

Interaction between alkali-metal ions M^+ in the deactivation process of quartz-embedded $Al-M^+$ centers

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The influence of the long- and short-range interactions between alkali-metal-ion compensators on the deactivation mechanism of $Al-M^+$ centers ($M=Li$ or Na) in quartz crystal during electrodiffusion is determined on the basis of a perturbation treatment of the Smoluchowski diffusion equation. Application to the deactivation rate of $Al-Li^+$ in the presence of another Li^+ ion shows that the asymmetry induced in the frequency jump of the first ion by the Coulombic interaction with the second appears to be a localized effect. When the second ion lies in adjacent wells of the $Al-Li^+$ center, as expected in the model of diffusion and compensation, it is shown that the first-ion diffusion can be enhanced by two orders of magnitude with respect to the single-ion diffusion model without compensation.

I. INTRODUCTION

Electrodiffusion is a common treatment¹⁻⁴ that allows the selective exchange of charge-compensating interstitial ions inside a quartz sample containing trivalent substitutional impurities (Al, B, . . .). Depending on the nature of the electrodes or on the ambient atmosphere, the radiation hardness of the material used for resonators can then be enhanced by this technique, as observed when alkali-metal ions forming $Al-M^+$ centers ($M=Li, Na$) are replaced by protons which give rise to $Al-OH^-$ entities.

Electrodiffusion experiments¹⁻⁴ are usually performed in a H_2 atmosphere for a quartz sample brought up to around the α - β phase transition ($T \simeq 750$ K) over a long period. The sample is swept with an electric field of 20 – 2000 $V\ cm^{-1}$ applied along the optical axis. The ionic current j is recorded as a function of time. The j -versus-time curves exhibit initial current densities of 10 – 100 $\mu A\ cm^{-2}$ which probably characterize the alkali-metal-ion escape, on the cathode side, with the concomitant replacement by protons. Then the currents decrease subsequently over a range of 5 min to 1 h, and, in the long-time regime, a nearly stationary behavior occurs, which is connected to the single proton diffusion inside the quartz channels. These experimental results thus show that a reliable interpretation of the electrodiffusion mechanism must take into account the simultaneous effect of the metal-alkali-ion migration and of the charge compensation by protons.

In a series of previous papers,⁵⁻⁹ we have given a detailed account of the theoretical approaches developed for the study of the diffusion mechanism. Preliminary calculations of the interaction potentials⁵ between the compensating ions and the bulk crystal have provided the basis tool for the treatment of the diffusion equations. Two types of models have then been discussed. In Refs. 6 and 7, the ion diffusion is described as a random process

at thermal equilibrium. The transport theory is based on the transit-time concept and applied to the ion jump from a potential well to the adjacent one. The jump frequency depends on the dynamics of the crystal through the consideration of effective mass and potential for the diffusive particle.

In the second type of model, the time evolution of the probability for finding the ion at a given position inside the diffusion channel is described within the framework of the Smoluchowski equation.⁸ In this case, the diffusion constant describes the dynamical influence of the surrounding medium (crystal and Al impurities).

A complete diffusion model⁹ which takes into account the influence of the electrode-quartz interface has also been presented to describe the M^+ escape and the proton penetration in the quartz sample, at the electrodes. It is shown that bulk and surface processes can have competitive contributions in the determination of the diffusion coefficient.

In all these models, the motions of the alkali-metal ions or of the protons are not mutually coupled. Such an assumption can be justified by considering the small impurity concentration¹⁰ in the sample (about 10 to 10^3 ppm). However, two features lead us to revisit this problem and to go beyond this hypothesis. First, the interactions between ions are specifically long range, and second, during the electrodiffusion process, protons or other diffusive ions are injected into the sample in such a way that the local ion concentration can reach large values. Various alkali-metal ions (Li^+, Na^+) and protons can in fact be present in a given diffusion channel and they can modify the diffusion mechanism through their mutual interactions.

A detailed study of this mechanism would require the determination of the dynamical electrical field due to all the other charged impurities on the diffusive ion. In this paper, we consider the pairwise influence only and calcu-

late the deactivation frequency of the $Al-M^+$ center when a second M^+ ion interacts with this center. The Smoluchowski diffusion equation is then modified by the ion interaction and it can be shown that it behaves as a Schrödinger-like equation for a system of two bosons embedded in an effective potential. This latter potential describes the mutual ion interaction and the interaction of each ion with the ambient crystal.

