# INFLUENCE OF DISLOCATIONS ON DIFFUSION KINETICS IN SOLIDS WITH PARTICULAR REFERENCE TO THE ALKALI HALIDES

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Preferential diffusion along dislocations may give rise to several limiting types of behaviour, in some of which the kinetics of diffusion remain, on a macroscopic scale, in apparent agreement with Fick's law. The various possible types of behaviour are classified, and the conditions required for each type are discussed in detail, with complete derivations where necessary. The features of each type of diffusion which will appear in different experimental techniques are discussed.

Self-diffusion in the alkali halides is discussed in the light of this classification. It is concluded that, for the anions, no simple model of enhanced mobility in a dislocation network (or grain boundaries) is in complete accord with all the known facts. It is suggested that the only reported autoradiographic experiment gives some evidence for a rather long-range effect of large-angle boundaries. By analogy, the external surface may cause abnormal distribution of vacancies throughout the region in which diffusion is usually studied.

Preferential diffusion along dislocations has been demonstrated by direct observation of concentration distributions on a microscopic scale both in metals <sup>1-3</sup> and in the alkali halides.<sup>4</sup> However, most experimental techniques do not give such detailed information. The well-known sectioning method gives a mean concentration in any plane normal to the diffusion co-ordinate, but does not distinguish between bulk and dislocations. The newer exchange technique, which has many practical advantages, is even less informative in this respect. Only the total mass flow into, or out of, a crystal is measured, and the concentration distribution must be inferred from the overall kinetics.

For anion diffusion in the alkali halides, all these techniques have yielded evidence that dislocations or grain boundaries are important in determining the value of the apparent diffusion coefficient.<sup>4-6</sup> Yet, in every case, the overall kinetics of diffusion are consistent with a simple transport process, throughout the solid phase, obeying Fick's law. Two ways in which such behaviour may arise have been suggested <sup>7</sup>, <sup>8</sup> without extensive discussion of the conditions required, and the general case (which certainly does not give Fick's law behaviour) has been solved for particular boundary conditions.<sup>9</sup>

The purpose of this paper is, first, to classify the possible types of behaviour, to show their relationship to each other and to derive precise conditions for each; and, secondly, to examine the existing data for the alkali halides on the basis of this classification. An important feature, which does not seem to have been pointed out previously, is that a particular type of behaviour should, in general, present entirely different aspects in different types of experiment. Most particularly there is no *single* type of behaviour for which the structure sensitivity should be detectable by all three experimental techniques (sectioning, exchange, and microscopic examination of concentration distributions).

Now for the alkali halides, it has been thought hitherto that the results of all types of experiment were consistent with each other, in general terms, in that all showed structure sensitivity and diffusion coefficients were reproducible from one method to another. The contention of the present paper is that comparison of these various results is significant only when it is carried out in a rigorous manner. When the classification here developed is used as the basis of such a comparison, the conclusions reached for the alkali halides are somewhat unexpected. The simplicity of the experimental results is apparently deceptive, and while a difference in diffusion coefficients between bulk and dislocations seems necessary, it is not in itself sufficient to account for the results.

In this respect, the autoradiographic study of iodide ion diffusion in KI is very significant, and its anomalous nature has not been sufficiently stressed previously. The concentration distribution is not compatible with any of the limiting cases described in the present paper as giving apparent Fick's law behaviour on a macroscopic scale; yet such behaviour is just what is observed in this system.

#### A CLASSIFICATION OF POSSIBLE TYPES OF BEHAVIOUR

Three principal types of behaviour are recognized here; the two which give rise to simple overall kinetics are called types A and C, and represent opposite limiting cases of the general type B. A transition from type A through B to C may be thought of as occurring, in a hypothetical model, as the mobility in the dislocation network is increased, by several orders of magnitude, starting from values not much greater than the bulk mobility. Another, and perhaps more significant, relationship between the three types is that, in any system in which diffusion can be studied continuously from very short to very long times, the behaviour will initially be type C, and will develop into type B and ultimately type A.

#### type A

In this limiting form at long times (or long diffusion distances, or diffusion coefficient in the dislocations not much greater than that in the bulk), every diffusing particle has wandered sufficiently far to have entered, migrated in, and left a large number of dislocations before any experimental measurement is made. Thus, each particle effectively "sees" a single diffusion coefficient representing the combined effects of bulk and dislocation network as regions in which the particle spends particular fractions of its time. The whole system will appear to obey Fick's law.

