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The Isotope Effect for Diffusion in Solids

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The theory of the isotope effect and its application to studies of migration in metals, ionic crystals, oxides, and other solids are discussed. Methods of measuring the isotope effect are briefly described. 96 references.

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I. INTRODUCTION

The study of diffusion processes in solids began several decades ago, and the results obtained have been presented in thousands of original papers and discussed in excellent textbooks and reviews[1-4]. We must nevertheless agree with the reviewer[1] who stated, when discussing diffusion in crystals of alkali metal halides, that "in spite of a large volume of careful work we still lack a detailed understanding of diffusion processes, even in materials as familiar as NaCl". Further developments in our theoretical models and in our experimental techniques are needed to provide a deeper understanding of the nature of migration processes in solids.

The migration of structural units in transport processes (diffusion, ionic conduction, thermo-diffusion, etc.) occurs by a series of jumps from one equilibrium position to the next. Many different models have been proposed to describe these elementary diffusion acts, but most of these models rely on the motion of two types of defect: vacancies (unoccupied crystal lattice sites) and interstitial atoms or ions, or combinations of these defects (divacancies, interstitial configurations, etc.).

We shall confine our discussion (except in the case of electrical conduction) to the direct methods of determining diffusion coefficients by monitoring the redistribution of the diffusing "impurity" atoms in the solid. In this context the term impurity includes labelled atoms, i.e. isotopic indicators (such as ^{22}Na or ^{24}Na) which are chemically almost indistinguishable from the atoms of the matrix (^{23}Na). In some cases (e.g. when nuclear isomers are used) the indicator atoms and the matrix atom have the same weight as well as being chemically identical. The macroscopic significance of the diffusion coefficient D follows directly from Fick's familiar laws, and its microscopic significance (in the simplest case of an isotropic medium) from the Einstein relationship $D = \langle R^2\rangle/6t$, where $\langle R^2\rangle$ is the mean square displacement in time t. For the displacement of a diffusing atom in a simple cubic lattice we can write

$$\langle \mathbf{R}^2\rangle = \omega a^2 t + \left\langle 2 \sum_{j,k} (\mathbf{a}_j \mathbf{a}_k) \right\rangle, \qquad (1)$$

where $\mathbf{a}_i$ is the elementary jump, $(\mathbf{a}_j\mathbf{a}_k)$ is the scalar product of vectors, $a = |\mathbf{a}_i|$, and ω is the jump "frequency" of the diffusing atom in unit time.

In the diffusion of a labelled atom each jump is correlated with the previous jump, and only a fraction of the jumps contributes to random diffusion. It is easy to see that in the vacancy mechanism the probability of a diffusion jump in any direction depends on the direction of the previous jump, since each jump of a diffusing labelled atom leaves behind a vacancy and thus increases the probability of a jump in the reverse direction. Clearly, if an atom carries out a "forward" jump followed by its correlated "backward" jump (to the initial position) the two jumps are mutually compensating. Thus the term $2 \sum_{j,k} (\mathbf{a}_j\mathbf{a}_k)$ in the right-hand side of Eqn.(1), which vanishes in the case of random motion, is not zero in the general case.

We shall introduce the concept of the correlation coefficient f, equal to the fractional number of jumps which make an effective contribution to the random diffusion: $\omega_{\text{eff}} = f\omega$. Hence Eqn.(1) can be re-written

$$D_T = \omega_{\text{eff}} a^2 t = f\omega a^2 t. \qquad (2)$$

The correlation factor f also appears in the expression [equivalent to Eqn.(2)]

$$D_T = D_{\text{real}} = f D_{\text{rand}},$$

where D_{rand} is the diffusion coefficient of the atom for fully random (spatially independent) successive diffusion jumps. Throughout this review we shall use the term self-diffusion coefficient to refer to the "real" diffusion coefficient of isotopically labelled atoms or ions (D_T). In most cases this quantity is independent (to a first approximation) of the difference in mass between the indicator atoms (for example, ^{22}Na or ^{24}Na) and the matrix atoms (^{23}Na), though of course diffusion isotope effects are the subject of this review.

In the case of self-diffusion in cubic crystals the correlation factor (to this approximation) is a purely geometric coefficient, depending only on the diffusion mechanism and on the crystal structure. As an example, the calculated correlation factors for self-diffusion in a face-centred cubic lattice (f.c.c.) are listed in Table 1.

Experimental measurement of the correlation factor should at least help to identify the elementary mechanism of the diffusion process. For the isotropic self-diffusion of particles having a single jump frequency ω the diffusion coefficient can be written $D = A\omega f$, where A includes geometric and other factors independent of the jump frequency.

Table 1. Calculated correlation factors for self-diffusion by different mechanisms in a b.c.c. lattice.

Diffusion mechanism	f_0
Vacancy	0.781
Divacancy	0.475
Interstitial	1.000
Relay:	
collinear jumps	0.667
non-collinear jumps	0.969

We shall now compare the diffusion coefficients for the atoms of two isotopes of mass m_α and m_β. We shall express their ratio as

$$D_\alpha/D_\beta = f_\alpha\omega_\alpha/f_\beta\omega_\beta. \quad (3)$$

The difference in mass between the isotopes leads to differences in the jump frequencies ω_α and ω_β, and hence in the correlation factors f_α and f_β (which depend on ω_α and ω_β). This statement is true both for self-diffusion and for the diffusion of impurities, since in self-diffusion the labelled atom (having a different mass) acts as an impurity atom with respect to the atoms of the host lattice. Hence f_α and f_β are true correlation coefficients for the impurity atoms. The correlation factor for "true" self-diffusion ($f = f_0$, see Table 1) is, strictly speaking, meaningful only in the ideal case when the diffusing atom and the matrix atom have identical jump frequencies. The approximate equality $f_\alpha \cong f_\beta \cong f_0$ is obeyed satisfactorily in most cases.

For the systems considered the correlation factor of the impurity can be expressed as $f = (u/\omega + u)$, where u is the jump frequency of the matrix atoms only. Assuming that this expression is valid for any labelled atom, i.e. that u is independent of the mass of the labelled atom, we can express f_α and f_β as

$$f_\alpha = u/(\omega_\alpha + u);\ f_\beta = u/(\omega_\beta + u). \quad (4)$$

Eliminating u and one of the correlation factors from (3) and (4) we obtain the following expression for the fractional difference between D_α and D_β:

$$\Delta D/D_\beta = f_\alpha\ \Delta\omega/\omega_\beta, \quad (5)$$

where $\Delta D = D_\alpha - D_\beta$, and $\Delta\omega = \omega_\alpha - \omega_\beta$.

Since the absolute value of the jump frequency cannot be determined in a diffusion experiment, for practical purposes the ratio $\Delta\omega/\omega$ in expressions such as (5) must be written as a function of the isotopic masses m_α and m_β. Treating the diffusional jump as the motion of an atom through a potential barrier, we write

$$\omega = \nu \exp(-Q/kT),$$

where Q is the energy (enthalpy) of activation of the jump, and ν is the mean vibrational frequency of the migrating atom.

Since Q denotes the height of the potential barrier, its value should be the same for chemically identical isotopes. Atomic vibration frequencies vary with the mass of the atom as $\nu \propto m^{-1/2}$. Hence

$$\Delta\omega/\omega_\beta = [(m_\alpha/m_\beta)^{-1/2} - 1]. \quad (6)$$

Combining (5) and (6) gives the following expression for the diffusion isotope effect:

$$E_\beta^\alpha = \frac{\Delta D/D_\beta}{(m_\beta/m_\alpha)^{1/2} - 1} = f_\alpha \simeq f_0. \quad (7)$$

Expressions like (6) and (7) were derived for conditions in which only the migrating atom is able to jump, and no allowance was made for changes in the state of the lattice. Obviously, allowing for the part played by the neighbours of the diffusing atom in the migration act must modify Eqn.(6) in the sense of decreasing the magnitude of the isotope effect. Introducing the correction coefficient

$$\Delta K = \Delta\omega/\omega_\beta \left[\left(\frac{m_\beta}{m_\alpha}\right)^{1/2} - 1\right]^{-1},$$

we convert Eqn.(7) into

$$E_\beta^\alpha = \frac{\Delta D/D_\beta}{(m_\beta/m_\alpha)^{1/2} - 1} \simeq f_0\Delta K. \quad (8)$$

An expression for the diffusion isotope effect in the form of Eqn.(8) was first proposed by Mullen[4]. Using the classical theory of reaction rates ΔK can be interpreted as the fraction of the kinetic energy of the diffusing atom at the saddle point associated with motion in the direction of the jump. Thus, ΔK can vary between zero and unity. It follows from Eqn.(8) that by measuring the isotope effect E_β^α it should be possible to evaluate the product $f\Delta K$: hence, in order to obtain the coefficient f (and thus to identify the diffusion mechanism) we must introduce additional information. We shall examine first of all the possibility of measuring (and interpreting) quantities such as the electrical conductivity σ (in the case of ionic conductors) and the activation volumes of diffusion or ionic conduction processes.

The well known Einstein–Nernst expression related the mobility μ and the diffusion coefficient D of a charged particle:

$$\mu/D = q/kT \quad (9)$$

where q is the charge of the particle, k is Boltzmann's constant, and T is the absolute temperature.

The electrical conductivity (resulting from the migration of charged particles in an electric field) is $\sigma = \mu qN$, where N is the number of current-carrying particles per unit volume. To simplify the discussion we shall consider the case of unipolar ionic conduction, for which we can write

$$D/\sigma = kT/q^2N. \quad (10)$$

In Eqns.(9) and (10) the quantity D is the "random" or "chaotic" diffusion coefficient, wheras the real diffusion coefficient D_T (measured experimentally with radioactive indicators) is related to σ by the generalised expression $D_T/\sigma = (kT/q^2N)f$.

Comparative measurements of the real self-diffusion coefficient D_T and of the ionic conductivity coefficient σ allow (in some cases) the coefficient f to be determined. Measurements of the quantity called the "activation volume" can also help to identify diffusion mechanisms. The diffusion coefficient D_T can be described with adequate generality by the expression[2]

$$D_T = \gamma a^2 f\nu \exp(-\Delta g/kT) = \gamma a^2 f\nu \exp\left(\frac{\Delta S}{k}\right)\exp\left(-\frac{\Delta H}{kT}\right),$$

where γ depends on the geometry of the crystal lattice, ν is

the frequency, and Δg, ΔS, and ΔH are the changes in thermodynamic potential, entropy, and enthalpy which accompany each diffusional jump. Using the standard thermodynamic relation $(\partial g/\partial p)_T = V$ (where p is pressure and V is volume) we can write to a good approximation

$$\left(\frac{\partial \ln D}{\partial p}\right)_T \simeq \left(\frac{\partial \Delta g}{\partial p}\right)_T = \Delta V,$$

where ΔV is called the activation volume. Using the Einstein–Nernst relation, the activation volume for ionic salts can be determined also from electrical conductivity data. The quantities Δg, ΔH, and ΔS can be expressed as sums of the free energy (enthalpy, entropy) of formation of the lattice defect responsible for the diffusion (i.e. Δg_f, ΔH_f, ΔS_f) and of the corresponding quantities for the migration process itself (Δg_m, ΔH_m, ΔS_m). In exactly the same way ΔV can be separated into its components ΔV_f (the activation volume of formation) and ΔV_m (the activation volume of migration).

