

## SELF-DIFFUSION IN ALKALI HALIDES CONTAINING F-CENTERS

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### ABSTRACT:

The self-diffusion in alkali halides containing F-centers is considered for crystals that have been irradiated and for crystals to which an electric field has been applied. The procedure is based on the determination of the density of vacancies in both cases and the use of the formulae for the self-diffusion coefficient for alkali halides which is a function of the density of vacancies. It is found that in the first case the diffusion constant depends on the intensity of irradiation and in the second case the diffusion coefficient depends on the F-centers existing in the alkali halide and the current passing through the specimen.

### 1. INTRODUCTION

The diffusion of ions in alkali halide crystals<sup>1-6</sup> has been studied for many years. Effects like the influence of surface roughness on the determination of diffusion constants<sup>7</sup> or the effects of Short-circuiting paths of diffusion coefficient measurements<sup>8</sup>, are known. The role of dislocations and other imperfections in the crystal has been taken into account in the determi-

nation of diffusion processes<sup>9</sup>. The purpose of this work is to determine the diffusion coefficient as a function of the F-center formation under different conditions. We find the vacancy number when the sample is irradiated with ionizing radiation and when an electric field is applied. This number is directly related to the expression for the coefficient of diffusion through the formula<sup>10</sup>

$$D = \frac{1}{3} a^2 \frac{N_V}{N_D} p \quad (1)$$

where  $a$  is the shortest interplanar distance,  $N_D$  is the density of positive ions per  $\text{cm}^3$ ,  $N_V$  is the density of vacancies and  $p$  the jump probability of a vacancy per second.

## 2. DIFFUSION IN A CRYSTAL WITH F-CENTERS IRRADIATION PRODUCED

There are many works on F-centers which make use of kinetic equations<sup>11,12,13</sup>; the differences between these approaches reside in which factors participate in the kinetic phenomena. Here we suppose the density of interstitials  $N_I$ , the density of vacancies  $N_V$  and the density of electrons in vacancies  $n_V$  as the more important factors for the kinetic process.

We assume that only Frenkel defects are produced and will call  $N_A$  the number of atoms per  $\text{cm}^3$  that lost electrons during the irradiation and  $n_A$  the electrons per  $\text{cm}^3$  which remain bound to the atoms of the lattice. The assumptions to establish the equations describing the behavior of the

$$\frac{dN_V}{dt}$$

are the following: the increase of  $N_V$  is proportional to the probability  $P$  of forming a Frenkel defect and its decrease is proportional to the interstitials  $N_I$  that are trapped in vacancies ( $N_V - n_V$ ). The proportionality constant involves the trapping section of an ion by a vacancy  $\sigma_{IV}$ . Thence we can put

$$\frac{dN_V}{dt} = P - \sigma_{IV} N_I (N_V - n_V) \quad (2)$$

In the same way  $n_V$  increases in time because there are  $n$  electrons in the conduction band that are susceptible to be trapped in vacancies ( $N_V - n_V$ ) with a probability  $\sigma_{eV}$  and diminishes due to thermal ionization  $I_{eV}$  of the F-center electron, due to interstitials being trapped by the F-centers with probability  $\sigma'_{IV}$ . Then

$$\frac{dn_V}{dt} = \sigma_{eV} n (N_V - n_V) - I_{eV} n_V - \sigma'_{IV} N_I n_V \quad (3)$$

Finally, electrons from the atoms of the lattice are lost proportionally to the ionization radiation rate  $E_R$  and to the thermal ionization probability  $I_{eA}$  and are recovered (when they return from the conduction band) with probability  $\sigma_{eA}$ ; that is,

$$\frac{dn_A}{dt} = -E_R + \sigma_{eA} n (N_A - n_A) - I_{eA} n_A \quad (4)$$

Moreover we have the electronic neutrality condition as:

$$n + n_V + n_A = N_A \quad (5)$$

and the constancy of atoms in the crystal as

$$N_I + N_V^0 = N_V$$

At this point we can find some useful relations minimizing the free energy of the crystal  $F$ <sup>14</sup>

$$F = WN_I - \epsilon_A n_A - \epsilon_V n_V - kT \ln \left[ \frac{S^n}{n!} \frac{N!}{(N - n_V)! N_V!} \times \right. \\ \left. \times \frac{N!}{(N - N_I)! N_I!} \times \frac{N_V!}{n_V! (N_V - n_V)!} \times \frac{N_A!}{n_A! (N_A - n_A)!} \right] \quad (6)$$

