SELF-DIFFUSION COEFFICIENT OF Na IN NaCl DURING THE X-RAY IRRADIATION ON THE SAMPLE

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ABSTRACT: The effect of irradiation in the self-diffusion process of Na in NaCl is considered using a model for diffusion processes which ignores the crystalline structure of the material. The effect of interstitial clusters presents in the sample during the self-diffusion process is to reducethe diffusion particles by absorption of the ions in motion. We found that this effect can be explained in terms of the number per interstitial agglomerates, its cross-section capture and the ions velocity. The experimental data are consistent with our model.

1. INTRODUCTION

Self-diffusion coefficient measurement of Na in NaCl on samples which were subjected to X-ray irradiation during the diffusion process were made a long time ago by Mapother[1]. Below the layer in which the diffusion rate is retarded, the diffusion rate for the irradiated sample is approximately the same as for the unirradiated sample. The occurrence of this effect depends upon the temperature at which the diffusion takes place. Data taken at 527 °C, 496 °C and 462 °C showed the same effect.

Recently Durand et al[2] have found that for temperatures higher than 400 °C clusters of F-centers are observed and he concludes that interstitial agglomerates are produced during the X-ray irradiation under the same experimental conditions as those of Mapother. The order of the radius for these agglomerates was about 10 Å.

The aim of this paper is to explain the effect of irradiation, in the diffusion process, using Durand's results.

2. DIFFUSION EQUATION

In the saturated state almost all the F centers are in the form of agglomerates. Each agglomerate contains about 10^2 F centers and the radius of the interstitial agglomerates is expected[2] to be of the same order (10 Å). Under these conditions we have ignored the the crystalline structure of the crystal. In the diffusion process we assume that the Na ions are dispersed or absorbed by the interstitial clusters. The distributions function $f(\mathbf{r}, \mathbf{v}, t)$ for the diffusing ions is the same as the one used in connection with techniques of kinetic theory, $\mathbf{r}$ is the position vector, $\mathbf{v}$ the velocity of the ions and t the time. The equation of motion for the distribution function is[3]

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla_r\right) f(\mathbf{r}, \mathbf{v}, t) = \left(\frac{\partial f}{\partial t}\right)_{\text{col}} - \left(\frac{\partial f}{\partial t}\right)_{\text{abs}} \tag{1}$$

assuming that there are no external forces. Here $(\partial f/\partial t)_{\text{col}}$ is the collision term and $(\partial f/\partial t)_{\text{abs}}$ represents the absorption term. We can write the absorption term in the following simple way

$$\left(\frac{\partial f}{\partial t}\right)_{\text{abs}} = n_c \sigma_c v f, \tag{2}$$

Where n_c is the number of agglomerates and σ_c the cross-section capture. For the collision term we can write, in the usual way

$$\left(\frac{\partial f}{\partial t}\right)_{\text{col}} = -\int n_i v f(\mathbf{r}, \mathbf{v}, t)\,\sigma(\alpha)\ \text{sen}\ \theta'\,d\theta'\,d\varphi'\,dt$$

$$+\int n_i v f(\mathbf{r}, \mathbf{v}', t)\,\sigma(\alpha)\ \text{sen}\ \theta'\,d\theta'\,d\varphi'\,dt \tag{3}$$

where n_i is the density of the diffusing ions, and $\sigma(\alpha)\, d\omega$ is the probability for one particle to be scattered through an angle σ into the solid angle element $d\omega$. The relation of σ with θ, θ', φ and φ' is

$$\cos\theta' = \cos\theta\,\cos\sigma + \mathrm{sen}\,\phi\;\mathrm{sen}\,\beta \tag{4}$$

$$\beta = 90 - \phi' + \phi\,. \tag{5}$$

The distribution function is approximated by the formula

$$f(\mathbf{r}, \mathbf{v}, t) = \frac{1}{4\pi m}\rho(\mathbf{r}, \mathbf{v}, t) + \frac{3}{4\pi m v^2}\,\mathbf{v}\cdot\mathbf{J}\,. \tag{6}$$