Theoretical models of the effect of high pressures on migration processes in solids allow some of these quantities to be calculated. For example, in the case of self-diffusion in metals the quantity $\Delta V^{1\nu}$ for diffusion by single vacancies is approximately $^1/_2$–$^3/_4$ of the atomic volume, and $\Delta V^{2\nu}$ for the divacancy mechanism is slightly less than $2\Delta V^{1\nu}$; the corresponding quantities for interstitial diffusion are very much smaller[2].

There are many other physical parameters whose measurement can help to establish the nature of the point in solids and hence to identify the diffusion mechanism. For example, useful measurements include anomalous thermal expansion, specific heat anomalies, high-precision density and lattice parameter measurements, relaxation studies, measurements of optical properties, etc. We shall refer to the results of these (and other) methods in our discussion of isotopic experiments.

II. THEORY OF THE ISOTOPE EFFECT

The general theory of diffusion in solids (and, in particular, the basic elements of the theory of isotope effects in diffusion) are discussed in many theoretical publications both by Eyring's theory of absolute reaction rates and by the dynamic variants of the theory, in both the harmonic and the anharmonic approximation. Eyring and Bigeleisen's general theory of the kinetic isotope effect predicts that the effect will be most marked when the isotopic atoms are loosely bound in the activated complex.

Zener[5] and others developed Eyring's theory of rate processes by treating the diffusion process as the motion of an atom through a potential barrier. They showed that the average jump frequency of the atom is related to its mass by the expression $\omega \propto m^{-1/2}$. In this model the elementary diffusion act is carried out by a single particle: the contribution from the crystal lattice is not considered. Other assumptions made in the model include: 1) an activated state can exist at the top of the potential barrier, and its life time is long enough to determine it thermodynamic properties; 2) irreversibility of the diffusion is produced by an unexplained mechanism which causes the migrating atom to lose so much energy that it is unable to re-cross the barrier in the backward direction.

Prigogine and Bak[6] proposed a theory in which irreversibility of the diffusion follows from the anharmonicity of the interactions between the normal modes of the matrix and those of the moving particle. Their model ignores the participation of the lattice atoms in the formation of the activated complex in the saddle-point configuration; a consequence of this model is that the diffusion coefficient is inversely proportional to the square of the mass of the migrating atom.

The contribution to the formation of the activated complex by the nearest neighbours of the diffusing atom can be allowed for by making the frequency of the jumps into a vacancy proportional to $(m^*)^{-1/2}$, where m^* is an effective mass whose value is determined by the highest and the lowest mass of the whole configuration. Rice and Frisch[7] allowed for the participation of the lattice in the saddle configuration and used a dynamic model free from the assumptions of the classical theory. According to their model the jump of a diffusing atom is the result of the fluctuations in its energy and momentum (quantity of motion) produced by the thermal vibrations. In order to calculate the amplitude of these fluctuations they introduce a definition of the reaction co-ordinate which allows for the displacement of both the migrating atom and the barrier atoms. This quantity can be treated as a measure of the extent to which the thermal motion has been able to overcome the resistance of the neighbouring atoms to the passage of the migrating particle. A jump is assumed to take place each time the reaction co-ordinate exceeds some critical distance. Thus, the basic feature of the dynamic theory is the assumption that a jump can occur only as a result of a specified type of fluctuation of the reacton co-ordinate, determined by the lattice geometry. However, the energy of this fluctuation cannot be calculated in the present state of the theory. The dynamic theory of diffusion has been developed also by other workers[8–12].

Discussion of the diffusion isotope effect from the standpoint of the dynamic theory produces results similar to those of the classical model. Hence, both theories can be used for practical purposes. The classical model has the advantage of being simpler, as well as offering the possibility of calculating the thermodynamic characteristics of the diffusion jump. Our discussion of the isotope effect will therefore be confined to this variant of the theory.

A problem still not fully solved is the mechanism by which the energy of the activated atom is dissipated when this atom has gone beyond the saddle point. Unless the energy is dissipated very rapidly the atom may retain enough energy to undergo the backward jump. Clearly, the diffusion problem is closely bound up with our interpretation of the isotope effect, i.e. with the physical significance of the term ΔK which appears in Eqn.(8).

The jump frequency of an atom in the saddle configuration (at the top of the potential barrier) should be given by an expression including the frequencies of the normal lattice modes for the initial configuration (ν_j) and for the activated complex (ν_j'). Le Claire[13] showed that one of the normal modes corresponding to the saddle configuration (of frequency ν_1') is unstable, and leads to the breakdown of that configuration and to completion of the jump. Changes in the mass of the migrating atom affect the frequency of this unstable mode only. By treating the jump as the motion of an atom at the saddle point through the potential barrier we demonstrate (in accordance with the above discussion) that ΔK is the fraction of the total kinetic energy of the system (at the saddle point) which is assigned to the migrating atom only. Thus the quantity ΔK provides information on the energetics of an individual act of diffusion, which is not obtainable by any other method.

Eqns.(7) and (8) apply only if the mechanism of the migration act involves only one particle (vacancy mechanism, direct interstitial mechanism, etc.). If the elementary displacement

requires the simultaneous motion of n atoms (as in the indirect interstitial or in the ring mechanism) Eqns.(7) and (8) become

$$E_{\beta}^{\alpha}=\frac{\Delta D}{D_{\beta}}\left[\left(\frac{m_{\beta}+(n-1)m_0}{m_{\alpha}+(n-1)m_0}\right)^{1/2}-1\right]^{-1}=f_{\alpha}\Delta K, \qquad (11)$$

where m_0 is the average mass of the matrix atoms.

Since ΔK allows for the contribution of the lattice atoms to the elementary diffusion act we can establish the relationship between this quantity and the relaxation of the atoms adjacent to the defect. This correlation was first investigated by Barr and Mundy[14], who expressed the activation volume for diffusion ΔV in units of the atomic volume and found that ΔK was numerically very similar to $\Delta V/V$. Le Claire[13] looked for a correlation between the kinetic energy of an atom at the saddle point and vibrating with the frequency ν_1', on the one hand, and the jump distance of this atom, on the other hand, and he obtained the following expression for ΔK:

$$\Delta K=\left[1+\frac{n}{3}\left|1-\Delta V_f\right|\right]^{-1}, \qquad (12)$$

where n is the number of relaxed atoms taking part in the saddle configuration. For the self-diffusion of Na atoms in metallic sodium we have $\Delta K = 0.50$ [15] and $\Delta V_f = 0.52$.[16] This gives, from Eqn.(12), $n = 6$, which is the same as the number of neighbours of a migrating atom in a body-centred cubic (b.c.c.) crystal. However, this agreement must be treated with some caution: very probably the number of relaxing atoms is greater than six, but their contribution to ΔK is not uniform. In the case of self-diffusion in metallic silver $\Delta K = 0.86$ [17] and $\Delta V_f = 0.70$. These values lead to $n = 1.6$, which is not surprising, since the number of relaxing atoms in the more closely packed f.c.c. structure must be smaller than in the b.c.c. lattice.

It is interesting to establish whether n is a constant, characteristic of a given type of crystal structure. If so, Eqn. (12) can be used to calculate ΔK values appropriate to the isotope effect in impurity diffusion. Most workers assume that ΔK_S for self-diffusion is equal to ΔK_{imp} for impurity diffusion: this assumption is consistent with the experimental fact that the activation volumes for impurtiy diffusion and for self-diffusion do not differ very markedly (for example, $\Delta V_{In/Ag}$ and $\Delta V_{Ag/Ag}$ differ by 5%; $\Delta V_{Sb/Ag}$ and $\Delta V_{Ag/Ag}$ differ by 10%).[2] Theoretical calculations for structures in which ΔK_S is not very different from 1 lead to the same conclusion: in the case of an f.c.c. lattice, for which $\Delta K_S = 0.9$,[17] substitutional impurities should have ΔK values differing from ΔK_S by not more than 8%.[9-11] However, the same is not true of crystals in which $\Delta K_S \ll 1$.

Theoretical calculations of ΔK have been reported for various crystal structures. Brown and coworkers[18] obtained $\Delta K = 0.998$ for NaCl, in excellent agreement (within experimental error) with the experimental value[19] $\Delta K = 0.93 \pm 0.09$. They also calculated ΔK for copper[20]. A comparison of ΔV and ΔK values is shown in Table 2.

Achar[12] used the dynamic theory of diffusion to calculate ΔK for several f.c.c. and b.c.c. metals. The results are consistent with experiment.

Eqn.(8) was obtained by classical statistical mechanics, without allowance for quantum effects. Experiment shows that this expression adequately describes the diffusion isotope effect in most systems. The only exception is the diffusion of the hydrogen isotopes, for which Eqn.(8) gives unacceptably low values of E. It has been clearly shown[13,21,22] that quantum effects cannot be ignored in the diffusion of such light isotopes. The contribution of quantum corrections to the hydrogen diffusion isotope effect has been discussed for Pt [23] and Nb [24] matrices. A study[25] of the diffusion of hydrogen, deuterium, and tritium in Ni and Cu has shown the need to allow for the anharmonicity of the lattice vibrations in addition to the quantum corrections.

Table 2. Calculated and experimental values[2] of ΔK and $\Delta V/V$.

Matrix	Isotope pair	ΔK_{calc}	ΔK_{exper}	$\Delta V/V$
Ag	^{105,111}Ag	0.80[12]	0.86±0.05[17]	0.90[34]
γ-Fe	^{55,59}Fe	—	0.74±0.08[29]	0.77[35]
Cu	^{64,67}Cu	0.82[12]	0.87±0.02[30]	0.90[36]
			0.92[20]	
Na *	^{22,24}Na	0.54[12]	0.50±0.05[15]	0.52[16]
α-Fe *	^{52,59}Fe	0.51[12]	0.56±0.05[31]	—
Zn **	^{65,69}Zn	—	0.93±0.08[32]	0.43[37]
NaCl	^{22,24}Na	0.99[18]	0.93±0.09[19]	1.20[38]
AgBr	^{105,111}Ag	—	0.66±0.02[33]	0.69[33]

*b.c.c. structure; ** close-packed hexagonal structure; in every other case f.c.c. structure.

