, 339 (1955)
20. K. Umeda and Kobayashi, J. Phys. Soc. Japan 13, 148 (1958)
21. H.B. Huntington, Phys. Rev. 61, 325 (1942)
22. The Radiochemical Manual, The Radiochemical Center, Amersham, Buckinghamshire (1962)
23. R. Schwarz, F. Heinrich and E. Hollstein, Zeitschrift fur Anorganische und Allegemein Chemie 229, 146 (1936)
24. C.G. Fink and V.M. Dokras, J. of Electrochemical Soc. 95, 80 (1949)
25. W.L. Mercer, Thesis Univ. of Leeds (1955). Also W.L. Mercer and R. Shuttleworth, to be published. Quoted from Le Claire.²
26. A.A. Zhukhovitsky, Conf. of the Academy of Sciences of the U.S.S.R. on the Peaceful Uses of Atomic Energy (July 1955), English Translation, p.63, U.S.A.E.C., Washington (1956)
27. R.L. Smith, F.E. Jaumot Jr. and J.A. Arné Jr., Phys. Rev. 94, 1407 (1954)
28. D.Y.F. Lai, "Diffusion in Body-Centered Cubic Metals", The American Society for Metals, Metals Park, Ohio, U.S.A., Chap.20 (1965)
29. J.R. Manning, Phys. Rev. Letters 1, 365 (1958)