IONIC MIGRATIONS IN CRYSTALLINE SOLIDS

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by
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İZMİR

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ABSTRACT

In this study, the diffusion which has a big importance in the new technology has been considered and in a crystal which include diffusible ions. It has been suggested to develope a new technique for determining diffusion coefficient of diffusing ions under the influence of a driving force such as an electric field. The study has a simple introduction to explain the importance of diffusion.

In Chapter Two, point defects, the formations and motions of point defects in a crystal, defect motion mechanisms, Fick's equations, atomic and continuum approaches to explain the diffusion, and the term of driving force in the event of diffusion have been considered.

In Chapter Three, some informations are given about the kinds of diffusion coefficients, the methods to measure the diffusion coeffcient and some terms about the diffusion in the literature.

In Chapter Four, it is given place to the numerical calculations to develop a new technique for determining diffusion coefficient which is the aim of this study.

ÖZET

Bu çalışmada, günümüz teknolojisinde büyük bir öneme sahip olan difüzyon kavramı üzerinde duruldu ve yayılabilir iyonlardan içeren bir kristal yapının içinde, difüze olan iyonların elektrik alan gibi bir sürücü kuvvetin etkisinde difüzyon katsayısını ölçebilmek için yeni bir teknik, önerilmeye çalışıldı. Çalışma, difüzyonun önemini belirten kısa bir girişe sahiptir.

İkinci bölümde, nokta kusurlar, nokta kusurların kristal içinde oluşumları ve hareketleri, kusur hareketi mekanizmaları, Fick denklemleri, difüzyon olayını açıklayabilmek için atomik ve süreklilik yaklaşımlar ve difüzyon olayındaki sürücü kuvvet kavramları üzerinde duruldu.

Üçüncü bölümde, difüzyon katsayısı çeşitleri, difüzyon katsayısı ölçme teknikleri ve bununla ilgili literatürde yer almış birkaç kavram hakkında bilgi verildi.

Dördüncü bölümde ise, çalışmanın amacı olan yeni bir difüzyon katsayısı ölçme tekniği geliştirebilmek için yapılan sayısal hesaplara yer verildi.

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CHAPTER ONE
INTRODUCTION

1.1. Introduction

An understanding of atomic transport in crystalline solids is essential to the understanding of solid state reactions as well as of many other phenomena. Namely, diffusion is responsible for many phenomena in materials science and engineering such as segregation, grain growth etc. Diffusion has been extensively studied since the end of last century, and many techniques have been employed by scientists to determine the diffusion coefficient. Traditionally, it is also possible to measure the diffusion process directly through determination of a concentration profile of the diffusing element.

'To develop a technique for determining diffusion coefficient' will be the aim of this study in which we considered the Ionic Migration in Crystalline Solids.

There are two main approaches to diffusion theory: 1. the atomic approach, where the atomic nature of the diffusing substance is explicitly considered; 2. the continuum approach, where the diffusing substance is treated as a continuous medium and the atomic nature of the diffusion process is ignored. Many useful equations result from the continuum approach. For example, general thermodynamic equations can be found which relate diffusion fluxes to thermodynamic driving forces. This approach in one sense simplifies the problem since it directly relates the initial and final states, but also it is limited in its result since it ignores the details of the atomic motions.

A more complete picture of diffusion phenomena is obtained if the atomic motions are considered. Equations can be found relating macroscopic quantities, such as atom jump frequencies. Often, several macroscopic diffusion quantities are related to the same atomic parameter. Thus, the atomic approach allows the various macroscopic quantities to be related to one another in ways not possible form a purely continuum approach.

In this study, we tried to develop a new technique for determining difussion coefficient, [D(T)] by considering the consantration profilles of the ions in an ionic crystal under the influence of an electric field (**E**).

CHAPTER TWO
ATOMIC MOTIONS AND POINT DEFECTS IN CRYSTALLINE SOLIDS

2.1. Introduction

There are minimum 10^{28} atoms in the volume of $1mm^3$ of a crystalline material. Therefore it is impossible to imagine a crystal without defects. Most of the defects in a crystalline material are;

- Point defects
- Line defects

In this chapter, point defects will be discussed with their formations, species, and motions in the crystal lattice, because these defects effect the electrical characteristics of semiconductors. Besides, the definitions of energy of formation, energy of motion, and activation energy will be expressed and the mechanisms of defect motions, diffusion in solids, and Fick's equations will be mentioned.

2.2. Point Defects

Point defects are also called zero dimensionally defects, because these defects grow in a volume which is so small and includes only one or two atoms. As we can see in the Figure 2.1., there are three kinds of point defects in a crystalline lattice,

- Vacancy (1)
- Interstitial (2)

- Impurities (3), (4).

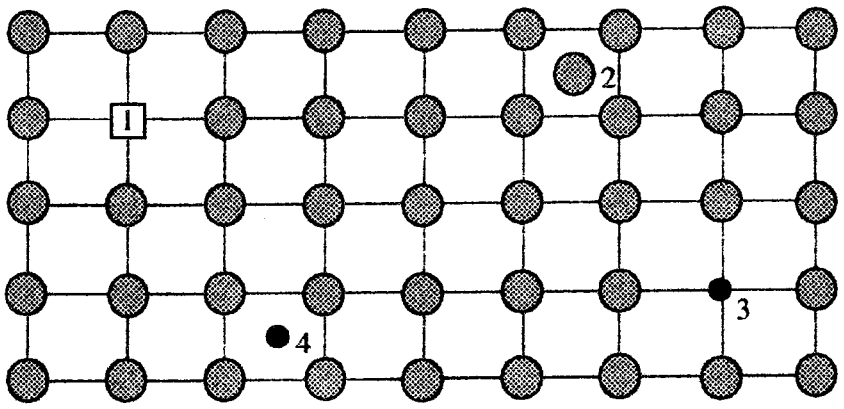

Figure 2.1. Point defects in crystalline structures

Vacancy and interstitial atoms are the natural defects of a crystalline lattice, but impurities can vaccinate to a structure and also they can be natural.

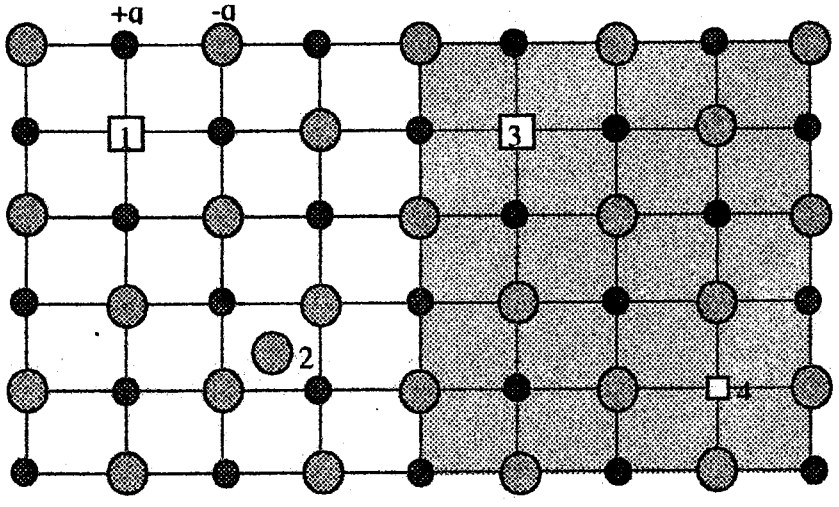

Figure 2.2. Frenkel and Schottky defects in ionic crystals

These defects which are written above, can grow in a crystal its bonds are van der Waals or covalent. But the situation is different in ionic crystals, because in an ionic crystal, the electrical charges must be neutral. That's why, in an ionic crystal, it is mentioned about Frenkel (1, 2, as we can see in Figure 2.2., for example CaF_2), and Schottky (3, 4, for example NaCl) defects. Besides, in an ionic crystal which includes only negative ion vacancies, the charge equilibrium can be obtained by trapping electrons into these vacancies (F centers).

2.3. The Vacancies in Crystalline Solids

Let us consider a solid at temperature T and its volume is constant. If the Gibbs Free Energy of this solid is minimum, the solid is thermal equilibrium. The Gibbs Free Energy of a solid with enthalpy H and entropy S;

$$G = H - TS \tag{2.1}$$

If ε_v is the energy to form an atom vacancy, the increase of entropy of a solid which includes n atom vacancies and N atoms, because of the defect of solid;

$$S_v = k_B \ln[\frac{(N+n)!}{(N!n!)}] \tag{2.2}$$

(The Boltzmann Equation). Therefore, the Gibbs Free Energy of the solid;

$$G_v = n\varepsilon_v - k_B T \ln[\frac{(N+n)!}{(N!n!)}] \tag{2.3}$$

with Stirling's formula,

$$\ln x! \approx (x+\frac{1}{2})\ln x - x + \frac{1}{2}\ln 2\pi \tag{2.4}$$

and for $1 \langle\langle n \langle\langle N$;

$$(\frac{\partial G_v}{\partial n})_{T,V} = \varepsilon_v - k_B T \ln(\frac{N+n}{n}) \tag{2.5}$$

as we have said before, if a solid is in thermal equilibrium,

$$(\frac{\partial G_v}{\partial n})_{T,V} = 0 \tag{2.6}$$

Thus, the vacancy concentration of a solid in thermal equilibrium at temperature T,

$$n \approx N \exp(-\varepsilon_v / k_B T) \tag{2.7}$$

obtained.

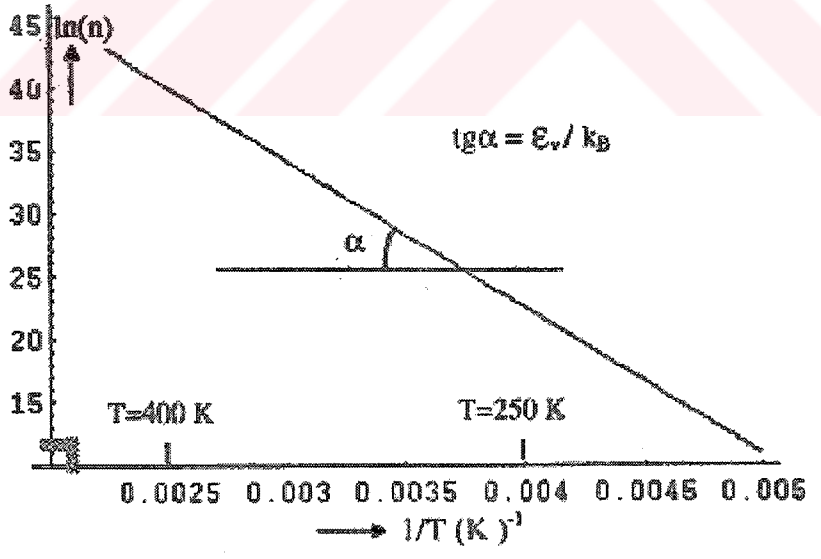

Figure 2.3. The graph of vacancy concentration depends on T in a crystalline solid

Figure 2.3. shows us $\ln(n) = f(1/T)$ relation for N=10^{30} atoms/cm^3 and $\varepsilon_v = 1\text{eV}$. With the help of Figure 2.3., we can obtain the energy of formation of a vacancy by measuring the change of any physical quantity, which is effected by the atom vacancy, depends on temperature in a solid.

Equation (2.7) can also be written as;

$$p = p_0 \exp(-\varepsilon_v / kT), \tag{2.8}$$

here, p is the probability of exist in a given location in a crystalline solid. For p, we can also write;

$$p = n/N \qquad p_0 = \exp(S/k) \quad \text{or} \quad p \to p_0 \quad \text{if} \quad T \to \infty \tag{2.9}$$

2.4. The Activation Energy of an Atom in a Crystalline Solid

In a crystalline solid, an atom moves from a lattice point to another. It is called "Atomic Diffusion". Figure 2.4. shows us the internal potantial energy between the atoms of a crystal.