The experimental value of E has been found to be temperature-dependent in several studies of the isotope effect in self-diffusion (for example, in the self-diffusion of ^{105,110}Ag in metallic silver[17] and in the self-diffusion of ^{22,24}Na in NaCl).[26] Since $E = f\Delta K$, the temperature dependence of the isotope effect may be due to a variation with temperature of either f, or ΔK, or both. The correlation factor in self-diffusion is a purely geometrical parameter, depending only on the type of lattice and on the diffusion mechanism; on the other hand, as was shown theoretically for Ag and Al,[12] the quantity ΔK should also be independent of temperature. Thus, in order to explain the temperature dependence of the isotope effect we must postulate the simultaneous operation of several diffusion mechanisms. Changes in the contribution of each mechanism to the overall diffusion process may account for the observed dependence of E on temperature.

Bakker[27] derived an expression for the isotope effect in the case of two simultaneous mechanisms (vacancy and divacancy diffusion) in an f.c.c. lattice:

$$E=\frac{D_1}{D_1+D_2}f_1\Delta K_1+\frac{D_2}{D_1+D_2}f_2\Delta K_2; \qquad (13)$$

where D_i, f_i, and ΔK_i are the diffusion coefficients and the isotope effects for each mechanism. The most general expression for the diffusion isotope effect in the case of diffusion by several simultaneous mechanisms is

$$\frac{\Delta D}{D_{\beta}}=\sum p_i\Delta K_i f_i\delta_{m_i}, \qquad (14)$$

where p_i is the fractional amount of diffusion by the stated mechanism, and δ_{m_i} is the mass term (for the vacancy and the direct interstitial mechanism $\delta_{m_i}=[(m_{\beta}/m_{\alpha})^{1/2}-1]$).[27] Eqns.(13) and (14) can be used to calculate the contribution of each mechanism to the overall diffusion process.

We shall now consider the limits of the validity of expressions of the type of (8), (11), and (14). Both the derivation and the practical use of these and similar expressions involve the following assumptions:

a) $\Delta f/f_{\beta}$ is small compared with unity, i.e. $f_{\alpha}=f_{\beta}=f_0$;

b) changes in mass affect only ω in Eqn.(2), and they have no effect on u;

c) the number of labelled atoms introduced into the crystal by diffusion is much smaller than the number of matrix atoms, and therefore the probability of finding an impurity atom among the nearest neighbours of a diffusing atom is negligibly small.

LeClaire has shown[13] that the measured diffusion isotope effect is only slightly affected by these assumptions, since the necessary corrections are less than 2% and therefore beyond the precision of the experiment (5–10%).

III. SELF-DIFFUSION IN PURE METALS

1. Face-centred Cubic Metals

Diffusion isotope effects have been studied in a large number of metals with a face-centred cubic lattice. In most cases the conclusion is that self-diffusion in f.c.c. metals is mainly by the single vacancy mechanism. A contribution from the divacancy mechanism is observed near the melting point.

Self-diffusion in copper has been studied in several laboratories[30,36]. We shall dwell mainly on Rothman and Peterson's results[30], obtained in an investigation of the effect of temperature on diffusion isotope effects. At relatively high temperatures (698–1061 °C) the diffusion is described by the following parameters: $D_0 = 0.78$ cm^2 s^{-1}, $Q = 2.18$ eV. From the diffusion of ^{64}Cu and ^{67}Cu in copper single crystals the ratio $D_{64}/D_{67} = 0.0155 \pm 0.0003$ was obtained, and found to be independent of temperature. These results led to the value $\Delta K = 0.87 \pm 0.02$, and to the conclusion that self-diffusion by the single vacancy mechanism is predominant in copper. The variation of E_{67}^{64} with temperature is negligibly small, showing that the contribution of divacancies to the diffusion process is slight.

The pressure dependence of the diffusion coefficient for self-diffusion in Cu [36,39] gives an activation volume of 0.9 of the atomic volume, corresponding to diffusion by the single vacancy mechanism or by a combination of the single vacancy and the divacancy mechanism. Mehrer and Seeger[40] arrived at the following series of optimum parameters for the defects in Cu by combining data on the temperature dependence of D and on the isotope effect with data[41] on high-temperature defect equilibria: $H_f^{1V} = 1.03$ eV, $\Delta S_f^{1V} = 0.3\ k$, $H_m^{1V} = 1.06$ eV, $\nu^{1V}\exp(\Delta S_m^{1V}/k) = 1.4 \times 10^{14}$ s^{-1}, $H_m^{2V} - H_b^{2V} = 0.54$ eV, $\Delta S_f^{2V} = 2k$, $\nu^{2V}\exp(\Delta S_f^{2V}/k) = 1.6 \times 10^{14}$ s^{-1}. Electron-microscopic studies by Bowden[42] have confirmed Mehrer and Seeger's interpretation (which allows for divacancy migration).

Self-diffusion in Ag has been studied by several workers. Rothman's results[17] show a small, systematic deviation from an Arrhenius dependence of ln D on $1/T$, which he ascribes to the presence of a second diffusion mechanism. The temperature dependence of the isotope effect for self-diffusion in Ag (Fig. 1) gives additional evidence for the presence of two diffusion mechanisms[17]. At low temperatures the E value corresponds to diffusion by the single vacancy mechanism ($\Delta K^{1V} = 0.92$), decreasing at higher temperatures to a level which suggests an increasing contribution from divacancies. Reimers and Bartdorff[43] also measured the temperature dependence of E: their results are less accurate than Rothman's but consistent with them.

Two extreme cases of the contribution of divacancies to self-diffusion in silver can be defined. On the one hand, the difference between E and f^{1V} can be ascribed wholly to the contribution from divacancies (i.e. $\Delta K^{1V} = 1$). Assuming $\Delta K^{1V} - \Delta K^{2V} = 1$, and $f^{2V} = 0.475$, we find that the divacancy contribution is a maximum ($D^{2V}/D^{1V} = 0.872$) at high temperatures ($E = 0.639$), falling to 0.263 at low temperatures ($E_{111}^{105} = 0.718$). Since only the single vacancy mechanism operates at low temperatures, i.e. $\Delta K^{1V} = 0.918$, and divacancy effects on E appear only at high temperatures, we can obtain $D^{2V}/D^{1V} = 0.12$ by assuming that ΔK is independent of temperature and that the contribution of divacancies at the melting point is a minimum for $\Delta K^{2V} = 0$. A critical analysis of all the experiment data[44] leads to the following set of thermodynamic parameters for the defects and for their mobility in metallic silver: $H_f^{1V} = 0.99$ eV, $H_m^{1V} = 0.86$ eV, $\Delta S_f^{1V} = 0.5\ k$, $H_m^{2V} - H_b^{2V} = 0.34$ eV, $H_m^{2V} = 0.58$ eV, $\Delta S_f^{2V} = 2.6\ k$.

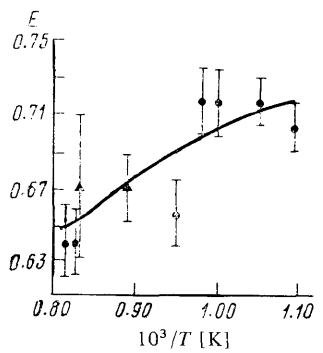


Figure 1. Isotope effect for self-diffusion in Ag: [17,33] the curve is taken from Mehrer's analysis[44] of these results.

Isotope effects for self-diffusion in Pd and γ-Fe have been measured accurately enough to identify the diffusion mechanism, but the temperature dependence of E was not measured to an accuracy sufficient to justify the calculation of the thermodynamic properties of the defects. Peterson[45] investigated the isotope effect for self-diffusion in Pd, and found $E = 0.79 \pm 0.04$ in a narrow region of temperature near the melting point. Since ΔK cannot be greater than unity, self-diffusion in Pd must take place by the single vacancy mechanism, with $(1 - \Delta K) \leq 0.02$. The experimental temperature range was too narrow to allow the contribution of divacancies to be detected, but the numerical value of the isotope effect suggests that this contribution is very small.

Published studies[29,46] of the isotope effect for self-diffusion in γ-Fe are consistent ($E_{59}^{55} = 0.53$–0.57), and suggest that the single vacancy diffusion mechanism predominates. The observed temperature dependence of E allows for some contribution from divacancies to the transport processes in γ-Fe.[29]

2. Body-centred Cubic Metals

Studies of self-diffusion in b.c.c. metals have yielded inconsistent results, and the diffusion parameters in these systems cannot yet be interpreted unambiguously. For most b.c.c. metals the diffusion coefficient near the melting point is ~10^{-7} cm^2 s^{-1}, as compared with ~10^{-8} cm^2 s^{-1} for f.c.c. metals. Interesting results were obtained for the self-diffusion effects in sodium. The model of self-diffusion in Na is more complicated than the model for f.c.c. metals, and is probably typical of the majority of metals which crystallise in a body-centred cubic lattice. The anomalously low value

of the ratio $\Delta D/D_{24} = 0.016$ was pointed out early on[14]: such a value of the mass effect may be due to an indirect interstitial mechanism, diffusion occurring along split interstitials. However, since the predominant defect in Na has been shown independently[16] to be a lattice vacancy, a diffusion model involving relaxed vacancies is proposed: this gives a lower value of f and explains the low value of E.

Later work in the same laboratory showed a decrease in the magnitude of the isotope effect near the melting point of sodium[15]: $\Delta D/D_{24} = 0.016$ at 40–84 °C, and $\Delta D/D_{24} = 0.013$ at $t > 84$ °C. Evidently, diffusion occurs by more than one mechanism at temperatures near the melting point, but the nature of these mechanisms has not been established. On the other hand, two models of the relaxed vacancy have been proposed for the region of constant E: $f_1 = 0.5$ and $\Delta K_1 = 0.72$, or $f_2 = 1$ and $\Delta K_2 = 0.36$. However, the authors are unable to choose between these models.

The isotope effect in Na has been calculated theoretically[18] for different types of defect. Agreement with experiment is best for the interstitial diffusion mechanism.

Mundy[28] attempted to explain unambiguously the mechanism of self-diffusion in sodium by carrying out a complex investigation over a range of hydrostatic pressures. His results, and in particular the irregularities in the plot of $\ln D = f(1/T)$, suggest that at least two diffusion mechanisms are operative: a high-temperature and a low-temperature mechanism. Within the high-temperature region two separate mechanisms can be distinguished. Thus, the total number of mechanisms involved is three. The dependence of self-diffusion on pressure at 14.8 and 91.4 °C indicates that at 14.8 °C approximately 2/3 of the diffusion takes place by the low-temperature mechanism, whereas at 91.4 °C this mechanism accounts for only 40% of the diffusion. When several mechanisms are possible an increase in pressure causes an increased contribution from the low-temperature processes. Therefore the decrease in the isotope effect at 91.4 °C becomes less marked when the pressure is raised to 7 kbar, though this effect may be due to the increase in the melting point of sodium at high pressures (145 °C at 7 kbar).