The possibility of this type of behaviour was first suggested in a brief paper by Hart,<sup>7</sup> who analyzed the situation very concisely on generalized "random walk" considerations. One aspect which is not stressed by this treatment (although it is implicit therein) is that, although the dislocation network is acting in such a way as to accelerate the diffusion, there are no marked concentration differences between bulk and dislocations. An autoradiographic experiment should not, therefore, yield a picture of the dislocation network in this case.

#### туре В

This is the most obvious, and most complicated, case. The overall diffusion distance from (or towards) the surface of the solid is of the same order of magnitude as the scale of the dislocation network, and the concentration distribution does not approximate to any simple form. Fick's law behaviour will not be observed.

Consider an experiment in which diffusing material is initially uniformly distributed through the solid, and the surface concentration is suddenly reduced to zero (as in the "exchange" technique). For type B diffusion, the concentration contour diagram has the form of "river-valleys" cutting back into the crystal. Near to the surface, the sides of the valleys slope gently, and as diffusion proceeds the valleys become very shallow throughout the region of effective diffusion; the process has then become type A. Returning to the earlier time, the valleys become narrower with increasing depth of penetration into the solid. At the earliest times,

the valleys are very narrow and, effectively, the material in the dislocation network may be considered mobile, while that in the bulk is not. This, as described below, is type C diffusion.

The first approximate treatment of the type B situation was given by Fisher.<sup>10</sup> Whipple <sup>9</sup> has published an exact solution, for the boundary conditions of an exchange experiment, for a crystal containing grain boundaries parallel to the direction of diffusion and of semi-infinite extent without cross-links. He concludes that Fisher's approximation appears incorrect. Lidiard and Tharmalingam <sup>8</sup> state that the total mass ejected from the crystal at time t will be proportional to  $t^{\frac{3}{2}}$ , instead of the usual  $t^{\frac{1}{2}}$  (for a Fick's law process); they omit to indicate that this is not general, but is a special case (see the condition given below).

#### туре С

This is the limiting form at short times, or very high diffusion coefficient in the dislocations, wherein it may be considered that diffusion is taking place only in the dislocation network, while material in the bulk is immobile. In this case, there is only one true diffusion coefficient (that for the dislocation network); but the apparent diffusion coefficient estimated experimentally will depend on the type of experiment, as follows.

(i) In a sectioning experiment, diffusion takes place into a crystal which initially contains none of the diffusing material. At a particular time, the amount of material which has diffused is determined as a function of distance of penetration into the crystal. From such data, the mean migration distance of a diffusing particle in the direction of diffusion is always correctly estimated. Thus, the true diffusion coefficient is calculated, whether the process concerned be a true bulk diffusion or the type C process here considered in the dislocation network only.

(ii) In an exchange experiment, diffusion takes place out of a crystal which initially contains diffusing material uniformly distributed throughout bulk and dislocation network. The experimentally measured quantity is the total amount of material which has diffused out of the crystal, as a function of time. This material has, in fact, diffused from the dislocation network only, and the true diffusion distance may be calculated only if the fraction of the total volume occupied by the dislocation network is known. In practice, the diffusion coefficient will usually be calculated as if all the material in the crystal were of equal mobility. To give the observed total amount of diffusion would, in these circumstances, require a shorter diffusion distance in the whole bulk than has actually occurred in the dislocations. The apparent diffusion distance and apparent diffusion coefficient are therefore much smaller than the true values.

Lidiard and Tharmalingam <sup>8</sup> have mentioned the possible occurrence of type C diffusion. They have not considered the dependence of the apparent diffusion coefficient on the type of experiment, but have discussed another important experimental matter, namely, the validity of the procedure in exchange experiments whereby diffusion is studied at several temperatures in one experiment.<sup>11</sup> They conclude that this procedure is correct both in simple bulk diffusion and in type C diffusion. In either case, the development of the concentration distribution depends on a single parameter ( $D_ct$  in the notation used below) and a change in temperature is equivalent to a change of time-scale. It only remains to point out that this is also true of type A diffusion, so that, in complete generality, whenever apparent Fick's law kinetics are observed, this experimental method is valid.

