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EFECT OF SURFACE IMPURITIES ON TRACER DIFFUSION IN IONIC CRYSTALS (*)

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Résumé. — Dans les expériences d'autodiffusion et de diffusion d'impuretés, des impuretés hétérovalentes présentes initialement à la surface des échantillons ou dans le traceur déposé peuvent co-diffuser avec le traceur. Dans les cristaux ioniques, des quantités même extrêmement faibles d'impuretés hétérovalentes, comparables à la concentration de traceur, peuvent introduire des lacunes extrinsèques dans la zone de diffusion qui modifient sensiblement les profils de diffusion du traceur. Un modèle de lissage sur ordinateur a été développé pour fournir une solution approchée au cas d'un traceur homovalent et d'une impureté hétérovalente inconnue co-diffusant par lacunes dans un solide ionique ainsi que dans le cas d'un traceur hétérovalent lorsque le traceur lui-même introduit des lacunes extrinsèques. Les solutions montrent une influence du temps de diffusion sur les profils et des écarts sensibles à la solution gaussienne de la source mince, même dans la région de profonde pénétration, indiquant que la pente limite n'est pas nécessairement une mesure valable de la diffusivité du traceur. Il est montré également que cet effet intervient au premier ordre dans la mesure des effets isotopiques dans les solides ioniques, en sorte que de légers écarts peuvent causer de graves erreurs dans la détermination de l'effet isotopique. Le programme est utilisé pour traiter les mesures expérimentales de l'influence de la pression sur l'autodiffusion de Na dans NaCl et de la durée de diffusion sur la diffusivité, apportant des valeurs précises de la diffusivité du traceur ainsi que de la quantité et de la diffusivité de l'impureté inconnue.

Abstract. — In tracer self-diffusion or impurity diffusion experiments heterovalent impurities initially present on the surface or in the deposited tracer may co-diffuse into a sample along with the tracer. In ionic crystals, even very tiny amounts of heterovalent impurity, comparable to the tracer concentration, may introduce extrinsic vacancies in the diffusion zone which markedly influence the measured diffusion profiles of the tracer. A computer fit model has been developed to provide an approximate solution for the case of a homovalent tracer and an unknown heterovalent impurity co-diffusing via vacancies in an ionic solid as well as for the case of a heterovalent tracer where the tracer itself introduces extrinsic vacancies. Solutions show a dependence of the profile shape on diffusion time and marked deviations from a Gaussian fit for a thin source, even for the deep penetration region, indicating that the limiting slope is not necessarily a valid measure of the tracer diffusivity. The effect is also shown to enter to first order in measurements of the isotope effect in ionic solids, so that small deviations may cause major errors in determination of the isotope effect. The program is used to fit experimental measurements of the pressure dependence of Na self-diffusion in NaCl and of the time dependence of the diffusivity, providing consistent values for the diffusivity of the tracer as well as for the amount and diffusivity of the unknown impurity.

1. Introduction. — The present problem was brought forcibly to our attention in an attempt to understand marked curvatures discovered in this laboratory by Martin et al. [1] in tracer penetration profiles for Na\textsuperscript{32} diffusing in NaCl under large hydrostatic pressure. The form of these profiles is shown in figure 1. These measurements were made using Harshaw NaCl single crystals with extremely thin layers of ICN carrier free Na\textsuperscript{32} tracer initially deposited on the surface, diffused and microtome-sectioned in the conventional manner. Zero-pressure measurements made with the same samples and tracer gave results in excellent agreement with those of Béníère [2] and disclosed no anomalies. No differences could be found by microchemical analysis between specimens diffused under pressure and those diffused in vacuum, nor any traces of contaminants other than those found in undiffused specimens. The effect, thus, could not be explained in terms of possible contamination introduced by the high pressure gas or the materials of the pressure chamber and internal furnace.

A review of the literature disclosed that curved tracer penetration profiles had been noted in NaCl self-diffusion measurements by Rothman et al. [3] as well as in several measurements of diffusion of divalent cations in monovalent ionic lattices [4], [5], [6], [7]. In these studies, an attempt had been made to correct for the extrinsic vacancies introduced.