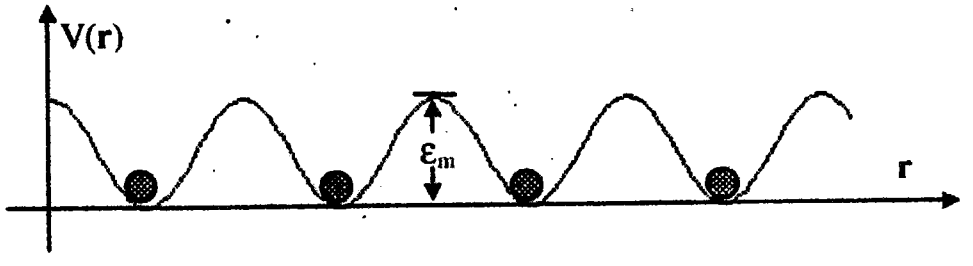

Figure 2.4. The crystal potential at a given direction

Here, ε_m depends on the properties of the atoms and the difference between atoms. An atom vibrates in a cell of potential by harmonic vibration motion, and if the atom passes over from a cell to another, it can move in the crystal. That's why, ε_m is called the energy of motion of an atom.

In thermal equilibrium, if the temperature of the solid is high enough, the atom can jump from a lattice vacancy to a neighbor vacancy with the frequency,

$$\Gamma = \omega q \tag{2.10}$$

here, ω is the frequency of vibration in the potential cell, and q is the probability of exchange,

$$q = q_0 \exp(-\varepsilon_m / k_B T) \tag{2.11}$$

Of course, there must be suitable neighbor vacancies in the neighborhood for the diffusion. If z is the number of neighbor vacancies and p is the probability of exist of them, the atom jump to neighbor vacancies with the frequancy,

$$\upsilon = zwqp \tag{2.12}$$

Thus, we can obtain,

$$\nu = zp_0 wq_0 \exp[-(\varepsilon_m + \varepsilon_v)/k_B T] \tag{2.13}$$

and,

$$\nu = \nu_0 \exp[-Q/k_B T] \tag{2.14}$$

here, $Q = (\varepsilon_v + \varepsilon_m)$ is the activation energy of an atom in the crystal.

2.5. The Mechanisms of the Motion of Defects

2.5.1. Introduction

The theory of atomic diffusion begins with the consideration of diffusion mechanisms. Let us consider this in the three phases of matter. In gases, where the molecules are widely seperated, it is asumed that each molecule travels in a straight line until it collides with another molecule (or with the walls of the container). This collision changes the speed and direction of molecule, and it then proceeds in the new direction until it collides with still another molecule, and so on. This approach has led to a satisfactory kinetic theory of diffusion in gases with diffusion coefficient being related to the average velocity and mean free path of the molecule.

In liquids, the situation is different and also more comlex. In liquids, a molecule cannot move freely between the molecules immediately surrounding it. Its motion is probably best described as an irregular jostling motion. This is quite difficult to treat accurately.

The transport and diffusion in amorphous solids, with no regular arrangement of atoms, is also difficult to treat.

In crystalline solids, it again is possible to describe the diffusion mechanisms in simple terms. The ordered crystal lattice restricts the possible atom motions and allows a simple description of each specific atom displacement. This contrasts with the situation in a gas, where a perfectly random arrangement of atoms is assumed, and in liquids and amorphous solids, which are neither really random nor really ordered.

In any crystal, there is a regular array of lattice sites which are energetically favored positions for atoms. The basic assumption made to explain diffusion is that each diffusing atom makes a series of jumps between the various equilibrium lattice

sites. These jumps are in more or less random directions and allow the atoms to migrate through the crystal.

A number of possible diffusion mechanisms can be distinguished, depending on the type of elemetary jump which takes the atom from one equilibrium site to another. Some of these mechanisms can be listed as fallows;

- Vacancy mechanism
- Exchange mechanism
- Ring mechanism
- Interstitial mechanism
- Interstitialcy mechanism.

2.5.2. Vacancy mechanism

In thermal equilibrium, any crystal at a temperature above absolute zero contains a certain number of vacant lattice sites. These vacancies provide an easy path for diffusion.

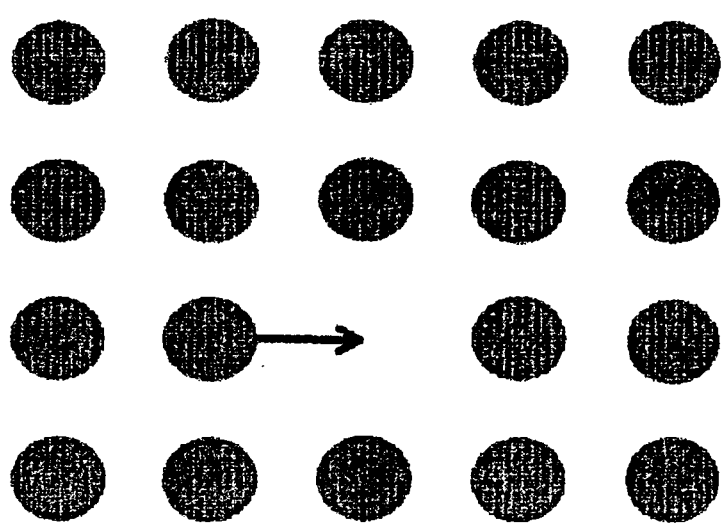

Figure 2.5. Vacancy mechanism, elementary jump

The elementary atom jump in the vacancy mechanism is the jump of an atom into a neighboring vacancy, as in Figure 2.5. The site previously occupied by the atom then is vacant, so that in effect the atom and vacancy merely exchage positions. Each atom moves through the crystal by making a series of exchanges with the various vacancies which from time to time are in its vicinity.

2.5.3. Exchange Mechanism

Possibly the simplest mechanism one can envision for the elementary jump is the direct interchange of two neighboring atom as showed in Figure 2.6.

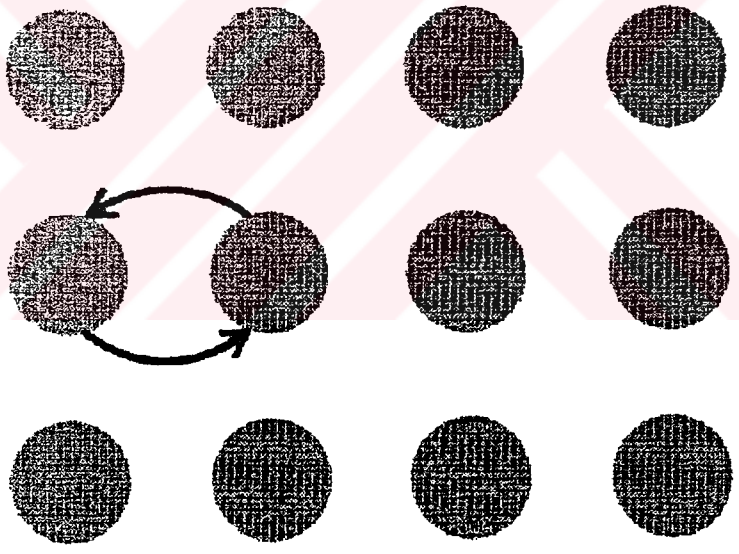

Figure 2.6. Exchange mechanism, elementary jump.

This mechanism is unlikely in crystals with tightly packed atom structures since each atom in this case is closely surrounded and hemmed in by its neighbors. The atoms would need to be considerably compressed before any two could squeeze past one another and interchange positions. On the other hand, this mechanism may be possible in very loosely packed crystals.

2.5.4. Ring Mechanism

A variation of the exchange is the ring mechanism, demonstrated in Figure 2.7.

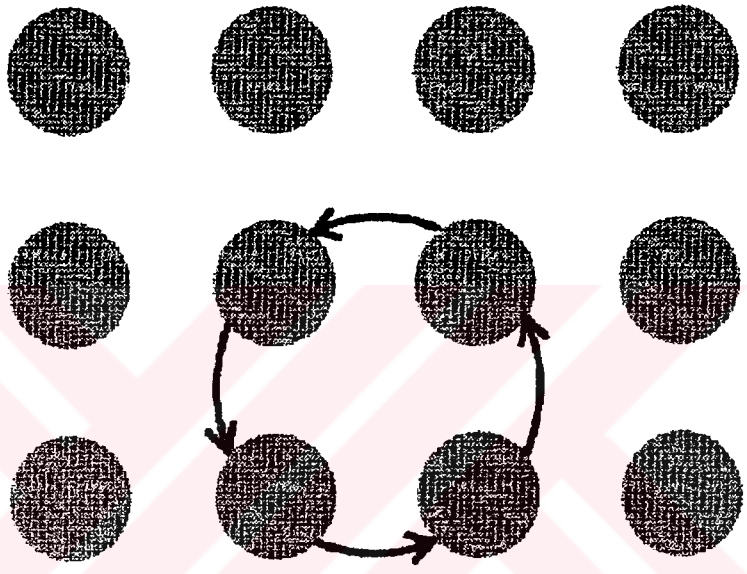

Figure 2.7. Ring mechanism, elementary jump.

Here a number of atoms (three or more) which are situated roughly in a ring move together so that the whole ring of atoms rotates by one atom distance. The compressions required here are not as grate as in a direct exchange mechanism. Nevertheless, this more complex mechanism also seems unlikely in most instances.

2.5.5. Interstitial Mechanism

The exchange and ring mechanisms are those which can operate in perfect crystals. When there are imperfections such as interstitials atoms, other mechanisms requiring considerable less energy can operate. One such mechanism is the

interstitial mechanism, also called the direct interstitial mechanism. Here an atom moves through the crystal by jumping directly from one interstitial site to another, as in Figure 2.8.

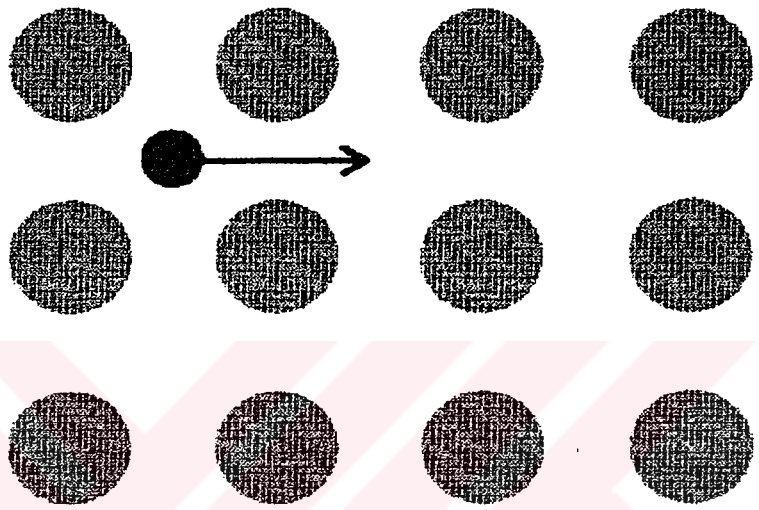

Figure 2.8. Interstitial mechanism, elementary jump.

This mechanism is particularly likely for diffusion of small impurity atoms, which easily fit into interstitial sites and in jumping don't greatly displace the solvent atoms from their normal lattice sites.

2.5.6. Interstitialcy Mechanism

When the interstitial atom is nearly equal in size to the lattice atoms or to the lattice atoms in a given sublattice, diffusion is more likely to occur by the interstitialcy mechanism, also called the indirect interstitial mechanism. Here the interstitial atom does not move directly to another interstitial site. Instead it moves into a normal lattice site and the atom which was originally at the lattice site is pushed into a neighboring interstitial site. We can see the interstitialcy mechanism in

Figure 2.9. The cooperative motion of the two atoms moves the interstitialcy, the region containing the additional atom, from one interstitial site to another. However, the original interstitial atom now occupies a normal lattice site. Two jumps of the interstitialcy are required to move an atom from one lattice site to another.

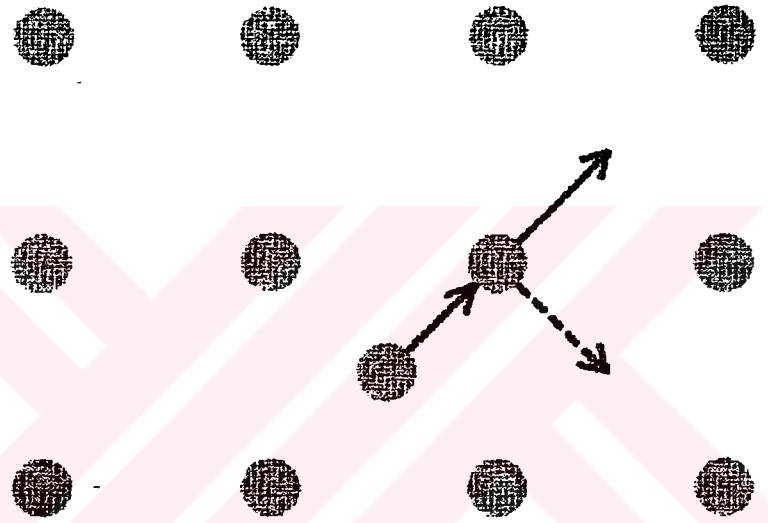

Figure 2.9. Interstitialcy mechanism.

