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MATERIALS SCIENCE RESEARCH
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MASS TRANSPORT PHENOMENA
IN CERAMICS

MATERIALS SCIENCE RESEARCH

PREFACE

The Eleventh University Conference on Ceramic Science held at Case Western Reserve University from June 3 - 5, 1974 was devoted to the subject of Mass Transport Phenomena in Ceramics. This book follows closely the form of the conference. While the active participation at the meeting was not recorded, it is clear that many of the contributors have benefited from the remarks, suggestions, and criticisms of the participants. Furthermore, the session chairmen -- Delbert Day (Univ. of Missouri), Wm. LaCourse (Alfred Univ.), W. Richard Ott (Rutgers Univ.), A.L. Friedberg (Univ. of Illinois), V. Stubican (Penn. State Univ.), and R. Loehman (Univ. of Florida) -- successfully kept the meeting to a reasonable schedule, but also stimulated the lively discussion.

The book divides naturally into four sections, focusing on correlation and coupling effects in diffusion in ionic materials, understanding of fast ion transport, diffusion and electrical conductivity in crystalline and glassy oxides and applications of diffusion to oxidation and other processes of current interest.

The editors have benefited from the cheerful help and assistance of many people. Mrs. Karyn Pletka typed the entire manuscript with unusual accuracy and tolerance. Mr. Makmod ElLeil, Ajit Sone, Leslie Major and Ms. Jenny Sang provided the subject index. The authors have been cooperative and understanding and we acknowledge our enjoyment in working with them.

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Cleveland, Ohio
March, 1975

A. R. Cooper
A. H. Heuer

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NON-RANDOM DIFFUSION IN IONIC CRYSTALS*

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ABSTRACT

Non-random diffusion can result both from the presence of atomic driving forces and from the motion of defects in a crystal. Defect-related non-random effects appear in two different ways in the kinetic diffusion equations, as correlation effects and as defect-wind effects. In the present paper, the origin and magnitude of these effects during diffusion in a driving force are discussed. Kinetic expressions for the drift velocity $<v_F>$ are derived from expressions for the effective frequencies of independent atom jumps and are related to the tracer diffusion coefficient D^*. For impurity diffusion in an electric field, deviations from the Nernst-Einstein relation result from defect-wind effects. Recently developed equations for the ionic-impurity drift-mobility when diffusion occurs via divacancies moving on one of the sub-lattices in the NaCl structure are summarized. Extensions of the simple equations derived here to more complex situations are discussed.

INTRODUCTION

Diffusion in crystals occurs by atoms following more-or-less random walks. Each atom moves through the crystal by making a series of elementary atom jumps from one lattice site to another. An atomic driving force will provide a bias to the directions of the individual jumps so that they are no longer random in direction. Thus, driving forces, such as electric fields, are one

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source of non-random effects. If each jump has the same bias, as
for self-diffusion in a constant driving force, effects from
driving forces are easily treated by making simple modifications
in the random walk equations. However, when the biases are not
constant or when other non-random effects occur, such as the
defect-related non-random effects discussed later in this paper,
the analysis is more complex.

A category of non-random effect which can arise even in the
absence of driving forces occurs when a given atom jump is
influenced by the directions of previous jumps taken by atoms and
defects in the crystal. The resulting "correlation effects" and
"defect-wind effects" can occur either with or without the presence
of atomic driving forces. These non-random effects do not provide
the same bias on each jump.

In the present paper, the origin and magnitude of correlation
and defect wind effects will be discussed, particularly for the
case where there is an atomic driving force. Electric field
effects will be emphasized and explicitly discussed. Nevertheless,
most of the equations will apply equally well to effects from other
driving forces and other sources of defect fluxes, such as tem-
perature gradients, stress fields, or gradients in concentration
or stoichiometry.

Electric field effects are empahsized here since they provide
a particularly straight-forward example of a driving force. Also,
electric fields have important effects on ions moving in ionic
crystals. In the present discussion, correlation and wind effects
resulting from motion of individual defects will be emphasized.
Non-stoichiometric crystals with large vacancy concentrations
would require a more complex treatment since interactions between
large groups of defects then should be considered.