The above classification takes into account the possible existence of two regions in which the diffusing material has different mobilities. It is easy to imagine more complicated situations. For example, diffusion is sometimes studied in pressed compacts,<sup>4, 5</sup> and here there could be three distinct regions: (i) the large-angle boundaries between crystals, (ii) the dislocation network within each crystal, (iii) the bulk of each crystal. Such complications do not require any addition to the classification given here, but only an elaboration of the same concepts suited to each individual case. Suppose, for example, that the concentrations in largeangle boundaries and dislocation networks remain approximately equal, but there is a wide discrepancy in concentration between the dislocation network and the bulk of each crystal. Then we may classify the situation as type A for regions (i) and (ii), but type C within each crystal.

# THE CONDITIONS FOR EACH TYPE OF DIFFUSION, AND THE VALUES OF TRUE AND APPARENT DIFFUSION COEFFICIENTS

In this section, the conditions required for each type of diffusion and the diffusion coefficient which will be measured by each type of experiment are summarized, with reasons wherever these can be given briefly. Where a detailed mathematical discussion is necessary, it is deferred to the following section.

Where detailed discussion is required, the principal regions of accelerated diffusion will be taken as the dislocations concentrated in low-angle boundaries. In deriving the condition for type-A diffusion, a simplified model will be used consisting of a spherical crystal composed of spherical grains all of equal size, the diffusion coefficient being greater in the surface layer of each grain than in the interior. The following notation will be used throughout:

 $a_c$  and  $a_g$ , crystal and grain size respectively (radii, in the simple model),

 $r_c$  and  $r_g$ , distance from centre of crystal and grain respectively,

- *l*, thickness of boundary layer on each grain,
- $D_g$ , bulk diffusion coefficient in interior of grain,
- $D_s$ , diffusion coefficient in grain boundaries or dislocations,
- $D_c$ , macroscopic diffusion coefficient for the solid as a whole (where this exists, e.g., in type A),
- $D_a$ , apparent diffusion coefficient derived from a particular experiment by a particular method of calculation,

 $C(r_c, r_g, t)$ , concentration at any point in the system,

 $\phi(r_c, t)$ , concentration in the grain boundaries,

f, fraction of total volume having the diffusion coefficient  $D_s$ .

#### туре А

CONDITIONS.—Lidiard and Tharmalingam<sup>8</sup> have given the condition that the scale of the dislocation network (i.e.,  $a_g$ ) should be small compared to the diffusion distance ( $\sim \sqrt{D_{ct}}$ ). Hart's condition that the migration time of particles between dislocations should be much less than t is the same, except that  $D_c$  is replaced by  $D_g$ ; and since  $D_g$  is smaller than  $D_c$  (perhaps even by orders of magnitude in some cases), this is the more restrictive condition :

$$a_g^2/D_g \ll t. \tag{1}$$

An analysis of the same situation by a different mathematical approach (using the simple model of spherical grains) is given in the next section, and suggests that condition (1) is numerically very restrictive, a factor of the order of  $10^{-5}$  being introduced on the right-hand side of the inequality.

It may sometimes be useful to consider condition (1) in a different form which displays the importance of the ratios of grain size to crystal size and of  $D_c$  to  $D_g$ . For a particular crystal size the sensitivity of the measuring device will require the removal from the crystal of some fixed minimum fraction of the diffusing material. This determines a minimum time,  $t_{\min} = ka_c^2/D_c$ , where k is usually less than unity. Applying inequality (1) to  $t_{\min}$ ,

$$D_{q}a_{c}^{2}/D_{c}a_{q}^{2} \gg 1.$$

If the grains are large, this condition is soon violated as  $D_c$  and  $D_s$  increase relative to  $D_g$ ; but if the grains are small, type-A diffusion may persist until  $D_s$  exceeds  $D_g$  by several orders of magnitude.