In the Figure 2.9., the solid arrows show displacements of the diffusing atoms during an elementary jump in a collinear interstitialcy mechanism. The dotted arrow shows an alternative (noncollinear) motion for the lattice atom.

This mechanism seems to be important for diffusion of silver in the silver halides, where the silver ions are much smaller than the halogen ions. The most common type of interstitialcy jump is the collinear jump where the two atoms both move along the same line. However, noncollinear jumps whereby the atoms move at an angle to one another can also occur. (Manning, 1968).

2.6. Diffusion in Solids and Fick's Equation

There is two main approaches to decribe the diffusion in solids;

- Atomic approach
- Continuum approach

We will begin with the atomic approach and by using it (and later, by using the other approach), we will try to describe the diffusion and the concepts of it, i.e., diffusion coefficient. And the diffusion coefficient will be our subject to study and to research in the following chapters.

2.6.1. Atomic Approach

Let us think a strucrure which is became by adding some atoms (A) in a line direction. This is demonstrated in Figure 2.10. Let the point $x = 0$ be an interstitial vacancy which is occupied by an impurity atom (B).

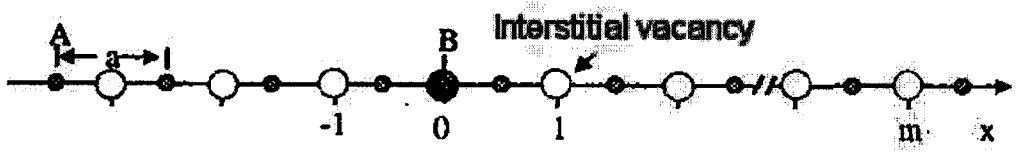

Figure 2.10. A crystal structure (one dimensional).

If we give some heat, Q, to the structure, the impurity atom, B, can move in the structure. Namely, B atom is became active, and this atom tries to jump to the

neighbor interstitial vacancies with frequency υ in the structure. Let the motion occur with interstitial mechanism.

In this event, there is no any driving force, that's why, the B atom's jump probability to the neighbor vacancies (in the both direction $+x$ and $-x$) is equal and ½. If the atom makes N jumps in the lattice, its probability of exist at $x = +ma$,

$$W(m,N) = \frac{N!}{(1/2)/(N+m)!(1/2)(N-m)!}(1/2)^N \tag{2.15}$$

We can write Eq.(2.15) in another form by using logarithm and Stirling's formula, Eq.2.4., for $m \langle\langle N$

$$\ln W(m,N) \approx -(1/2)\ln N + \ln 2 - (1/2)\ln \pi - (m^2/2N^2) \tag{2.16}$$

thus, we can obtain,

$$W(m,N) = \left(\frac{2}{\pi N}\right)^{1/2} \exp\left(-\frac{m^2}{2N}\right) \tag{2.17}$$

Eq.2.17. is B atom's , which is active in the interstitial vacancy at $x = 0$, probability of exist at $x = +ma$ after N jumps in one dimensional structure. $W(m,N)$ is a discontinuous (discreete) function depends on m. $W(m,N)$ is demonstrated in Figure 2.11. We can rewrite this function as a continuous function form depends on x. Let the continuous function be $W(x,N)$. With a constant, A, for $x = ma$,

$$W(x,N) = AW(\frac{x}{a},N) \tag{2.18}$$

can be written. This continuous function is also a probability distribution function. Thus, we can write this for it;

$$\int_{-\infty}^{+\infty} W(x,N)dx = A\int_{-\infty}^{+\infty}\left(\frac{2}{\pi N}\right)^{1/2}\exp\left(-\frac{x^2}{2Na^2}\right)dx = 1 \qquad (2.19)$$

for $m\langle\langle N$ and $N\to\infty$.

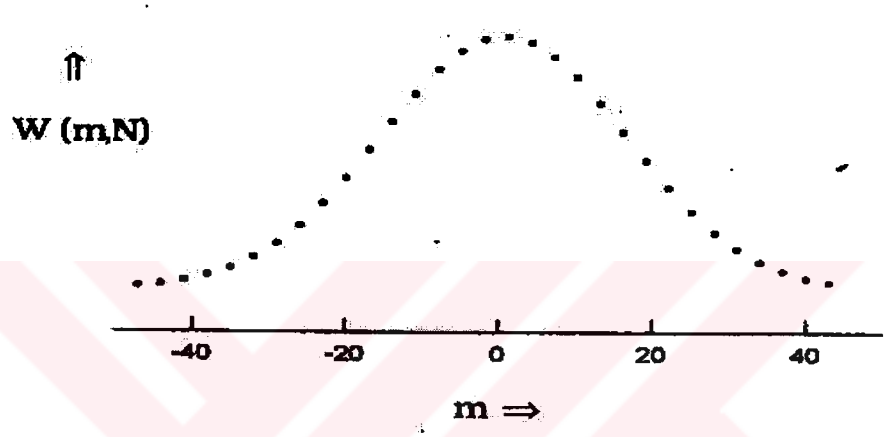

Figure 2.11. $W(m,N)$ distribution function for N=160.

From this integral, it can be obtained; $A=(2a)^{-1}$. Thus,

$$W(x,N)=\left(\frac{1}{2\pi Na^2}\right)^{1/2}\exp\left(-\frac{x^2}{2Na^2}\right). \qquad (2.20)$$

Eq.2.20. is the probability of exist of B atom at x point.

υ is the B atom's frequency of jump to neighbor interstitial vacancies. If, t is the time interval which in B atom is active, we can write $N = \upsilon t$. Therefore, we can obtain,

$$W(x,t) = \left(\frac{1}{2\pi a^2 vt}\right)^{1/2} \exp\left(-\frac{x^2}{2vta^2}\right) . \qquad (2.21)$$

Here, υa^2 is depends on temperature, and for one dimensionally this event $\upsilon a^2 / 2$ is called "Diffusion Coefficient, $D(T)$". For three dimensionally event the diffusion coefficient is $D(T) = \upsilon a^2 / 6$. Therefore, Eq. (2.21) becomes,

$$W(x,t) = \frac{1}{2(\pi t D(T))^{1/2}} \exp\left(-\frac{x^2}{4tD(T)}\right) . \qquad (2.22)$$

Eq. (2.22) is the probility of exist of B atom, which is been activated with temperature T at $x = 0$ and $t = 0$, at $t = t$ and $x = x$.

In a three dimensionally similar structure, if S_0 is the concentration of B atoms at $x = 0$ and $t = 0$, the concentration $c(x,t)$ at $t = t$ and $x = x$;

$$c(x,t) = S_0 W(x,t)$$

$$c(x,t) = \frac{S_0}{2(\pi t D(T))^{1/2}} \exp\left(-\frac{x^2}{4tD(T)}\right) \qquad (2.23)$$

The graph of $c(x,t)$ is drawn in Figure 2.12. for different times, t_1, t_2, t_3. Here, diffusion coefficient is given Arrhenius Equation;

$$D(T) = D_0 \exp(-Q / k_B T) \qquad (2.24)$$

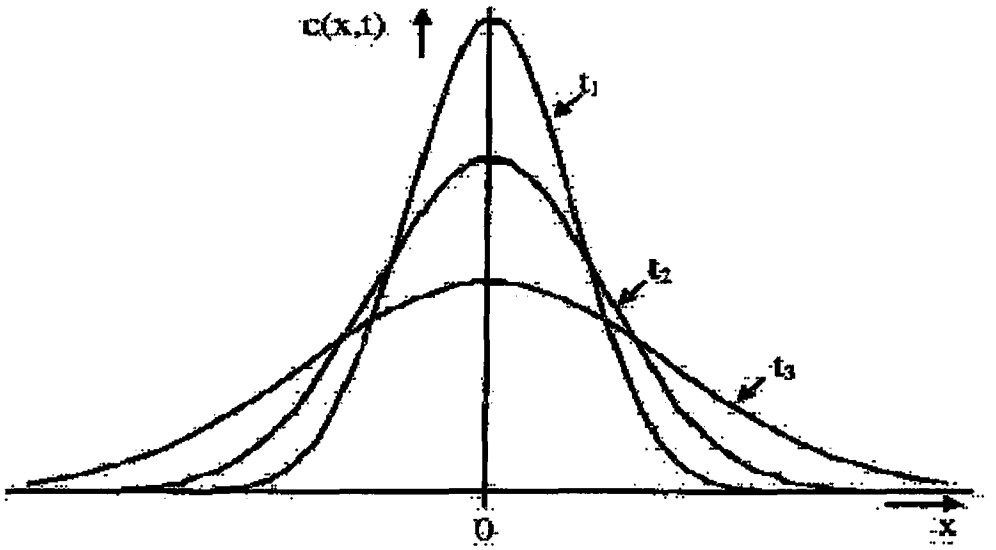

Figure 2.12. The graphics of $c(x,t)$ functions for $t_1 \langle t_2 \langle t_3$.

2.6.2. Continuum Approach

Let $c(x,t)$ be the concentration of B atoms which have the diffusion coefficient $D(T)$ and diffuse because of the difference of concentration in the $+x$ direction in any crystal structure which is formed by A atoms. (Figure 2.13.)

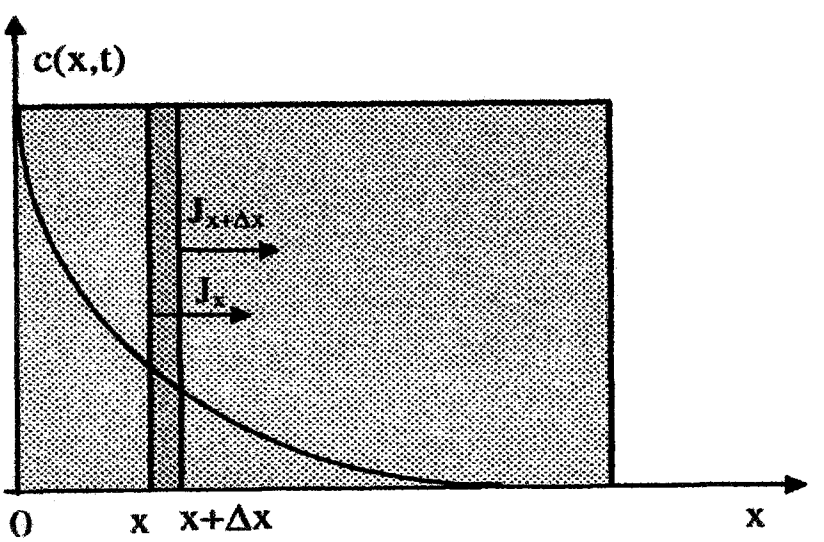

Figure 2.13. The change of $c(x,t)$ in any media.

