On the Correlation Factor for Diffusion in the f.c.c.- and NaCl-Structure

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The correlation factor for impurity diffusion in the f.c.c.-structure by means of a vacancy mechanism is calculated as a function of nine distinct vacancy-atom exchange rates.

Furthermore an expression is derived for the correlation factor for diffusion of aliovalent impurities in the NaCl-structure including an electrostatic impurity-vacancy interaction.

Introduction

If one considers diffusion of an aliovalent ion in an ionic crystal by means of a vacancy mechanism, one has to take into account an electrostatic interaction between this ion and the vacancy. This is so because both the impurity and the vacancy will carry an effective charge of opposite sign[1]. This interaction has a Coulombic form[1,2].

However, the interaction energy will depart from the Coulombic value as the impurity-vacancy distance decreases to the nearest neighbour position.

This interaction will have an influence on e.g. the correlation factor for diffusion, a quantity which plays an essential role in the interpretation of diffusion and isotope effect measurements. We have calculated this influence for the NaCl-structure using the method of calculation developed in[3,4].

However, as a first step we have to compute the correlation factor for diffusion in a nine-frequency model in the f.c.c.-structure without an electrostatic impurity-vacancy interaction.

Calculation of the Correlation Factor

A) Diffusion in the f.c.c.-Strukture in a nine-Frequency Model without Electrostatic Impurity-Vacancy Interaction

So far the correlation factor for diffusion in the f.c.c.-structure by means of a vacancy mechanism has been calculated in a model, which distinguishes five different exchange rates of the vacancy, namely w_2, being the impurity-vacancy exchange rate, w_1, the rate of exchange of a vacancy neighbouring an impurity with any of the solvent atoms that are also nearest neighbours of the impurity, k_1, the rate of exchange of the vacancy with any atom, resulting in a dissociation of the vacancy from the impurity, the associating jump frequency k_2, and the jump frequency w_0 in the pure solvent.

The result is[5,6,7,3]

$$f = (2\,w_1 + 7\,F\,k_1)/(2\,w_1 + 2\,w_2 + 7\,F\,k_1)\,, \tag{1}$$

where

$$7\,F = 7 - \frac{10\,\alpha^4 + 180.5\,\alpha^3 + 927\,\alpha^2 + 1341\,\alpha}{2\,\alpha^4 + 40.2\,\alpha^3 + 254\,\alpha^2 + 597\,\alpha + 436} \tag{2}$$

and

$$\alpha = k_2/w_0\,. \tag{3}$$

However, among the k_1-jumps we notice jumps to second, third and fourth nearest neighbours of the tracer, so it seems reasonable to distinguish three quantities k_1, namely k_1, k_1' and k_1'', respectively and also k_2, k_2' and k_2'' [3]. In such a nine-frequency model we have obtained the following expression for f

$$f = \frac{2\,w_1 + 2\,F_1\,k_1 + 4\,F_2\,k_1' + F_3\,k_1''}{2\,w_1 + 2\,w_2 + 2\,F_1\,k_1 + 4\,F_2\,k_1' + F_3\,k_1''} \tag{4}$$

where

$$2\,F_1 = 2 - \frac{274\,\alpha+130\,\alpha'+24.9\,\alpha''+153\,\alpha\alpha'+34.7\,\alpha\alpha''+19.7\,\alpha'\,\alpha''+27.3(\alpha')^2+19.4\,\alpha(\alpha')^2+3.04(\alpha')^2\alpha''+17.0\,\alpha\alpha'\,\alpha''+2\,\alpha(\alpha')^2\alpha''}{442+274\,\alpha+269\,\alpha'+58.1\,\alpha''+153\,\alpha\alpha'+34.7\,\alpha\alpha''+30.2\,\alpha'\,\alpha''+36.3(\alpha')^2+19.4\,\alpha(\alpha')^2+3.75(\alpha')^2\alpha''+17.0\,\alpha\alpha'\,\alpha''+2\,\alpha(\alpha')^2\alpha''} \tag{5}$$

$$4\,F_2 = 4 - \frac{130\,\alpha+534\,\alpha'+81.9\,\alpha''+321\,\alpha\alpha'+56.0\,\alpha\alpha''+71.7\,\alpha'\,\alpha''+109(\alpha')^2+58.2\,\alpha(\alpha')^2+11.2(\alpha')^2\alpha''+41.5\,\alpha\alpha'\,\alpha''+6\,\alpha(\alpha')^2\alpha''}{442+274\,\alpha+269\,\alpha'+58.1\,\alpha''+153\,\alpha\alpha'+34.7\,\alpha\alpha''+30.2\,\alpha'\,\alpha''+36.3(\alpha')^2+19.4\,\alpha(\alpha')^2+3.75(\alpha')^2\alpha''+17.0\,\alpha\alpha'\,\alpha''+2\,\alpha(\alpha')^2\alpha''} \tag{6}$$