Section II is devoted to the theoretical development of the diffusion equation. This equation is then solved in Sec. III for long and short interionic distances and the deactivation frequency for the $Al-M^+$ center is determined as a function of the relative position of the two M^+ ions. Discussion of the results and comparison with the vanishing interaction limit are presented in Sec. IV for the case of two interacting Li^+ ions.

II. THEORETICAL MODEL

A. Diffusion equation

Let us consider an optical channel in a quartz sample, i.e., a channel along the optical axis of the crystal, as representing the diffusion path for alkali-metal ions. Two ions M^+ in this channel interact through the usual long-range Coulomb potential. The first ion labeled 1 is assumed to be located at the immediate proximity of the trivalent impurity (Al^{3+}) and it behaves as a charge compensator by forming an $Al-M^+$ center. The position of this ion along the \mathbf{Z} axis of the channel with respect to the Al atom taken as the origin is defined by Z_1 . The second ion, noted 2, can move along the channel and has

an instantaneous position Z_2 .

The distribution probability $P(\mathbf{Z}_1, \mathbf{Z}_2, t)$ for the two ions to be at the positions Z_1 and Z_2 at time t satisfies, in the Smoluchowski approach, the equation¹¹

$$\frac{\partial P(\mathbf{Z}, t)}{\partial t} = D_0 \sum_{i=1}^2 \frac{\partial}{\partial Z_i} \left[\frac{\partial}{\partial Z_i} - \beta F_i \right] P(\mathbf{Z}, t), \quad (1)$$

where $\mathbf{Z} = (Z_1, Z_2)$, $\beta = (k_B T)^{-1}$, and D_0 characterizes the diffusion constant for a single particle. The force experienced by the i th ion ($i=1,2$),

$$F_i \equiv - \frac{\partial V(\mathbf{Z})}{\partial Z_i}, \quad (2)$$

is obtained from the definition of the total interaction potential V :

$$V(\mathbf{Z}) = V_1(Z_1) + V_2(Z_2) + V_{12}(\mathbf{Z}). \quad (3)$$

The first two contributions in Eq. (3) take into account the interaction of each ion with the surrounding medium (the crystal and the trivalent impurity) whereas the third one characterizes the ion-ion interaction.

The solutions of Eq. (1) are written as a series expansion in the basis of the eigenfunctions $P_n(\mathbf{Z})$ as^{11,13}

$$P(\mathbf{Z}, t) = \sum_{n=0}^{\infty} A_n e^{-\lambda_n t} P_n(\mathbf{Z}), \quad (4)$$

where the A_n 's are coefficients and λ_n defines the n th eigenvalue connected to the steady eigenfunction $P_n(\mathbf{Z})$ which satisfies the equation

$$\sum_{i=1}^2 \left[\frac{\partial^2 P_n(\mathbf{Z})}{\partial Z_i^2} + \left(\frac{\partial^2 U_i(Z_i)}{\partial Z_i^2} + \frac{\partial^2 U_{12}(\mathbf{Z})}{\partial Z_i^2} \right) P_n(\mathbf{Z}) + \left[\frac{\partial U_i(Z_i)}{\partial Z_i} + \frac{\partial U_{12}(\mathbf{Z})}{\partial Z_i} \right] \frac{\partial P_n(\mathbf{Z})}{\partial Z_i} \right] + D_0^{-1} \lambda_n P_n(\mathbf{Z}) = 0. \quad (5)$$

The reduced potentials U_i are defined as $U_i = V_i / k_B T$. We then introduce the new eigenfunctions $\varphi_n(\mathbf{Z})$ as

$$\varphi_n(\mathbf{Z}) = \exp\left[\frac{1}{2}(U_1 + U_2 + U_{12})\right] P_n(\mathbf{Z}) \quad (6)$$

and substitute this expression into Eq. (5) in order to obtain a Schrödinger-like eigenequation as

$$(H_1 + H_2 + U_{12}^*) \varphi_n(\mathbf{Z}) = K_n \varphi_n(\mathbf{Z}). \quad (7)$$

The Hamiltonian for the i th ion is written as

$$H_i = - \frac{\partial^2}{\partial Z_i^2} + U_i^*(Z_i) \quad (8)$$

and the new effective potentials are defined as

$$U_i^*(Z_i) = \frac{1}{4} \left[\frac{dU_i}{dZ_i} \right]^2 - \frac{1}{2} \frac{d^2 U_i}{dZ_i^2}, \quad (9)$$

$$U_{12}^*(\mathbf{Z}) = \frac{1}{4} \sum_{i=1}^2 \left[\left(\frac{\partial U_{12}(\mathbf{Z})}{\partial Z_i} \right)^2 + 2 \frac{\partial U_{12}}{\partial Z_i} \frac{dU_i}{dZ_i} - 2 \frac{\partial^2 U_{12}(\mathbf{Z})}{\partial Z_i^2} \right]. \quad (10)$$