The number of diffusing atoms in $+x$ direction into any surface at x per unit time and per unit cross-section is proportional with the gradient of concentration which is in the same direction;

$$J_x = -D(T)\frac{\partial c(x,t)}{\partial x} \tag{2.25}$$

This equation is called "Fick's first law". The number of increasing B atoms in per unit volume of Δx and at per unit time in x , $x+\Delta x$ and at t , $t+\Delta t$;

$$\frac{\Delta c(x,t)}{\Delta t} = \frac{(J_x - J_{x+\Delta x})}{\Delta x} \quad , \tag{2.26}$$

for $\Delta x \to 0$ and $\Delta t \to 0$;

$$\frac{\partial c(x,t)}{\partial t} = -\frac{\partial J}{\partial x} \, . \tag{2.27}$$

From Eq. (2.27) and Eq. (2.25), we can obtain,

$$\frac{\partial c(x,t)}{\partial t} = D(T)\frac{\partial^2 c(x,t)}{\partial x^2} \tag{2.28}$$

This is "Fick's second law" which has constant coefficient. The solution of Eq. (2.28) depends on the boundary conditions. If,

$$\text{For } t = 0 \, , \; c(x,t) = S_0 \text{ and}$$

$$t \geq 0 \; , \; c(\pm\infty, t) = 0$$

and if $c_F(k,t)$ is the Fourier transform of the concentration $c(x,t)$, we can write;

$$\frac{dc_F(k,t)}{dt} = -k^2 D(T) c_F(k,t) \tag{2.29}$$

With constant temperature ($D(T) \rightarrow D$), the general solution of Eq. (2.29) is;

$$c_F(k,t) = \frac{S_0}{\sqrt{2\pi}} \exp(-k^2 Dt) \tag{2.30}$$

Here, we can use Fourier transform again to obtain $c(x,t)$

$$c(x,t) = \frac{S_0}{2\pi} \int_{-\infty}^{+\infty} e^{-(k^2 Dt + ikx)} dk \tag{2.31}$$

With the $[k\sqrt{Dt} + \frac{ix}{\sqrt{4Dt}}] = u$ transform and Cauchy Theorem,

$$c(x,t) = \frac{S_0}{2\sqrt{\pi Dt}} \exp(-\frac{x^2}{4Dt}) \tag{2.32}$$

Equation (2.32) is the same with Eq. (2.23), namely, we have found the same result with using two different approaches; Atomic approach and Continuus approach. If the boundary conditions is $c(0,t) = S_0$; $t \geq 0$, $c(\pm\infty, t) = 0$, the solution of Eq. (2.28) will be,

$$c(x,t) = S_0 \left[1 - erf \frac{x}{2\sqrt{D(T)t}} \right] \tag{2.33}$$

If there is a driving force, i.e., any electrical field **E**, Eq. (2.32) changes a little;

$$c(x,t) = \frac{S_0}{2\sqrt{\pi Dt}} \exp(-\frac{(x-vt)^2}{4Dt}) \tag{2.34}$$

2.7. Definition of Driving Force

The term "driving force" can be used several different ways in connection with diffusion. The thermodynamic driving forces include not only forces on the individual atoms but only entropy of mixing terms, which give a "force" proportional to the concentration gradient of the diffusing species. Thus, the thermodynamic driving forces should be carefully distinguished from the other driving forces.

A driving force is defined as being any influence which makes the jump frequency for a jump in one direction between two given sites differ from that for a jump in the opposite direction between these same two sites. Driving forces include not only actual forces, such as those from an electric field, but also effective forces from other sources. Driving forces also include gradients of stress, electrical potential, temperature or chemical potential. In the literature, the concentration gradient of a diffusing species often is called a "driving force for diffusion". However, a simple concentration gradient does not make it any easier for a paricular atom to cross a barrier in one direction than in the opposite direction.

Even in the absence of driving forces the heights of energy barriers may depend on position. This occurs, for example, in an alloy of variable composition if the energy of motion depends on the composition. Then, the jump frequences are the same for jumps in either direction across a given barrier; but, for a jump from any given lattice site, the barrier to the right is easier to cross than the barrier to the left. This changes the diffusion equations in some respects. These effects are seperate from effects due to driving forces. (Manning, 1968).

CHAPTER THREE
THE MEASURING TECHNIQUES OF DIFFUSION COEFFICIENT

3.1. Introduction

In this chapter, some different methods will be concerned to examine the impurity concentration distribution arising from diffusion and to determine the diffusion coefficient. These all are based on the asumption that entry of a given type of ion or atom into a sample resulted from the temperature, surface concentration c_0.

3.2. Diffusion Coefficients

Equation (2.24) can be used to define a "diffusion coefficient" regardless of what forces or gradients are present. This leads to the definition of various kinds of diffusion coefficients.

3.2.1. Tracer Diffusion Coefficient

A particularly simple situation is that for diffusion of tracer isotope (in very dilute consentration) in an otherwise homogeneous crystal with no driving forces. Then the only factor that can lead to a net flow of tracer atoms is the concentration gradient of the tracer itself. A diffusion coefficient measured under these circumstances will be designated as D^* and will be called the "tracer diffusion coefficient". The term "self

diffusion coefficient" will refer to the special case where the tracer atoms are of the same species as the nontracer atoms in the crystal.

It of course is possible to introduce tracer atoms into nonhomogeneous crystals and measure their diffusion. We shall restrict the term "tracer diffusion coefficient", however, and have it refer only to diffusion in homogeneous crystals with no driving forces. This name seems appropriate since only tracer measurements allow diffusion coefficients to be measured directly in these crystals.

3.2.2. Effect of Driving Forces

When there is a driving force, atoms on the average have a greater than random probability of jumping in the direction of the driving force, for example $+x$ direction, than in the other directions. The driving force thus gives each atom an average drift velocity $\langle v \rangle_F$ in the direction of the driving force and contributes a term $c\langle v \rangle_F$ to the atomic flux. The subscript F here indicates that only the drift velocity arising from driving forces is included. This distinction is necessary since a diffusion coefficient gradient (which is not a driving force) contributes to the drift velocity $\langle v \rangle$ but not to the atom flux J across any given plane.

If we include driving forces, the diffusion equation becomes

$$J = -D^*(\partial c / \partial x) + c\langle v \rangle_F \tag{3.1}$$

The term $-D^*(\partial c / \partial x)$ arises merely because more atoms of the diffusing species are available on one side of the diffusion plane than on the other. The origin of this term is similar to that of the single term found for tracer diffusion with no driving forces. On the other hand, the term $c\langle v \rangle_F$ arises because the individual atoms have a preferred direction of jump.

The coefficient D^* in (3.1) does not to need to equal the tracer diffusion coefficient except in the absence of driving forces; however, it almost always does equal this coefficient at least to first order in small quantities. Also, it has the same basic origin. Hence, it is reasonable to use the same symbol D^* for this coefficient as for the tracer diffusion coefficient.

3.2.3. Intrinsic Diffusion Coefficients

In several important instances, the driving force F and hence the drift velocity $\langle v \rangle_F$ are proportional to $(\partial c / \partial x)$. Then it is useful to combine the terms on the right side of Eq. (3.1) so that

$$J_i = -D_i^I (\partial c_i / \partial x) \tag{3.2}$$

with

$$D_i^I = D_i^* - \frac{c_i \langle v \rangle_{Fi}}{(\partial c_i / \partial x)} \tag{3.3}$$

Here D_i^I is the intrinsic diffusion coefficient of species i, and the subscripts i indicate that the quantities are those for species i. Driving forces which are proportional to $(\partial c / \partial x)$ are those from (1) the diffusion potential in ionic crystals and (2) nonideal contributions to the chemical potential.

As an example, let us consider an ideal solid solution so that effect (2) goes to zero. Then let us consider interdiffusion of two species of cations in an ionic crystal where the anions remain fixed in position. If diffusion of the cation sublattice occurs by a vacancy mechanism, the two species of cations can have different values of D^*. In the absence of driving forces, this would lead to a flux of cation A,

$$J_A = -D_A^*(\partial c_A / \partial x) \tag{3.4}$$

and of cation B,

$$J_B = -D_B^*(\partial c_B / \partial x) \tag{3.5.}$$

With only two species of cations, $(\partial c_A / \partial x) = -(\partial c_B / \partial x)$. Then, if $D_A^* \neq D_B^*$, a net flux of cations might be expected, since according to (3.4) and (3.5),

$$J_A + J_B = (D_B^* - D_A^*)(\partial c_A / \partial x) \neq 0 \tag{3.6}$$

The net flux of electric charge, however, must equal zero in steady state, since otherwise local charge neutrality could not be maintained everywhere. Thus, when both cation species have the same charge q, there must be zero net flux of cations $(J_A + J_B = 0)$. In practise, a diffusion potential arises, creating an electric field E_d just large enough to make the cationflux equal zero. The driving force F from this field equals qE_d , where q is the cation charge; and, in general, $\langle v \rangle_{Fi} = FD_i^* / kT$. Thus, from Eq. (3.1)

$$J_A = -D_A^*(\partial c_A / \partial x) + qE_d D_A^* c_A / kT \tag{3.7}$$

$$J_B = -D_B^*(\partial c_A / \partial x) + qE_d D_B^* c_B / kT \tag{3.8}$$

Setting $J_A + J_B = 0$ and solving for E_d yields

$$E_d = \frac{kT}{q} \frac{(D_A^* - D_B^*)(\partial c_A / \partial x)}{D_A^* c_A + D_B^* c_B} \tag{3.9}$$

Thus, the driving force is proportional to $\partial c_A / \partial x$. For the atom flux, we obtain

$$J_A = -J_B = -\frac{D_A^* D_B^*}{N_A D_A^* + N_B D_B^*} \frac{\partial c_A}{\partial x} \tag{3.10}$$

where $N_A = c_A / (c_A / c_B)$ and $N_B = c_B / (c_A / c_B)$. The intrinsic diffusion coefficient D_A^I is the coefficient of $-\partial c_A / \partial x$ in (3.10),

$$D_A^I = \frac{D_A^* D_B^*}{N_A D_A^* + N_B D_B^*} \tag{3.11}$$

Since $J_A = -J_B$ and $(\partial c_A / \partial x) = -(\partial c_B / \partial x)$, it also fallows in this particular case that $D_A^I = D_B^I$.

In Eqs. (3.7) to (3.11) we see one example of a calculation of intrinsic diffusion coefficients in terms of tracer diffusion coefficients. Other examples can be for (1) nonideal solid solutions in metal alloys and (2) diffusion potentials when divalent ionic impurities.

If we include nonideal solutions in the present treatment, an additional factor $[1 + (\partial \ln \gamma_i / \partial \ln N_i)]$ appears on the right hand side of (3.11). Here γ_i is the activity coefficient of species i.

3.2.4. Interdiffusion Coefficients

When two species of atoms intermingle, their rate of mixing depends on the diffusion rates of both species. An interdiffusion coefficient can be defined to measure this rate of mixing, as in Eq. (3.14) below. For diffusion in an isolated system, this gives the rate at which the original concentration gradient disappears.

When the two species in an interdiffusion experiment have unequal intrinsic diffusion coefficients, there is a net atom flux across any plane in the diffusion zone. This causes the crystal to swell on one side of the diffusion plane and shrink on the other side. Each lattice plane in the diffusion zone thus acquires a velocity v_K with respect to a reference plane fixed at one end of the crystal. The flux J_i' of species i with respect to this reference plane is given by

$$J_i' = J_i + c_i v_K \tag{3.12}$$

where J_i is the flux of species i across the lattice plane in the diffusion zone. In general, J_i is given by (3.1). Thus,

$$J_i' = -D_i^* (\partial c_i / \partial x) + c_i \langle v \rangle_{Fi} + c_i v_K \tag{3.13}$$

The interdiffusion coefficient $\tilde{D}$ is defined in terms of J_i',

$$J_i' = \tilde{D}(\partial c_i / \partial x) \tag{3.14}$$

In a two component crystal of constant dimentions and atom density, it is necessarily true that $J_A' = -J_B'$ and $(\partial c_A / \partial x) = -(\partial c_B / \partial x)$. For such a crystal, the same value of $\tilde{D}$ is found whether in (3.14) is species A or species B.

In the situation treated in Eqs. (3.7) to (3.11), v_K equals zero. Thus, the intrinsic diffusion coefficient D_A^I in (3.11) also is the interdiffusion coefficient. In metal alloy interdiffusion, however v_K usually is not zero, and $\tilde{D} \neq D_A^I \neq D_B^I$.

3.2.5. Discussion

There are three types of diffusion coefficients which can be defined from Eq. (2.24); 1. tracer diffusion coefficient, 2. intrinsic diffusion coefficient and 3. interdiffusion coefficient. Of this three, the tracer diffusion coefficient is the most basic, since it is directly related to the atom jump frequencies. The term diffusion coefficient will always refer to the tracer diffusion coefficient.

3.2.6. Partial Diffusion Coefficients

In multi-component systems, it is not always convenient to use an expression such as Eq. (2.24) for the atom flux, since the diffusion coefficient then would be a very complex quantity, depending not only on concentration gradients of various species. Instead, is is more convenient to use the expression,

$$J_i = -\sum_k D_{ik}\left(\partial c_k / \partial x\right) \tag{3.15}$$

This equation explicitly allows for the possibility that the flux J_i of species i may depend on the concentration gradient $\left(\partial c_k / \partial x\right)$ of any species in the crystal. The summation includes all species k in the crystal including species i.

