

CONTRIBUTION OF ASSOCIATED VACANCIES TO SELFDIFFUSION OF CATIONS IN NaCl CRYSTALS

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The contribution of vacancies, associated into tightly-bound complexes with divalent cation admixtures, to the selfdiffusion coefficient of cations has been mathematically expressed. Considered was the model of a complex limited to the ground state and the first excited state as well as that including all excited states of the complex which can be reached by a direct jump from the ground state.

INTRODUCTION

In NaCl, selfdiffusion of cations is intermediated by a vacancy mechanism. As vacancies may be free or associated into complexes with divalent admixtures, diffusion flow consists of two components. The component resulting from migration of free cation vacancies is characterized by the diffusion coefficient D_f , while the component carried by associated cation vacancies has the diffusion coefficient D_a . The component connected with the associated vacancies is important especially in crystals doped with divalent cation admixtures.

Since free vacancies carry also the electric current in the crystal, D_f will be apparently connected with the cation component of ionic conductivity. In the region of temperatures where the concentration of thermally produced vacancies is negligible, the relation

$$D_f = 3.13 a^2 w_0 (1 - p) c \quad (1)$$

will be valid [1]; a is the anion-cation distance, w_0 the probability of the jump of the free vacancy into a definite neighbouring site in 1 second, p the degree of association of admixtures into complexes, i. e. the ratio of the concentration of the admixture associated into complexes with vacancies to the total concentration of the admixture c (in molar fractions).

The theoretical expression of D_a is known only for complexes tightly bound in the ground state [2]. In this case we have

$$D_a = \frac{4}{3} f(w_2/w_1) c p w_1 a^2 \quad (2)$$

where w_1 and w_2 are the probabilities of the jump of an associated vacancy into another definite associated position and into the position of the admixture, respectively, in 1 second. The correlation function $f(w_2/w_1)$ for selfdiffusion by a mechanism of vacancies associated into complexes tightly bound in the ground state is known for the NaCl lattice for various values of the ratio w_2/w_1 [2, 3]. In this case the selfdiffusion coefficient of cations D will be determined by the relation

$$D = D_f \left[1 + \frac{4}{3 \times 3.13} \frac{w_1}{w_0} f(w_2/w_1) \frac{p}{1-p} \right]. \quad (3)$$

Experiments with the NaCl + CaCl₂ crystals have shown that within the temperature range of 300–600 °C, where the concentration of thermally produced vacancies is negligible, the following empirical relation was valid [4]

$$D = D_f \left[1 + C \frac{p}{1-p} \right]. \quad (4)$$

The experimentally obtained values of the coefficient C depended, in agreement with equation (3), only on temperature, but they were always substantially higher, as those obtained from equation (3), applying the experimentally determined temperature dependences of w_0 [4], w_1 [5, 6] and w_2 [7, 8]. Consequently it appears that the required condition of complexes tightly bound in the ground state is too strict.

For this reason, we have made an attempt to express mathematically the contribution of associated vacancies to the selfdiffusion coefficient of cations for more complicated structures of the admixture-vacancy complexes and to find relations analogous to equation (3) for various models of complexes. A comparison of these theoretically determined dependences D on the concentration of the admixture and on temperature with experimentally obtained data makes it possible to determine the most probable structure of the complex [4].

THEORY

It follows from theoretical calculations [9, 10] and some experiments [11, 12] that the energy of association of the complexes in the ground state, i. e. those with a vacancy in the nearest neighbouring position from the admixture, should not differ in NaCl from that of the excited complexes, i. e. those with a vacancy at a distance of $2a$ from the admixture, by more than 10 %. It is consequently probable that the complex will not be bound only in the ground

state and that its reorientation will also include vacancy jumps from the ground state into the excited state with the frequency of w_3 and vice versa with the frequency of w_4 .

