ON PROBLEMS OF DEFORMATION OF PENETRATION PLOTS FOR THE DIFFUSION OF DIVALENT IMPURITIES IN ALKALI HALIDES

О ПРОБЛЕМЕ ДЕФОРМАЦИИ ДИФФУЗИОННЫХ ПРОФИЛЕЙ ПРИ ДИФФУЗИИ ДВУВАЛЕНТНЫХ ПРИМЕСЕЙ В АЛКАЛИЧЕСКИХ ГАЛОГЕНИДАХ

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A deformation of the diffusion profiles often takes place close to the crystal surface, when we investigate divalent impurity diffusion in alkali halides [1—5]. The profile anomaly is characterized in general by a lowering of the concentration of the diffusing species near the crystal surface, which process may lead to the formation of a plateau [5]. In some cases even a maximum lying deeply in the diffusion region has been observed [1, 4]. Most of the attempts to explain the deformation of the profiles resulted in the conclusion that near the surface of the crystals there exists a region, the properties of which differ from those of the homogeneous bulk. If we assume this conclusion to be valid, the assumption of the existence of a gradient in the diffusion coefficient near the surface of the crystal is substantiated. The purpose of the present paper is to investigate the influence of the gradient in the diffusion coefficient on the character of the diffusion profiles.

When we consider planar diffusion along the abscisa in the case of a gradient of the diffusion coefficient, the flow J of atoms is given by the relation [6]

$$J = -\frac{\partial}{\partial x}[cD(x)],$$

(1)

where c is the concentration of the diffusing substance, $D(x)$ stands for the diffusion coefficient. The continuity equation which respect to (1) takes the form

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left\{\frac{\partial}{\partial x}[cD(x)]\right\} = D(x)\frac{\partial^2 c}{\partial x^2} + 2D'(x)\frac{\partial c}{\partial x} + D''(x)c.$$

(2)

The solution $c(x, t)$ of the equation represents the distribution of the diffusing impurity in the crystal and can be calculated numerically. Let us consider the planar diffusion through unit area into a semiinfinite medium. The crystal is assumed to be divided into layers of thickness d. The duration of the diffusion is also divided into intervals τ. The magnitude of the particular intervals has to obey the

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condition $D\tau/d^2 < 1/2$, which express the condition for the convergence of the solution (2) [7]. The mean concentration of the impurity in the i-th layer will be denoted by c_i^l. If we assume the intervals to be sufficiently small, the particular derivatives in (2) can be rewritten by means of finite differences [7]. Then we obtain

$$c_i^{l+1} = c_i^l + \left\{ [D(x)]_i \frac{c_{i+1}^l - 2c_i^l + c_{i-1}^l}{d^2} + 2[D'(x)]_i \frac{c_{i+1}^l - c_i^l}{d} + [D''(x)]_i \, c_i^l \right\} \tau . \qquad (3)$$

Equation (3) enables us to calculate the distribution of the impurity concentration in a given layer by means of the data characterizing the preceding time inte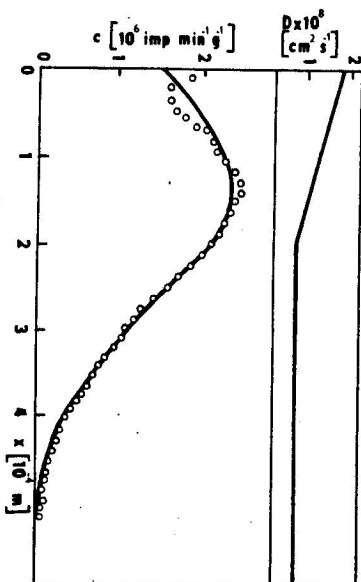rval. The respective values of $[D(x)]_i$, $[D'(x)]_i$, resp. $[D^*(x)]_i$ for particular layers should be determined from an assumed x-dependence of the diffusion coefficient. The diffusion profile $c(x, t)$ for any time can be calculated by the solution (3) for sufficiently high numbers of cycles, starting from the initial conditions.

The value of the calculated profiles was similar to the nature of the real measured ones in those cases when a negative gradient of the diffusion coefficient was used in the calculations, i.e. when dependence $D(x)$ vs x near the surface exhibited a tendency to rise. A few calculated diffusion profiles and the corresponding dependence $D(x)$ vs x are shown in Fig. 1. For the formation of the observed deformation of the diffusion profiles a change in the diffusion coefficient at the surface of less than 10% suffices.

Especially marked deformations of diffusion profiles have been observed by Rothman et al. [1] in the diffusion of Zn^{2+} in NaCl crystals. Rothman has ascribed that effect to the occurence of OH⁻ anions in NaCl crystals. We have observed the same effect in the diffusion of Ba^{2+} in NaCl in the case when the crystals were subjected to an atmosphere containing water vapor before diffusion annealing. Such a diffusion profile and the corresponding theoretical one are shown in the Fig. 2. The theoretical profile was calculated taking into account the dependence $D(x)$ vs x on the upper half of Fig. 2.

The existence of the gradient of the diffusion coefficient is probably created by OH⁻ anion groups in the crystal. This seems to be in agreement with the results given in paper [8], in which the influence of the concentration of OH⁻ anions on the selfdiffusion of Na⁺ in NaCl crystals was studied. In this case the increase of the selfdiffusion coefficient by a value of 10—15 % was caused by the occurence of a $2—5\times10^{-6}$ mol fraction of OH⁻ anions in the crystals.

Fig. 1. Theoretical diffusion profiles. The dependence $D(x)$ vs x is shown in the upper half of the figure. D_x means diffusion coefficient characteristic for crystal volume. The broken curves represent diffusion profiles in absent of diffusion coefficient gradient. [a] $t = 2.4\times10^5$ s, $D_x = 6.0\times10^{-9}$ cm²s⁻¹, b) $t = 2.4\times10^5$ s, $D_x = 2.2\times10^{-8}$ cm²s⁻¹].
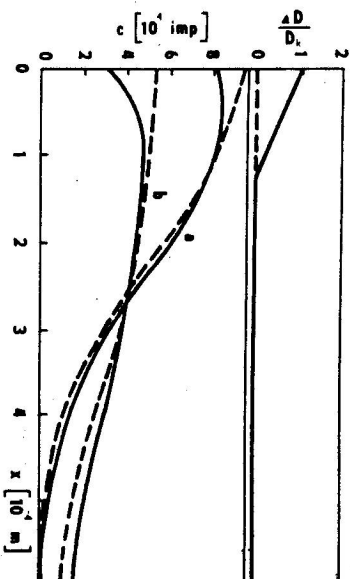

Fig. 2. Experimental diffusion profile which takes place during the diffusion of Ba^{2+} into NaCl crystals containing OH⁻ anions. The theoretical diffusion profile was calculated taking into account the dependence $D(x)$ vs x given in the upper half of the figure ($t=1.38\times10^4$ s, $T=910$ K, $D_x=8.3\times10^{-9}$ cm²s⁻¹).

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