NON-RANDOM DIFFUSION VIA MONOVACANCY MECHANISM

Correlation and defect wind effects depend strongly on the
diffusion mechanism. When diffusion proceeds by the simple inter-
stitial mechanism with no atomic driving forces, the individual
interstitial atoms can follow truly random walks. The kinetic dif-
fusion equations then may be obtained from the simple mathematical
theory of random walks. On the other hand, for most other diffu-
sion mechanisms, especially those which require a mobile defect at
a neighboring site, the individual atoms do not follow random walks.
The direction of an atom jump, for example, will depend on which
particular neighboring site is occupied by a defect at the time of
the jump. Consequently, when diffusion of atoms occurs via motion
of vacancies, divacancies, interstitialcies, crowdions, or even
more-complex mobile defects, defect-dependent non-random diffusion

will occur [1,2,3].

To illustrate the origin of these defect-dependent non-random effects, let us consider diffusion by the monovacancy mechanism. In this mechanism, the elementary atom jump involves the jumping of an atom into a neighboring vacant lattice site. These vacant sites, or vacancies, are assumed to be present in thermodynamic equilibrium in concentrations which depend on $\exp(-E_f/kT)$ where E_f is the formation energy for vacancies, k is Boltzmann's constant and T is the absolute temperature. In discussing the monovacancy mechanism, one assumes that each vacancy moves independently in that it is not bound to other vacancies and does not interfere with diffusion processes involving other vacancies. By contrast, in the divacancy mechanism, it is assumed that vacancies move as part of vacancy pairs.

With respect to non-random diffusion, the important thing about the vacancy mechanism, and also the divacancy mechanism, is that an atom cannot move until a vacancy arrives at a site neighboring on it. Thus, the independent diffusion process is not the single atom jump but instead requires a sequence of jumps. In this sequence, the vacancy is first created at a vacancy source. Then the vacancy moves through the crystal by exchanging with the various atoms in the crystal until it arrives at a site neighboring on the diffusing atom i. After arrival, the vacancy can exchange with atom i one or more times. Finally the vacancy will move permanently away and be destroyed at a vacancy sink.

This sequence of interrelated vacancy jumps may be contrasted to the situation in the simple interstitial mechanism, where the atom jumps directly from one interstitial site to another, with the direction of each atom jump being independent of the direction of jump of any other neighboring atom or defect. On the other hand, for diffusion via an interstitialcy mechanism, an interstitialcy must approach the atom much as described above for diffusion via a vacancy mechanism.

In principle, one must follow the complete paths of the vacancies if one wishes to determine the kinetic diffusion processes affecting the particular atom i. In simple situations, however, there are several ways to simplify the calculation.

To present the defect-dependent non-random diffusion equations in as simple a form as possible while still allowing discussion of the influence of driving forces on these equations, attention will be restricted to high-symmetry crystals, such as cubic crystals, with mirror symmetry across all lattice planes normal to the diffusion direction. The diffusion direction x will be chosen normal to low-index planes separated by a regular interplanar spacing b, and it will be assumed that the x components of

the possible atom jumps are all +b, zero, or -b. Thus, an atom or vacancy cannot reach a lattice plane that is 2b away without stopping at a lattice site one interplanar distance away in that direction. As examples, <100>-diffusion directions in a variety of cubic structures satisfy these rules provided that only jumps to nearest neighbor sites are allowed. Also, <100>-diffusion directions in tetragonal or orthorhombic crystals would be suitable. In cubic crystals diffusion is isotropic, so this arbitrary choice of diffusion direction does not make the result any less general.

Driving forces can be expected to create a net vacancy flux, which normally will be distorted in the vicinity of an impurity atom i. (A distortion is expected unless the diffusion properties of i are identically the same as those of all other atoms in the crystal.) Nevertheless, if there is a mirror crystal symmetry plane passing through i normal to the flux, the average vacancy concentrations on this plane will not be altered from those in the absence of a flux. Thus, sites along this plane will maintain equilibrium vacancy concentrations and for present purposes can be treated as effective vacancy sources-and-sinks. Any sequence of vacancy jumps thus is regarded as terminated when the vacancy reaches this symmetry plane (but not terminated by exchange with atom i itself since after such an exchange the atom and vacancy still are not on the same plane). Further jumps by the vacancy starting from the symmetry plane will begin a new independent sequence, uncorrelated to the previous sequence. Since the only way for a vacancy during a single jump sequence to move from one side of atom i to the other is by exchange with atom i itself, a single vacancy sequence cannot provide atom i with two consecutive jumps in the same sense. Instead jumps by atom i from a single vacancy sequence will cause alternate +b and -b displacements and the net displacement from any sequence will be either ±b or zero.