where  $W$  is the thermal energy to form a Frenkel defect,  $\epsilon_V$  is the electron energy level of the vacancy,  $\epsilon_A$  the electron energy level of an electron in an atom of the lattice, and  $N$  the number of the atoms per  $\text{cm}^3$  in the lattice. Taking

$$\left( \frac{\partial F}{\partial n_V} \right)_{n_A, N_V} = 0 \quad (7)$$

and using Eq. (5) in the form

$$\left( \frac{\partial n}{\partial n_V} \right)_{n_A, N_V} = -1 \quad (8)$$

we obtain,

$$N^2 \exp \left( - \frac{W}{kT} \right) = (N_V - N_V^0)(N_V - n_V) \quad (9)$$

In the same way minimizing  $F$  with respect to  $N_V$  and  $n_V$  and using Eqs. (5) and (6) we have

$$S \exp \left( - \frac{\epsilon_V}{kT} \right) n_V = n(N_V - n_V) \quad (10)$$

and

$$n(N_A - n_A) = S \exp \left( - \frac{\epsilon_A}{kT} \right) n_A \quad (11)$$

where  $S$  is the electronic density in the band.

Now, when  $E_R = 0$ , we get, from Eq. (4),

$$\frac{dn_A}{dt} = 0$$

and

$$\sigma_{eA} n_e n = I_{eA} n_A \quad (12)$$

Now we suppose that

$$\frac{dn_A}{dt} = 0 \text{ but } E_R \neq 0.$$

These describe the equilibrium between intrinsic lattice defects and free electrons for some (arbitrary) given non-equilibrium total electron concentration  $n_e = n + n_V = N_A + n_A$ . In this manner we can write Eq. (12) in the form

$$\sigma_{eA} n (N_A - n_A) = I_{eA} n_A \quad (13)$$

and on using Eq. (11), Eq. 13) becomes

$$\sigma_{eA} S \exp(-\epsilon_A/kT) = I_{eA} \quad (14)$$

In this "semi-equilibrium" condition Eq. (4) can be written as

$$\sigma_{eA} n_e n - I_{eA} n_A - E_R = 0 \quad (15)$$

and upon adding the term  $n_e \sigma_{eA} S \exp(-\epsilon_A/kT)$  to both members of the last equations we have,

$$\begin{aligned} n_e \sigma_{eA} S \exp(-\epsilon_A/kT) - E_R + \sigma_{eA} n_e n &= \\ = \sigma_{eA} S \exp(-\epsilon_A/kT) N_A + n_A [I_{eA} - S \exp(-\epsilon_A/kT) \sigma_{eA}] & \end{aligned} \quad (16)$$

which can be reduced utilizing Eq. (14), to give

$$n_e [\sigma_{eA} S \exp(-\epsilon_A/kT) + \sigma_{eA} n] = E_R + \sigma_{eA} N_A S \exp(-\epsilon_A/kT) \quad (17)$$

Now, from Eq. (9) supposing that  $N_V^0 \ll N_V$  leads to

$$N^2 \exp(-W/kT) = N_V(N_V - n_V) \quad (18)$$

combining this with Eq. (10) there results

$$\frac{N^2 \exp[-(W - \epsilon_V)/kT]}{S n_V} = \frac{N_V}{n} \quad (19)$$

On the other hand it is a common fact<sup>15</sup> that  $n \ll n_V$ ; so that we may suppose that  $n_e \approx n_V$  if  $N_V^0 \ll N_V$  where  $N_V^0$  is the density of vacancies initially in the perfect crystal.

So from Eq. (19) we have

$$n = \frac{n_e^2}{N^2} S \exp[(W - \epsilon_V)/kT] \quad (20)$$

and putting this result in Eq. (17) we can find

$$n_e \approx \left[ \left( \frac{N^2 \exp((\epsilon_V - W)/kT)}{S \sigma_{eA}} \right) \left( E_R + \sigma_{eA} S \exp\left(-\frac{\epsilon_A}{kT}\right) \right) \right]^{1/3} \quad (21)$$

Assuming that

$$\exp\left(-\frac{\epsilon_A}{kT}\right) \ll n_e^2 \exp[(W - \epsilon_V)/kT] \quad (22)$$

and taking into account that  $n_e \gg N_V^0$ , we can conclude that  $n_e \approx N_V$  and hence Eq. (21) can be rewritten as

$$N_V \simeq \left( \frac{E_R N^2 \exp [(\epsilon_V - W)/kT]}{S\sigma_{eA}} \right)^{1/3}$$

Therefore the expression for the diffusion coefficient is

$$D = \frac{1}{3} \frac{a^2 \nu}{N^0} \left( \frac{E_R N^2}{S\sigma_{eA}} \right)^{1/3} \exp [(\epsilon_V - W - 3\epsilon_j)/3kT] \quad (23)$$

where  $\nu$  is the frequency and  $\epsilon_j$  is the activation energy associated with a jump. In deriving Eq. (23) we have neglected the thermal entropy<sup>16</sup> and the change in the vibrational frequency of the atoms next to holes<sup>17</sup>.