The corresponding reduced eigenvalues K_n are expressed as

$$K_n = D_0^{-1} \lambda_n. \quad (11)$$

The lowest value $K_0 = 0 = \lambda_0$ corresponds to the eigenfunction $\varphi_0(\mathbf{Z})$ which is simply written from Eq. (6) as

$$\varphi_0(\mathbf{Z}) = \exp\left[-\frac{1}{2}(U_1 + U_2 + U_{12})\right]. \quad (12)$$

This ground-state eigenfunction is connected to the steady-state solution of the Smoluchowski equation which can be written as

$$P(\mathbf{Z}, t) = \varphi_0^2(\mathbf{Z}) + \sum_{n=1}^{\infty} A_n e^{-\lambda_n t} \varphi_0(\mathbf{Z}) \varphi_n(\mathbf{Z}), \quad (13)$$

where the first term in the series ($n=0$) characterizes the Boltzmann probability for the equilibrium canonical distribution.

We then have to solve a Schrödinger-like equation [Eq. (7)] from the usual techniques of quantum mechanics instead of the initial Smoluchowski equation [Eq. (1)]. Note that the ionic interaction potential U_{12} does not occur in the expression of the effective potentials U_i^* . These potentials can then be modeled⁸ with the single requirement that they lead to ground-state eigenfunctions $\varphi_0^{(i)}(Z_i)$ which give physically convenient potentials through the equations:

$$U_i = -2 \ln \varphi_0^{(i)}(Z_i), \quad i = 1, 2. \quad (14)$$

The remaining effective potential U_{12}^* can then be determined from the knowledge of the potentials U_i and U_{12} from Eq. (10).

B. Deactivation rate

The ion-ion interaction is described as the sum of two contributions, as

$$U_{12}(|Z_1 - Z_2|) = \frac{1}{k_B T} \left[\frac{q_1 q_2}{|Z_1 - Z_2|} + V_{12}^c(|Z_1 - Z_2|) \right]. \quad (15)$$

The Coulombic contribution depends on the effective charges of the two ions inside the crystal and the second contribution characterizes a repulsive core potential which has been chosen, for simplification, such that

$$V_{12}^c = \begin{cases} 0 & \text{for } |Z_1 - Z_2| \geq 2r_0 \\ \infty & \text{for } |Z_1 - Z_2| < 2r_0, \end{cases} \quad (15')$$

where $2r_0$ defines the van der Waals diameter for ion pair. Two different approaches are used for the determination of the eigensolutions of Eq. (7), depending on the distance $|Z_1 - Z_2|$ between the two ions. For distances larger than the distance between adjacent wells along the diffusion path, we assume that the deactivation rate of the center formed by an Al impurity and the first ion is perturbatively influenced by the interaction with the second ion. The center Al- M^+ experiences thus the slowly varying Coulombic potential [Eq. (15)] as an external potential, with Z_2 playing the role of a parameter. The eigenequation can then be reduced, in this case, to a single-variable equation:

$$[H_1 + U_{12}^*(Z_1)]\varphi_n(Z_1) = K_n \varphi_n(Z_1), \quad (16)$$

where the effective potentials U_1^* and U_{12}^* are defined by Eqs. (9) and (10).

In contrast, at short distance $|Z_1 - Z_2|$, Eq. (7) must be viewed as the dynamical equation of two ions located in the close neighborhood of the Al impurity. If we assume that the two ions are identical, the eigensolutions will then obey symmetry conditions.

In the two approaches, the single-particle Hamiltonian H_i [Eq. (8)] must be solved and its eigenfunctions are used to determine the solutions of the two-particle Hamiltonians $H_1 + U_{12}^*$ or $H_1 + H_2 + U_{12}^*$.

1. Single-ion eigensolutions

The eigensolutions connected to the Hamiltonian H_i are obtained, as in Ref. 8, for the effective potential U_i^* schematized in Fig. 1. This potential exhibits five square wells of equal width L and it is symmetrical with respect to the plane $Z_i=0$. The parameters L , V'_0 , V''_0 , d' , and d'' which define these wells are calculated according to the requirement given by Eq. (14). Their values are determined in such a way they lead to an adequate fit of the potential U_i .