In NaCl, the most probable is the model of a complex including the ground state with twelve possible orientations as well as the first excited state with six possible orientations. In equilibrium the following relation for the distribution of associated vacancies to both states must be valid

$$\frac{1}{6} p_0 w_3 = \frac{1}{3} p_1 w_4 \quad (5)$$

where p_0 and p_1 are the degrees of association in the ground state and in the excited state, respectively. At the same time

$$p = p_0 + p_1 \quad (6)$$

is valid and therefore

$$p_1 = \frac{1}{2} \frac{p_0 w_3}{w_4} \quad (7)$$

$$p_0 = \frac{p}{1 + \frac{1}{2} w_3/w_4}. \quad (8)$$

According to the theory of correlated jumps [13]

$$D = \frac{1}{6} f I \Gamma^2 \quad (9)$$

(Γ being the jump distance, I the frequency of jumps of the diffusing tracer ion and f the corresponding correlation function). From each ground position the associated vacancy may carry out four jumps to another ground position and two jumps to an excited position. The vacancy can reach the ground state from each excited position by four jumps. Therefore

$$\Gamma = 12c(1-p)w_0 + 12 \times \frac{1}{12} c p_0 4w_1 + 6 \times \frac{1}{12} c p_0 4w_3 + 12 \times \frac{1}{6} c p_1 2w_4. \quad (10)$$

The first member on the right side of equation (10) is the contribution of free vacancies to the jumps of the tracer, the second member represents the jumps of the tracer in the ground sphere of the complex, the third member corresponds to the jumps of the tracer from the excited sphere of the complex into the ground sphere, while the fourth member corresponds to the opposite jumps. Direct jumps between the sites of the excited sphere are not possible owing to their great distance from one another. In calculations tightly bound complexes

were considered, i. e. the dissociation of complexes was neglected. Inserting relations (7) and (8) into (10) we obtained

$$r = 12c \left[(1-p)w_0 + \frac{1}{3} \frac{p}{1 + \frac{1}{2} w_3/w_4} (w_1 + w_3) \right] \quad (11)$$

Substituting equation (10) into equation (9) yields (as $r = \sqrt{2}a$)

$$D = 4a^2c \left[(1-p)w_0 \times 0.78 + \frac{1}{3} \frac{p}{1 + \frac{1}{2} w_3/w_4} \left(X_1 + X_2 \frac{w_3}{w_1} \right) w_1 \right] \quad (12)$$

0.78 being the correlation factor for cation selfdiffusion by free vacancies [2], X_1 and X_2 correlation functions for the other types of jumps. Applying equation (1) we obtain

$$D = D_f \left[1 + \frac{1}{3 \times 0.78} \frac{p}{1-p} \frac{w_1/w_0}{1 + \frac{1}{2} w_3/w_4} \left(X_1 + X_2 \frac{w_3}{w_1} \right) \right] \quad (13)$$

$$C = \frac{1}{3 \times 0.78} \frac{w_1/w_0}{1 + \frac{1}{2} w_3/w_4} \left(X_1 + X_2 \frac{w_3}{w_1} \right) \quad (13a)$$

This type of complexes gives dependence $D(p)$, which is in agreement with that obtained experimentally [4] and with the independence of the coefficient C on the concentration of the admixture. However, the temperature dependence of C cannot be theoretically determined until the correlation functions X_1 , X_2 have been tabulated.

The simplified model of a complex, including all direct vacancy jumps from the ground state of the complex into an excited state with equal probability, can be evaluated also quantitatively. In NaCl such an excited complex would have 42 possible orientations. The excited state can be reached from the ground state by seven jumps and from the average excited state (not all the excited positions are equivalent) the ground state can be reached by two various jumps. We are still considering tightly bound complexes and exclude vacancy jumps between the sites of the excited sphere. In analogy with equation (10) we obtain

$$r = 12c(1-p)w_0 + \frac{1}{12} 12cp_0^4 w_1 + \frac{1}{12} 42cp_0^2 w_3 + \frac{1}{42} 12cp_1^7 w_4 \quad (14)$$

To obtain an equilibrium distribution of associated vacancies the following relation must be valid

$$\frac{7}{12} p_0 w_3 = \frac{7}{42} p_1 w_4 \quad (15)$$

It follows from equations (6) and (15) that

$$p_1 = \frac{p_0 w_3}{w_4} \frac{7}{2} \quad (16)$$

$$p_0 = \frac{p}{1 + \frac{7}{2} w_3/w_4} \quad (17)$$

$$r = 12c \left[(1-p)w_0 + \frac{1}{3} \frac{p}{1 + \frac{7}{2} w_3/w_4} \left(w_1 + \frac{7}{2} w_3 \right) \right] \quad (18)$$

