

Deactivation of Al-M^+ and Al-OH^- centers in quartz by use of the Smoluchowski approach

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(Received 20 October 1988)

The problem of deactivation of alkali-metal ions M^+ ($M=\text{Li,Na}$) or of protons H^+ which form, with Al^{3+} impurities present in quartz crystal, Al-M^+ or Al-OH^- centers is studied with use of the Smoluchowski equation. For special forms of the interaction potential between M^+ (H^+) and the crystal, semianalytical solutions of the transport equation are obtained, which lead to a straightforward calculation of the distribution function $P(\xi, t)$ of the ion (proton) in the vicinity of the Al impurity. The results are compared to experimental data on ionic current density and to those derived from a transit-time approach of a transport theory previously developed.

I. INTRODUCTION

From an empirical point of view, the importance of alkali-metal ions in relation to frequency stability of quartz resonators is now well-accepted¹ since many experiments (infrared, electron-spin resonance, acoustic and dielectric losses, and electrical-conductivity measurements) have shown² that these ions can migrate in quartz channels parallel to the c axis for special physical conditions (temperature, electrical field, and irradiation). Electrodiffusion is a post-growth treatment which allows the selective exchange of charge compensating interstitial ions (replacement of alkali-metal ions near aluminum impurity centers by protons or holes), in order to enhance the radiation hardness of the material used for resonators. The time behavior of the ionic current due to ion migration is a quantitative test of the sweeping efficiency in quartz crystals.

The microscopic interpretation of electrodiffusion is, however, a somewhat complicated problem which rests on the knowledge of the dynamics of the interstitial ions and of the ambient solid medium. Preliminary information on the interaction potentials experienced by the alkali-metal ions is required. *Ab initio* self-consistent-field molecular-orbital calculations have been performed^{3,4} on clusters with a reduced number of atoms around an aluminum center and with an alkali-metal ion or a proton in the close vicinity of this center. Although accurate and rich in information, these numerical potentials³ are nevertheless difficult to use in dynamical models; indeed, the whole potential surface, and not only the region in the vicinity of the Al centers, must be known. So, semiempirical potentials,⁵ surely less accurate but analytical everywhere in space, and reflecting the trends and the overall behavior of the *ab initio* version, are better suited. With this simplified version of the potential experienced either by an alkali-metal ion or a proton at any point of a quartz channel containing an impurity aluminum, it was possible^{5,6} to determine the trajectories of these intersti-

tial ions. These trajectories can be approximately described by helices with varying radius and path, and with axis collinear to the c axis of the quartz channel. Note, in passing, that the trajectory is described by a single reaction coordinate ξ which takes account of the three-dimensional (3D) nature of the diffusion process. Indeed, ξ is different from the component z of the instantaneous position of the ion along the c axis in the sense that it is a function of x and y at each z location, through the equation of the trajectory. The motion of the ion M^+ can be regarded as a succession of jumps in potential wells described by the spatial distribution of oxygen and silicon atoms of quartz.

Several theoretical models can be used to describe the dynamics of the interstitial ion or of the proton. In previous papers,^{6,7} a transport theory of the ion based on the transit-time concept was developed to determine the diffusion constant and the ionic current density of the three alkali-metal ions Li^+ , Na^+ , and K^+ and of the proton H^+ in quartz channels containing Al centers. In this transport theory, the ion jumps from one potential well to the adjacent one in the channel, with a frequency which depends on an effective ion mass. This effective mass takes into account the spatial distortion of the crystal as the ion moves. The residence time is thus the time spent by the ion in a given well before it escapes into another one. This time, much longer than the jumping time, is a function of the potential structure, barrier heights between the wells, distances between the well minima, and overall behavior of the well shape, but it does not depend on the dynamical history of the ion inside the wells and of the jumps themselves. Beside its very partial use of the dynamical information, this transport theory is a typical equilibrium thermodynamical approach since the parameters which characterize the ionic diffusion are obtained from the detailed balance equation, leading to stationary solutions only. In spite of these approximations, the transit-time concept method can provide diffusion coefficients and values of the ionic current density in fair