$$F_3 = 1 - \frac{24.9+81.9\,\alpha'+58.1\,\alpha''+50.7\,\alpha\alpha'+34.7\,\alpha\alpha''+30.2\,\alpha'\,\alpha''+16.7(\alpha')^2+9.05\,\alpha(\alpha')^2+3.75(\alpha')^2\alpha''+17.0\,\alpha\alpha'\,\alpha''+2\,\alpha(\alpha')^2\alpha''}{442+274\,\alpha+269\,\alpha'+58.1\,\alpha''+153\,\alpha\alpha'+34.7\,\alpha\alpha''+30.2\,\alpha'\,\alpha''+36.3(\alpha')^2+19.4\,\alpha(\alpha')^2+3.75(\alpha')^2\alpha''+17.0\,\alpha\alpha'\,\alpha''+2\,\alpha(\alpha')^2\alpha''} \tag{7}$$

and

$$\alpha = k_2/w_0\,, \quad \alpha' = k_2'/w_0\,, \quad \alpha'' = k_2''/w_0\,. \quad (8)-(10)$$

The quantities F_1, F_2 and F_3 have the physical meaning that they are the probabilities that the vacancy does not return to the impurity after a k_1, k_1' and k_1''-jump respectively.

Calculating this, we have supposed that the vacancy is "effectively lost" beyond the nineth shell, which consists of all those positions which can be reached by the tracer in at least nine jumps. I.e., when the vacancy has passed this boundary it is assumed not to return at all to the impurity, or to return from random direction.

The equations given above are rather complex. However, it will be clear that when the physically less realistic five-frequency model is applied, it takes not much sense to attach great value to very accurately calculated coefficients in the expression (2) for F. In the case of self-diffusion the expression for f [Eq. (4)] is reduced to the value .7818, which is almost equal to the exact value .7815[8].

We have not given details of the calculations here, because we have proceeded in exactly the same way as in[3,4].

B) Diffusion in the NaCl-Structure Including Coulomb Vacancy-Impurity Interaction

At larger separations the interaction energy between a divalent cation impurity and a vacancy in e.g. NaCl is given by [1,2]

$$E = -\,e^2/4\pi\varepsilon r\,, \tag{11}$$

where $-e$ is the charge of the electron, ε is the dielectric constant and r is the impurity-vacancy distance. When a vacancy jumps from position $\boldsymbol{r}_i$ to position $\boldsymbol{r}_j$ the difference in electrostatic energy between the initial and final state is

$$\Delta E = (e^2/4\pi\varepsilon)\,[1/r_i - 1/r_j]\,. \tag{12}$$

We shall suppose — as in[4] — that, when the atom is situated in the saddle point halfway between these positions a change of half this amount has occurred. The corresponding jump frequency is then given by

$$w_{ij} = w_0 \exp\left\{-\frac{c}{k\,T}\left[\frac{1}{r_i} - \frac{1}{r_j}\right]\right\}, \tag{13}$$

w_0 being the exchange rate for cation self-diffusion. c is defined as

$$c = e^2/8\pi\varepsilon a\,, \tag{14}$$

where a is the lattice parameter. So in Eq. (13) r_i and r_j are expressed in terms of this lattice parameter.

To get a notion of the value of c we shall calculate c for the case of NaCl. For NaCl we have $a = 5.6$ Å and $\varepsilon = 5.6\,\varepsilon_0$, which yields

$$c \cong 0.23\ \text{eV}\,. \tag{15}$$

If we proceed in the same way as in [4], we find expressions for F_1, F_2 and F_3. The coefficients are given in Table 1, calculated for seven shells around the tracer and for several values of $c/k\,T$.

To make clear what happens to the quantities F_1, F_2 and F_3, when there is an electrostatic interaction between the vacancy and the impurity we shall proceed as follows. Let us suppose that the difference in activation energy of the jumps k_2, k_2' and k_2'' is caused exclusively by the difference in the Coulomb part of the energy, i.e. we make the assumption that there is no difference in the elastic

Table 1. The coefficients occuring in the expressions (5), (6), and (7) for various values of $c/k\,T$, taking the sevenht shell as a boundary.