DIFFUSION COEFFICIENTS.—The diffusion process may be visualized as a rapid equilibration of each grain with its boundary, accompanied by transport to the external surface solely along the boundaries. This is kinetically analogous to diffusion accompanied by a rapid reversible chemical reaction with an immobile species.<sup>12</sup> The diffusion coefficient is diminished by a factor representing the extra material to be transported, i.e., in the case of reaction, 1+K (K = equilibrium constant), and in the present case the ratio (1/f) of total volume to grain boundary volume :

$$D_c = f D_s = 3D_s l/a_g.$$

More generally, since bulk and grain boundary diffusion are proceeding in parallel under the same concentration gradient at any  $r_c$  and t, their contributions to mass flow are in proportion to their diffusion coefficients and the fraction of the solid involved in each process. Hence,

$$D_{c} = f D_{s} + (1 - f) D_{a}.$$
 (3)

This is identical to the expression for  $D_1$  in Hart's paper.  $D_c$  is, in effect, a true diffusion coefficient applicable to all particles of the diffusing species. Hence the apparent diffusion coefficient  $D_a = D_c$  for all types of experiment.

#### туре В

This most general situation is established whenever the conditions for types A and C are both violated. There is one limiting case in which a simple law is obeyed; for the conditions of an exchange experiment, the total amount of material which has left the crystal at time t is proportional to  $t^{\frac{3}{2}}$  if

$$(D_a t)^{\frac{1}{2}} \gg l. \tag{4}$$

туре С

CONDITIONS.—The diffusion distance in the bulk must be small compared to the thickness of a grain boundary, so that material discharged from the bulk into the boundaries is negligible; thus

$$(D_a t)^{\frac{1}{2}} \ll l. \tag{5}$$

It is shown below that this condition is required for Whipple's general solution to reduce to the form describing type-C diffusion. For this behaviour to be experimentally observable, l would usually have to be much greater than the extent of the core of a dislocation.

DIFFUSION COEFFICIENTS.—Since particles are mobile in some regions of the solid and immobile in others, there is no diffusion coefficient  $D_c$  applicable to the motion of all particles in the solid. However, in all experiments where measurements are on a macroscopic scale, Fick's law will appear to be obeyed and various apparent diffusion coefficients  $D_a$  may be calculated according to the type of experiment and the assumptions made in the calculation. It will most commonly be assumed that the process is simple Fick's law diffusion in which  $D_a$  is applicable to all particles in the solid. On this basis,  $D_a$  will be related to  $D_s$  as follows.

(i) Exchange experiment.—For unit area of the crystal face, of which a fraction f is occupied by the terminations of grain boundaries, amount of material which has left crystal by time  $t = f(2D_st/\pi)^{\frac{1}{2}}$ . If the transport process is assumed to have involved the whole crystal, and not just the fraction f, with diffusion coefficient  $D_a$ , amount of material which has left crystal at time  $t = (2D_at/\pi)^{\frac{1}{2}}$ . Equating the two expressions, we have

$$D_a = f^2 D_{s^*} \tag{6}$$

(ii) Sectioning experiment.—The concentration distribution at any time in the grain boundaries corresponds to

$$\ln\left(\phi_2/\phi_1\right) = (y_1^2 - y_2^2)/4D_s t,\tag{7}$$

where y is distance in the direction of diffusion. The measured mean concentration in any section is  $f\phi$ , and use of this in place of  $\phi$  in eqn. (7) will result in a correct estimation of  $D_{s}$ .

#### DERIVATION OF THE CONDITIONS

TYPE A.—The following treatment refers to unit initial concentration in the crystal and zero concentration at its surface for t>0. For the simple model of spherical grains, let us assume the situation to be established in which  $C(r_c, r_g, t)$  nowhere greatly exceeds  $\phi(r_c, t)$ , transport to the surface is solely along grain boundaries, and  $D_c \sim D_s l/3a_g$ . Then <sup>12</sup>

$$\phi(r_c, t) = \frac{-2a_c}{\pi r_c} \sum_{m=1}^{\infty} \frac{(-1)^m}{m} \sin \frac{m\pi r_c}{a_c} \exp\left(-D_c m^2 \pi^2 t/a_c^2\right).$$
(8)