The standard techniques of quantum mechanics are then applied to the eigenequation connected to H_i and the symmetric eigenfunctions are written as

$$\begin{aligned} \varphi_n^{iS}(Z_i) &= A_n^{iS} \sin \sqrt{K_n^{iS}}(Z_i + g), \quad -g \leq Z_i \leq -f, \\ \varphi_n^{iS}(Z_i) &= B_n^{+iS} e^{-\gamma_n^{+iS}(Z_i + f)} \\ &\quad + B_n^{-iS} e^{\gamma_n^{+iS}(Z_i + f)}, \quad -f \leq Z_i \leq -c, \\ \varphi_n^{iS}(Z_i) &= C_n^{+iS} \sin \sqrt{K_n^{iS}}(Z_i + c) \\ &\quad + C_n^{-iS} \cos \sqrt{K_n^{iS}}(Z_i + c), \quad -c \leq Z_i < -b, \\ \varphi_n^{iS}(Z_i) &= n D_n^{+iS} e^{-\gamma_n^{+iS}(Z_i + b)} \\ &\quad + D_n^{-iS} e^{\gamma_n^{+iS}(Z_i + b)}, \quad -b \leq Z_i \leq -a, \\ \varphi_n^{iS}(Z_i) &= E_n^{iS} \cos \sqrt{K_n^{iS}} Z_i, \quad -a \leq Z_i \leq a, \end{aligned} \quad (17)$$

whereas the antisymmetric eigenfunctions can be obtained from Eqs. (17) by changing index S into A everywhere it appears, and the cosine function by a sine in the range $-a \leq Z_i \leq a$, only.

The reduced coefficients γ_n^{+i} and γ_n^{+i} are defined as

$$\begin{aligned} \gamma_n^{+i} &= (V'_0 - K_n^{+i})^{1/2}, \\ \gamma_n^{+i} &= (V''_0 - K_n^{+i})^{1/2} \end{aligned} \quad (18)$$

and the parameters B , C , D , and E can be expressed in terms of L , V'_0 , V''_0 , d' , d'' , K_n and of the remaining parameters A which are determined by orthonormalization of the eigenfunctions (cf. Table I).

In the range $a \leq Z_i \leq f$ the solutions φ_n^{iS} and φ_n^{iA} satisfy the symmetry relations

$$\begin{aligned} \varphi_n^{iS}(Z_i) &= \varphi_n^{iS}(-Z_i), \\ \varphi_n^{iA}(Z_i) &= -\varphi_n^{iA}(-Z_i). \end{aligned} \quad (19)$$

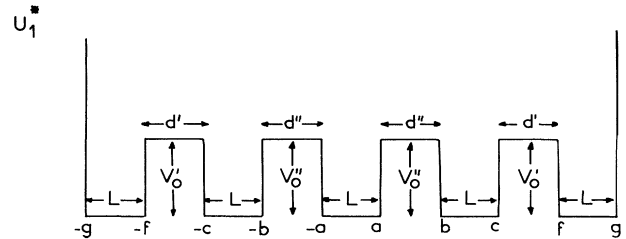


FIG. 1. Effective potential U_i^* defined by Eqs. (9) and (14). The values of the parameters V'_0 , V''_0 , d' , d'' , and L are given in Table I for Li^+ .

TABLE I. Coefficients B^i , C^i , D^i , and E^i of the eigenfunction $\varphi^i(Z_i)$.
$$\begin{aligned}
B_n^{\pm i} &= \frac{A_n^i}{2} \left[\sin \sqrt{K_n^i} L \mp \frac{\sqrt{K_n^i}}{\gamma_n^i} \cos \sqrt{K_n^i} L \right] \\
C_n^{+i} &= \frac{\gamma_n^i}{\sqrt{K_n^i}} (B^{-i} e^{\gamma_n^i d'} - B^{+i} e^{-\gamma_n^i d'}) \\
C_n^{-1} &= B^{+i} e^{-\gamma_n^i d'} + B^{-i} e^{\gamma_n^i d'} \\
D_n^{\pm i} &= \frac{1}{2} \left[C_n^{+1} \pm \frac{\sqrt{K_n^i}}{\gamma_n^i} C^{-i} \right] \sin \sqrt{K_n^i} L + \frac{1}{2} \left[C^{-i} \mp \frac{\sqrt{K_n^i}}{\gamma_n^i} C^{+i} \right] \cos \sqrt{K_n^i} L \\
E_n^{iS} &= (D_n^{+iS} e^{-\gamma_n^i d''} + D_n^{-iS} e^{\gamma_n^i d''}) / \cos(\sqrt{K_n^i} L / 2) \\
E_n^{iA} &= (D_n^{+iA} e^{-\gamma_n^i d''} + D_n^{-iA} e^{\gamma_n^i d''}) / \sin(\sqrt{K_n^i} L / 2)
\end{aligned}$$