Table 1a. The coefficients occuring in the denominator of the expressions (5), (6), and (7) (all expressions have the same denominator).

$c/k\,T$	0	1	2.5	5
coeff. of $\alpha(\alpha')^2\alpha''$	2	2	2	2
coeff. of $\alpha\alpha'\alpha''$	17.0	16.0	14.6	13.1
coeff. of $\alpha(\alpha')^2$	19.4	18.8	18.3	18.0
coeff. of $(\alpha')^2\alpha''$	3.75	3.24	2.61	1.85
coeff. of $\alpha'\alpha''$	30.3	24.2	17.5	10.6
coeff. of $(\alpha')^2$	36.5	30.6	23.9	16.6
coeff. of $\alpha\alpha''$	34.8	30.2	25.1	20.1
coeff. of $\alpha\alpha'$	154	139	122	107
coeff. of α''	58.4	42.6	27.1	13.7
coeff. of α'	270	207	143	83.5
coeff. of α	277	228	178	136
constant	448	304	176	80.0

Table 1b. The coefficients occuring in the numerator of Equation (5).

c/kT	**0**	**1**	**2.5**	**5**
coeff. of $\alpha(\alpha')^2\alpha''$	2	2	2	2
coeff. of $\alpha\alpha'\alpha''$	17.0	16.0	14.6	13.1
coeff. of $\alpha(\alpha')^2$	19.4	18.8	18.3	18.0
coeff. of $(\alpha')^2\alpha''$	3.02	2.73	2.32	1.75
coeff. of $\alpha'\alpha''$	19.5	16.6	12.9	8.58
coeff. of $(\alpha')^2$	27.3	24.2	20.2	15.2
coeff. of $\alpha\alpha''$	34.8	30.2	25.1	20.1
coeff. of $\alpha\alpha'$	154	139	122	107
coeff. of α''	24.6	19.5	13.7	7.67
coeff. of α'	130	108	83.5	56.5
coeff. of α	277	228	178	136

Table 1c. The coefficients occurring in the numerator of Equation (6).

c/kT	0	1	2.5	5
coeff. of $\alpha(\alpha')^2\alpha''$	6	6	6	6
coeff. of $\alpha\alpha'\alpha''$	41.4	39.5	37.2	34.3
coeff. of $\alpha(\alpha')^2$	58.4	56.8	55.0	54.0
coeff. of $(\alpha')^2\alpha''$	11.2	9.73	7.84	5.54
coeff. of $\alpha'\alpha''$	71.7	58.3	43.1	26.8
coeff. of $(\alpha')^2$	110	91.8	71.7	49.8
coeff. of $\alpha\alpha''$	55.3	51.4	46.1	39.8
coeff. of $\alpha\alpha'$	322	299	275	255
coeff. of α''	81.3	62.6	42.5	22.7
coeff. of α'	536	422	302	186
coeff. of α	130	108	83.5	56.5

Table 1d. The coefficients occurring in the numerator of Equation (7).

c/kT	0	1	2.5	5
coeff. of $\alpha(\alpha')^2\alpha''$	2	2	2	2
coeff. of $\alpha\alpha'\alpha''$	17.0	16.0	14.6	13.1
coeff. of $\alpha(\alpha')^2$	8.98	9.88	10.3	11.3
coeff. of $(\alpha')^2\alpha''$	3.75	3.24	2.61	1.85
coeff. of $\alpha'\alpha''$	30.3	24.2	17.5	10.6
coeff. of $(\alpha')^2$	16.6	15.2	13.3	10.5
coeff. of $\alpha\alpha''$	34.8	30.2	25.1	20.1
coeff. of $\alpha\alpha'$	50.3	51.0	52.1	54.7
coeff. of α''	58.4	42.6	27.1	13.7
coeff. of α'	81.3	62.6	42.5	22.7
coeff. of α	24.6	26.2	28.6	33.2

contribution to the saddle point energy for vacancy jumps to second, third and fourth nearest neighbour positions (cf. the five-frequency model). Then it is easy to see that

$$\frac{\alpha'}{\alpha} = \frac{k_2'}{k_2} = \exp\left\{\frac{c}{k\,T}\left(\frac{1}{r_2} - \frac{1}{r_3}\right)\right\}, \qquad (16)$$

$$\frac{\alpha''}{\alpha} = \frac{k_2''}{k_2} = \exp\left\{\frac{c}{k\,T}\left(\frac{1}{r_2} - \frac{1}{r_4}\right)\right\}. \qquad (17)$$