Thus the experimental results show that self-diffusion in sodium involves at least two mechanisms. The following pairs of mechanisms have been proposed for the two-process model: 1) a vacancy and an interstitial, and 2) a vacancy and a divacancy. By associating (in the first variant) the interstitial mechanism with the low-temperature region and the vacancy mechanism with the high-temperature region we can explain many experimental results. However, this model does not allow us to explain the variation of E with temperature. On the other hand, the temperature dependence of the isotope effect is easily explained by postulating two types of divacancy whose relative contribution to the transport of matter varies with temperature. Evidence for this model is provided by the similarity of the activation volumes for the two high-temperature processes ($\Delta V_2/V = 0.68 \pm 0.21$, and $\Delta V_3/V = 0.68 \pm 0.25$ at 91.3 °C).[28]

For the model which includes three self-diffusion mechanisms Mundy[28] suggests the following processes: a low-temperature (interstitial) process with $\Delta D/D = 0.018$ and two high-temperature processes with $\Delta D/D = 0.014$ and 0.003 respectively. The latter value is surprisingly small, and we have to use Eqn. (11) to calculate the number of atoms taking part in the elementary act: the result is $n = 20$. This is not too surprising, since neutron diffusion experiments in liquid sodium have shown that at temperatures slightly above the melting point ~30 atoms are involved in each diffusion jump. We may assume that the concentration of vacancies increases steeply near the melting point, and therefore the relaxation around one vacancy may affect other vacancies. This type of interaction may lead the formation of regions within the crystal in which diffusion is a polyatomic process.

Studies of isotope effects in self-diffusion in α-Fe [31,46] and δ-Fe [47] have been reported. The results are mutually consistent, the E values in α-Fe and δ-Fe being similar to those in Na at the same reduced temperatures (i.e. at temperatures referred to the melting point of the appropriate metal, T/T_f). The complex temperature dependence of the isotope effect in α-Fe, δ-Fe, and Na suggests that the migration of atoms in these b.c.c. metals occurs by the same mechanism. In order to test this hypothesis with a higher-melting b.c.c. metal, Mundy and coworkers[48] studied the isotope effect of chromium, and they again observed a decrease in the E_{51}^{48} value for the effect with increase of temperature (0.52–0.31 at 1440–1810 °C). The high values of the Arrhenius parameters (as in the case of self-diffusion on vanadium) are consistent with a predominantly divacancy migration mechanism in chromium, with a negligibly small contribution from single vacancies. The temperature dependence of the isotope effect is explained (as in the case of sodium) by the participation of two types of divacancy in the transport process.

Evidently, further work on diffusion isotope effects in other b.c.c. metals is needed to solve the problem of anomalous diffusion in these materials, which are industrially important.

3. Close-packed Hexagonal Metals

Isotope effects in the self-diffusion in zinc, which has an anisotropic lattice, have been reported[32,49]. At 289–418 °C the self-diffusion coefficients parallel (∥) and perpendicular (⊥) to the sixth-order symmetry axis are different, but the isotope effects are identical (within experimental error) in the two directions, and do not depend on temperature. The numerical values of the diffusion isotope effect suggest transport by a single vacancy mechanism in both directions, without a significant contribution from divacancies, i.e. $f_\parallel = f_\perp$ and $\Delta K_\parallel = \Delta K_\perp$. Different configurations of barrier atoms for these two cases can be proposed from geometrical considerations. However, the experimental values of ΔV are identical for both directions[37].

Stein and coworkers[50] proposed a method of calculating the correlation factor for self-diffusion in close-packed hexagonal metals by the single vacancy and divacancy mechanism. The results have been compared with experimental data[49] on the isotope effect for self-diffusion in zinc. The calculated correlation factor was shown to be the upper limit of the diffusion isotope effect.

IV. ISOTOPE EFFECTS IN HETERO-DIFFUSION IN METALS

Mundy and McFall[51] studied the diffusion of copper in metallic lithium, and observed deviations from linearity in the $\ln D = f(1/T)$ plots, which they ascribed to the presence of two diffusion mechanisms. The numerical value of the diffusion isotope effect ($E_{Cu/Li} = 0.11 \pm 0.03$) is incompatible with both the vacancy and the direct interstitial mechanism. For the vacancy mechanism the E value should be ≅0 (i.e. $f_{Cu/Li} \to 0$), whereas for interstitial diffusion E should be close to unity. Assuming a dissociative mechanism for the dissolution of Cu in Li, involving an equilibrium between the numbers of copper atoms in normal lattice sites and in interstitials respectively, the authors[51] conclude that diffusion takes place by a direct interstitial and a vacancy mechanism simultaneously. The two mechanisms are thought to contribute to a similar extent

to the transport process, since they involve comparable activation energies for diffusion. These considerations led the authors to the values $E = 0.17$ and $E = 0.05$ for the two mechanisms respectively. By measuring the diffusion isotope effects of $^{105,110}Ag$ and $^{22,24}Na$ in lithium Mundy and McFall[52] were able to compare experimental results with conclusions from the dynamic theory of diffusion.

An interesting example of the use of the isotope effect in identifying the diffusion mechanism of an impurity is provided by the fast diffusion of $^{105,110}Ag$ in lead[53]. An interstitial diffusion mechanism is almost invariably assumed to account for the abnormally fast diffusion of an impurity. The vacancy mechanism is excluded by the very small effect of the added impurity on the rate of self-diffusion. However, the effect cannot be explained on the assumption that the diffusion occurs wholly by an interstitial mechanism. To resolve this problem, the diffusion isotope effect of Ag in Pb was measured. The result[53] was $E_{Ag/Pb} = 0.25 \pm 0.05$, and the effect of the Ag impurity of $E_{Ag/Pb}$ was undetectable (addition of 0.08 at.% of Ag giving $E = 0.26 \pm 0.02$). The effect of temperature on $E_{Ag/Pb}$ was also negligibly small. These experimental observations were explained by postulating that the diffusion of Ag in Pb involves two mechanisms, though the contribution of the interstitial mechanism is predominant (80%). The remaining 20% is ascribed to any mechanism in which the diffusion of the impurity is directly linked to the diffusion of the solvent. Typical of these mechanisms is diffusion by impurity–vacancy pairs, with the silver atoms in interstitial sites. The relatively small contribution from the pair diffusion mechanism (20%) explains the failure of Ag additions to accelerate the self-diffusion in Pb. On the other hand, this small contribution from impurity–vacancy pairs to the overall diffusion process tends to obscure the influence of this mechanism on the isotope effect and to make the isotope effect temperature-independent.

Thus it is firmly established that most of the transport of Ag in Pb occurs by the interstitial mechanism. We also know that in this case $E \cong 1$, whereas the experimental value is $E = 0.25$. Since there is no reason to assume that either ΔK or f is very different from unity in this case, we must conclude that according to Eqn.(11) $n \neq 1$, i.e. several particles are involved in the elementary migration act. The most important defect in solutions of silver in lead is the split interstitial. If this defect consists (as in the present case) of two Ag atoms the presence of the impurity should accelerate the diffusion much more substantially than is found in practice. If on the other hand the split interstitial is composed of one Ag atom and one Pb atom, the Ag atom can perform one migration act by jumping from this defect into a normal site of the lead lattice. In this case $n = 3$, and if $f = 1$ and $\Delta K = 1$ the E value calculated from Eqn.(11) is 0.20, which agrees with the experimental value[53].

The isotope effects in the diffusion of cadmium (E_{115}^{109}) [54] and copper (E_{67}^{64}) [55] in lead were studied for the same purpose, i.e. in order to identify the hetero-diffusion mechanism. In the latter case the isotope effect ($E_{67}^{64} = 0.23 \pm 0.08$) was found to be close to the corresponding value for the diffusion of $^{105,110}Ag$ in Pb,[53] suggesting a similarity between the migration mechanisms of the impurities in the two systems. We should note that because of the low solubility of copper in lead the concentration dependence of the rate of diffusion could not be studied over a significantly wide range. Thus, the measurement of the isotope effect is the only method available for identifying the hetero-diffusion mechanism.

It should be remembered that in a pure metal the correlation factor f_0 is a constant, and depends only on the type of crystal structure and on the diffusion mechanism, whereas in impurity diffusion the correlation factor depends on the jump frequencies of the impurity atoms and of the solvent atoms. Therefore the quantity f_{imp} obtained from measurements of the diffusion isotope effect can be combined with other data (such as the dependence of the self-diffusion coefficient on the impurity concentration) to give the ratio of the jump frequencies of impurity and matrix atoms. For example, data on the isotope effect for the diffusion of zinc in silver[2] and data on the effect of zinc impurities on the rate of self-diffusion in Ag have allowed this ratio to be calculated for different temperatures. Results from studies of isotope effects accompanying the diffusion of Fe in Ag and Cu,[4] of cadmium in zinc[49], etc. have been interpreted in a similar way.

V. DIFFUSION IN ALKALI METAL HALIDE CRYSTALS AND IN SILVER HALIDES

Work on diffusion isotope effects in alkali metal halide crystals and in silver halides has been confined mainly to determining the contribution of vacancy pairs to the overall diffusion, and to evaluating the parameter n in Eqn.(11) for the case of simultaneous motion of two (or more) ions, since the indirect interstitial mechanism appears to operate in silver halides. From the results, thermodynamic parameters describing the migration under hetero-diffusion conditions have been calculated. The experimental data are summarised in Table 3.

Table 3. Experimental values of the diffusion isotope effect in single crystals of alkali metal halides and silver halides.

Solvent	Δt, C°	$E_\beta^{\alpha*}$	References
	$^{22,24}Na$		
NaCl	644	0.727	13
NaCl	600—750	0.75	67
NaCl	622—797	0.695—0.485	26
NaBr	730—798	0.65	68
KCl	574—772	0.441—0.689	67
KBr	600—695	0.523—0.637	67
RbCl	380—707	0.107—0.362	65
AgCl	180—450	0.989	69
	$^{131,137}Cs$		
CsI	470—600	0.54	60
	$^{6,7}Li$		
LiF	600—750	0.42	59
AgCl	250—400	0.75	70
	$^{105,111}Ag$		
AgCl	239—253	0.0076	33
AgBr	175—337	0.0045	33

* In the case of $^{105,111}Ag$ the $\Delta D/D_\beta$ values are given

1. Contribution of the Divacancy Mechanism

As was stated above, the concentration of vacancy pairs increases steeply in many crystal structures at temperatures close to the melting point, and the contribution of vacancy pairs to the diffusion process increases correspondingly. The presence of a second diffusion mechanism will be reflected also by the magnitude of the isotope effect.