In this equation, the D_{ik} may be called partial diffusion coefficients, since each seperate turn $-D_{ik}\left(\partial c_k / \partial x\right)$ contributes only part of the total flux J_i. Normally, the D_{ik} for $i \neq k$ are small compared to that for $i = k$. Still the cross-terms (where $i \neq k$) are not necessarily zero. Nonzero cross-terms arise whenever the driving force on an i atom depends on the concentration gradient of a different species k.

In general, the partial diffusion coefficients can be desingnoted as either intrinsic or interdiffusion coefficients, depending on the reference axes use to describe the flux J_i. When fluxes are referred to the ends of the specimen, interdiffusion

coefficients are obtained. If the diffusion plane is the reference plane, however, the D_{ik} are intrinsic diffusion coefficients. The full intrinsic diffusion coefficient as defined in Eq. (3.2) is given by

$$D_i^I = D_{ii}^I + \sum_{k \neq i} D_{ik}^I \frac{(\partial c_k / \partial x)}{(\partial c_i / \partial x)} \tag{3.16}$$

A similar equation can be written for the interdiffusion coefficient. For a binary system, where $(\partial c_A / \partial x) = -(\partial c_B / \partial x)$, we find $D_A^I = D_{AA}^I - D_{AB}^I$.

3.2.7. Defect Diffusion Coefficient

In the case of diffusion via a vacancy mechanism movement of a particle is associated with a movement of a vacancy in the opposite direction. If the vacancy concentration c_V is small with respect to the particle concentration c_i, the individual jump frequences Γ_V and Γ_i are releted as follows:

$$\frac{\Gamma_i}{\Gamma_V} = \frac{c_V}{c_i} = N_V \tag{3.17}$$

where N_V is the mole fraction of vacancies. From this relation it follows that the self-diffusion (tracer) coefficient D_i of the atoms i is related to the self-diffusion coefficient D_V of the vacancies via:

$$D_i = D_V N_V \tag{3.18}$$

This only holds when there are only particles of type i on the sublattice under consideration. If this is not the case the equation has to be modified by introduction of a corelation factor.

The reletion can be generalised to

$$\sum_i D_i N_i = \sum_d D_d N_d \tag{3.19}$$

where i indicates the different mobile species and d the different types of defects (vacancies, interstitials,...).

3.2.8. Chemical Diffusion Coefficient

In N-component diffusion the chemical diffusion coefficient or interdiffusion coefficient $\tilde{D}_{ij}$ is obtained from the flux $\tilde{J}_i$ of species i, with concentration c_i, measured with respect to the laboratory frame of reference by applying Fick's First law (expressed here in one dimension):

$$\tilde{J}_i = -\sum_{j=1}^{N-1} \tilde{D}_{ij} (\partial c_i / \partial x) \tag{3.20}$$

From irreversible thermodynamics one can show that for isotropic, one-dimensional diffusion there are $(N-1)N/2$ independent coefficients $\tilde{D}_{ij}$. These coefficients are sometimes called partial diffusion coefficients.

3.2.9. Conductivity Diffusion Coefficient

The conductivity diffusion coefficient $D_i(\sigma_i)$ of a mobile, charged particle i is derived from the measured partial electrical conductivity of that species, σ_i, by the Nernst-Einstein equation, which will be discussed in the following sections,

$$D_i(\sigma_i) = \frac{kT}{c_i q_i^2} \sigma_i \tag{3.21}$$

where k is the Boltzmann constant, T the thermodynamic temperature, c_i the concentration of i expressed in number of particles per unit volume and q_i the electrical charge of the particle.

3.2.10. Effective Diffusion Coefficient

In alloys or compounds transport of material can occur under the influence of a driving force, at constant composition in the whole sample. Examples are found in viscous creep and sintering processes. In this case the fluxes of the diffusing species must be coupled. In an ionic crystal a similar condition holds due to the necessity of preserving electroneutrality. For a compound A_rB_s with tracer diffusion coefficients D_A^* and D_B^* the effective diffusion coefficient D_{eff} is given by:

$$D_{eff} = \frac{D_A^* D_B^*}{rD_B^* + sD_A^*} \tag{3.22}$$

which is often known as Herring's formula.

If $D_A^* \rangle\rangle D_B^*$, then $D_{eff} \approx D_B^*/s$, i.e. the fluxex determined by the slower diffusing species. In interdiffusion the two species diffuse in oppsite directions, while in the case of material transport migration occurs in the same direction. In the case of ionic crystals one uses the term ambipolar diffusion.

3.3. The Techniques

It is assumed that each diffusion process study is characterised by a concentration independent diffusion coefficient D. The concentration distribution would be given by (Jost, 1952)

$$c(x,t) = c_0 erfc\left(x/2\sqrt{Dt}\right) \tag{3.23}$$

where x denotes a coordinate axis directed into the sample from a plane surface and and *erfc* denotes the error function complement

$$erfcy = 1 - erfy \quad , \; erfy = erf\frac{x}{2\sqrt{Dt}} \tag{3.24}$$

The methods are;

- Observation on colour change
- Measurement of I.R. absorption coefficients.
- Radiactive tracer measurements

The first method is based on the microscopic measurement of the penetration depth of colour change, resulting from a diffusion process, generally in an originally green Sm^{2+} doped calcium fluoride crystal. This method was previously used to measure the activation energy for diffusion of O^{2-} ions by Muto and Awazu (1968).

Infrared spectroscopic measurements, following the variation in intensity of absorption lines due to local mode vibrations of H^- or D^- ions in association with other impurities, can be used to study the diffusion of these impurities in fluorite crystals. It is well known that the total absorption at a particular wavelength λ is proportional to the number of absorbing centers in the beam. Therefore the absorption due to an infinitely thin slice between the planes x and $x + dx$ with cross-sectional faces perpendicular to the beam can be expressed as

$$dJ_\lambda = -J_\lambda \sigma(\lambda) c(x) dx \tag{3.25}$$

where J_λ denotes the intensity of radiation of wavelength λ at distance x, $\sigma(\lambda)$ denotes the absorption cross-section and $c(x)$ the concentration of the centre in the slab. If the total thickness of the absorbing sample is d, the transmitted intensity $J_\lambda(d)$ is related to the incident intensity $J_\lambda(0)$ by

$$\log\left(\frac{J_\lambda(d)}{J_\lambda(0)}\right) = -\sigma(\lambda)\int_0^d c(x)dx \tag{3.26}$$

After removing a thin layer of thickness ξ at $x = 0$, the corresponding relation is

$$\log\left(\frac{J_\lambda'(d)}{J_\lambda'(0)}\right) = -\sigma(\lambda)\int_\xi^d c(x)dx \tag{3.27}$$

Two ways of analysing the experimental measurements of $J_\lambda'(d)/J_\lambda'(0)$ as a function of successive removals of thin surface layers have been considered in Özbay (1971). Substraction of (3.26) from (3.27) gives

$$\begin{aligned}\log\left(\frac{J_\lambda'(d)}{J_\lambda'(0)}\right) - \log\left(\frac{J_\lambda(d)}{J_\lambda(0)}\right) &= \sigma(\lambda)\int_0^\xi c(x)dx \\ &= \sigma(\lambda)\bar{c}\,\xi\end{aligned} \tag{3.28}$$

where $\bar{c}$ denotes the mean concentration in the layer last removed, and is expressed as proportional to measured quantities so that the shape of the function $c(x)$ may be deduced. Alternatively the integral $I(\xi) = \int_\xi^d c(x)dx$ may be computed from an assumed form of $c(x)$, corresponding to certain assumptions concerning the diffusion process involved and the measured intensity ratios then compared with the function $I(\xi)$.

Figure 3.1. indicates the intensity measurements in relation to a simple absorption line displayed on the recorder chart of a spectometer, the wavelength corresponding to maximum absorption being chosen for measurements of $J_\lambda(d)$ and $J_\lambda(0)$.

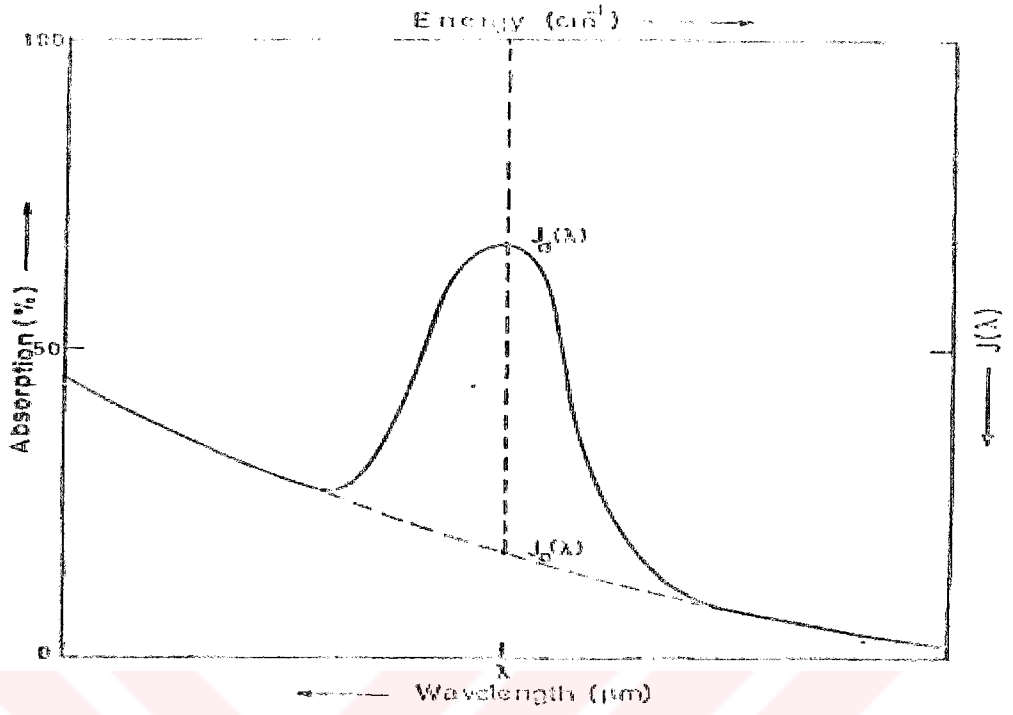

Figure 3.1. Intensity measurement in relation to a single absorption band displayed on the recorder chart of a spectrometer.

Of course, the width of the line may be partly due to instrumental and other causes affecting resolution and $\sigma(\lambda)$ in the above equations will then represent an effective cross-section. Provided the line shape does not vary appreciably with the concentration $c(x)$ this should not affect the determination of $c(x)$, in relative terms, from the above analysis. A similar condition is necessary to justify the selection of a particular point on the line (point of maximum absorption) for the intensity measurements.

3.4. A Method of Obtaining Diffusion Coefficients

When a crystalline solid is heated in a gaseous atmosphere the concentration distribution of the diffusion ions (atoms) is given, in conditions of simple diffusion kinetics, by an error function curve i.e.,

$$c(x,t) = c_0 erfc\left(x/2\sqrt{Dt}\right) \tag{3.29}$$

where c_0 is the constant surface concentration at $x = 0$ at the given temperature and t is the diffusion time. This curve is illustrated in Figure 3.2. where $x/2\sqrt{Dt}$ is represented by y.

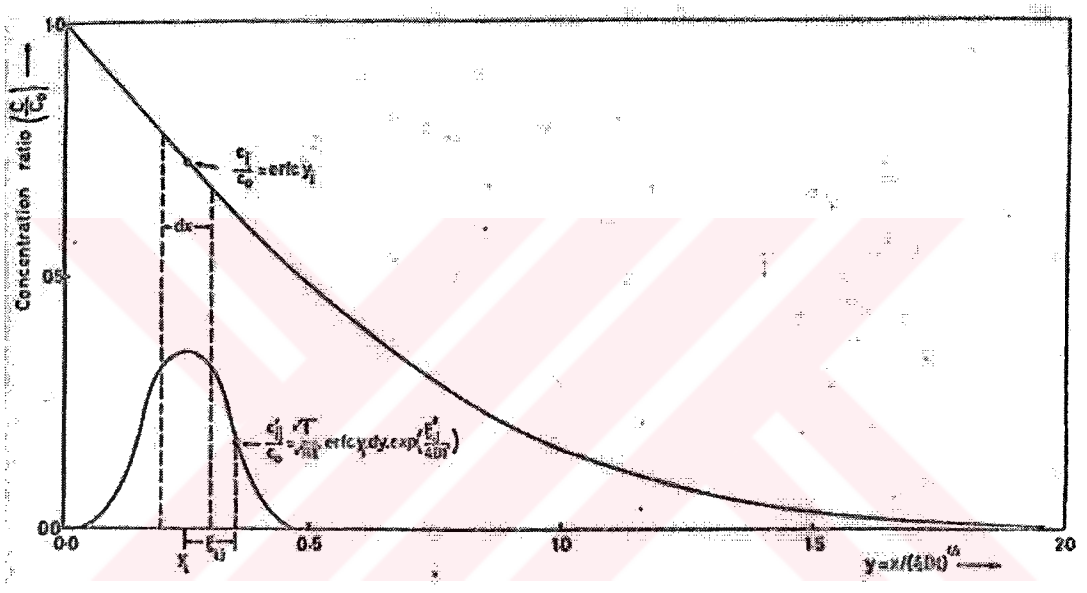

Figure 3.2. Concentration distribution of diffusing species given by an error function complement curve, and re-distribution of the content of a slab dx after subsequent heat treatment in vacuum.