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by the divalent tracers by calculating diffusivities from the slope of the deep portion of the penetration profile or by computer fitting using the procedure first proposed by Lidiard [8]. Use of either of these procedures failed to provide consistent results for the high pressure diffusion data, particularly in comparison to previous measurements of the effect of pressure on ionic conductivity in NaCl [9], [10].

Attention was then focused on the problem of finding a solution to the diffusion equation for the general case of co-diffusion via a vacancy mechanism of a homovalent tracer and a heterovalent impurity from a thin source into an insulating crystal lattice. An approximate solution was found which predicted a quantitative time dependence for the effect, which was verified in a preliminary experiment. The solution specifies a computer fitting procedure which permits determination of the best-fit value of the true tracer diffusivity, as well as means for estimating the concentration and diffusivity of the unknown impurity. The general solution and preliminary experimental verification are described in detail elsewhere [11]. A synopsis of this treatment and result are given in the following sections.

2. Theoretical model. — In the theoretical model, we assume that the local tracer diffusivity is proportional to the local vacancy concentration, and is, therefore, a linear function of the local heterovalent impurity concentration. To avoid the complexities of dealing with coupled flux equations, the solution proceeds in two stages:

2.1 The impurity is assumed to have a Gaussian distribution, unaffected by its own extrinsic vacancies, and we solve for the effect of the resulting excess vacancies on the profile of the co-diffusing monovalent tracer. This solution can be found exactly to terms of first order in the impurity concentration.

2.2 The impurity distribution is no longer assumed to be Gaussian, but is presumed to be affected in the same manner as that found for the tracer in step 1. The first order solution is iterated until convergence is found. This non-Gaussian distribution of the extra vacancies is used to find the tracer penetration profile which is still exact to first order and approximate to second order in the impurity concentration. Finally, second order correction terms are included in the iterated solution for the impurity and an improved tracer penetration curve is found, which is compared to the measured tracer profile. A best least-squares fit is obtained.

The principle basic assumption in this procedure is that the actual diffusivities of both the tracer and impurity are given by simple expressions of the form

$$D(x, t) = D_0 + y c_i(x, t), \quad (1)$$

where $D_0$ is the true diffusivity in the absence of extrinsic vacancies, $y$ is a constant (the same for both tracer and impurity), and $c_i(x, t)$ is the local impurity concentration. The impurity concentration is thus assumed sufficiently small that effects due to impurity complexes may be neglected. Use of the same value of $y$ for both tracer and impurity corresponds to the assumption that the product of entropic terms and the motion energies and correlation factors are approximately the same for both impurity and tracer, so that the difference in actual diffusion rates can be explained in terms of preferential pairing of impurities and vacancies only. The solution would be changed only slightly by modifying this assumption.

The final solution for the impurity concentration, $c_i$, is given by

$$c_i = \frac{N c_i(z, t)}{A(4 D_0 t)^{1/2}} \quad (2)$$

and for the logarithm of the tracer concentration, $c_t$,

$$\ln c_t = \ln c_0(t) - \frac{x^2}{4 D_0 t} + \alpha^2 \frac{r^{3/2}}{(r + 1)^2} \int_0^t e_t(\xi, t) \, d\xi - \frac{\alpha r^{1/2}}{(r + 1)} e_t(z, t) +$$

$$+ \frac{\alpha^2 e_t^2(z, t)}{2} \left(1 - \frac{1}{r(r + 1)}\right) - \frac{\alpha^2 r^2}{(r + 1)^2} \left[\int_0^t e_t(\xi, t) \, d\xi\right]^2. \quad (3)$$
The tracer diffusion coefficient $D_t$ is given by

$$D_t = D_{o} \left(1 + \frac{\alpha}{r^{1/2}} e_n(z, t)\right).$$

In the equations,

$D_{o}$ = true diffusivity of impurity,

$D_{t}$ = true diffusivity of tracer,

$\alpha$ = an expansion parameter related to the constant

\begin{equation}
\alpha = \gamma \frac{N}{AD_{o}^{1/2}} (4D_{o} t)^{1/2}
\end{equation}