Attempts have been made in recent years to calculate the contribution of vacancy pairs to the diffusion of Na^+ ions in

sodium chloride. Nelson and Friauf[56] measured the self-diffusion coefficients of Na^+ in NaCl and also monitored (at the same time) the migration of this ion in an electric field, and concluded that the contribution from vacancy pairs was ~40%. Though the contacts to the crystal during the measurements in an electric field were far from ideal, the results obtained in this way are more accurate than those of independent measurements of D and σ.

Beniere and coworkers[57] calculated the contribution of vacancy pairs to the diffusion of the sodium ion in sodium chloride (~10%) from measurements of D_{Cl} in NaCl samples containing small amounts of bivalent cation impurities. The addition of bivalent cations is known to lower the concentration of single anion vacancies, and therefore at sufficiently high concentrations of M^{2+} the anions should migrate almost exclusively along vacancy pairs. However, these workers[57] based their calculations on the assumed equivalence[58] of cation and anion diffusion by the divacancy mechanism. By combining this (to say the least) arguable assumption with their experimental results on D_{Cl}, D_{Na}, and σ they obtained[57] $f^{1V} = 1$.

Rothman and coworkers[26] studied the isotope effect in the self-diffusion of Na in NaCl. Measurements of E_{24}^{22} in NaCl had been carried out even earlier[19], but the effect of temperature on this parameter had not been observed, and it had been concluded[57] that correlation is absent in the diffusion of Na in NaCl (i.e. $f = 1$). Rothman[26] observed a change in E_{24}^{22} in NaCl: from 0.484 at 796.6 °C to 0.624 at 589.3 °C. By ascribing the lack of constancy of the isotope effect to an increasing contribution from divacancies to the diffusion process they evaluated[26] this contribution at different temperatures. This calculation is more complex for an ionic crystal than for a metal, since f becomes a function of the ratio of the jump frequencies of the anion (ω_a) and of the cation (ω_c) into the divacancy, and it can vary from zero to 0.782. The value of ΔK^{2V} for divacancy diffusion is also unknown.

Rothman and coworkers[26] define two limiting cases for the participation of divacancies in the transport process: 1) assuming that $E^{2V} = 0$ at the melting point, and noting that $E^{1V} = 0.624$, they estimate the minimum contribution from vacancy pairs at the melting point to be 22%; 2) assuming that at 796.6 °C the diffusion is wholly along divacancies they find $E^{2V} = 0.484$. Then, if $\Delta K_2 \leq 0.8$, we have $f^{2V} \leq 0.6$ and $\omega_a/\omega_c < 0.5$. Using these values they obtain[26] the maximum value of $D_2/(D_1 + D_2) = 53\%$ at 589 °C. A more critical analysis of the experimental results suggests that the most reasonable of all the possible values of E^{2V} is <0.2: in this case $f^{2V} \leq 0.25$ and $\omega_a/\omega_c \leq 0.1$. Adopting these values we find that the difference in activation energy between the two diffusion mechanisms is $\Delta Q = Q^{2V} - Q^{1V} = 0.82$–$0.9$ eV, and the contribution of vacancy pairs to diffusion near the melting point is 30–45%.

Using the ratio $\omega_a/\omega_c \leq 0.1$ to interpret the results of Beniere and coworkers[57] we find that the contribution of vacancy pairs at 800 °C is 50%, i.e. not very different from Rothman's value[26]. Also, with this value of $D_2/(D_1 + D_2)$ Beniere's results[57] give an f_{1V} value nearer to 0.78 than to 1, in good agreement with Nelson and Friauf's value[56].

Self-diffusion isotope effects have been studied also in single crystals of LiF [59] and CsI.[60] In both cases the migration mechanism was found to be by single vacancies.

2. Self-diffusion Istope Effect in Systems with Frenkel' Defects

In all the systems discussed so far the predominant defects are vacancies. As an example of the application of the isotope effect to structures containing Frenkel' defects we shall consider the diffusion of $^{105,111}Ag$ in AgCl.[33]

Studies[61-63] of ionic conduction in AgCl and AgBr single crystals (both pure and doped with divalent cations) have shown that most of the Ag ions migrate by the direct interstitial mechanism in pure AgCl and AgBr. The variation of the quantity $\Phi = \mu_i/\mu_V$ with temperature and pressure (where μ_i and μ_V are the mobilities of the interstitial ions and of the vacancies) has also been studied[61,62]. Self-diffusion can take place by indirect interstitial mechanisms involving collinear (frequency ν_1) or non-collinear jumps. Non-collinear jumps of two types are possible (frequencies ν_2 and ν_3). Peterson and coworkers[33] consider only the ν_1 and ν_2 jumps, pointing out that the ν_3 jump is energetically unfavourable, and they arrive at the following expression for the effect of mass on self-diffusion in silver halides:

$$\frac{D_\alpha}{D_\beta} - 1 = \frac{\Delta D_{tot}}{D_{\beta,\,tot}} = \frac{\Delta D_v}{D_v}\left(\frac{D_v}{D_{tot}}\right) + \frac{\Delta D_i}{D_i}\left(1 - \frac{D_v}{D_{tot}}\right);$$

where $\Delta D_V/D_V$ and $\Delta D_i/D_i$ are the relative differences between the self-diffusion coefficients of the two isotopes for the vacancy and the interstitial mechanism, and $\Delta D_{tot}/D_{tot}$ is the experimentally observed mass effect.

Introducing the functions $F_1(\chi)$ and $F_2(\chi)$, relating the frequencies of the collinear and the non-collinear jump ($\chi = \nu_1/\nu_2$), Peterson and coworkers obtain[33]

$$\Delta D_{tot}/D_{tot} = \alpha_1 \Delta K_1 + \alpha_2 \Delta K_2 + \alpha_v \Delta K_v, \qquad (15)$$

where

$$\alpha_1 = [1 - (M_\alpha/M_\beta)^{1/2}] F_1(\chi)\,[1 - D_v/D_{tot}],$$
$$\alpha_2 = [1\,(M_\alpha/M_\beta)^{1/2}] F_2(\chi)\,[1 - D_v/D_{tot}],$$
$$\alpha_v = [1 - (M_\alpha/M_\beta)^{1/2}] f_v D_v/D_{tot},$$

and $M_\alpha = [m_\alpha + (n-1)m_0]$, $M_\beta = [m_\beta + (n-1)m_0]$ for $n = 2$. The ratio D_V/D_{tot} can be obtained from the expression

$$\frac{D_v}{D_{tot}} = \frac{f_v}{(D_{tot}/D_v)\,(1 - \Phi)},$$

where f_V is the correlation factor for the vacancy mechanism. Thus, by using Eqn.(15), the quantities α_1, α_2, and α_V can be calculated for different temperatures.

In order to determine ΔK_V Peterson and coworkers[33] measured the isotope effect for the self-diffusion of $^{105,111}Ag$ in AgBr doped with $CdBr_2$, because diffusion in this system is entirely (100%) by the vacancy mechanism. The best agreement between experiment and calculation was obtained by putting $\Delta K_1 = 1$ and $\Delta K_2 = 0.1$ (note that ΔK_V is constant in very case, $\Delta K_V = 0.66$). This result suggests that the interaction between the migrating atom and the lattice is weak during a collinear jump, whereas during a non-collinear jump the interaction is substantial. This conclusion is confirmed by other experimental results, showing that the activation energy is much lower for the collinear than for the non-collinear jump ($Q_1 = 0.058$ eV, $Q_2 = 0.274$ eV). The difference between the pre-exponential factors is even more striking ($D_{01} = 6.1$ cm^2 s^{-1}, $D_{02} = 1090$ cm^2 s^{-1}), indicating a large entropy of activation for the ν_2 jumps (due to the large number of particles taking part in this process).

3. The Isotope Effect in Hetero-diffusion

Tosi and Doyama[64] calculated the energy of formation (H_f) and the energy of migration (H_m) of cation vacancies in NaCl, KCl, and RbCl, the energy of migration of Na^+, K^+, and Rb^+ impurities in these chlorides, and the impurity–vacancy bond energy (H_b) for these impurities. They obtained[64] a very small value for the energy of migration of Na in RbCl (0.22 eV) in comparison with the H_m value for the migration of Rb^+.

The activation energy for the hetero-diffusion in the "intrinsic" (high-temperature) region is given by the expression

$$Q_{\text{intr}} = \frac{1}{2}H_f + H_m - k\left(\partial \ln f/\partial \frac{1}{T}\right)_{\text{intr}} + H_b.$$

In the "extrinsic" (low-temperature) region, in which no new defects are formed and therefore the term $\frac{1}{2}H_f$ can be ignored, we have

$$Q_{\text{extr}} = H_m - k\left(\partial \ln f/\partial \frac{1}{T}\right)_{\text{extr}} + H_b.$$

Experimental measurements of the temperature dependence of f in both regions give $\frac{1}{2}H_f$ and $(H_m + H_b)$, which can be compared with the calculated values[64]. Peterson and Rothman[65] measured the diffusion coefficients of Na in RbCl and the diffusion isotope effect of $^{22,24}Na$ at different temperatures. Plots for evaluating the ratio $[\partial \ln f/\partial (1/T)]_{\text{extr}}$ are shown in Fig. 2. The experimental results give $Q_{\text{intr}} = 2.06 \pm 0.02$ eV, $Q_{\text{extr}} = 0.59 \pm 0.01$ eV, $[\partial \ln f/\partial (1/T)]_{\text{intr}} = -0.19 \pm 0.02$ eV, $[\partial \ln f/\partial (1/T)]_{\text{extr}} = 0.05 \pm 0.03$ eV. They also obtained[65] $(H_m + H_b) = 0.65$ eV, and $\frac{1}{2}H_f = 1.22$ eV. According to Tosi and Doyama's calculations[64] the interaction energy of the Na^+ ion with a vacancy in RbCl is 0.1 eV. Taking $H_b = 0.1$ eV, we find $H_m = 0.55$ eV, in contrast to the calculated value[64] $H_m = 0.22$ eV. As expected from the theory, the energy of migration of the Na^+ ion is experimentally found to be higher than the energy of migration of the native rubidium ions. The experimental value $\frac{1}{2}H_f = 1.22$ eV also differs significantly from the calculated values (1.05 eV;[64] 1.12 eV),[66] but the migration energy calculated by the conventional ionic model is usually lower than the experimental value in all the alkali metal halide crystals. This discrepancy can be ascribed[66] to an excessive allowance for the polarisation energy of the ions surrounding the vacancy.