The grains being presumed small enough for each to be specified by a single  $r_c$ ,  $\phi$  may be used as a boundary condition to find C in each grain, and the description of the process is self-consistent if the expression thus obtained justifies the original assumption that  $C \sim \phi$ . We may write  $C = C_1 + C_2$ , where  $^{12}$ 

$$C_{1} = \frac{-2D_{g}}{r_{g}a_{g}} \sum_{n=1}^{\infty} (-1)^{n} n\pi \sin \frac{n\pi r_{g}}{a_{g}} \exp\left(-D_{g}n^{2}\pi^{2}t/a_{g}^{2}\right) \int_{0}^{t} \exp\left(D_{g}n^{2}\pi^{2}\lambda/a_{g}^{2}\right) \phi(\lambda) \mathrm{d}\lambda,$$
(9)

$$C_2 = \frac{-2a_g}{\pi r_g} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r_g}{a_g} \exp\left(-D_g n^2 \pi^2 t/a_g^2\right).$$
(10)

From eqn. (6) and (7),

$$C_{1} = \frac{4D_{g}a_{c}}{r_{g}r_{c}a_{g}}\sum_{n}\sum_{m}(-1)^{n}n\pi\sin\frac{n\pi r_{g}}{a_{g}}\frac{\exp\left(-D_{c}m^{2}\pi^{2}t/a_{c}^{2}\right)-\exp\left(-D_{g}n^{2}\pi^{2}t/a_{g}^{2}\right)}{(D_{g}n^{2}\pi^{2}t/a_{g}^{2})-(D_{c}m^{2}\pi^{2}t/a_{c}^{2})}$$
$$\frac{(-1)^{m}}{m\pi}\sin\frac{m\pi r_{c}}{a_{c}}.$$
 (11)

We require that  $C_1 \sim \phi - C_2$ ; this condition is fulfilled if the term  $(D_c m^2 \pi^2 / a_c^2)$  in the denominator of eqn. (11) can be neglected, i.e., all summations in *m* must be adequately represented by their terms up to  $m_{\text{max}}$ . Thus, for n = 1,  $m = m_{\text{max}}$ , we must have approximately

$$(D_g n^2 \pi^2 / a_g^2) \ge 10 (D_c m^2 \pi^2 / a_c^2),$$

or

$$D_g a_c^2 / D_c a_g^2 \ge 10 m_{\text{max}}^2, \tag{12}$$

which may be compared with eqn. (2).

The most slowly convergent series in m to be considered is

$$\sum_{m=1}^{m_{\max}} \frac{(-1)^m}{m\pi} \sin \frac{m\pi r_c}{a_c} = -\sum_{m=1}^{m_{\max}} \frac{1}{m\pi} \sin m\pi \left(1 - \frac{r_c}{a_c}\right) = -\frac{1}{\pi} \sum_{m=1}^{m_{\max}} \frac{\sin x}{x} \delta x, \quad (13)$$

where

$$x = m\pi \left(1 - \frac{r_c}{a_c}\right), \quad \delta x = \pi \left(1 - \frac{r_c}{a_c}\right)$$

At positions close to the surface of the crystal, this series converges very slowly, and  $m_{\max}$  may be estimated by considering the behaviour of  $\int_0^{x_{\max}} [(\sin x)/x)] dx$ . This function oscillates about the value  $\pi/2$ , the oscillations becoming small at  $x_{\max} \sim 10\pi$ . Hence

$$10\pi = m_{\max}\pi \left(1 - \frac{r_c}{a_c}\right). \tag{14}$$

Since the approximation must be good down to distances  $(r_c - a_c)$  small compared to the diffusion distance, say to  $10^{-1} (D_c t)^{\frac{1}{2}}$ ,

$$m_{\rm max} \sim 10^2 a_c / (D_c t)^{\frac{1}{2}},$$
 (15)

and from eqn. (12) and (15),

$$a_g^2/D_g \leqslant 10^{-5}t.$$
 (16)

This is a somewhat more precise form of eqn. (1). If there is a significant contribution from bulk diffusion, the condition must become numerically less restrictive, since it is not required in the limit  $D_s = D_g$ . However, the condition will not be relaxed markedly while the grain boundaries are carrying a substantial proportion of the total mass flow.

