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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

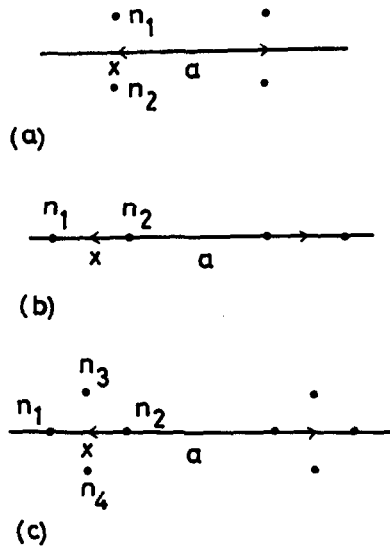$$n(x, t) = \frac{1}{2\sqrt{\pi D_0 t}} e^{-x^2/4D_0 t}. \tag{2}$$

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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

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

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

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

and, similarly,

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

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

$$\frac{\partial s}{\partial t} = 2D_0 \frac{\partial^2 s}{\partial x^2}, \qquad (6)$$

and

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

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

$$\frac{\partial n_1}{\partial t} = -p_0(n_1 - n_2) - p[n_1 - n_2(x - a)]$$
$$\cong -(p_0 + p)(n_1 - n_2) - pa\frac{\partial n_2}{\partial x} + \tfrac{1}{2}pa^2\frac{\partial^2 n_2}{\partial x^2}, \quad (8)$$

and

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

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

$$\frac{\partial s}{\partial t} = pa\frac{\partial d}{\partial x} + \tfrac{1}{2}pa^2\frac{\partial^2 s}{\partial x^2},$$
$$\frac{\partial d}{\partial t} = -2(p_0 + p)d - pa\frac{\partial s}{\partial x} - \tfrac{1}{2}pa^2\frac{\partial^2 d}{\partial x^2}. \qquad (10)$$

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

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

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 $\omega_2 \cong (1/2)pa^2q^2$. 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,

$$
\frac{\partial n_1}{\partial t} = -(p_0 + p)(n_1 - n_2)
$$

$$
- (p_0 + 2p)[2n_1 - (n_3 + n_4)]
$$

$$
- pa\frac{\partial n_2}{\partial x} + \tfrac{1}{2}pa^2\frac{\partial^2}{\partial x^2}[n_2 + 2(n_3 + n_4)],
$$

$$
\frac{\partial n_2}{\partial t} = -(p_0 + p)(n_2 - n_1)
$$

$$
- (p_0 + 2p)[2n_2 - (n_3 + n_4)]
$$

$$
+ pa\frac{\partial n_1}{\partial x} + \tfrac{1}{2}pa^2\frac{\partial^2}{\partial x^2}[n_1 + 2(n_3 + n_4)], \quad (12)
$$

$$
\frac{\partial n_3}{\partial t} = -(p_0 + 2p)[3n_3 - (n_1 + n_2 + n_4)]
$$

$$
\frac{\partial n_4}{\partial t} = -(p_0 + 2p)[3n_4 - (n_1 + n_2 + n_3)]
$$

$$
+ pa^2\frac{\partial^2}{\partial x^2}(n_1 + n_2 + n_3 + n_4).
$$

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

$$
\frac{\partial s_1}{\partial t} = -2p_0(s_1 - s_2) + \tfrac{1}{2}pa^2\frac{\partial^2 s_1}{\partial x^2} + 2pa^2\frac{\partial^2 s_2}{\partial x^2},
$$

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

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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