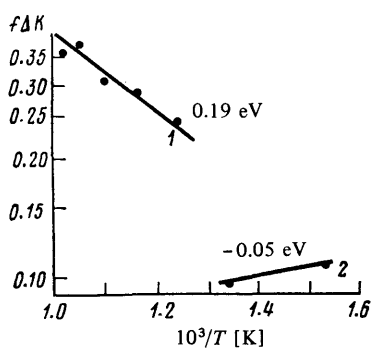


Figure 2. Isotope effect for the diffusion of Na in RbCl in (*1*) the intrinsic region and (*2*) the impurity region[65].

In order to determine $\frac{1}{2}Hf$ Peterson and coworkers[65] assumed that $(H_m + H_b)$ is the same in the intrinsic and the extrinsic state, i.e. that the energy needed to exchange a Na^+ ion with a vacancy and the bond energy are independent of whether the vacancy is free or attached to a multivalent impurity. This assumption was not tested experimentally.

The changed sign of $[\partial \ln f/\partial (1/T)]$ observed on going from the intrinsic to the extrinsic region has been explained qualitatively as follows[65]. In the intrinsic region the Na^+ ion can exchange places with a vacancy very much faster than any of the neighbouring Rb^+ ions. At 575 °C the rate of the Na^+–vacancy exchange (ω_2) is 10 times greater than the rate of the Rb^+–vacancy exchange (ω_0) if all the other jump frequencies are assumed to be equal. On raising the temperature ω_2 increases more slowly than ω_0, i.e. $H_m(Na^+) < H_m(Rb^+)$. This leads to low values of the correlation factor for the diffusion of the impurity, increasing with temperature. On the other hand, in the extrinsic region some of the vacancies may be bound to multivalent impurity ions. If these ions exchange places with vacancies more seldom than sodium ions the correlation factor should be much lower than in the intrinsic region. On the other hand, if H_m for the multivalent ion is intermediate in value between $H_m(Na^+)$ and $H_m(Rb^+)$ the correlation factor will be independent of temperature, or it may even increase as the temperature falls. This behaviour is consistent with both the temperature dependence and the low value of E observed experimentally in the extrinsic region.

VI. DIFFUSION IN TRANSITION METAL OXIDES

Unlike the majority of ionic compounds, many transition metal oxides can exist in non-stoichiometric compositions. These oxides contain non-stoichiometric defects whose concentration depends on temperature and on the oxygen partial pressure. We shall discuss only the oxides NiO, CoO, and FeO, all of which have the NaCl structure and can be described by the general formula $M_{1-x}O$ (in which cation vacancies are assumed to be the main non-stoichiometric defect). In order to preserve the electrical neutrality of the crystal an equal number of electron holes must be produced. At high temperatures the localised electron holes can migrate from one cation site to the next, giving rise to p-type semiconductivity.

In the absence of defect association the formation of cation vacancies in $M_{1-x}O$ can be described by the expression

$$\frac{1}{2}O_2 + \alpha M^{2+} \rightarrow O^{2-} + V_c^{\alpha'} + \alpha M^{3+},$$

where $V_c^{\alpha'}$ is a cation vacancy (negatively charged with respect to the lattice), M^{2+} and O^{2-} are a metal cation and an oxygen anion in their respective lattice sites, and M^{3+} is a cation bearing a localised hole. Obviously, the concentration of cation vacancies and of holes will be proportional to $p_{O_2}^{1/n}$ at a given temperature, where p_{O_2} is the equilibrium partial pressure of oxygen and $n = 2(\alpha + 1)$. Thus, if the electrical conductivity and the self-diffusion of cations are determined exclusively by electron holes and cation vacancies we expect both the cation self-diffusion coefficients and the electrical conductivity to be a function of p_{O_2}.

1. Self-diffusion in NiO and CoO

The effect of oxygen partial pressure on the self-diffusion of cations in NiO and CoO was studied by Volpe and Reddy[71], who found values of n (in the expression $D \propto p_{O_2}^{1/n}$) of 2.9, 3.3, and 3.6 for CoO at 1000, 1150, and 1350 °C respectively, and

6.25 and 5.0 for NiO at 1245 and 1380 °C respectively. The deviation of the n value from 4 (or 6) shows that the single defect model is incapable of interpreting the experimental results adequately. Non-integral values of n can be explained by postulating more than one type of ionised cation vacancy. Since electron holes are more mobile than cation vacancies, the ionised state of a cation vacancy can change many thousands of times during the life time of the vacancy. Hence, if more than one type of ionised cation vacancy is contributing to the equilibrium, a migrating vacancy can have an effective negative charge α which is not necessarily an integer. If we adopt this approach we must introduce a distinction between the mobilities of neutral, singly charged, and doubly charged vacancies in these materials.

Recent work on isotope effects in the self-diffusion of cations has helped to identify the diffusion mechanisms in CoO and NiO crystals. Measurements[72] of the diffusion of ^{55,60}Co in CoO gave $E_{60}^{55} = 0.58 \pm 0.01$ (independent of temperature between 1081 and 1411 °C). The temperature-independence of the isotope effect is evidence that the self-diffusion of Co in CoO involves only one mechanism, and the observed value of E_{60}^{55} suggests a single vacancy mechanism with $\Delta K = 0,75$. Volpe and coworkers[73] also studied the isotope effect for the self-diffusion of ^{57,66}Ni in NiO crystals, and obtained the value $E_{66}^{57} = 0.61 \pm 0.02$, independent of temperature in the range 1201–1678 °C. In an earlier paper[71] the same workers had suggested that a temperature-dependent (interstitial) mechanism may be needed, in addition to the vacancy mechanism, to account for the diffusion of cations in nickel oxide. However, their measurement of the isotope effect clearly shows that in NiO (as in CoO) cation transport occurs exclusively by the single vacancy mechanism, with $\Delta K = 0,78$.

2. Self-diffusion in $Fe_{1-x}O$

The wüstite lattice always contains an apparent excess of oxygen (at 1400 °C the range of compositions is $Fe_{0,95}O$–$Fe_{0,84}O$). The non-stoichiometric excess of oxygen is shown (by X-ray diffraction) to be due to a large number of cation vacancies[74]. At these high concentrations of defects we can no longer use the simple model of individual vacancies, and we must allow for the formation of defect associations (or clusters). Extended defects may give rise to whole regions having the spinel (Fe_3O_4) structure in wüstite. Thus, cluster formation perturbs the direct relationship between the diffusion coefficient and the departure from stoichiometry (x). Not surprisingly, early studies of this relationship gave inconsistent results. For example, a study of diffusion in $Fe_{1-x}O$ with radioactive indicators gave D values increasing with the extent of non-stoichiometry[75], whereas the D values calculated from chemical diffusion coefficients decrease as x increases.

A detailed study of the mechanism of diffusion of cations in wüstite and of the formation of clusters in this material (and its effect on diffusion) was based on measurements[76] of the diffusion coefficients and of the diffusion isotope effect of ^{52,59}Fe in $Fe_{1-x}O$. The results indicate a non-linear relationship between D and x. At high temperatures (1200 °C) and compositions in the range $0.05 \leq x \leq 0.10$ the D values increase by 20% as x increases, but at 800 °C they fall by 40%, and at 1000 °C they are almost independent of x. The measurements of the isotope effect are summarised in Fig. 3, which shows a plot of $E = f(x)$ for different temperatures.

As was pointed out above, the numerical values of E for NiO and CoO are consistent with the single-vacancy mechanism ($f = 0,78$ and $\Delta K = 0,78$ and 0,75 respectively), and are independent of temperature and composition. In wüstite of a given composition E is independent of temperature, but it decreases as the deviation from stoichiometry increases. This effect can be ascribed to changes in the correlation factor if we assume ΔK to be constant for wüstite and for NiO and CoO (a plausible assumption, since all three oxides have the same crystal structure). The fact that the E values are lower in FeO than in NiO and CoO suggests a contribution to the diffusion process from divacancies and even higher-order associations. The experimental results show that the iron cations diffuse by exchanging places with mobile vacancies, with a single mechanism operating over the whole range of composition (as shown by the constancy of the isotope effect parameters at different temperatures but constant x).[76]

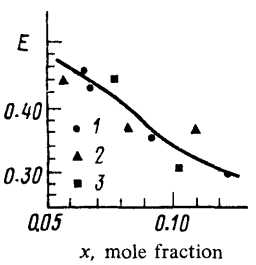


Figure 3. Isotope effect for the self-diffusion of ^{52,59}Fe in $Fe_{1-x}O$ as a function of x [76] at different temperatures: *1*) 1200, *2*) 1000, *3*) 807 °C.

At high concentrations of vacancies clusters are formed: different models of the cluster are discussed in Ref. 77. These defect associations are less mobile than single vacancies, and they show a higher degree of correlation, leading to lower E values at high x. Macroscopic diffusion along free vacancies tends to decrease as the deviation from stoichiometry increases. At a well defined temperature D is independent of x, since the increase in the concentration of free vacancies is balanced by the decrease in mobility and by the increased correlation effect (i.e. by the decrease in f). Lastly, if the temperature is increased still further the higher-order clusters begin to break down, causing D to increase with x.

3. Diffusion of Co in NiO

In order to throw light on the detailed features of impurity diffusion processes, and also to explain the influence of the interaction between impurity cations and defects on the self-diffusion of cations in oxides, Chen and Peterson[78] studied the isotope effect for the diffusion of Co in NiO, and also the simultaneous diffusion of Co and Ni in $(Ni_{1-c}Co_c)O$ crystals. The experimental values of $(f\Delta K)_{Co}$ in NiO increase from 0.45 ± 0.01 and 1179 °C to 0.61 ± 0.01 at 1649 °C. Using the value $\Delta K = 0.78$ obtained for the self-diffusion of Ni in NiO the authors[78] evaluated f_{Co} for the given temperature range (see Fig. 4). These values of f_{Co} were then used to calculate the ratio of the jump frequencies of the impurity ions and the solvent ions, from which was finally obtained the ratio of the diffusion coefficients of Co and Ni (D_{Co}/D_{Ni}) in pure NiO.

The D_{Co}/D_{Ni} values calculated from the diffusion isotope effect agree well with the values obtained directly from experiments on the simultaneous diffusion of Co and Ni in NiO. This agreement between calculation and experiment confirms the validity of the assumptions made in the calculation (including a low value of the energy H_b for the interaction between an impurity cation and a vacancy, i.e. $H_b \ll kT$).

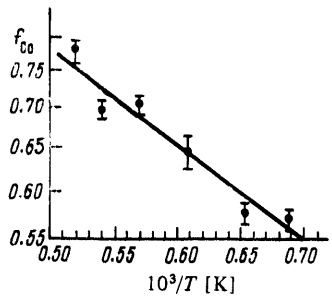


Figure 4. f_{Co} against $1/T$ for the diffusion of Co in NiO.[76]

VII. OTHER APPLICATIONS OF THE DIFFUSION ISOTOPE EFFECT

All the examples considered so far are typical of the practical application of the diffusion isotope effect in detailed studies of migration processes in metals and in ionic crystals. However, the possibilities of the isotopic method are not limited to these systems: the method can be used also to study van-der-Waals and molecular crystals.