TYPES B AND C.—Let us consider the concentration gradient at the surface (y = 0) in a grain boundary aligned normal to the surface, from which the total mass flow out of the boundary may be obtained by time integration. Using Whipple's <sup>9</sup> solution for "semi-infinite grains", and altering the initial and boundary conditions to those for outward diffusion,

$$\left(\frac{\partial\phi}{\partial y}\right)_{y=0} = \frac{1}{(\pi D_g t)^{\frac{1}{2}}} \left\{ 1 - \frac{1}{2} \int_0^{\Delta} \frac{d\sigma}{\sigma^{\frac{3}{2}}} \operatorname{erfc}\left(\sqrt{\frac{\Delta - 1}{\Delta - \sigma}} \frac{\sigma - 1}{2\beta}\right) \right\},\tag{17}$$

where

$$\Delta = D_s/D_g$$
 and  $\beta = (\Delta - 1)l/2(D_g t)^{\frac{1}{2}}$ 

The main contribution to the integral is from  $\sigma = 1$  to a value  $\sigma_{max}$  given by

$$\left(\frac{\Delta-1}{\Delta-\sigma_{\max}}\right)^{\frac{1}{2}}\frac{\sigma_{\max}-1}{2\beta} \sim 1,$$
(18)

and two limiting situations arise.

(i)  $D_g t/l^2 \leq 1$ , leads to type-C diffusion.  $\sigma_{\max} \sim \Delta$ , and integration with the approximation erfc x = 1-x, x < 1 shows that

$$(\partial \phi/\partial y)_y = 0 \sim (\pi D_g t)^{-\frac{1}{2}} \Delta^{-\frac{1}{2}} (1 + \text{terms of order } Dt/l^2) \sim (\pi D_s t)^{-\frac{1}{2}}.$$
(19)

Thus diffusion out of the grain boundary occurs with no disturbance from the bulk.

(ii)  $D_g t/l^2 \ge 1$  leads to Lidiard and Tharmalingam's <sup>8</sup> expression for type-B diffusion.  $\sigma_{\max} \sim 1+2\beta$ , and in place of the term  $\Delta^{-\frac{1}{2}}$  in (19) we have a term in  $\beta^{-\frac{1}{2}}$ . Thus  $(\partial \phi/\partial y)_y = 0 \propto t^{-\frac{1}{2}}$  and total mass flow  $\propto t^{\frac{3}{2}}$ .

#### SELF-DIFFUSION IN THE ALKALI HALIDES

The data which will be analyzed are the exchange experiments of Morrison et al.<sup>6, 11</sup> on anion diffusion in NaCl and KCl, and the sectioning experiments of Laurent and Bénard <sup>4, 5</sup> on cation and anion (except  $F^-$ ) diffusion in NaCl, KF, KCl, KBr, KI, CsF and CsCl; the latter study also includes autoradiographic experiments on the diffusion of both ions in KI. In almost all cases, the kinetics agree with Fick's law. The exceptions are some of the exchange experiments at very low temperatures, where diffusion distances are only a few atomic layers, and at very high temperatures, where the "semi-infinite solid" approximation breaks down at very short times.

Of the cations, caesium alone shows that the effect of grain boundaries is important by giving an apparent diffusion coefficient  $D_a$  linearly dependent on the concentration f of grain boundaries, in sectioning experiments. It might be noted in passing that, where such dependence is not found, it is only type A which is eliminated. Type C should give  $D_a = D_s$ , independent of f, in a sectioning experiment, but should be detectable by both autoradiography and exchange experiments. For K<sup>+</sup> in KI, autoradiography eliminates type C.

In summary, there is no evidence for any influence of grain boundaries in sodium and potassium-ion diffusion; the evidence on caesium is not very extensive, but its behaviour appears similar to that of the anions discussed below.

The difficulty which arises in interpreting the data for anion diffusion may be seen by comparing the results of exchange and sectioning experiments. For annealed single crystals of NaCl and KCl, which have not been subjected to mechanical stress after annealing, apparent diffusion coefficients are closely reproducible between the two kinds of study in the temperature range common to both ( $\sim$ 550-700°C). The effect of dislocations is shown as follows: if an exchange experiment is carried out on a crystal mechanically stressed after annealing, or if a sectioning experiment is carried out on a pressed compact,  $D_a$  has higher values than for annealed single crystals. In the sectioning experiments,  $D_a$  varies linearly with f.