After one exchange with atom i in a given direction, the vacancy is in the proper position to cause a reverse jump, moving the atom in the opposite direction. Such a second jump would cancel the effect of the first jump. Similarly, the fourth exchange of the vacancy with i will cancel the third exchange, the sixth exchange will cancel the fifth exchange, and so on. After an odd number of exchanges the net displacement of i equals b, the interplanar spacing; and after an even number of exchanges the net displacement is zero.

After the vacancy has arrived at a site α, neighboring on atom i on the +x side, it will have a probability P_+ of eventually causing a +b jump of atom i. This jump may occur on the next jump of the vacancy or the vacancy may first wander away from atom i and only later return to exchange with it without arrival of the vacancy at any effective vacancy sink. After a P_+ exchange the vacancy will be on the -x side of atom i in proper position

to cause a -b jump. The probability of the vacancy causing such a -b jump (again on any of its subsequent jumps before arrival at an effective vacancy sink) is defined as P_-. If there is a driving force, P_- will differ from P_+; but, in the absence of a driving force, P_- equals P_+ since the only distinction between P_+ and P_- is the direction in which the exchange occurs.

The frequency ν_+ with which atom i undergoes a displacement, always of magnitude b, in the +x direction therefore is:

$$\nu_+ = \nu_{\pi+} \ [P_+ - P_+P_- + P_+P_-P_+ - P_+P_-P_+P_- + \ . \ . \ . \ .] \qquad (1)$$

where $\nu_{\pi+}$ is the frequency of arrival of fresh vacancies at sites α neighboring on i on the plane on the +x side of i. (These vacancies then are in the proper position to allow a +b jump of atom i on the next jump.) The sum involving P_+ and P_- terms in Eqn. (1) gives the probability of the vacancy causing a net atom displacement +b after arrival at site α. Thus, ν_+ is the effective frequency of independent displacements +b.

In Eqn. (1), the initial term P_+ within the brackets represents the probability of an initial exchange of an α-site vacancy with atom i. The second term P_+P_- represents the probability of a two-jump sequence where the second jump cancels the effect of the first jump. Hence, this term appears with a minus sign. The third term represents the probability of a three-jump sequence, again providing a net displacement +b of atom i, and so on.

A fresh vacancy is defined as one which in its sequence of jumps has not previously arrived at a site from which it could cause a +b or -b jump of the tracer. As noted previously, any vacancy which arrives at the mirror symmetry plane passing through atom i normal to the diffusion direction ends one sequence of jumps and in effect becomes a new fresh vacancy during its subsequent path. Thus, in its subsequent path it again can have a first arrival at a site α.

In Eqn. (1), $\nu_{\pi+}$ represents a sum over all possible paths from any vacancy source (or effective fresh vacancy source on the mirror symmetry plane) to any site α which will allow a +b jump of atom i. For simplicity, it is assumed in the present equation that all α sites are equivalent to each other. Then $\nu_{\pi+}$ is a simple scalar quantity, while still representing a sum over all α sites. This condition will be satisfied in any crystal which has sufficient rotational or mirror symmetry around the diffusion direction that rotations or reflections of the crystal can be applied to bring any site α into the original position of any other site α and these rotations or reflections also reproduce in the transformed orientation all other lattice sites in the original orientation. In such a situation, a vacancy at any one α site has the

same effect of diffusion along the x-axis as does a vacancy at any
other α site. This condition will be satisfied by many crystals
(cubic, tetragonal, orthorhombic) for which the previously-
introduced mirror symmetry normal to the diffusion direction
applies.

P_+ can be expressed in terms of the possible vacancy jump
frequencies from sites α. In particular, P_+ depends on the jump
frequency w_{2+} for a vacancy on site α to cause a +b jump of atom
i and on the competing jump frequencies $w_{+\pi}$ for the vacancy to
start a path which leads it away from site α to an effective
vacancy sink without exchanging with atom i or returning to any
site α. Here $w_{+\pi}$ represents the sum over all jumps (to any sites)
which actually start a vacancy on such a path of non-exchange
and non-return. In $w_{+\pi}$, one must exclude paths which eventually
return the vacancy to a site α or which involve a direct jump from
one site α to another site α. Detailed calculations show that
these α to α transitions do not affect P_+.