$r$ = ratio of true diffusivities of impurity and tracer, $D_{o}/D_{t}$

$N$ = number of impurity ions on initial surface,

$z = x^2/4D_{o} t$,

$t$ = diffusion time,

$A$ = area of initial surface,

$e_n(z, t) = \frac{\exp\left(-z^2 + \frac{\alpha z}{r^{3/2}} \int_0^z E_{a-1}(\xi, t) d\xi - \frac{\alpha^2}{2 r^{3/2}} E_{a-1} - \frac{\alpha^2}{4 r^3} \left[\int_0^z E_{a-1}(\xi, t) d\xi\right]^2\right)}{\int_0^\infty \exp\left(-z^2 + \frac{\alpha z}{r^{3/2}} \int_0^z E_{a-1}(\xi, t) d\xi - \frac{\alpha^2}{2 r^{3/2}} E_{a-1} - \frac{\alpha^2}{4 r^3} \left[\int_0^z E_{a-1}(\xi, t) d\xi\right]^2\right) dz}.$

In (5), the $E_n$ are terms arising from the first order solution given by

$$E_n(z, t) = \frac{\exp\left(-z^2 + \frac{\alpha z}{r^{3/2}} \int_0^z E_{a-1}(\xi, t) d\xi - \frac{\alpha^2}{2 r^{3/2}} E_{a-1} - \frac{\alpha^2}{4 r^3} \left[\int_0^z E_{a-1}(\xi, t) d\xi\right]^2\right)}{\int_0^\infty \exp\left(-z^2 + \frac{\alpha z}{r^{3/2}} \int_0^z E_{a-1}(\xi, t) d\xi - \frac{\alpha^2}{2 r^{3/2}} E_{a-1} - \frac{\alpha^2}{4 r^3} \left[\int_0^z E_{a-1}(\xi, t) d\xi\right]^2\right) dz}.$$

with the normalization condition that, for any value of $n$,

$$c_n = \frac{N}{A(4D_{o} t)^{1/2}} E_n(z, t).$$

These are successive iterations starting with

$$E_0(z) = 2 \pi^{-1/2} \exp(-z^2).$$

For fitting the cases described in the next section, iteration to $n = 3$ has been sufficient for the most curved cases.

Best fit values for $D_{o}$, the true tracer diffusivity, and for the expansion parameter $\alpha$ (proportional to the impurity concentration) and the diffusivity ratio $r$ are found by comparing various trial fits of eq. (3) to the measured tracer profile. Typically, values of $D_{o}$ can be found to within at worst $10\%$, and values of $\alpha$ and $r$ to within at worst a factor of two. For small values of $\alpha$ (small impurity effect) the precision in determination of $D_{o}$ is improved, while there is greater uncertainty in determination of values of $r$ and $a$.

Figures 2 and 3 show the form for the tracer profiles (eq. (3)) for various values of $r$ and $a$. The case for $r = 1$ is particularly significant, since these are the solutions for self-diffusion of a divalent tracer, subject to the effect of its own extrinsic vacancies. The form of the curves is quite similar, in most respects, to those given by the Lidiard model [8], but the values of $D_{o}$ deduced from the present program indicate a correction term about twice that given by the Lidiard model. The use of the "limiting slope" of the curve as a valid measure of the tracer diffusivity is found to be very suspect, particularly for

Fig. 2. — Computer generated penetrations plots for a given diffusivity ratio $r$. The plots become more curved as $a$ increases.

Fig. 3. — Computer generated penetrations plots for a given $z$. The apparent value of the diffusivity calculated from the limiting slope deviates increasingly from $D_{o}$ as $r$ increases, although the apparent curvature near the origin decreases.
cases of large $r$; this may be seen in figure 2 by comparison of the limiting slopes of the curves to a $45^\circ$ line, corresponding to $D_{r0}$.