Let the region $y\rangle 0$ be subdivided into n slices each of thickness dx and uniform cross-sectional area. The number of diffusing ions (atoms) per unit volume in the slice i, for infinitely small magnitudes of dx, can be expressed as $c_i dx$, and;

$$c_i dx = 2c_i\sqrt{Dt}dy \tag{3.30}$$

where c_i denotes the concentration at y_i. Now suppose this sample with an initial distribution of diffusing ion (atom) is re-heated in vacuum at the same temperature, as it was heated in atmosphere, the concentration distribution would then take a new form arising from the internal diffusion of these ions (atoms). This new distribution curve can be calculated provided that certain assumption are made, i.e. each slice behaves as a thin layer of diffusing species. Thus after annealing for time t' in vacuum, the concentration at the distance ξ_{ij} from y_i (Figure 3.2.), produced by the diffusion of species in slab i will be given the well known thin film solution of Fick's equation,

$$c_{ij} = \frac{2c_i\sqrt{Dt}dy}{2\sqrt{\pi Dt}}\exp\left(-\frac{\xi_{ij}^2}{4Dt'}\right) \tag{3.31}$$

Since the temperature has not been changed only a single diffusion coefficient is present. For $t = t'$ we obtain, from equations (3.29) and (3.31),

$$\frac{c_{ij}}{c_0} = \left(\frac{1}{\sqrt{\pi}}erfcy_i\right)dy\ \exp\left(-\frac{\xi_{ij}^2}{4Dt}\right) \tag{3.32}$$

where ξ_{ij} is the distance in either direction normal to the slab. The resulting distribution after both heat treatments can thus be regarded as a superposition of the distributions from the individual slabs; it is given by a function $c_j' = \sum c_{ij}$ which is the final concentration in the jth slab. The sum over all i and j of c_{ij}/c_0 values on each y_n axis will give the concentration ratio c'/c_0 as a function of y.

In taking the sum of the individual distributions it is assumed that during the heat treatment in vacuum diffusion out of the sample was negligible, the crystal surface behaving as a reflecting barrier. The calculated concentration distribution in the Ph. D. Thesis of Özbay (1971) for these conditions are plotted in Figure 3.3. (curve 2)

together with the error function complement curve (curve 1) representing the distribution after the first heat treatment in the oxygen atmosphere.

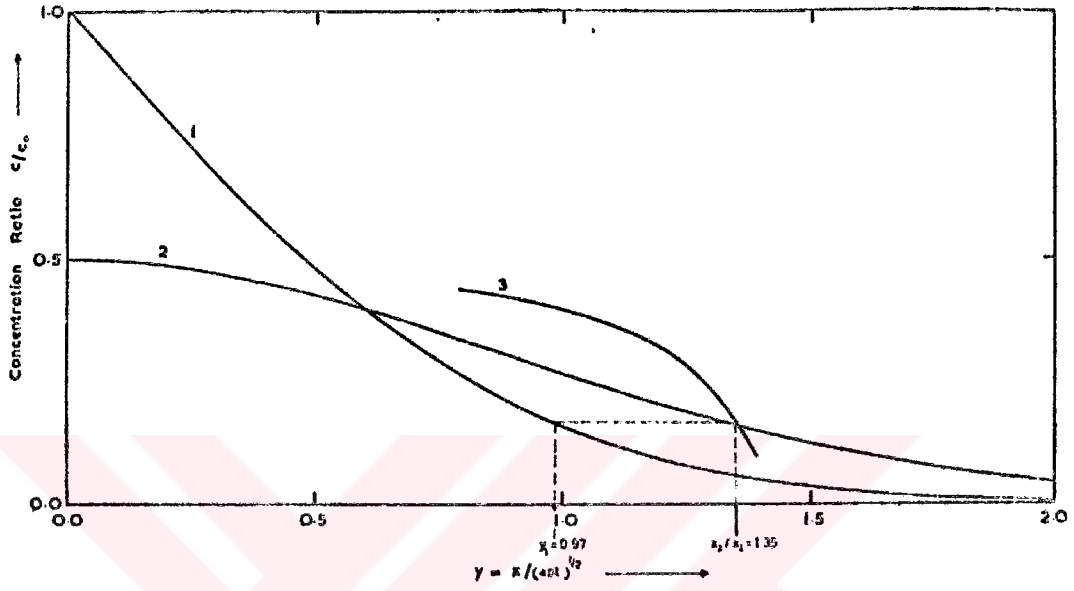

Figure 3.3. Calculated distribution curves of diffusing impurities, when a crystal was heated in gaseous atmosphere (curve 1) and then re-heated in vacuum at the same temperature for the same time (curve 2). Curve 3 shows the variation of the ratio of y values corresponding to equal concentrations c and c' as ordinate.

In an experiment the colour boundary will occur at coordinates $x = x_1$ after the first heat treatment (in atmosphere) and at $x = x_2$ after the second (in vacuum) and these two points should correspond to the same critical concentration of the compensator (O^{2-}). Curve 3 shown in Figure 3.3. gives the ratios of y values and therefore also of x values, corresponding to equal concentrations c and c' as ordinate. From the measured ratio x_2 / x_1 it is therefore possible to determine the critical concentration as a fraction of c_0 and thus to read off the corresponding value

of y_1 or $x_1/2\sqrt{Dt}$. The diffusion coefficient D may then be evaluated using the known value of time t for each one of these two heat treatments. Similar cases could be constructed for any reasonable ratio of the times t and t'. In the works of Özbay (1971) the choise $t = t'$ was was found to suit the experimental situation , i.e. to give suitable values for x_2/x_1.

3.5. Diffusion Coefficient by the Method of Random Walks

In this section we follow the motion of an atom or ion over a large number n of jumps and average the result over all similar ions. Let the displacement of an ion after n jumps be R. If we suppose the initial positions of all the ions on to a common origin, we shall obtain a practically continiuous distribution of end points of he vectors R. This distribution will be a spherically symmetrical solution of the general diffusion equation

$$\frac{\partial c}{\partial t} = D\nabla^2 c \tag{3.33}$$

corresponding to initial conditions in which all the difusing ions are concenrtrated at the origin. It is well known that this solution of (3.33) leads to the relation

$$\overline{R^2(t)} = 6Dt \tag{3.34}$$

where t is the time necessary for the performance of n jumps. $\overline{R^2(t)}$ can be evaluated directly as follows

$$\overline{R^2(t)} = \overline{\left(\sum_i \vec{r}_i\right)^2}$$

$$= \sum_{i=1}^{n} \overline{r_i^2} + 2 \sum_{i=1}^{n-1} \sum_{j=1}^{n-i} \overline{\vec{r}_i \cdot \vec{r}_{i+j}} \tag{3.35}$$

where successive jumps are denoted by r_1, r_2, r_3, ..., r_i,...etc. We assume that the individual jump vectors are of equal magnetude r. Then,

$$\overline{R^2(t)} = nr^2 + 2r^2 \sum_{i=1}^{n-1} \sum_{j=1}^{n-i} \overline{\cos \vartheta_{i,i+j}} \tag{3.36}$$

where $\overline{\cos \vartheta_{i,i+j}}$ is the average value of the cosine of the angle between the ith and the $(i+j)$th jump of an ion. When the jumps of an ion completely random and uncorrelated with previous jumps, $\overline{\cos \vartheta_{i,i+j}}$ must be zero and

$$\overline{R^2(t)} = nr^2 = \Gamma t r^2 \quad \text{(uncorrelated).} \tag{3.37}$$

where Γ is the average number of jumps made by every ion in unit time. Eqs. (3.34) and (3.37) give

$$D = \frac{1}{6} \Gamma r^2 \quad \text{(uncorrelated)} \tag{3.40}$$

Within the stated limitation to no correlations this equation is very general, since it has been derived without consideration of the jump mechanism and without spesification of the type of lattice (except that it be isotopic). As a simple example we may consider the self-diffusion of the cations in a NaCl type lattice. Let the molar fraction of cation vacancies be x and let w_0 be the probability per unit time that a vacancy jump from one position to another particular position. Then the average jump frequency, Γ, for a normal cation is $12xw_0$. If a is the anion-cation seperation, then $r = \sqrt{2}a$ and the self-diffusion coefficient, by (3.40) is,

$$D = 4a^2 w_0 x \tag{3.41}$$

If we calculate the cation vacancy contribution to the conductivity, we get

$$\sigma_+ = 4Nxa^2 e^2 w_0 / kT \tag{3.42}$$

where N is the number of cations per volume $\left\{= 1/(2a^3)\right\}$. From (3.41) and (3.42) we see that

$$\frac{\sigma_+}{D} = \frac{Ne^2}{kT} \tag{3.43}$$

as it must do. Eq.(3.43) is also called "Nernst-Einstein relation".

3.6. Correlation Factor and the Haven Ratio

We will use q indice for ionic conductivity and t for tracer coefficient in this section. In a normal ionic solid where the lattice defect concentration is small $\left(\langle 10^{-4}\right)$, the ionic conductivity measures the motion of the defects. Since one jump of a defect is uncorrelated with the next, defect motion is truly random and the diffusion coefficient obtained from ionic conductivity, as in previous section, is given by

$$D_\sigma = \frac{1}{6}\Gamma_q {r_q}^2 \tag{3.44}$$

where Γ_q and r_q are the defect-jump frequency and the distance, respectively, and 1/6 is the appropriate geometric factor for three dimensional motion in a cubic crystal. The value of D_σ is obtained from the ionic conductivity (σ) using the Nernst-Einstein relation

$$D_\sigma = \frac{\sigma kT}{Nq^2} \tag{3.45}$$

where N is the concentration of the mobile species, q is the electric charge, and kT has the usual meaning.

The tracer diffusion experiment measures the motion of independent and identifiable tracer atoms. Since for many jump processes successive atomic jumps of the tracer are correlated, it is necessary to write

$$D_t = \frac{1}{6}\Gamma_t r_t^2 f_t \tag{3.46}$$

where Γ_t and r_t are the tracer atom jump frequency and jump distance, respectively, and f is the correlation factor that takes account of the non-random nature of the tracer jump. Combination of Eqs. (3.44) and (3.46) gives

$$\frac{D_t}{D_\sigma} = \left(\frac{r_t}{r_\sigma}\right)^2 \frac{\Gamma_t}{\Gamma_\sigma} f_t \tag{3.47}$$

The Haven ratio, H_R, was introduce by LeClaire to help make clear that a comparison of D_t and D_σ is not solely depend on the correlation factor f for tracer diffusion. In interstitialcy diffusion, for instance, two atoms move for each defect jump, and the effective charge also moves a greater distance than the tracer atom. The effect of differences between r_t and r_q can be seen in Table 3.1. by comparison of f_t and H_R . In general each diffusion mechanism has a unique theoretical value for H_R and consequently careful measurements of H_R have proved valuable in identifying diffusion mechanism. The determination of H_R within a few percent requires the comparison of accurate values of the absolute

magnitudes of D_t, σ and N. We will just express the determination of D_t in the following section. The temperature dependence of the tracer diffusion coefficient is given by

$$D_t = D_0 \exp(-Q_t / kT) \tag{3.48}$$

where Q_t in the activation energy for the diffusion process and for normal ionic solids will be the sum of a defect formation energy ε_v and a migration energy (energy of motion) ε_m for the mobile species as in the Chapter Two. In solid electrolytes the number of mobile ions is large and fixed so that $Q_t = \varepsilon_m$. The slope of Eq. (3.48) will only equal ε_m if one diffusion process is operative over the range of temperature measurement and if f_t which is contained within D_0, is temperature independent. Where the mobile ion jumps by means of two nonequivalent sites, f_t will be temperature dependent.