The corresponding eigenvalues K_n^{iS} and K_n^{iA} can only be determined numerically; the symmetric eigenvalue K_n^{iS} satisfies the equation

$$(A_n^{iS})^{-1} \left[E_n^{iS} \sqrt{K_n^{iS}} \sin \sqrt{K_n^{iS}} \frac{L}{2} + D_n^{+iS} \gamma_n^{iS} e^{-\gamma_n^{iS} d''} - D_n^{-iS} \gamma_n^{iS} e^{\gamma_n^{iS} d''} \right] = 0 \quad (20)$$

and the antisymmetric one K_n^{iA} can be obtained by changing the index S into A and the sine function into cosine.

The eigensolutions K_n^i and φ_n^i are then replaced into Eq. (13) to determine the probability of finding the i th ion at the position Z_i , at time t .

2. Long-range eigensolutions

When the location Z_2 of the second ion is considered as a parameter ($Z_2 = -R$ for instance), the effective ion-ion interaction obtained from Eqs. (10) and (15) can be readily written as

$$U_{12}^*(Z_1, R) = -\frac{\alpha}{|Z_1 + R|^3} \left[1 - \frac{\alpha}{4|Z_1 + R|} - \frac{d \ln \varphi_0^{1S}(Z_1)}{dZ_1} (Z_1 + R) \right] \quad (21)$$

with

$$\alpha = q_1 q_2 / k_B T. \quad (21')$$

Within this particular approach, the ratio Z_1/R is much smaller than unity and the potential $U_{12}^*(Z_1, R)$ can be expanded as a Taylor series with respect to Z_1/R up to the second order, as

$$\begin{aligned}
U_{12}^*(Z_1, R) &\simeq \frac{\alpha}{R^3} \left[\frac{\alpha}{4R} - 1 + R \frac{d}{dZ_1} \ln \varphi_0^{1S}(Z_1) \right. \\
&+ \frac{Z_1}{R^2} \left[3 - \frac{\alpha}{R} - 2R \frac{d}{dZ_1} \ln \varphi_0^{1S}(Z_1) \right] \\
&+ \frac{Z_1^2}{R^3} \left[\frac{5\alpha}{2R} - 6 \right. \\
&\left. \left. + 3R \frac{d}{dZ_1} \ln \varphi_0^{1S}(Z_1) \right] \right]. \quad (22)
\end{aligned}$$

The usual perturbation theory truncated at the second order allows the ground state eigenvalue K_0^1 to be calculated for the first ion, influenced by the Coulombic interaction with the second one, as

$$K_0^1 \simeq K_0^{1S} + \langle U_{12}^* \rangle_{0S}^1 + \sum_m \sum_{\beta=A,S} \frac{|\langle U_{12}^* \rangle_{0S, m\beta}^1|^2}{K_0^{1S} - K_m^{1\beta}}, \quad (23)$$

where the first matrix element corresponds to the average value of U_{12}^* in the ground state while the second element characterizes a transition from φ_{0S}^1 to $\varphi_{m\beta}^1$, $\beta=A, S$. The sum is restricted to $m=4$ and 5 for the symmetric and antisymmetric states, respectively. This order ensures convergence of the expansion.

Moreover, the first excited state K_1^1 is twofold degenerate. The degenerate perturbation theory must be used in this case to calculate the splitting of the eigenvalue K_1^1 due to the potential U_{12}^* . The perturbation expansion is limited to the first order for the quadratic term (Z_1^2/R^2) in Eq. (22), whereas the second order gives the first non-vanishing contribution for the linear term (Z_1/R). We then obtain the new eigenvalues K_1^{1+} and K_1^{1-} as the solutions of the determinant Δ :

$$\begin{aligned}
\Delta &= \langle U_{12}^* \rangle_{1\beta}^1 \sum_{m \neq 1} \sum_{\beta'=A,S} \frac{\langle U_{12}^* \rangle_{1\beta m \beta'}^1 \langle U_{12}^* \rangle_{m \beta' 1 \beta'}^1}{K_1^{1S, A} - K_m^{1\beta'}} \\
&- (K_1^{1\pm} - K_1^{1S, A}) \delta_{\beta\beta'}. \quad (24)
\end{aligned}$$

Application of these calculations to the other excited eigenstates would then lead to the determination of the eigensolutions which describe the probability for finding the first ion M^+ at a position Z_1 at time t (with the initial condition $Z_1=0$ at $t=0$) in presence of the second ion M^+ at a distance $|R| \gg |Z_1|$.