Where $\rho(\mathbf{r}, \mathbf{v}, t)$ is the particle density

$$\rho(\mathbf{r}, t) = m\int f(\mathbf{r}, \mathbf{v}, t)\, d^3v \tag{7}$$

and $\mathbf{J}(r, \mathbf{v}, t)$ is the mass flow vector

$$\mathbf{J}(\mathbf{r}, t) = m\int \mathbf{v} f(\mathbf{r}, \mathbf{v}, t)\, d^3v\,. \tag{8}$$

Then from Eqs. 3 and 6 we obtain

$$\left(\frac{\partial f}{\partial t}\right)_{\mathrm{col}} = -\frac{3n_i J}{4\pi m}\int_0^{2\pi} d\phi' \int_0^{\pi} \sigma(\sigma)\,[\cos\theta - \cos\theta']\;\mathrm{sen}\,\theta'\, d\theta' \tag{9}$$

and using Eqs. 4 and 5 there results

$$\left(\frac{\partial f}{\partial t}\right)_{\mathrm{col}} = -\frac{3n_i J}{4\pi m}\int_0^{2\pi} d\phi' \int \cos\theta\,[1 - \cos\sigma]\;\mathrm{sen}\,\theta'\, d\theta' \tag{10}$$

because

$$\int_0^{2\pi} \cos(90 - \phi' + \phi)\, d\phi' = 0\,. \tag{11}$$

The momentum transfer cross section σ_m is defined by

$$\sigma_m = \iint [1 - \cos \alpha]\, d\phi' \operatorname{sen} \theta' d\theta' . \tag{12}$$

Now we can write the Eq. 1 in the following form:

$$\frac{1}{4\pi m} \frac{\partial \rho}{\partial t} + \frac{3}{4\pi m v^2} \mathbf{v} \cdot \frac{\partial \mathbf{J}}{\partial t} + \frac{\mathbf{v} \cdot \nabla \rho}{4\pi m} + \frac{3\mathbf{v} \cdot \nabla(\mathbf{v} \cdot \mathbf{J})}{4\pi m v^2} \simeq$$

$$- \frac{3n_i J}{4\pi m} \cos \theta \sigma_m - n_c \sigma_c v \left\{ \frac{\rho}{4\pi m} + \frac{3\mathbf{v} \cdot \mathbf{J}}{4\pi m v^2} \right\} \tag{13}$$

The term $\partial \mathbf{J}/\partial t$ can be neglected when we are dealing with the relatively slow rates of changes involved in diffusion. Additionally we suppose that $\nabla \rho$ and $\mathbf{J}$ are in the same direction. Therefore on the basis of symmetry we can separate Eq. 13 into two equations which serve to determine ρ and $\mathbf{J}$ in terms of $\mathbf{r}$, $\mathbf{v}$ and t.

Those terms which change sign when the direction of $\mathbf{v}$ is reversed give us the equation:

$$\frac{\mathbf{v} \cdot \nabla \rho}{4\pi m} \simeq - \frac{3n_i \mathbf{J} \cdot \mathbf{v} \sigma_m}{4\pi m v} - \frac{3n_c \sigma_c \mathbf{v} \cdot \mathbf{J}}{4\pi m v} \tag{14}$$

or

$$\mathbf{J} \simeq - \frac{v}{3m (n_i \sigma_m + n_c \sigma_c)} \nabla \rho \tag{15}$$

Next we consider those parts of Eq. 13 which do not change sign when $\mathbf{v}$ is reversed. All but one of the terms are independent of θ and the direction of $\mathbf{v}$, but the term in $\mathbf{v} \cdot \nabla(\mathbf{v} \cdot \mathbf{J})$ is a function of θ. This, of course is an indication that the assumption for the distribution function was only an approximate one. The relation can be approximately satisfied by averaging over all directions of $\mathbf{v}$. The only complicated term can be reduced by using Eq. 15. That is

