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A NOTE ON OFF-CENTRE DIFFUSION

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Within a one-dimensional model of off-centre diffusion it is shown that the diffusion coefficient depends on the number of off-centre sites and on their orientation relative to the host lattice.

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IT IS WELL KNOWN [1, 2] that substitutional impurity ions may occupy off-centered positions in an ionic host lattice, as a consequence of the balance between the repulsion and the polarization forces. These off-centre sites surround the normal lattice sites, in a configuration which is dictated mainly by the high-symmetry directions of the lattice. On the other hand, it is also known [3] that the diffusion coefficients of the solute ions in ionic crystals (as, for example, alkali halides) may acquire high values, sometimes by orders of magnitude higher than the self-diffusion coefficients. Recently, it has been suggested [4] that these vacancy-mediated fast diffusion processes are due to the off-centre positions occupied by the impurity ions. Indeed, the activation energy is considerably lowered in an off-centre configuration, thereby enhancing the transfer frequency.

Another source of variability of the diffusion coefficients, although to a lesser extent, is provided by the increase in the number of available sites brought by the off-centre configurations. A competi-

the diffusing particle moving among the various off-centre sites around the same normal site and the transfer time from one group of off-centre sites to another. In addition, geometric restrictions may appear on the transfer processes from one site to another, depending on the number of the off-centre sites and their orientation with respect to the host lattice. These questions are addressed in the present

Note within a simple one-dimensional model of off-centre diffusion.

To start with, we shall establish first the diffusion equation for a one-dimensional chain of sites, equally spaced by the distance a . Let $n(x, t)$ be the average concentration of diffusing particles at distance x and time t . We assume that the diffusion process is described by a transfer frequency p of the particles between the nearest-neighbouring sites placed at $x \pm a$. The various representations of the transfer frequency p , depending on the particular transfer mechanisms, are disregarded here, in particular its temperature dependence (which, as it is well known, is usually given by an Arrhenius-type law at high temperatures). We shall be interested, as usual, in variations of $n(x, t)$ over distances much larger than a and over time intervals much longer than p^{-1} , such that the diffusion proceeds by slight perturbations of the initial concentration. We may then write down

$$\frac{\partial n}{\partial t} = p[n(x+a) - n] - p[n - n(x-a)]$$

$$\cong pa^2 \frac{\partial^2 n}{\partial x^2} = D_0 \frac{\partial^2 n}{\partial x^2},$$

where $D_0 = pa^2$ is the diffusion coefficient. As is well known the solution of this equation for an initial concentration $n_0(x) = \delta(x)$ is given by

$$n(x, t) = \frac{1}{2\sqrt{\pi D_0 t}} e^{-x^2/4D_0 t}. \quad (2)$$

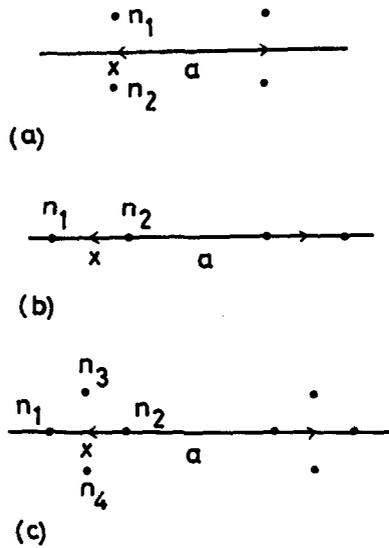


Fig. 1. Various off-centre configurations discussed in the present diffusion model.

In many experiments the initial concentration $n_0(x)$ extends uniformly from $x = 0$ to $x = -\infty$; the solution is then

$$n(x, t) = \frac{1}{2} [1 - \text{erf}(x/2\sqrt{D_0 t})], \tag{3}$$

where erf stands for the error function.