Physically the reason for omitting α to α transitions may be
seen from the definition of P_+. In the calculation of P_+, one
must follow the vacancy until it either exchanges with atom i or
permanently moves away by reaching an effective vacancy sink.
There is unit probability that one of these two events will even-
tually occur and P_+ is the probability of the former, i.e.,
exchange with atom i. The relative probabilities of an eventual
w_{2+} jump or $w_{+\pi}$ jump path are the same regardless of which α site
contains the vacancy. Thus, transitions from one α site to another
do not affect P_+ and these transitions may be omitted from further
consideration.

The expression for P_+ therefore is simply

$$P_+ = w_{2+} / (w_{2+} + w_{+\pi}) \tag{2}$$

Also

$$1 - P_+ = w_{+\pi} / (w_{2+} + w_{+\pi}) = P_+ w_{+\pi} / w_{2+} \tag{3}$$

Summing the series in Eqn. (1) yields

$$\nu_+ = \nu_{\pi+} P_+ (1-P_-P_+)^{-1} (1-P_-) \tag{4}$$

This equation may be recast into a form which explicitly displays
the correlation factor and a familiar expression for the jump fre-
quency. Upon application of Eqn. (3) relating P_+ to $1-P_+$, one
obtains

$$\nu_+ = \frac{\nu_{\pi+}}{w_{+\pi} N_{V\alpha} z_\alpha} \frac{(1-P_+)(1-P_-)}{(1-P_-P_+)} w_{2+} N_{V\alpha} z_\alpha \tag{5}$$

where $N_{v\alpha}$ is the equilibrium vacancy concentration at site α and z_α is the number of equivalent sites α. According to Eqn. (5), the effective jump frequency ν_+ of jumps +b can be expressed as the product of four factors,

$$\nu_+ = G_+ \, f \, \Gamma_{b+} \, z_\alpha \tag{6}$$

where

$$\Gamma_{b+} = w_{2+} \, N_{v\alpha} \tag{7}$$

$$f = (1-P_+) \, (1-P_-P_+)^{-1} \, (1-P_-) \tag{8}$$

$$G_+ = \nu_{\pi+}/w_{+\pi} \, N_v \, z_\alpha \tag{9}$$

Here Γ_{b+} is the basic jump frequency for an atom to jump to a given site in the +x direction. This basic frequency is the jump frequency which would apply if the only non-random effects were those from driving forces, i.e., in the absence of defect-related non-random effects. These defect-related non-random effects appear in Eqn. (6) as the correlation factor f and the vacancy wind factor G_+.

The basic jump frequency Γ_{b+} will be affected by driving forces along the x-axis since these driving forces influence the vacancy jump frequency w_{2+}. By contrast, the correlation factor f is unaffected by driving forces to first order, since P_+ and P_- appear symmetrically in Eqn. (8). The vacancy wind factor G_+ given in Eqn. (9) is unity if there are no vacancy fluxes. A driving force normally will provide a vacancy flux and make G_+ differ from unity.

In Eqn. (9), $\nu_{\pi+}$ is the frequency with which vacancies leave vacancy sources-and-sinks at sites π and travel to sites α neighboring on the atom, with the α sites here being those on the +x side of the atom. Similarly, $w_{+\pi} \, N_{v\alpha} \, z_\alpha$ is the frequency with which vacancies follow the reverse paths from sites α to sites π. If there is a net vacancy flux, vacancies will travel more frequently in one sense along these paths than the other. Thus, a net vacancy flux makes G_+ differ from unity, whereas in the absence of such a flux G_+ equals unity. This general conclusion will apply even when there are interactions between defects.

To first order in the driving forces, Eqn. (8) reduces to

$$f = \frac{1 - P}{1 + P} \tag{10}$$

where P is the average of P_+ and P_-. Physically the correlation factor occurs here because a vacancy can exchange with an atom more than once during a single independent sequence of jumps.