$$\frac{3\mathbf{v}\cdot\nabla(\mathbf{v}\cdot\mathbf{J})}{4\pi m v^2} = -\frac{v}{3m\,(n_i\sigma_m + n_c\sigma_c)}\Bigg[v_x\left\{v_x\frac{\partial^2\rho}{\partial x} + v_y\frac{\partial^2\rho}{\partial x\partial y} + v_z\frac{\partial^2\rho}{\partial x\partial z}\right\} +$$

$$+ v_y\left\{v_x\frac{\partial^2\rho}{\partial x\partial y} + v_y\frac{\partial^2\rho}{\partial y} + v_z\frac{\partial^2\rho}{\partial z\partial y}\right\} +$$

$$+ v_z\left\{v_x\frac{\partial^2\rho}{\partial x\partial z} + v_y\frac{\partial^2\rho}{\partial y\partial z} + v_z\frac{\partial^2\rho}{\partial z^2}\right\}\Bigg] \tag{16}$$

When these terms are averaged over all directions of $\mathbf{v}$ the cross terms containing factors of the general type $v_x v_y$, etc., all average to zero, whereas the terms in v_x^2 , v_y^2 or v_z^2 each average to $1/3\ v^2$. Therefore the second. equation arising from Eq. 13 is

$$\frac{\partial\rho}{\partial t} \simeq \frac{v}{3m\,(n_i\sigma_m + n_c\sigma_c)}\nabla^2\rho - n_c\sigma_c v\rho \tag{17}$$

3. COMPARISON WITH THE EXPERIMENT

The solution of Eq. 17 with the boundary conditions used by Mapother is[4] given by

$$\rho = \rho_0/\sqrt{4\pi Dt}\ \exp\left(-\frac{r^2}{4Dt} - n_c\sigma_c v t\right) \tag{18}$$

and

$$D = \frac{v}{3m\,(n_i\sigma_m + n_c\sigma_c)} \tag{19}$$

This solution corresponds qualitatively to the experimental results of Mapother. To check the numerical result we have extrapolated the straight line in fig. 1 of reference 1 which corresponds to the irradiated sample; we have used the deepest points in this figure. If our model is correct we must approximately have

$$n_c \sigma_c v t = \ln \frac{800}{460} \qquad (20)$$

Since the diffusion time t is known from Mapother's data, σ_c can be obtained from Durand's experiment, for v we can use a formula given by Seitz[5]

$$v \simeq \sqrt{\frac{D}{t}}$$

for D we use again the value obtained by Mapother, we get the following value for n_c

$$n_c \simeq 3 \times 10^{15} .$$

Now, if we suppose that in the saturated state all the interstitials form agglomerates and there are about 10^{18} of them, that is, of the order of magnitude of the number of F centers in the saturated state, we obtain from Durand's data 2×10^2 of interstitials in each cluster. On the other hand, the volume of one cluster is expected to be of the order of $4/3\,\pi\, 10^{21}\ \mathrm{cm}^3$. Using the volume occupied by a chlorine ion, we obtain 1.8×10^2 interstitials in each agglomerate.

To check the value of D we use the formula

$$D = \frac{v}{3(n_i \sigma_m + n_c \sigma_c)} \simeq 10^{-11}\ \mathrm{cm}^2/\mathrm{sec}$$

and we use the experimental data. Therefore we have the same result as Mapother.

4. CONCLUSION

We have developed a model for diffusion processes which ignores the crystalline structure of the material; the effect of the interstitial clusters is to reduce the diffusing particles by absorption of the ions in motion.

A decrease in the concentration of both the diffusing particles and the diffusion coefficient is predicted in agreement with experiment but the quantitative comparison with experiment is difficult and unsatisfactory because of the uncertainty in the parameters which enter the theoretical equations.

The more important information for the construction of this model was the paper by Durand et al .

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RESUMEN

Se estudió el efecto de la radiación sobre el proceso de auto-difusión de Na en NaCl usando un modelo que ignora la estructura cristalina de la muestra. Se obtiene después de algunas simplificaciones la ecuación de difusión modificada por un término que es función del número de conglomerados de intersticiales en el cristal. su sección de captura y la velocidad de los iones. El resultado obtenido usando este modelo es consistente con los datos experimentales.