Let us now suppose that we have an off-centre configuration as that shown in Fig. 1(a), where there are two off-centre sites around each normal site

slightly displaced along a direction perpendicular to the chain axis. We shall assume that the motion among the off-centre sites belonging to the same group is described by a frequency p_0 , while the transfer frequency from one group of sites to another is p . As has been remarked above, this latter frequency is, usually, much higher than the transfer frequency p used in equation (1) for describing the on-centre diffusion, as a result of the lowering of the activation energy barrier. However, we shall not make this distinction explicitly, though we shall keep it in mind. The equations for the two concentrations $n_{1,2}(x, t)$ can readily be written as

$$\begin{aligned} \frac{\partial n_1}{\partial t} &= -p_0(n_1 - n_2) + p[n_1(x+a) - n_1] \\ &\quad + p[n_2(x+a) - n_1] - p[n_1 - n_1(x-a)] \\ &\quad - p[n_1 - n_2(x-a)] \\ &\cong -(p_0 + 2p)(n_1 - n_2) + pa^2 \frac{\partial^2}{\partial x^2} (n_1 + n_2), \end{aligned} \tag{4}$$

and, similarly,

$$\frac{\partial n_2}{\partial t} = -(p_0 + 2p)(n_2 - n_1) + pa^2 \frac{\partial^2}{\partial x^2} (n_1 + n_2). \tag{5}$$

Introducing $s = n_1 + n_2$ and $d = n_1 - n_2$ we get

$$\frac{\partial s}{\partial t} = 2D_0 \frac{\partial^2 s}{\partial x^2}, \tag{6}$$

and

$$\frac{\partial d}{\partial t} = 2(p_0 + 2p)d. \tag{7}$$

Usually, we are interested in the total concentration s (we may take, for example, $d_0(x) = 0$ whence $d(x, t) = 0$) which, as one can see from equation (6), diffuses twice as fast as in the previous on-centre case: the corresponding diffusion coefficient $D = 2D_0$ is simply multiplied by the number of the newly introduced off-centre sites, as expected.

A more interesting case appears when the two off-centre sites are displayed along the chain axis, as shown in Fig. 1(b). Obviously, the transfer processes between $n_1(x)$ and $n_1(x \pm a)$, as well as the transfer processes between $n_2(x)$ and $n_2(x \pm a)$, are forbidden in the present nearest-neighbour diffusion model. With the same frequencies as above the equations for the two concentrations $n_{1,2}(x, t)$ read

$$\begin{aligned} \frac{\partial n_1}{\partial t} &= -p_0(n_1 - n_2) - p[n_1 - n_2(x-a)] \\ &\cong -(p_0 + p)(n_1 - n_2) - pa \frac{\partial n_2}{\partial x} + \frac{1}{2} pa^2 \frac{\partial^2 n_2}{\partial x^2}, \end{aligned} \tag{8}$$

$$\frac{\partial n_2}{\partial t} = -(p_0 + p)(n_2 - n_1) + pa \frac{\partial n_1}{\partial x} + \frac{1}{2} pa^2 \frac{\partial^2 n_1}{\partial x^2}, \tag{9}$$

or, using the sum $s = n_1 + n_2$ and the difference $d = n_1 - n_2$,

$$\frac{\partial s}{\partial t} = pa \frac{\partial d}{\partial x} + \frac{1}{2} pa^2 \frac{\partial^2 s}{\partial x^2}, \tag{10}$$

$$\frac{\partial d}{\partial t} = -2(p_0 + p)d - pa \frac{\partial s}{\partial x} - \frac{1}{2} pa^2 \frac{\partial^2 d}{\partial x^2}.$$

A Fourier decomposition of s and d leads to the eigenvalue equation

$$\begin{cases} (\omega - \frac{1}{2} pa^2 q^2) s_q + ipaq d_q = 0, \\ - ipaq s_q + [\omega - 2(p_0 + p) + \frac{1}{2} pa^2 q^2] d_q = 0. \end{cases} \tag{11}$$

Usually $p_0 \gg p$, and, as we have said above, we are interested in the long wavelength limit $aq \ll 1$. Within these approximations we get the two eigenfrequencies $\omega_1 \cong 2p_0$ and $\omega_2 \cong (1/2)pa^2 q^2$. It is now easy to find out that for the initial condition $s_0(x) = \delta(x)$ the solution is given by the diffusion law (2) with D_0 replaced by the diffusion coefficient $D = (1/2)D_0$. As expected, the diffusion is slower in this case due to

the fact that the particles spend more time around each normal site.