These observations obviously indicate type-A diffusion and no other situation (type C would give different values of  $D_a$  from the two experimental techniques, and  $D_a$  would not depend on f in the sectioning experiments). Yet, in all the experiments, the condition for type A is violated. Thus, for the work of Morrison *et al.*,  $t\sim 10^5$  sec and the minimum value which can be reasonably assigned to  $a_g$  is  $5 \mu$  (the half-distance between isolated dislocations, measured maximum concentration  $\sim 10^6$  cm<sup>-2</sup>). Condition (16) becomes  $D_g \ge a_g^2 \ge 2.5 \times 10^{-7}$  cm<sup>2</sup> sec<sup>-1</sup>, whereas the maximum  $D_c$  at any temperature  $\sim 10^{-9}$  cm<sup>2</sup> sec<sup>-1</sup>. Laurent and Bénard's experimental conditions are not very much different; from their published examples for KBr (polycrystalline) and KBr and KCl single crystals (taking  $a_g > 5 \mu$ ), condition (16) is violated in all cases by factors between  $10^2$  and  $10^5$ .

Morrison *et al.* have suggested that type-A diffusion may be possible if the region of accelerated diffusion is a fairly extensive "space-charge" region in which the concentrations of vacancies are disturbed by the presence of a dislocation. The existence of such space-charges has been discussed by Lehovec <sup>13</sup> for external surfaces and Eshelby *et al.*<sup>14</sup> for dislocations. To the present author the required relaxation of condition (16) appears possible in these circumstances either (i) if the space-charge is much more extensive than the 200 Å used by Morrison *et al.* in their estimation of  $D_s/D_g$ , or (ii) if the dislocation network is itself mobile and capable of traversing all regions of the crystal, so that the concentration distribution is smoothed out to that of type A.

In this connection, the autoradiographic study reported by Laurent and Bénard 4 (for I<sup>-</sup> diffusion in a pressed compact of KI) is of great interest. If the situation disclosed by this study is to be placed anywhere in the classification given in the present paper, it must clearly be type B. Yet when precisely similar specimens are studied by the sectioning method, simple Fick's law behaviour is found. It appears to the present author that Laurent and Bénard have not sufficiently stressed the anomalous nature of this result.

To consider this point more rigorously, it should be recognized that Whipple's solution is not appropriate to these experiments. The boundary conditions for which Whipple's solution applies are those of an exchange experiment; for a sectioning experiment, the dependence of concentration on time and spatial coordinates should have an entirely different functional form. However, an exact solution is not necessary to establish that apparent Fick's law behaviour should

not be observed in this case. Even supposing that the solution for these boundary conditions gives an effective concentration distribution of the form  $(\pi D_c t)^{-\frac{1}{2}} \exp(-y^2/4D_c t)$  for a particular grain size, this cannot remain true for a larger grain size. The distribution must then be the sum of two terms of this type, with different diffusion coefficient  $D_c$  and  $D_g$ .

While it is not within the scope of this paper to consider any situation more complicated than a simple increased mobility for diffusing material in a particular geometrical region, one tentative suggestion may perhaps be made. The autoradiographs referred to above show several interconnected regions (presumably large-angle boundaries), the thickness of which is of the order of a millimetre, in which I<sup>-</sup> diffusion is apparently accelerated. Now the total distance from the external surface in which the process has been studied is only 0.6 mm; it is thus possible that the whole region in which diffusion is studied is abnormal by virtue of the influence of the external surface, if this influence is only as extensive as that of the large-angle boundaries.

Suppose that, in the interior of the compact, the vacancies (or vacancy-pairs) responsible for anion diffusion are concentrated at the large-angle boundaries. To account for the observed results, it is then required that the external surface should have the effect of "spreading out" the vacancy distribution without changing the total number of vacancies to be found in any section parallel to the external surface.

In general terms, the mobility of the ions depends on the number, distribution and mobility of the vacancies (of the appropriate kind) in the lattice. Any explanation on the lines suggested above requires the grain boundaries to affect the number and distribution of the vacancies rather than their mobility. It is then reasonable that, as found experimentally by Laurent and Bénard, the activation energy of  $D_a$  does not change when its absolute value is increased by increasing the concentration of grain boundaries. This interpretation differs from that of Morrison *et al.*, who have found that the activation energy of  $Cl^-$  diffusion in NaCl, in a fairly low temperature range, can be changed between two limiting values according to the extent of annealing. They have assigned the two limits as being the activation energies of  $D_s$  and  $D_g$ .

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