### 3. DIFFUSION IN A SAMPLE WITH F-CENTERS PRODUCED BY AN APPLIED ELECTRIC FIELD.

For simplicity we think in a semicircular disk of uniform thickness  $d$ . The periphery of the disk is used as the anode, and an edge placed at the centre along the thickness of the disk serves as the cathode. The electrical conductivity of the crystal at any point may be written as  $n_V e \mu_F$  where  $e$  is the electronic charge and  $\mu_F$  the mobility of the F-centers.

The electric field for a current  $I$  passing through the specimen will be given by

$$E = - \frac{I}{\pi r n_V \mu_F e d} \quad (24)$$

where  $r$  is the distance from the cathode. The rate of change of  $n_V$  due to this field is<sup>18</sup>

$$\frac{\partial n_V}{\partial t} = D_F \frac{\partial^2 n_V}{\partial r^2} - \frac{\partial}{\partial r} (n_V \mu E) \quad (25)$$

Then we can write Eq. (25) like

$$\frac{\partial n_V}{\partial t} = D_F \frac{\partial^2 n_V}{\partial r^2} - \frac{I}{\pi d e r^2} \quad (26)$$

or

$$\frac{\partial n_V}{\partial t} = \frac{\partial^2}{\partial r^2} \left( D_F n_V + \frac{I}{\pi d e} \ln r \right) \quad (27)$$

as  $r$  does not depend on  $t$  Eq. (27) can be rewritten

$$\frac{\partial \left( n_V + \frac{I}{D_F \pi d e} \ln r \right)}{\partial t} = D_F \frac{\partial^2}{\partial r^2} \left( n_V + \frac{I}{D_F \pi d e} \ln r \right) \quad (28)$$

the solution to the Eq. (28) is known<sup>19</sup> and we can put

$$n_V = - \frac{I}{D_F \pi d e} \ln r + \frac{A}{D_F t^{\frac{1}{2}}} \exp \left( - \frac{r^2}{4 D_F t} \right) \quad (29)$$

If time is measured from the instant of application of the electric field and if the current reaches its equilibrium value in a time much smaller compared with the duration of coloration, we have

$$I = n_V = 0 \quad \text{at} \quad t = 0$$

Now, under the same conditions as those of the last section  $N_V \approx n_V$

$$D = \frac{1}{3} \frac{a^2 \nu}{N_0} \left[ - \frac{I}{D_F \pi d e} \ln \tilde{r} + \frac{A}{D t^{\frac{1}{2}}} \exp \left( - \frac{\tilde{r}^2}{4 D_F t} \right) \right] e^{-\epsilon_j / kT} \quad (30)$$

where we note that  $D$  depends of  $\tilde{r}$ . Besides the result is approximate because the diffusion of the metallic impurity is not along  $r$ , it is perpendicular to the largest diameter of the crystal, and then we use an average on  $r$ , called  $\tilde{r}$  in Eq. (30).



## 4. CONCLUSIONS

We have given two different expressions for the diffusion coefficient. In the first case  $D$  depends on the rate of radiation energy and it is possible to obtain directly the activation energy as function of  $W$  and  $\epsilon_V$ . In section 3 we have treated a very particular case and we have made many simplifications in order to obtain a simple mathematical solution to the problem. In any case we hope to have given one approximate solution to the real case. The dependence on the thermal entropy and another factors that we have not taken into account have been mentioned in section 2.

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## RESUMEN

Se calcula el coeficiente de autodifusión para halogenuros alcalinos en los cuales existen centros F formados por irradiación de la muestra y también por aplicación de un campo eléctrico. El método consiste en determinar teóricamente el número de vacancias que existen en los cristales con centros F y substituir esa expresión en la fórmula para el coeficiente de autodifusión. En el caso de cristales irradiados se encuentra que el coeficiente de autodifusión, depende de la intensidad de irradiación. En el caso del cristal al cual se ha aplicado un campo eléctrico se encuentra que el coeficiente de autodifusión, depende del coeficiente de difusión de los centros F en el halogenuro alcalino considerado y de la corriente que pasa a través de la muestra.