Motion of the atom itself changes the local probability of a
vacancy being on the +x or −x side of the atom.

By contrast, the vacancy wind factor arises because of motion
of other atoms. When there is a driving force along the x-axis
motion of these other atoms (i.e., other than the atom i whose
jump frequency ν_+ is being calculated) will bring vacancies up
to sites α by paths contributing to $\nu_{\pi+}$ more frequently than
motion of these other atoms will carry vacancies in the opposite
direction along these paths.

Atomic driving forces which bias the directions of individual
atom jumps are not the only influences which can yield a net
vacancy flux and hence cause G_+ to differ from unity. For example,
various types of concentration gradients or stoichiometry gradients
can also produce net vacancy fluxes. In the present discussion,
however, attention will be restricted to vacancy fluxes resulting
from atomic driving forces, and particularly from electric fields.

Equation (6) yields the effective jump frequency ν_+ for an
atom jump in the +x direction. A similar equation is found for
the effective jump frequency ν_- in the −x direction,

$$\nu_- = G_- \, f \, \Gamma_{b-} \, z_\alpha \qquad\qquad (11)$$

where f again is given by Eqn. (8), Γ_{b-} is obtained from Eqn. (7)
merely by replacing all subscripts + with subscripts −, where the
− subscript refers to atom jumps in the −x direction, and G_- is
obtained from Eqn. (9) by replacing subscripts + with subscripts −,
where the − subscript refers to a site in the −x direction from
the atom.

CALCULATION OF DIFFUSION COEFFICIENT D* AND
DRIFT VELOCITY $\langle v_F \rangle$ FROM EFFECTIVE JUMP FREQUENCIES

The basic kinetic diffusion equation for planar diffusion in
the x-direction relates the atom flux J to the concentration c and
concentration gradient $\partial c/\partial x$ of the diffusing species,

$$J = -D^* \, (\partial c/\partial x) + \langle v_F \rangle \, c \qquad\qquad (12)$$

This equation contains two measureable coefficients, the tracer
diffusion coefficient D* and the drift velocity from atomic
driving forces $\langle v_F \rangle$. If atomic driving forces are the only non-
random effects which occur, as for diffusion by a simple intersti-
tial mechanism, D* and $\langle v_F \rangle$ are related by the well-known Nernst-
Einstein equation [4],

$$\langle v_F \rangle / D^* = F/kT \qquad\qquad (13)$$

where F is the atomic driving force. For diffusion in an electric field E

$$F = q E \qquad (14)$$

where q is the charge of the diffusing ion. The drift mobility μ is defined as the drift velocity in unit electric field. Thus,

$$\langle v_F \rangle = \mu E \qquad (15)$$

and for the specific case of an electric field, the Nernst-Einstein equation becomes

$$\frac{\mu}{D^*} = \frac{q}{kT} \qquad (16)$$

When defect-related non-random effects occur, as for diffusion by a vacancy mechanism, it is found that the Nernst-Einstein equation no longer applies. The deviations which are found can be described by considering the ways in which the effective jump frequencies v_+ and v_- differ from the basic jump frequencies Γ_{b+} and Γ_{b-}.

In terms of effective jump frequencies, if v_+ and v_- are independent of location in the crystal, as for diffusion in a homogeneous crystal with a constant electric field,

$$D^* = \frac{1}{2} b^2 (v_+ + v_-) \qquad (17)$$

and

$$\langle v_F \rangle = b(v_+ - v_-) \qquad (18)$$

These equations are very similar in appearance, the only differences being the square and half which appear in Eqn. (17) and the fact that the v's are added in Eqn. (17) but subtracted in Eqn. (18). Because of this similarity, it is not surprising that D^* and $\langle v_F \rangle$ can be related to one another.

When Eqns. (6) and (11) are inserted into Eqn. (17), one finds

$$D^* = \frac{1}{2} z_\alpha b^2 f (G_+ \Gamma_{b+} + G_- \Gamma_{b-}) \qquad (19)$$

To first order, G_+ and G_- can be written as

$$G_\pm = 1 \pm \Delta G \qquad (20)$$

where G is a small quantity calculated from Eqn. (9). Also

$$\Gamma_{b\pm} = \Gamma_{bo} \exp(\pm bF/2kT) \qquad (21)$$