The same formalism has been applied to an investigation of the possible influence of co-diffusion of heterovalent impurities on measurements of the isotope effect in alkali halides. The impurity effects are found to enter to first order in the isotope effect measurement. If we define the isotope effect, $\beta$, in the usual way in terms of the ratio of diffusivities of two isotopes of different mass,

$$\beta_{\text{meas}} \approx \beta_{\text{true}}(1 - \alpha), \quad (8a)$$

if deduced from a plot with $x^2/4D t$ as abscissa, and by

$$\beta_{\text{meas}} \approx \beta_{\text{true}}(1 - 0.6 \alpha), \quad (8b)$$

if the abscissa is $\ln c_1$ (the difference arising from the fact that the errors compensate in the latter plot). There is only a slight dependence of $\beta_{\text{meas}}$ on the diffusivity ratio $r$, and to first order the $r$ dependence can be ignored. The potential error which can be introduced by the impurity effect may be judged from figure 4. A value of $\alpha = 0.2$ introduces almost negligible curvature in the tracer penetration plot over several decades, but would introduce an error of 20% (eq. (8a)) or 12% (eq. (8b)) in the measured value of the isotope effect, depending on the choice of variable for the abscissa. A more exact correction to $\beta_{\text{meas}}$ can be obtained by using the best fit values for $\alpha_1$, $r_{11}$, and $D_1$ from the penetration profile to calculate $(\ln c_1 - \ln c_2)$ versus $\ln c_1$ where

$$D_2 = D_1(1 + \beta([m_2/m_1]^{1/2} - 1)), \quad \alpha_2 = \alpha_1(1 + \beta([m_2/m_1]^{1/2} - 1))^{1/2},$$

and $r_2 = r_1(1 + \beta([m_2/m_1]^{1/2} - 1))$. The percent error is independent of the choice of $\beta$.

3. Experimental check. — The model has been used to fit two separate sets of experimental data: the high pressure data for Na$^{22}$ diffusion of NaCl [1] mentioned earlier, and a set of three measurements of the diffusion of Na$^{22}$ in NaCl in which the diffusion time was deliberately varied at constant temperature to scale the values of $\alpha$ in a known manner.

To find an exact value for the true tracer diffusivity from a measured non-linear penetration curve one must know precise values for both the concentration and diffusivity of the impurity for the run, to specify exact values for $\alpha$ and $r$. Such data, naturally, are not ordinarily available. In the present instance, not even the identity of the impurity is known, although it may be Mg, since the Na$^{22}$ tracer is produced by a Mg$^{24}(d, \alpha)$ reaction in a cyclotron, and considerable residual Mg is expected in the as-received tracer. Alternatively, the contaminant could be Ca, inadvertently introduced in storing samples in a dessicator or even from residual detergent used to clean sample holders.

The chief merit of the present program is that it permits deduction of values for the «true» tracer diffusivity within a precision of the order of magnitude of the scatter of the data (usually a few percent) and approximate values (within a factor of 2) for $\alpha$ and $r$, with no prior knowledge about the impurity. Tables I and II show the values for the true tracer diffusivity and $\alpha$ and $r$ calculated for the two sets of experimental data. In table I, it is evident that the calculated values for $\alpha$ scale in the ratio 1:2:3.8 while the square roots of the corresponding diffusion times scale in the ratio 1:2:4, in excellent agreement. Values of $r$ for the three runs are equal within better than a factor of 2. Similar consistency is evident in the high pressure data shown in table II, although there is somewhat greater scatter in the deduced values of $r$ and $\alpha$ (here, of course, these are both temperature

![Fig. 4. Simulated data and computer fits showing the effect of co-diffusion of heterovalent impurities on isotope effect measurements for two «practical» cases of small $\alpha$ where the curvature of the penetration profile would be lost in the scatter of the data.](image)

<table>
<thead>
<tr>
<th>Curve in figure S</th>
<th>Time $10^4$ s</th>
<th>Diff. coef. $10^{-10}$ cm$^2$/s</th>
<th>$\alpha$</th>
<th>$r$</th>
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<td>0.67</td>
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<tr>
<td>$b$</td>
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<td>1.4</td>
<td>1.36</td>
<td>2.1</td>
</tr>
<tr>
<td>$c$</td>
<td>1.9</td>
<td>1.3</td>
<td>2.52</td>
<td>1.9</td>
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EFFECT OF SURFACE IMPURITIES ON TRACER DIFFUSION IN IONIC CRYSTALS