Parker and coworkers[79] studied the diffusion of the krypton isotopes $^{78,86}Kr$ in solid argon, and found $E_{86}^{78} = 0.48 \pm 0.25$. This result suggests that the diffusion of Kr in solid Ar involves either a divacancy mechanism or a single vacancy mechanism with $f = 0.78$ and $\Delta K = 0.6$. The low value of ΔK is not surprising, since it can be shown that heavy impurity atoms have very small values of ΔK. Barton[80] calculated the isotope effect for this system theoretically, and obtained $\Delta K = 0.75-0.85$ (a value at the upper limit of experimental results). The calculated value of E_{86}^{78} for the divacancy mechanism is also not too different from the experimental value[79]. However, within the limitations of the model used it is not possible to select the preferred mechanism.

Fox and Sherwood[81] used the mass effect to identify the diffusion mechanism in solid benzene single crystals. The molecules $^{14}C\,^{12}C_5H_6$ and $^{12}C_6\,^2H_5\,^3H$ were used as tracers because their molar volumes are similar (and their spectral characteristics almost identical) to those of ordinary benzene. The authors therefore treated the labelled molecules as "isotopes" of benzene. The measured value $E = 0.8$ suggests mass transport by a single vacancy mechanism, with $f = 0.78$ and $\Delta K = 1$. Similar measurements were carried out on single crystals of naphthalene[82]. The equations for the diffusion isotope effect in solids have been used[83] to interpret data on the isotope effect in liquids. The diffusion of perdeuterobenzene and of ordinary benzene has been studied in chlorobenzene, n-octane, and cyclohexane. The results, which show a negligibly small "isotope effect" for the diffusion of benzene, made the authors conclude[83] that diffusion in these systems is controlled primarily by the viscosity of the solvent.

The diffusion isotope effect has been studied also in glasses (systems in which the structural units have no long-range order). Le Claire[84] observed a small isotope effect for the diffusion of sodium in a sodium silicate glass ($E_{24}^{22} = 0.24$) and concluded that mass transport in this system is by a relay mechanism. Similar measurements were made in other laboratories with the aim of determining the correlation factor or of identifying the mechanism of diffusion in glass[85,86].

A typical application of the diffusion isotope effect to the study of transport processes in disordered crystals was described by Robinson and Peterson[87], who measured the isotope effect for the diffusion of silver along the grain boundaries of metallic silver. The experimental value $\Delta K = 0.46$ can be used to select a series of f and ΔK values compatible with both experiment and theory[88]. The closest agreement between experiment and calculation was obtained for $\Delta K = 0.70-0.76$ and a correlation factor corresponding to the following vacancy–dislocation bond energies: 0.2 eV (vacancy at the centre of the dislocation), and 0.15 eV (vacancy at one interatomic distance from the centre of the dislocation). A measurement[87] of the isotope effect for the diffusion of silver in polycrystalline copper gave much lower values ($E = 0.16$), showing that the diffusion of silver impurity in copper has a high correlation, i.e. that the differences in the vacancy–dislocation bond energy are large. As a result, the silver tends to accumulate along the dislocations.

The separation of isotopes by diffusion has been studied also in geochemistry, because it yields information on the physicochemical conditions of natural processes and on their time scale. The isotopic variations of Mg, Ca, K, and Li in minerals have been examined in detail[89], and the migration parameters obtained have been used to reconstruct the thermal history of the minerals and to determine the temperature and time of their formation.

VIII. METHODS OF MEASURING THE DIFFUSION ISOTOPE EFFECT

According to Eqn.(8) the measurement of the diffusion isotope effect in practice reduces to determining the relative difference between the diffusion coefficients of the migrating isotopes. In order to obtain the E value with a precision of 5% the ratio $\Delta D/D_\beta$ must be measured with an error not exceeding 0.1%. In most experiments the parameters D_α and D_β cannot be measured to better than $\pm(1-2)\%$, and since the difference between the diffusion coefficients is usually between 2 and 3% this difference lies within the experimental uncertainty and is therefore not experimentally detectable.

The problem can be overcome by monitoring the diffusion of the two isotopes simultaneously. Since the diffusion conditions are identical, errors in the measurement of the diffusion temperature and time do not influence the ratio $\Delta D/D_\beta$. In an experiment of this type the precision of the measurement of $\Delta D/D_\beta$ is determined by the precision with which the isotope concentrations c_α and c_β are known. The ratio c_α/c_β can be determined by radio-isotope and mass-spectroscopic techniques to better than 0.1%. The most convenient (and therefore most often used) method is the radioactive indicator methods, which we shall examine in detail.

Mass-spectroscopic methods have been used in geochemical studies to measure the natural abundance ratios of stable isotopes[89]. The methods can be used also to study isotope effects in the diffusion of elements lacking convenient radioactive isotopes. Thus, E_7^6 for the diffusion of $^{6,7}Li$ in Na,[90] AfCl,[70] and TiO_2 [91] has been measured mass-spectrocopically. In this method of analysis the diffusion isotope effect can be calculated by the procedure proposed by Naumov and Ptashnik[70,92]. In the interpretation of mass-spectrometric data on the diffusion isotope effect it is very important to allow for the isotope fractionation which takes place in the ion source during the measurement. Neglect of this factor can lead to spuriously high (ten-fold, or even hundred-fold) results.

By using the radiometric method the concentration of the migrating isotopes can be determined in three ways.

1. If the difference between the half-lives $T_{1/2}^{\alpha}$ and $T_{1/2}^{\beta}$ is fairly large the ratio c_α/c_β can be determined by analysing the time dependence of the total activity.

$$c_{tot} = c_\alpha \exp(-\lambda_\alpha t) + c_\beta \exp(-\lambda_\beta t),$$

where c_{tot} is the measured total activity, λ_α and λ_β are the decay constants, and t is time (measured from the beginning of the experiment).

At present this procedure is the most widely used. If the half-life of one of the isotopes ($T_{1/2}^{\alpha}$, say) is small enough, a second measurement is made at time $t \geq 10T_{1/2}^{\alpha}$, when the short-lived isotope has decayed almost completely and the measured activity corresponds to the concentration of the long-lived isotope c_β. The concentration of the short-lived isotope is then given by the difference $c_\alpha = c_{tot} - c_\beta$.

2. If the isotopes used in the experiment are γ-emitters with their strongest spectral lines at sufficiently different energies, and if the isotopes decay to a significant extent during the measurement, the activity ratio of the isotopes can be expressed as

$$\frac{c_\alpha}{c_\beta} = \frac{(\lambda_\alpha/\lambda_\beta)(A_\alpha/A_\beta)\exp[(\lambda_\alpha - \lambda_\beta)t][1 - \exp(-\lambda_\beta\tau)]}{1 - \exp(-\lambda_\alpha\tau)};$$

where A_α and A_β are the areas under the gamma peak (corrected for background), t is the time elapsed from the beginning of the measurement on a series of samples, and τ is the time of the measurement of one particular sample.

3. If the chosen isotopes emit different radiations (one β-emitter and one γ-emitter, say) it is still possible to determine the concentrations of both isotopes simultaneously by placing the sample between suitable detectors.

We have dealt only with the measurement of the activity ratio of the migrating isotopes (c_α/c_β). We shall now show that this is sufficient for determining E_β^α. In this case of diffusion from a thin layer the concentration of the isotope (c) varies with the depth of penetration (x) and diffusion time (t) according to the expression

$$c = c_0 \exp(-x^2/4Dt),$$

where D is the diffusion coefficient of the isotope. For two isotopes we obtain the ratio

$$\frac{c_\alpha}{c_\beta} = \frac{c_{0\alpha}}{c_{0\beta}} \exp\left[-\frac{x^2}{4D_\alpha t} + \frac{x^2}{4D_\beta t}\right] = \frac{c_{0\alpha}}{c_{0\beta}} \exp\left[\frac{x^2}{4D_\alpha t}\left(\frac{D_\alpha}{D_\beta} - 1\right)\right];$$

$$\ln\frac{c_\alpha}{c_\beta} = \text{const} + \frac{x^2}{4D_\alpha t}\left[\frac{D_\alpha}{D_\beta} - 1\right] = \text{const} - \left[\frac{D_\alpha}{D_\beta} - 1\right]\ln c_\alpha.$$

Thus the relative difference between the diffusion coefficients of the isotopes can be obtained by analysing plots of $\ln(c_\alpha/c_\beta) = f(\ln c_\alpha)$. In this procedure the precision of the determination of the quantity $[D_\alpha/D_\beta - 1]$ depends primarily on the precision with which the relative activities of the isotopes (c_α/c_β) can be measured.

Because of the smallness of the diffusion isotope effect, most workers carry out a blank experiment (in parallel with the measurement of the concentration of the diffusing isotopes) in which the activity of an aliquot of the initial mixture of isotopes is monitored. A zero slope of the $\ln(c_\alpha/c_\beta) = f(\ln c_\alpha)$ plot for the blank experiment confirms that the observed effect arises wholly from diffusion phenomena.

The greatest care is needed in carrying out the isotope experiment. Not less than 10^6 counts should be used in the measurements of activity (in order to minimise the statistical error). In addition to $\ln(c_\alpha/c_\beta) = f(\ln c_\alpha)$ it is useful to plot also the relationship $\ln c_{\alpha,\beta} = f(x^2)$, which should be a straight line. The activity should change by at least three orders of magnitude with depth of penetration, because deviations from normal bulk diffusion, leading to distortions in the linear plot, can only be detected at considerable depths. The blank experiment is an essential part of the procedure. The importance of adhering to all these precautions is well illustrated by published measurements of the isotope effect for the diffusion of Ag in Pb. Herzig and coworkers[93] found $E_{111}^{105} = 1$, but a redetermination of the isotope effect in this system[53] gave $E_{111}^{105} = 0.25$. The latter value of the diffusion isotope effect satisfactorily explains the fast diffusion of Ag in Pb. This very large discrepancy between experimentally measured values of the isotope effect can be ascribed to the failure by Herzig and coworkers[93] to observe all the above precautions.

Isotope diffusion has been studied also in an electric field[59]. In this case the separation of the isotopes is more substantial, and can be used in practice to produce enrichment of the initial mixture with one of the isotopes. The precision of the measurement of the diffusion isotope effect increases with the extent of separation achieved. In these measurements the relative difference between the diffusion coefficients of the isotopes is replaced by its equivalent relative difference between the mobilities of the isotopes ($\Delta D/D_\beta = \Delta\mu/\mu_\beta$). Detailed discussions of the measurement of the diffusion isotope effect with the help of an electric field, and of the advantages of this method, are given in Refs.70 and 92.