It is interesting to connect the long-time regime of $P(Z, t)$ which corresponds to the Boltzmann equilibrium distribution for $t \rightarrow \infty$ with the jump frequency for the first ion from its initial well to an adjacent one.⁸ This jump frequency k_0' corresponds to the so-called deactivation frequency of the Al- M^+ center, and it is written as

$$k_0'(R) = (K_1^{1-} - K_0^1) D_0 \int_{\text{adjacent well}} e^{-(U_1 + U_{12})} dZ_1, \quad (25)$$

where K_0^1 and K_1^{1-} are the ground and the first excited eigenvalues calculated in Eqs. (23) and (24). The presence of the second ion at a distance R gives rise to an obvious

asymmetry of the deactivation frequency depending on whether the integral is over the right or left adjacent well.

3. Short-range eigensolutions

When the distance between the two ions decreases in such a way that they can both be considered in the close neighborhood of the Al impurity, the solutions of the Smoluchowski equation are determined by a perturbation treatment on the basis of the eigensolutions of $H_1 + H_2$. Indeed the perturbation U_{12}^* modifies only slightly the

ground and first excited eigenvalues of the Hamiltonian $H_1 + H_2$ and the treatment is obviously valid.

An interesting case corresponds to two identical ions M^+ since the probability $P(Z_1, Z_2, t)$ must be symmetrical with respect to the exchange of the two particles. From Eq. (12), $\varphi_0(Z_1, Z_2)$ is also symmetrical, so that the eigenfunctions $\varphi_n(Z_1, Z_2)$ are themselves symmetrical with respect to the ion permutation. The Schrödinger-like equation must then be solved within the framework of the Bose-Einstein statistics.

The effective potential U_{12}^* is given by

$$U_{12}^*(Z_1, Z_2) = - \frac{2\alpha}{|Z_1 - Z_2|^3} \left[1 - \frac{\alpha}{4|Z_1 - Z_2|} - \frac{1}{2}(Z_1 - Z_2) \left(\frac{d \ln \varphi_0^{1S}(Z_1)}{dZ_1} - \frac{d \ln \varphi_0^{2S}(Z_2)}{dZ_2} \right) \right], \quad (26)$$

where φ_0^{1S} and φ_0^{2S} are the ground eigenstates of the two identical ions. The eigenfunctions ψ_n of the operator $H_1 + H_2$ are written as the symmetrized product of the functions $\varphi_{n_1}^1(Z_1)$ and $\varphi_{n_2}^2(Z_2)$ connected to the independent ion Hamiltonians with the corresponding eigenvalues $K_{n_1}^{1S,A}$ and $K_{n_2}^{2S,A}$. They are given as

$$\psi_n(Z_1, Z_2) = \frac{1}{\sqrt{2}} [\varphi_{n_1}^1(Z_1) \varphi_{n_2}^2(Z_2) + \varphi_{n_1}^1(Z_2) \varphi_{n_2}^2(Z_1)]. \quad (27)$$

The usual perturbation theory can then be applied to the ground-state level up to the second order, as in Eq. (23), whereas the first excited eigenvalues are degenerate and the degenerate perturbation treatment must be developed in this case [Eq. (24)]. The main difference with Sec. II B 2 is the replacement of $\varphi_{n_i}^i(Z_i)$ by $\psi_n(Z_1, Z_2)$ [Eq. (27)].

The deactivation frequency for the Al- M^+ center, when the other identical M^+ ion is confined at a distance r in the same region, takes the generalized form

$$k_0'(r) = (K_1 - K_0) D_0 \times \frac{\int_{\text{adjacent well}} dZ_1 \int_{\text{well around } r} dZ_2 e^{-(U_1 + U_2 + U_{12})}}{\int_{\text{space}} dZ_1 \int_{\text{well around } r} dZ_2 e^{-(U_1 + U_2 + U_{12})}}. \quad (28)$$

K_1 and K_0 are the ground and the first excited eigenvalues of the total Hamiltonian $H_1 + H_2 + U_{12}^*$. r characterizes the location of a well minimum close to the Al center. The central well corresponds to the Al- M^+ center while the adjacent one is occupied by the second ion M^+ when $r = 2c/3$. The range of the values for r is

$2c/3 \leq r \leq c$. The integral ratio in Eq. (28) characterizes the conditional probability for the deactivation of the Al- M^+ center when another M^+ ion is located in a well around r , on one side or on the other side of the Al well. Since the ion-ion distance is small in this case, we thus expect a stronger asymmetry in the right or left jump frequency for the first ion.