However, this hindrance process has a rather low weight in more realistic off-centre configurations, as, for example, that shown in Fig. 1(c). In a similar way we may write down the equations in this case,

$$\begin{cases} \frac{\partial n_1}{\partial t} = -(p_0 + p)(n_1 - n_2) \\ \quad - (p_0 + 2p)[2n_1 - (n_3 + n_4)] \\ \quad - pa \frac{\partial n_2}{\partial x} + \frac{1}{2} pa^2 \frac{\partial^2}{\partial x^2} [n_2 + 2(n_3 + n_4)], \\ \frac{\partial n_2}{\partial t} = -(p_0 + p)(n_2 - n_1) \\ \quad - (p_0 + 2p)[2n_2 - (n_3 + n_4)] \\ \quad + pa \frac{\partial n_1}{\partial x} + \frac{1}{2} pa^2 \frac{\partial^2}{\partial x^2} [n_1 + 2(n_3 + n_4)], \\ \frac{\partial n_3}{\partial t} = -(p_0 + 2p)[3n_3 - (n_1 + n_2 + n_4)] \\ \quad + pa^2 \frac{\partial^2}{\partial x^2} (n_1 + n_2 + n_3 + n_4), \\ \frac{\partial n_4}{\partial t} = -(p_0 + 2p)[3n_4 - (n_1 + n_2 + n_3)] \\ \quad + pa^2 \frac{\partial^2}{\partial x^2} (n_1 + n_2 + n_3 + n_4). \end{cases} \quad (12)$$

Introducing $s_{1,2} = n_{1,3} + n_{2,4}$ and $d_{1,2} = n_{1,3} - n_{2,4}$ we get from equation (12) in the long-wavelength limit and for $p_0 \gg p$ the following two main equations

$$\begin{cases} \frac{\partial s_1}{\partial t} = -2p_0(s_1 - s_2) + \frac{1}{2} pa^2 \frac{\partial^2 s_1}{\partial x^2} + 2pa^2 \frac{\partial^2 s_2}{\partial x^2}, \\ \frac{\partial s_2}{\partial t} = -2p_0(s_2 - s_1) + 2pa^2 \frac{\partial^2}{\partial x^2} (s_1 + s_2), \end{cases} \quad (13)$$

whose dominant diffusion eigenmode is $\omega \cong$

$(13/4)pa^2q^2$, i.e. a diffusion coefficient $D = (13/4)D_0$. It is easy to see that this is the expected result. Indeed, looking on Fig. 1(c) we see that there are 2 ways for particle 1 to be transferred to the sites 3 and 4 at $x + a$, 3 ways for particle 2 to be transferred to the sites 1, 3, 4 at $x + a$ and, similarly, 4 ways for each of the particles 3 and 4 to be transferred to the $x + a$ -group of off-centre sites; which makes a total amount of $2 + 3 + 2 \cdot 4 = 13$, which divided by the number 4 of the off-centre sites gives the factor found above for the diffusion coefficient. If we include the other two off-centre sites placed on the second

calculation that the diffusion coefficient is increased by a factor 33/6.

In conclusion one may say that the off-centre diffusion coefficient depends on the number of the off-centre sites and on their relative orientation with respect to the host lattice. Extension of the present one-dimensional model to three-dimensional crystals reveals interesting anisotropic properties of the off-centre diffusion coefficient, depending on both the two elements mentioned above as well as on the diffusion

mechanism of diffusion.

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