In analogy with equations (12), (13) we obtain

$$D = 4a^2c \left[(1-p)w_0 \times 0.78 + \frac{1}{3} \frac{p}{1 + \frac{7}{2} w_3/w_4} w_1 \left(X_1 + \frac{7}{2} X_2 w_3/w_1 \right) \right] \quad (19)$$

$$D = D_f \left[1 + \frac{1}{3 \times 0.78} \frac{p}{1-p} \frac{w_1/w_0}{1 + \frac{7}{2} w_3/w_4} \left(X_1 + \frac{7}{2} X_2 w_3/w_1 \right) \right] \quad (20)$$

$$C = \frac{1}{3 \times 0.78} \frac{w_1/w_0}{1 + \frac{7}{2} w_3/w_4} \left(X_1 + \frac{7}{2} X_2 w_3/w_1 \right) \quad (20a)$$

The correlation functions X_1 and X_2 for this model of complex, commonly used for metals, are tabulated [13] for different w_2/w_1 , w_3/w_1 and w_4/w_0 ratios. As the complexes in metals are only loosely bound, (equation (19) is not valid for metals) the tabulated value of w_0 [13] denotes also the probability of all vacancy jumps from the excited state leading not to the ground one. We neglected these jumps in our calculations because in NaCl the association energy of the ground and of the first excited state is fairly high and thus the probabilities of these jumps are low. In the case of tightly bound complexes, the jumps of free vacancies with a probability of w_0 have no influence on the motion of the complexes and on the correlation functions. Hence only the maximum tabulated value of w_4/w_0 ($= 10^5$) could be used.

The latter model of the complex is not entirely adequate in NaCl, because the association energy of the vacancy varies considerably with its distance

from the admixture and consequently the corresponding probabilities of the jumps into various non-equivalent sites of the excited sphere vary, too. However, it enables to estimate the value of the coefficient C for complexes not limited to the ground state only. The theoretically predicted form of the dependence D/g for this type of complexes is in agreement with the experimentally obtained form (4) and in agreement with the experiments the theoretically predicted C should depend only on temperature.

CONCLUSION

We expressed mathematically the contribution of cation vacancies, associated into complexes with divalent cation admixtures, to the selfdiffusion of the cations in ionic crystals of the NaCl type for tightly bound complexes existing also in some excited states. We considered: 1) the model of a tightly bound, complex limited to the ground state and to the first excited one, i. e. with a vacancy at a distance of $(2a)^2$ or of $2a$ from the admixture and 2) the model including all excited states of the complex which can be reached by direct jumps from the ground state.

In both cases under consideration, as well as in the case of complexes limited to the ground state only, theoretical considerations led to the dependence of the diffusion coefficient on the degree of association, which can be written in the form of equation (4), which was experimentally verified [4]. The quantitative theoretical calculations of the coefficient C were accomplished only for complexes in the ground state (equation (3) with $w_0 = 8.22 \times 10^{13} \exp(-0.74/kT)$ [4]; $w_1 = 9 \times 10^{13} \exp(-0.702/kT)$ [5]; $w_2 = 10^{14} \exp(-0.9/kT)$ [8]) and for our model sub 2). The quantitative evaluation of the

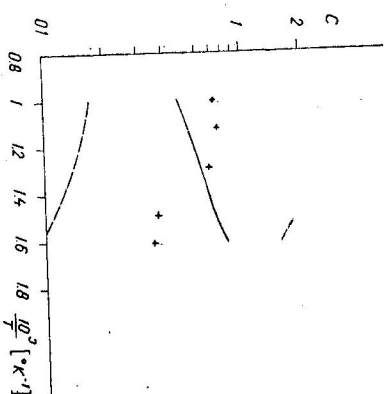


Fig. 1. Temperature dependence of the coefficient C given by the ratio of the contribution of one associated vacancy to that of one free vacancy to the selfdiffusion coefficient of cations in the NaCl + CaCl_2 crystals (+ — experimentally determined values; dashed line — calculated according to equation (20); full line — calculated according to equation (3)).

most probable model sub 1) has to be completed by the calculation of the necessary correlation functions.

The extension of the term complex to excited states, (model sub 2)) improved the agreement between the theoretically predicted and the experimentally determined C (Fig. 1) [4]. Full agreement of both values has not been achieved, most probably because of the fact that the model sub 1) would be more adequate and also because the temperature dependences of the jump probabilities used in theoretical calculations ($w_1 = 9 \times 10^{13} \exp(-0.76/kT)$; $w_2 = 9 \times 10^{13} \exp(-0.68/kT)$; $w_4 = 9 \times 10^{13} \exp(-0.63/kT)$) [12] are not yet sufficiently verified.

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