III. NUMERICAL APPLICATION AND DISCUSSION

The method is applied to the calculation of the deactivation rate of the Al-Li⁺ center when a second Li⁺ ion is located along the optical channel of an electrodiffused quartz sample at $T = 750$ K. The effective charge of Li⁺ inside quartz is equal⁵ to $0.3e$ (e being the electronic charge) and we take $r_0 = 0.7$ Å for the ionic radius of Li⁺ [Eq. (15')].

The parameters for the square potential U_i^* which yield the better fit to the potential U_i are given in Table II. The potential U_i experienced by the first Li⁺ ion and due to its interaction with the Al impurity and the crystal is drawn in Fig. 2. The corresponding eigenvalues $K_n^{1S,A}$

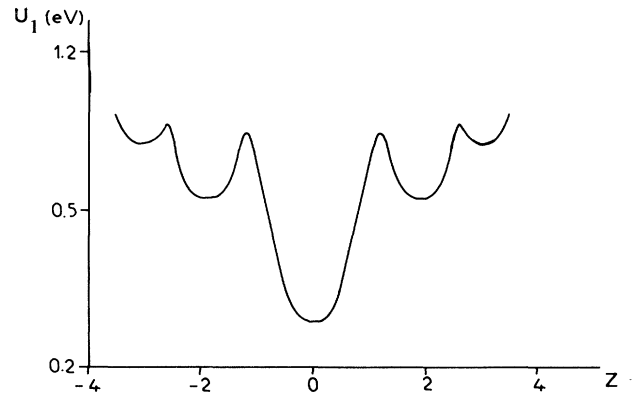


FIG. 2. Potential U_i for the Al-Li⁺ center along the direction of the z optical axis of quartz. The origin of Z is at the Al ion position and Z is in units of $c/3$ ($c = 5.456$ Å for SiO₂).

TABLE II. Potential parameters for U_i^* .

V_0' (Å ⁻²)	V_0'' (Å ⁻²)	L (Å)	d' (Å)	d'' (Å)
29.33	24.19	1.819	0.455	1.637

TABLE III. Symmetric and antisymmetric eigenvalues $K_n^{iS,A}$ (\AA^{-2}) for the Al-Li⁺ center.

n	K_n^{iS}	K_n^{iA}
0	1.983	
1	2.004	2.004
2	2.459	2.459
3	7.888	7.790
4	9.759	7.888
5	16.794	9.759
6	17.170	17.162
7	21.571	21.570

are presented in Table III. As expected from Eq. (20), the ground-state eigenvalue is not degenerate and symmetrical. The two levels $n=1$ and $n=2$ are twofold degenerate, whereas the higher symmetrical and antisymmetrical eigenvalues are generally distinct. Note also that the first three levels are very close and much lower than the other excited levels $n \geq 3$. This feature leads to fast convergence with time of the solution $P(Z_i, t)$ [Eq. (13)].

When the second ion is located at a distance $R \geq 2c$ from the Al impurity, the numerical computation of the zeros of the determinant Δ [Eq. (24)] leads to the occurrence of the two distinct excited eigenvalues K_1^{1+} and K_1^{1-} (connected to $n=1$). Figure 3 exhibits the different behavior of the quantities $K_1^{1+} - K_0$ and $K_1^{1-} - K_0$ as a function of the distance R . When R is large, these quantities are equal, as expected from results of Table III for a single Li⁺ ion, while, as R decreases, the difference increases. We present in Fig. 4 the deactivation frequency of the Al-Li⁺ center when the second ion is located at the left side of this center. The presence of this second ion favors appreciably the deactivation rate k'_{0r} toward the right well and decreases the jump frequency k'_{0l} toward the left well. At large distance R , the rate recovers its symmetry.

For distances r shorter than $2c$, the right and left rate asymmetry increases dramatically, then the deactivation takes place into the right well only. The relative values of the first eigenvalues K_n are given in Table IV. Figure 5 exhibits the rate $k'_{0r}(R)$ for distances ranging from $2c/3$ to $7c$. The value $k'_{0r}(2c/3)$ is about two orders of magnitude greater than that of $k'_{0r}(\infty)$. Note also that the value of $k'_{0r}(r)$ strongly decreases for $r \leq 5c/3$ and the asymmetry thus appears as a localized effect. This is a

TABLE IV. Eigenvalue difference $K_n - K_0$ (\AA^{-2}) of the Hamiltonian $H_1 + H_2 + U_{12}^*$.