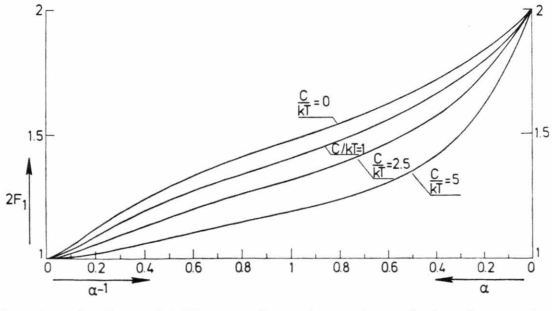

Fig. 1a. A plot of $2F_1$ as a function of $\alpha = k_2/w_0$ for various values of c/kT if the only difference in activation energy between k_2, k_2' and k_2'' jumps is due to Coulombic interaction, and taking the seventh shell as a boundary.

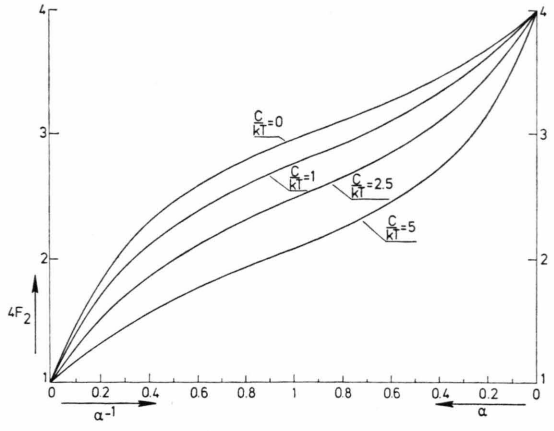

Fig. 1b. A plot of $4F_2$ as a function of $\alpha = k_2/w_0$ for various values of c/kT, if the only difference in activation energy between k_2, k_2' and k_2'' jumps is due to Coulombic interaction, and taking the seventh shell as a boundary.

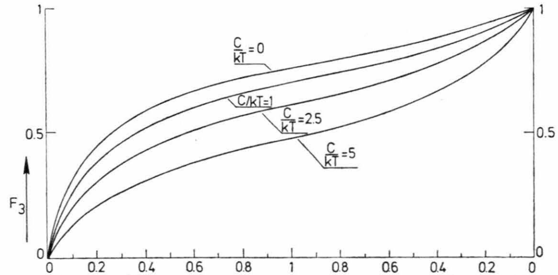

Fig. 1c. A plot of F_3 as a function of $\alpha = k_2/w_0$ for various values of c/kT, if the only difference in activation energy between k_2, k_2' and k_2'' jumps is due to Coulombic interaction, and taking the seventh shell as a boundary.

After substituting (16) and (17) in Eq. (5), (6) and (7) we obtain F_1, F_2 and F_3 as a function of α. Thus, in this case it is possible to make a plot of F_1, F_2 and F_3 versus α. We have performed this for different values of c/kT, again for seven shells around the tracer, and we see that Coulombic interaction causes a decrease of F_1, F_2 and F_3 in agreement with our expectation: as a result of an electrostatic interaction the vacancy will have a tendency to remain in the neighbourhood of the tracer, so there is less probability that the vacancy dissociates definitively from the tracer (Fig. 1). The consequence is that f will be smaller than without electrostatic interaction. This result is essentially the same as has been calculated by Mehrer[9] and by Bakker and Mirani[4, 10] for diffusion of group V impurities in silicon and germanium.

In particular an interesting case occurs when

$$w_2 \gg w_1 + F_1 k_1 + 2 F_2 k_1' + \tfrac{1}{2} F_3 k_1'' , \qquad (18)$$

because the diffusion coefficient then becomes

$$D \sim w_1 + F_1 k_1 + 2 F_2 k_1' + \tfrac{1}{2} F_3 k_1'' , \qquad (19)$$

So in this case D is completely determined by the jump frequencies of the host-ions, whereas the jump frequency of the diffusing ion itself does not occur explicitly. In the case

$$w_2 \ll w_1 + F_1 k_1 + 2 F_2 k_1' + \tfrac{1}{2} F_3 k_1'' \qquad (20)$$

$f = 1$ and furthermore

$$D \sim w_2 . \qquad (21)$$

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