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In conclusion we note that the importance of the diffusion isotope effect as a new method of gaining information on the details of migration processes in solids is recognised by the inclusion of special chapters on the advantages and applications of this method in all the recently published reviews and monographs devoted to diffusion[94-96].

REFERENCES

1. J.Hladik (Editor), "Physics of Electrolytes" (Translated into Russian), Moscow, 1978.
2. A.S.Nowick and J.J.Burton (Editors), "Diffusion in Solids (Recent Developments)", Academic Press, New York, 1975.
3. J.Manning, "Kinetics of the Diffusion of Atoms in Crystals" (Translated into Russian), Izd.Mir, Moscow, 1971.
4. J.G.Mullen, Phys.Rev., 121, 2649 (1961).
5. C.Zener, "Imperfections in Nearly Perfect Crystals", J.Wiley, New York, 1952.
6. I.Prigogine and T.Bak, J.Chem.Phys., 31, 1368 (1959).

7. S.Rice and H.Frisch, J.Chem.Phys., **32**, 1026 (1960).
8. C.Flynn, Phys.Rev., **171**, 682 (1968).
9. M.D.Feit, Phys.Rev., **B3**, 1223 (1971).
10. M.D.Feit, Phys.Rev., **B5**, 2145 (1972).
11. H.R.Glyde, Phys.Rev., **180**, 722 (1969).
12. B.N.Achar, Phys.Rev., **B2**, 3848 (1970).
13. A.D.Le Claire, Phil.Mag., **14**, 1271 (1966).
14. S.Z.Bokshtein (Editor), "Diffuziya v Metallakh s Ob"emno-tsentrirovannoi Reshetkoi" (Diffusion in Body-centred Cubic Metals), Izd.Metallurgiya, Moscow, 1969, p.180.
15. J.Mundy, L.Barr, and F.Smith, Phil.Mag., **14**, 785 (1966).
16. N.Nachtrieb, J.Weil, E.Catalano, and A.Lowson, J. Chem.Phys., **20**, 1189 (1952).
17. S.Rothman, N.Peterson, and J.Robinson, Phys. Status Solidi, **39**, 635 (1970).
18. R.Brown, J.Vorster, N.March, R.Perrin, and R.Bullough, Phil.Mag., **23**, 555 (1971).
19. L.Barr and A.D.Le Claire, Proc.Brit.Ceram.Soc., **1**, 109 (1964).
20. R.Brown, Z.Naturforsch., **26a**, 77 (1971).
21. J.Ebisuzaki, W.Kass, and M.O'Keeffe, Phil.Mag., **15**, 1071 (1967).
22. J.Ebisuzaki, W.Kass, and M.O'Keeffe, J.Chem. Phys., **46**, 1375 (1967).
23. J.Ebisuzaki, W.Kass, and M.O'Keeffe, J.Chem. Phys., **49**, 3329 (1968).
24. J.Sussmann and J.Wersmann, Phys.Status Solidi, **53(b)**, 419 (1972).
25. R.Katz, M.Guinan, and R.Borg, Phys.Rev., **B4**, 331 (1971).
26. S.Rothman and A.Lascar, J.Phys.Chem.Solids, **33**, 1061 (1972).
27. N.Bakker, Phys.Status Solidi, **31**, 271 (1969).
28. J.Mundy, Phys.Rev., **B3**,2431 (1971).
29. T.Neumann and R.Imm, J.Phys.Chem.Solids, **29**, 1613 (1968).
30. S.Rothman and N.Peterson, Phys.Status Solidi, **35**, 305 (1969).
31. V.Irmer and Feller-Kniepmeier, J.Appl.Phys., **43**, 953 (1972).
32. N.Peterson and S.Rothman, Phys.Rev., **163**, 645 (1967).
33. N.Peterson, L.Barr, A.D. Le Claire, J.Phys., **C6**, 2020 (1973).
34. C.Tomizuka, Symposium "Progress in Very High Pressure Research. Proceedings of the International Conference (France, 1960)", J.Wiley, New York, 1961.
35. R.Hannemann, R.Ogilvie and H.C.Gatos, Trans. AIME, **233**, 691 (1965).
36. M.Beyeler and J.Adda, J.Phys.(Paris), 29, 345 (1968).
37. M.Norton and C.Tomizuka, Bull.Amer.Phys.Soc., **15**, 390 (1970).
38. D.Yoon and D.Lazarus, Phys.Rev., **B5**, 4935 (1975).
39. P.McArdle, Bull.Amer.Phys.Soc., **13**, 489 (1968).
40. H.Mehrer and A.Seeger, Phys.Status Solidi, **35**, 313 (1969).
41. R.Simmons and R.Ballufi, Phys.Rev., **129**, 1533 (1963).
42. H.Bowden and R.Ballufi, Phil.Mag., **19**, 1001 (1969).
43. P.Reimers and D.Bartdorff, Phys.Status Solidi, **50**, 305 (1972).
44. H.Mehrer and A.Seeger, Phys.Status Solidi, **39**, 647 (1970).
45. N.Peterson, Phys.Rev., **136A**, 568 (1964).
46. C.Walter and N.Peterson, Phys.Rev., **178**, 922 (1969).
47. C.De Gonzalez and N.De Reca, J.Phys.Chem.Solids, **32**, 1067 (1971).
48. J.Mundy, C.Tse, and W.McFall, Phys.Rev., **B13**, 2349 (1976).
49. A.Batra, Phys.Rev., **159**, 487 (1967).
50. E.Stein, H.Mehrer, and A.Seeger, Phys.Status Solidi, (b), **75**, 361 (1976).
51. J.Mundy and W.McFall, Phys.Rev., **B8**, 5477 (1973).
52. J.Mundy and W.McFall, Phys.Rev., **B7**, 4363 (1973).
53. J.Miller, J.Mundy, L.Robinson, and R.Loess, Phys. Rev., **B8**, 2411 (1973).
54. J.Miller and W.Edelstein, Phys.Rev., **188**, 1081 (1969).
55. J.Mundy, J.Miller, and S.Rothman, Phys.Rev., **B10**, 2275 (1974).
56. V.Nelson and R.Friauf, Chem.Solids, **31**, 825 (1970).
57. F.Beniere, M.Beniere, and M.Chemla, Chem.Solids, **31**, 1205 (1970).
58. K.Tharmalingam and A.Lidiard, Phil.Mag., **6**, 1157 (1961).
59. V.B.Ptashnik, Fiz.Tverdogo Tela, **13**, 3212 (1971).
60. S.M.Klotzman, J.P.Polikarpova, G.A.Tatarinova, and A.N.Timofeev, Phys.Status Solidi, (b), **63**, 153 (1974).
61. H.Abbink and D.Martin, J.Phys.Chem.Solids, **27**, 205 (1966).
62. A.N.Murin, I.V.Murin, and V.P.Sivkov, Fiz.Tverdogo Tela, **15**, 142 (1973).
63. B.G.Lur'e, A.N.Murin, and I.V.Murin, Vestnik Leningrad.Univ., **4**, (22), 131 (1968).
64. M.Tosi and M.Doyama, Phys.Rev., **151**, 642 (1966).
65. N.Peterson and S.Rothman, Phys.Rev., **177**, 1329 (1969).
66. J.Boswara and A.Lidiard, Phil.Mag., **16**, 805 (1967).
67. F.Nicolas, Thesis, Paris, 1971.
68. A.N.Murin, I.V.Murin, V.I.Portnyagin, and A.M.Andreev, Fiz.Tverdogo Tela, **15**, 2838 (1973).
69. P.Süptiz, Phys.Status Solidi, **12**, 555 (1965).
70. V.B.Ptashnik, Fiz.Tverdogo Tela, **13**, 1066 (1971).
71. M.Volpe and J.Reddy, J.Chem.Phys., 53, 1117 (1970).
72. W.Chen, N.Peterson, and W.Reeves, Phys.Rev., **186**, 887 (1969).
73. M.Volpe, N.Peterson, and J.Reddy, Phys.Rev., **B3**, 1417 (1971).
74. M.Hayakawa, J.Cohen, and T.Reed, J.Amer.Ceram. Soc., **55**, 100 (1972).
75. P.Hembree and J.Wagner, Trans.Met.Soc,AIME, **245**, 1547 (1969).
76. W.Chen and N.Peterson, J.Phys.Chem.Solids, **36**, 1097 (1975).
77. F.Koch and J.Cohen, Acta Cryst., **B25**, 275 (1969).
78. W.Chen and N.Peterson, J.Phys.Chem.Solids, **33**, 881 (1972).
79. E.Parker, B.Smith, and H.Glyde, Phys.Rev., **188**, 1371 (1969).
80. J.Barton, Phys.Rev., **B2**, 5010 (1970).
81. R.Fox and J.Sherwood, Trans.Faraday Soc., **67**, 3364 (1971).
82. E.Hampton and J.Sherwood, J.Chem.Soc.Faraday Trans., **71**, 1392 (1975).
83. J.Shankland, P.Dunlop, and L.Barr, Phys.Rev., **B12**, 2249 (1975).
84. H.Euring, D.Henderson, and W.Jost (Editors), "Physical Chemistry", Vol.10, Ch.5, Academic Press, New York, 1970.
85. V.A.Zhabrev, V.V.Moiseev, and V.N.Sigaev, Fiz. Khim.Stekla, **1**, 475 (1975).
86. C.Lim and D.Day, J.Amer.Ceram.Soc., **60**, 473 (1977).
87. J.Robinson and N.Peterson, Surface Sci., **31**, 586 (1972).

88. M.Doyama and R.Cotterill, Supl.Jap.Inst.Met., **9**, 55 (1968).
89. A.A.Alferovskii, Thesis, Leningrad, 1974.
90. A.N.Naumov and G.A.Ryskin, Fiz.Tverdogo Tela, **7**, 695 (1965).
91. O.Johnson and H.Krause, J.Appl.Phys., **37**, 668 (1966).
92. A.N.Naumov and V.B.Ptashnik Fiz.Tverdogo Tela, **8**, 3590 (1966).
93. C.Herzig, T.Neumann, and D.Wolter, Z.Naturforsch., **26a**, 1477 (1971).
94. A.N.Murin, Symposium "Khimiya Nesovershennykh Ionnykh Kristallov" (Chemistry of Imperfect Ionic Crystals), Izd.Leningrad.Univ., 1975, p.270.
95. V.Boldyrev and K.Meier (Editors), "Festkörperchemie (Beitrage aus Forschung und Praxis)", VEB, Leipzig, 1973.
96. B.S.Bokshtein, S.Z.Bokshtein, and A.A.Zhukhovitskii, "Termodinamika i Kinetika Diffuzii v Tverdykh Telakh" (Thermodynamics and Kinetics of Diffusion in Solids), Izd.Metallurgiya, Moscow, 1974.

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