Table 3.1. Theoretical values of correlation factors and Haven ratios

Lattice	Mechanism	f_t	H_R
2D Honeycomb	Vacancy	0,333	0,333
	Interstitial	1,000	1,000
	Interstitialcy	0,900	0,600
3D fcc	Vacancy	0,781	0,781
	Interstitial	1,000	1,000
	Interstitialcy (C)	0,667	0,333
	Interstitialcy (Nc1)	0,970	0,727
	Interstitialcy (Nc2)	0,964	1,446
C-Collinear; Nc-Noncollinear; Type 1 & 2			

It may be necessary to express the correlation factor. When the motion of a diffusing species is dependent on the precense of a defect on a neighboring site, e.g. a tracer diffusing by a vacancy mechanism, the jumps of the diffusing species will not be random, but are correlated. The correlation factor, f , is a measure of the deviation of the diffusing atoms from the random walk. For a tracer it is defined as the ratio of the tracer diffusion coefficient D_i^* and the self-diffusion coefficient, D_i:

$$f = D_i^* / D_i \tag{3.49}$$

For the random walk, $f = 1$ by definition. In general f is less than unity, but it can be larger than unity and in such cases the motion is called channelling.

3.7. Experimental Measurement of D_t

In solid electrlytes where D_t is in the range 10^{-5} to 10^{-8} cm^2/s and σ is in the range 1 to 10^{-3} $1/\Omega cm$, the required measurement accuracy can only be attained using special techniques or special care with existing methods.

Measurements of D_t are commonly made by observation of the redistribution of radiactive tracer atoms from some prescribed initial condition. The value of D_t is then obtained from a suitable solution of Fick's law. Ideally the method used should examine the redistribution of the radioactive tracer in such a way that any possible disturbing influence (interfacial kinetics, grain boundary diffusion, etc.) on the bulk diffusion properties can be readily observed. One method that meets this requirement and which has been frequently used for the accurate determination of D_t is the serial sectioning method (SSM). A thin layer of radioactive tracer is deposited onto one end of a sample which is then annealed, sectioned and the sections counted. The method should result in a Gaussian depth dependence of the concentration and deviations (which can be mostly readily observed when the concentration change is

$\geq 10^2$) are a strong indicator of the presence of other kinetic processes contributing to that of bulk diffusion. In ionic solids where bulk diffusion coefficients are $\leq 10^{-8}$ cm^2/s, interface reactions and surface diffusion are usually so much more rapid that the SSM profiles are Gaussian until deep into the sample, where grain boundary or dislocation effects can be of influence. In solid electrolytes bulk diffusion is sufficiently fast that interface reactions can affect the whole profile and effects of grain boundaries may be small.

Sectioning is usually performed at room temperature where, in most solids, the diffusion coefficients are essentially zero, and the concentration profile obtained at the anneal temperature is frozen at the temperature of sectioning. In solid electrolytes Q_t is sufficiently small (0,1 – 0,3 eV) that even at room temperatures the concentration profile is not frozen, and corrections must be made for diffusion occuring during the process of sectioning. When a nondestructive profiling technique is available, the changes in the profile at room temperature can be observed and appropriate corrections made. Some solid electrolytes undergo a phase transition to a normal ionic conductor as the temperature is lowered, and so the concentration profile is frozen below the phase transition. In cases where room temperature does not freeze the profile, sectioning can be carried out under liquid nitrogen.

Measurements of D_t have also been made using the exchange technique. The technique follows the out diffusion of radioactive tracers form a sample of solid electralyte into a well-stirred molten salt bath. A measurement of the radioactivity remaining in the sample or in the salt bath after a given time interval, compared to the initial radioactivity concentration allows D_t to be determined. The method has the advantage that the high diffusion rates and low activation energies that create problems with the SSM are readily handled by the exchange technique in Mundy (1979). However this adventage is at the expence of a measured profile so that interface reactions could alter the the measured value of D_t but still not be observable from the experimental data. The diffusion kinetics can be checked by observing radioactivity at a series of time intervals. The accurancy of the method can

be limited by the measurements of the linear dimensions of the sample which may be diffucult unless large regular shaped, samples are available.

CHAPTER FOUR
THE CALCULATIONS

4.1. Introduction

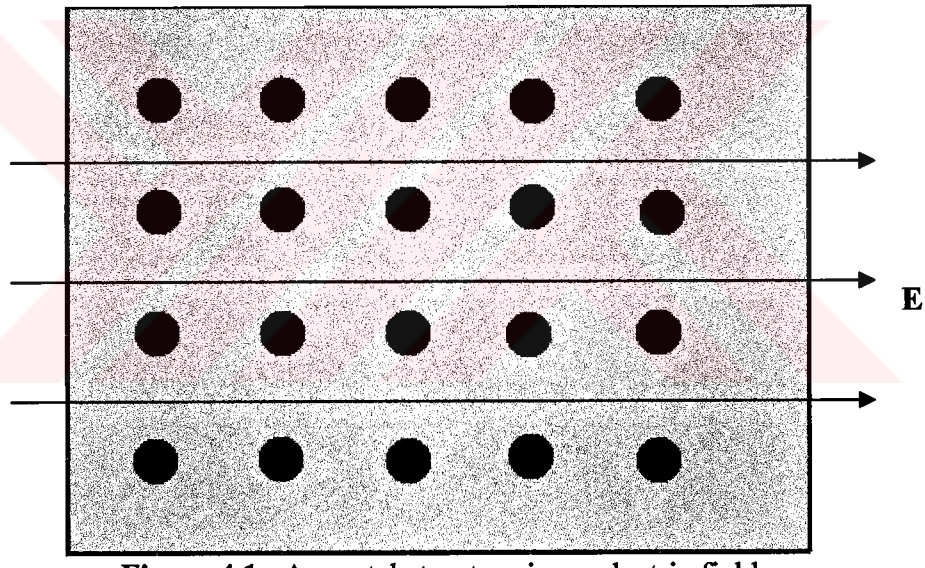

Figure 4.1. A crystal structure in an electric field

If a crystal which includes diffusible ions, for example a crystal with two different ions one of which can easily diffuses through the sample, in an electric field, the ions will be swept in the direction of the electric field. At the begining the concentration of these ions has homogeneous distribution. We will consider with this concentration distribution and the calculations about it in this chapter. Figure 4.2. shows us the concentration distribution in a crystalline sample. And we will start with the differential of the concentration in the sample,

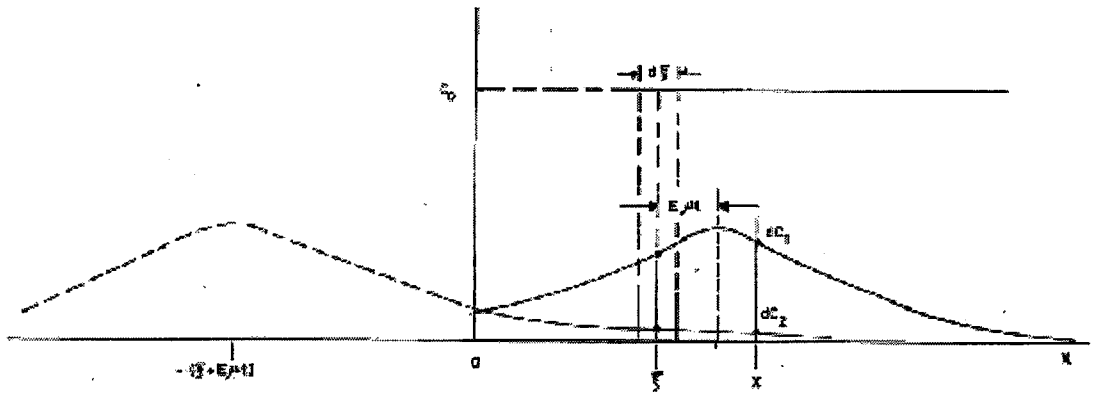

Figure 4.2. The concentration distribution

$$dc(x) = dc_1 + dc_2 \tag{4.1}$$

$$= \frac{c_0 d\xi}{2\sqrt{\pi Dt}} \exp\left[-\frac{(x-\xi-E\mu t)^2}{4Dt}\right] + \frac{c_0 d\xi}{2\sqrt{\pi Dt}} \exp\left[-\frac{(x+\xi+E\mu t)^2}{4Dt}\right]$$

$$= \frac{c_0 d\xi}{2\sqrt{\pi Dt}} \left\{ \exp\left[-\frac{(x-\xi-E\mu t)^2}{4Dt}\right] + \exp\left[-\frac{(x+\xi+E\mu t)^2}{4Dt}\right] \right\}$$

For c_1 ,

$$c_1 = \int_0^{\infty} \frac{c_0 d\xi}{2\sqrt{\pi Dt}} \exp\left[-\frac{(x-\xi-E\mu t)^2}{4Dt}\right] \tag{4.2}$$

Using this transform $\frac{x-\xi-E\mu t}{\sqrt{4Dt}}=-y \longrightarrow d\xi=(\sqrt{4Dt})dy$

$$c_1=\int_{\frac{(x-E\mu t)}{\sqrt{4Dt}}}^{\infty}\frac{c_0 dy}{2\sqrt{\pi}}\exp\left[-y^2\right] \tag{4.3}$$

$$=\frac{c_0}{\sqrt{\pi}}\left[\int_{\frac{(x-E\mu t)}{\sqrt{4Dt}}}^{0}\exp\left[-y^2\right]dy+\int_0^{\infty}\exp\left[-y^2\right]dy\right]$$

or

$$c_1=\frac{c_0}{\sqrt{\pi}}\left[\int_0^{\infty}\exp\left[-y^2\right]dy-\int_0^{\frac{(x-E\mu t)}{\sqrt{4Dt}}}\exp\left[-y^2\right]dy\right] \tag{4.4}$$

Here $\int_0^{\infty}\exp\left[-y^2\right]dy=\frac{\sqrt{\pi}}{2}erf(\infty)$, $erf(\infty)=1$ and

$$\int_0^{\frac{(x-E\mu t)}{\sqrt{4Dt}}}\exp\left[-y^2\right]dy=\frac{\sqrt{\pi}}{2}erf\left[-\frac{(x-E\mu t)}{\sqrt{4Dt}}\right] \tag{4.5}$$

We obtain,

$$c_1 = \frac{c_0}{2}\left[1 + erf\left[\frac{(x - E\mu t)}{\sqrt{4Dt}}\right]\right] \tag{4.6}$$

With the same way, for c_2, we obtain

$$c_2 = \frac{c_0}{2}\left[1 - erf\left[\frac{(x + E\mu t)}{\sqrt{4Dt}}\right]\right] \tag{4.7}$$

Therefore, from (4.6) and (4.7), for $c(x)$;

$$c(x) = \frac{c_0}{2}\left[2 + erf\left[\frac{(x - E\mu t)}{\sqrt{4Dt}}\right] - erf\left[\frac{(x + E\mu t)}{\sqrt{4Dt}}\right]\right] \tag{4.8}$$

Using these abbraviation; $\frac{x}{\sqrt{4Dt}} = \xi$ and $\frac{E\mu t}{\sqrt{4Dt}} = A$, we obtain;

$$c(\xi) = c_0\left[1 + \frac{1}{2}erf(\xi - A) - \frac{1}{2}erf(\xi + A)\right] \tag{4.9}$$

Here $c(\xi)$ is a function of two independent variable; ξ and A. In this equation, we can take A as a constant between suitable boundaries and we can obtain numerical change of the function $\left[\frac{c(\xi)}{c_0}\right]_A = f(\xi)$. Here A is between 0,2 - 2,0 and this is plotted in Figure 4.3.

$$\left[\frac{c(\xi)}{c_0}\right]_A = f(\xi) \quad , \quad \text{A= 0.2, 0.4, 0.6, ..., 1.8, 2.0}$$

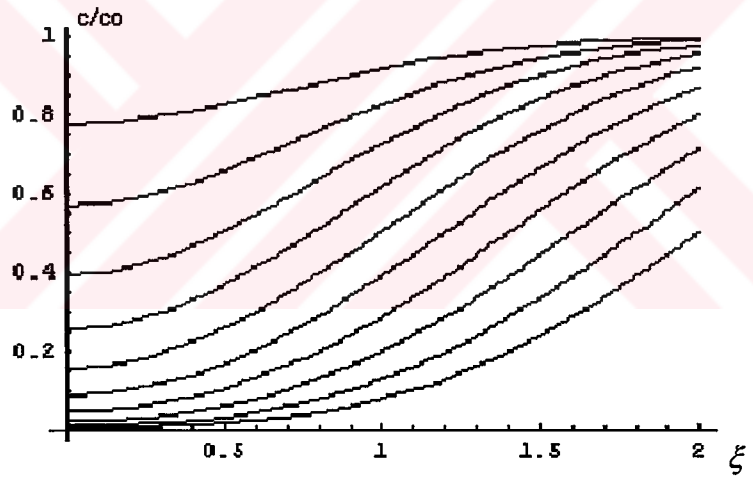

Figure 4.3. The plot of $c/c_0 = f(\xi)$

Now, let us find the change of ξ depending on A by taking $c(\xi)/c_0$ as a constant. For that, in Figure 4.3. , if we draw a line that is parallel to ξ axis at any $c(\xi)/c_0$, we can take the ξ value which intersects with any curve as the A value of that curve.