Table II

<table>
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<tr>
<th>Temperature</th>
<th>Pressure (kbar)</th>
<th>Time (10^4 s)</th>
<th>Estimate of Na^{22} deposited (10^{11} atoms)</th>
<th>Diff. coeff. (10^{-10} \text{cm}^2/\text{s})</th>
<th>(\alpha)</th>
<th>(r)</th>
</tr>
</thead>
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<tr>
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<td>8.1</td>
<td>0.00</td>
<td>0.6</td>
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<td>4.2</td>
<td>0.27</td>
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<td>0.51</td>
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<td>28.0</td>
<td>1.3</td>
<td>0.27</td>
<td>3.4</td>
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</tbody>
</table>

(*) The initial impurity concentration is presumed proportional to the initial tracer concentration. These values are rough estimates and are included only to indicate the general scaling of \(\alpha\) with impurity concentration. No precise comparison, particularly for cases of differing \(T\) and \(P\), is merited.

and pressure dependent, and depend on varying initial impurity concentrations which can only be estimated roughly \textit{a posteriori}).

Figure 1 shows the fits of the computer-generated penetration curves to the actual points for some of the high pressure data of table II, while figure 5 shows similar fits for the time dependence data of table I. In all cases, the fits are within the scatter of the actual experimental points. Figure 6 shows the corrected results for the high-pressure results.

Figure 7 shows the \textit{«goodness of fit»} for the program applied to the intermediate time run b of table I. The numbers indicate the variances multiplied by a factor of 1 000 between the computer generated profiles and the experimental points for various assumed values of the true tracer diffusivity (the factor plotted as the ordinate) and the diffusivity ratio \(r\). The value of \(\alpha\) is chosen by the program to give the best least-squares fit for each \(F, r\) pair; the result given in table I corresponds to the point marked by the asterisk in figure 6. From deduced values of \(\alpha\), we conclude that the initial divalent impurity concentration is about two orders of magnitude greater than the initial Na^{22} concentration, which is consistent with values deduced from the actual specific activity of the tracer as received (about 10 mCi/mg, compared to a theoretical value of 6 Ci/mg). Since only a few

![Fig. 5. Penetration plots for Na^{22} diffusion in NaCl as a function of diffusion time. Solid lines are computer fits. Points labeled \(+\) are excluded from the fitting program.](image-url)
be detected by Auger spectroscopy, but we were unable to find a cooperative Auger spectroscopist willing to contaminate his system with Na$^{22}$.)

The errors introduced by co-diffusion of heterovalent impurities in the present study are not, of course, unique to the system of Na$^{22}$ diffusing in NaCl. Similar problems may be expected to occur in any studies of self-diffusion in insulators, and are inescapable in measurements of diffusion of heterovalent tracers. Clearly, in anticipation of these possible difficulties, several precautions must be taken by the experimentalist. Most important are the following:

1) Radiotracers must be procured with a view to results compared. If there is any difference between minimizing possible heterovalent contamination introduced in preparation of the tracer. In the case of heterovalent tracers, maximum possible specific activity is essential. All tracers should be stored only in non-glass containers in which all residues from detergent cleaning solutions have been removed, and can be diluted only with truly deionized water, not «distilled» water which has been stored in glass bottles and obtained using a glass condenser.

2) Specimens to be diffused should be prepared immediately before use, and should not be stored in a dessicator using «Drierite» or any other calcium-based dessicant.

3) Only the minimum amount of tracer needed for a valid diffusion measurement should be deposited on the surface.

4) As a final check, diffusion measurements with homovalent tracers should be repeated at each temperature for two very different diffusion times and the results compared. If there is any difference between the values of diffusivity calculated from the two slopes, the full computer fit program should be used to calculate the true diffusivity: in the case of measurements with heterovalent tracers, only the computer fit values should be used for any value of the diffusion time.

References

DISCUSSION

W. J. FREDERICKS. — Did you look for Mg\(^{++}\) in your tracer?

D. LAZARUS. — Yes by mass spectrographic analysis but saw nothing. We were unable to find anyone to do an Auger Analysis. It could be either Mg\(^{++}\) because \(^{22}\)Na is prepared from \(^{22}\)Mg or it could be Ca\(^{++}\) leached from glass storage bottles or from storage in desiccators.

W. J. FREDERICKS. — Yes, many ions leach from glass. What kind of host crystals did you use?

D. LAZARUS. — Harshaw crystals.