n	$K_n - K_0$
0	0
1	0.138
2	0.170
3	0.323
4	0.904
5	0.905

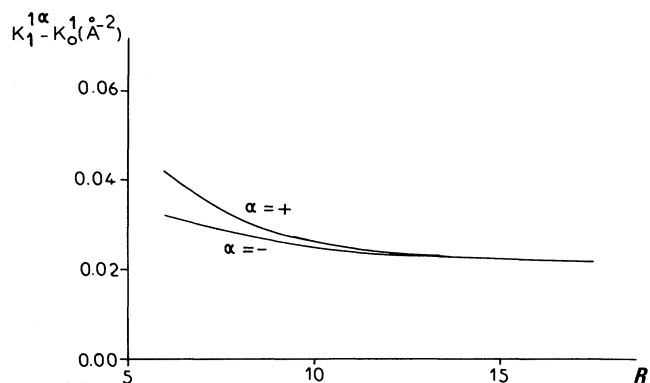


FIG. 3. Behavior of the eigenvalue differences $K_1^{1+} - K_0^{1+}$ (\AA^{-2}) and $K_1^{1-} - K_0^{1-}$ (\AA^{-2}) vs the ion-ion distance R (in units of $c/3$) for $R \geq 6$.

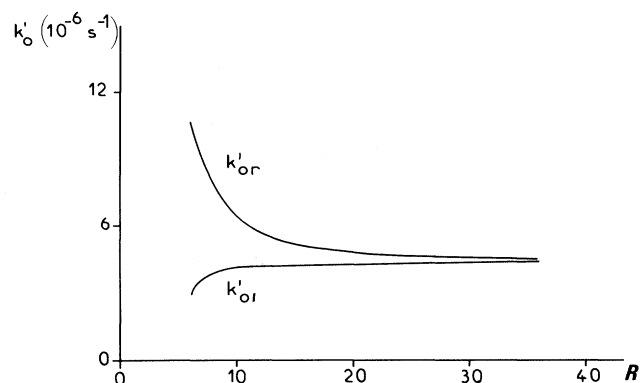


FIG. 4. Deactivation rates (s^{-1}) of the Al-Li⁺ center by jump of the Li⁺ into the right (k'_{0r}) and left (k'_{0l}) adjacent wells when the second alkali-metal ion is located at the left side of the center and at a distance $R \geq 6$ (in units of $c/3$).

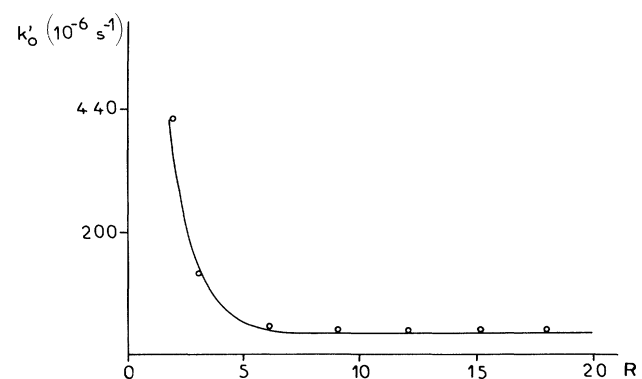


FIG. 5. Deactivation rate k'_{0r} (s^{-1}) of the Al-Li⁺ center by Li⁺ jump into the right adjacent well vs the distance R of the second alkali-metal ion (in units of $c/3$) for $r > 2$.

puzzling feature since the ion-ion Coulombic interaction is a long-range process. In fact, it must be realized that the effective potential U_{12}^* occurring in the Schrödinger-like equation [Eq. (7)] depends on the second derivative of the ion-ion interaction which introduces a limited range of the initial potential.

IV. CONCLUSION

The electrodiffusion mechanism leading to alkali-metal ion sweeping of quartz samples must be viewed as a complex phenomenon. In a first step, the deactivation rate of an $Al-M^+$ center can be described through the probability for the M^+ ion escape from the potential well due to the trivalent impurity. In fact, the density of alkali-metal ions and of proton compensators can be locally large. So, in a second step, it is necessary to consider the influence of these ions in the deactivation process. We have shown here that the presence of another ion in the close neighborhood of an $Al-M^+$ center can enhance the deactivation

rate by two orders of magnitude. As a consequence, the ionic current density in quartz, which is proportional to this rate, can be increased in the same ratio.

The model has been applied here to the interaction between lithium ions only. The main differences which would occur in a substitution of Li^+ by Na^+ or H^+ would be the value of the effective ionic charges. These charges are not too different for these species and the present results for Li^+ can be extended, at least qualitatively, to the diffusion-compensation mechanism with other ions or protons. Note also that the local character of the ion-ion interaction provides a justification of the initial pairwise potential hypothesis. Many-body interactions between ions are probably negligible.

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