Therefore, by using numerical calculations and the constant values c/c_0 = 0.1, 0.2,..., 0.9 , we can draw the relation between ξ and A.

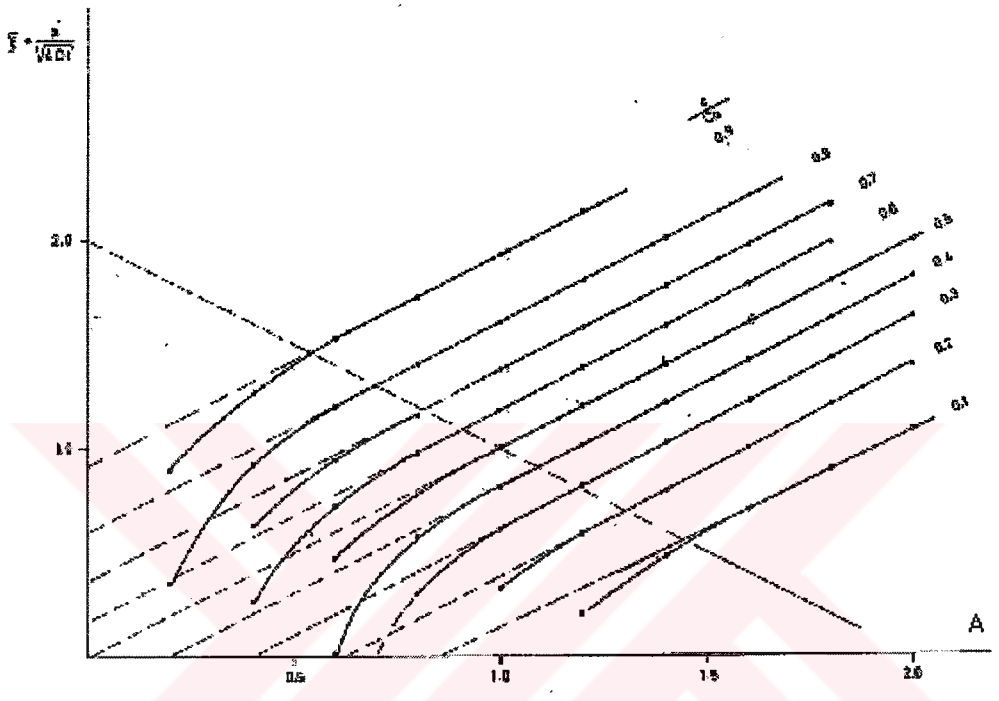

Figure 4.4. The relation between ξ and A, $\xi = f(A)$.

As we can see in Figure 4.4. on the right side of the line that connects the points $(\xi = 2 \ ; \ A = 0)$ and $(\xi = 0 \ ; \ A = 2)$, at any c/c_0 value, we can assume the function $\xi = f(A)$ as a line that has a slope $m = 1$. Thus, for that area and for constant c/c_0 ratio, we can write,

$$\xi = \eta + A \tag{4.10}$$

or

$$x = \sqrt{4Dt}\eta + \mu tE \tag{4.11}$$

This equation gives, at constant temperature and time, the position of the cross-section which has constant concentration in the crystal depending on electric field.

In transparent crystals, at the situation of occuring colour change by diffusing ions in the concentration higher than a given concentration (for example, diffusing of stimulated F^- ions in $CaF_2 : Sm^{++}$ crystal), the line that given by (4.11) can obtain experimentally. Thus, by measuring the slope of the line, we can obtain the diffusion coefficient D ,

$$m' = \mu t = \frac{Dq}{kT} t \tag{4.12}$$

Here q is the charge of the ion, k is the Boltzmann constant, T is the temperature of diffusion and t is the time of diffusion.

4.2. Numerical Calculations

In this section, we will see how to explain to draw Figure 4.4. theoretically by using numerical calculations with a computer program, Mathematica 4.0. For that, we will use Eq. (4.9) and assume constant values of $c(\xi)/c_0$.

By using Eq. (4.9), we obtained the plot $\xi = f(A)$. ξ and A are not independent from each other. Before, we found the roots of another form of Eq. (4.9) with computer. And with the numerical values obtained, draw the lines of $\xi = f(A)$. In the fallowing two pages, there are the calculations for $c/c_0 = 0{,}2$ and $c/c_0 = 0{,}3$.

For $c(\xi)/c_0 = 0{,}2$

```
f x_ :=0.5 Erf x- A - 0.5 Erf x+A +0.8
aa :=x . FindRoot f x , x, 1.4
bb =Table A, aa , A, 0.9, 2, 0.05
```

```
0.9, - 0.0388111 , 0.95, 0.220278 , 1., 0.323582 ,
1.05, 0.402857 , 1.1, 0.470979 , 1.15, 0.532711 ,
1.2, 0.590442 , 1.25, 0.645555 , 1.3, 0.698927 ,
1.35, 0.751132 , 1.4, 0.802557 , 1.45, 0.853464 ,
1.5, 0.904034 , 1.55, 0.954383 , 1.6, 1.00459 ,
1.65, 1.05472 , 1.7, 1.10479 , 1.75, 1.15483 ,
1.8, 1.20486 , 1.85, 1.25487 , 1.9, 1.30488 ,
1.95, 1.35488 , 2., 1.40488
```

```
ListPlot bb, PlotJoined® True
```

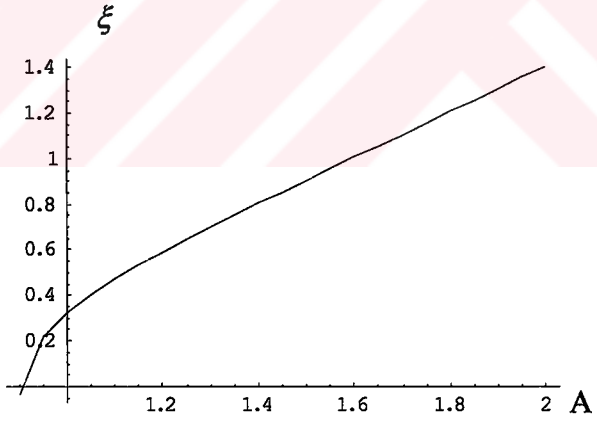

Figure 4.5. The plot of $\xi = f(A)$ for $c/c_0 = 0{,}2$

... Graphics ...

For $c(\xi)/c_0 = 0{,}3$

```
f x_ :=0.5 Erf x- A - 0.5 Erf x+A +0.7
aa :=x . FindRoot f x , x, 1.4
bb =Table A, aa , A, 0.9, 2, 0.05
  0.9, 0.475463 , 0.95, 0.543441 , 1., 0.605405 ,
 1.05, 0.663457 , 1.1, 0.71888 , 1.15, 0.772515 ,
1.2, 0.824928 , 1.25, 0.87651 , 1.3, 0.927533 ,
 1.35, 0.978183 , 1.4, 1.02859 , 1.45, 1.07884 ,
 1.5, 1.12899 , 1.55, 1.17908 , 1.6, 1.22913 ,
 1.65, 1.27916 , 1.7, 1.32918 , 1.75, 1.37918 ,
 1.8, 1.42919 , 1.85, 1.47919 , 1.9, 1.52919 ,
 1.95, 1.57919 , 2., 1.62919
ListPlot bb, PlotJoined® True
```

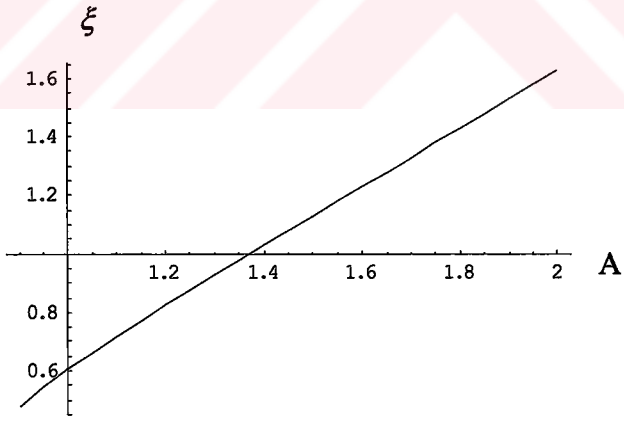

Figure 4.6. The plot of $\xi = f(A)$ for $c/c_0 = 0{,}3$

...Graphics...

```
songr = Show Out 4 , Out 9 , Out 31 , Out 35 ,
            Out 39 , Out 56 , Out 60 , Out 64 , Out 69
```

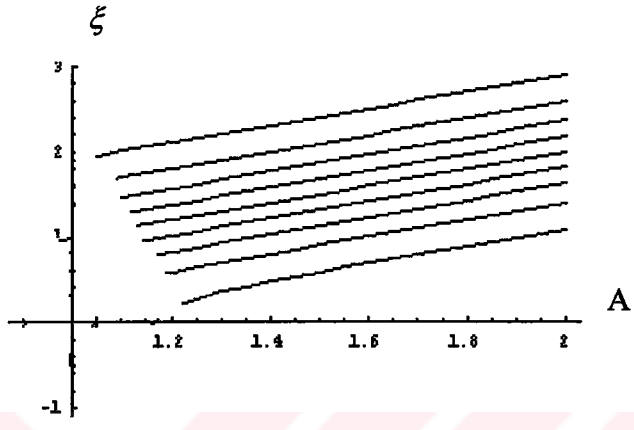

Figure 4.7. The plot of $\xi = f(A)$ for $c/c_0 = 0{,}1 - 0{,}2 - \ldots - 0{,}9$

```
... Graphics ...
```

Finally as we can see in this section, in an experiment, if we find out three points and values for drawing these lines, we can obtain the diffusion coefficient D by measuring the slope of the lines.

CHAPTER FIVE
CONCLUSION

5.1. Conclusion

In the present study, we have suggested a new technique to determine diffusion coefficient of the source ions in the ionic crystal.

As we can see in the study, in any crystal material, if the penetration of constant concentration profile of the diffusing atoms (limit concentration motion) is observable, one can measure three different depths as mentioned in Figure 4.4. and, calculate the diffusion coefficient by measuring the slope of the line. This is a new technique for determining diffusion coefficient.

For example, the CaF_2 crystal becomes green Sm^{++} substitution of the Ca^{++} side. Substitutions of O^{--}on the nearby F^- side makes the crystal transparent. For instance, if we diffuse O_2 into a crystal which is dopped with Sm^{++} homogenously, we can determine the diffusion coefficient from the motion of the boundary of green and tranparent areas. We can also determine the diffusion coefficient with chemical method by using same way, observing the motion of different coloured areas.

The motion of boundary is obtained like that; in any crystal, we determine different thicknesses. Therefore, under the same potential, we can change the electric field. During this process, time and temperature is constant. Finally, we can observe the boundary of concentration dx .

As we said before, diffusion is very important in the technology. For a simple example, if we know the diffusion coefficient of O_2 in any material, we can also know when this material is rusted. Also, we can change the physical properties of

semiconductors by diffusing some foreign atoms. We can dopp impurities into a crystal and clean out some not needed impurities from the crystal.

Some impurity centers that controlling the some physical properties of semiconductors anneals by the diffusion process. This is very important fact when some sensitive devices are concerned.

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