agreement with experimental measurements.⁶

However, an improvement of the dynamical treatment in each well and more severe tests on the accuracy of the interaction potential require the use of continuous theories rather than this discrete method. Indeed, the electrodiffusion mechanism, which takes place in H₂ ambient, is a typical diffusion-compensation phenomenon.⁷ When the alkali-metal ion M⁺ escapes from the well created by the Al center, it is replaced by a proton, in order to satisfy the requirement of local electrical neutrality of the solid. The inclusion of the dynamical coupling between the two partners M⁺ and H⁺ is not straightforward in the discrete method, but it could be introduced in a simple way in continuous dynamical methods, through the M⁺-H⁺ ionic potential.

Among the continuous transport theories⁸ including a larger part of the dynamical information, a phenomenological Langevin equation approach⁹ could be developed for the reaction coordinates ξ along the c direction of the ion in the channel, as

$$m\ddot{\xi} + m\gamma\dot{\xi} + \frac{\partial V}{\partial \xi} = f(t), \quad (1)$$

where m , γ , V , and f are the ion mass, the medium viscosity, the interaction potential, and the random force due to the remaining solid. Such a method has been extensively used to describe the rapid transport of ions in superionic conductors.⁹⁻¹¹ It is, however, time consuming for trajectories implying very complicated forms of interaction potentials such as those considered in quartz crystals.

The Fokker-Planck-equation approach^{9,12} of the dynamics of the ion is another alternative which leads to the determination of the probability density $P(\xi, v, t)$ of finding the ion at the position ξ with velocity v at time t . In the high-viscosity limit, for which the mean free path of the ion is smaller than the typical distance where the interaction potential V can be regarded as constant, the Fokker-Planck equation reduces to the Smoluchowski one and the probability $P(\xi, t)$ is given by the equation¹²

$$\frac{\partial P(\xi, t)}{\partial t} = \frac{\partial}{\partial \xi} \left[\frac{D}{k_B T} \frac{\partial V(\xi)}{\partial \xi} P(\xi, t) \right] + D \frac{\partial^2 P(\xi, t)}{\partial \xi^2}, \quad (2)$$

where k_B is the Boltzmann constant, T is the temperature, and $D = k_B T / m\gamma$ characterizes the diffusion constant.

Equation (2) is the starting equation of our dynamical model for the diffusion of alkali-metal ions M⁺ or of protons H⁺ in a quartz channel. It is used here to determine the transport characterizations of M⁺ and H⁺ in the neighborhood of Al³⁺ impurities. One of the main advantages of Eq. (2) over Eq. (1) is that semianalytical solutions of $P(\xi, t)$ can be obtained,^{14,15} thus reducing in a considerable way the computational task.

In Sec. II, we briefly present the analytical solutions of Eq. (2) for the considered potential, and in Sec. III we apply the method to the calculation of the jumping frequen-

cy of M⁺ ions and H⁺. A comparison of the results with those derived from the discrete transport theory is also done (Sec. IV).

II. SOLUTIONS OF THE SMOLUCHOWSKI EQUATION

Following the methods of Van Kampen¹⁴ and Reichl,¹⁵ the solutions of Eq. (2) are written as a series expansion in terms of eigenfunctions, with an exponential time behavior, as

$$P(\xi, t) = \sum_{n=0}^{\infty} A_n e^{-\lambda_n t} P_n(\xi). \quad (3)$$

The constants A_n can be determined once the probability at $t=0$ is specified, and the set $\{\lambda_n\}$ defines the eigenvalues connected to the (time-independent) eigenfunctions $P_n(\xi)$ which satisfy the equation

$$\frac{d^2 P_n(\xi)}{d\xi^2} + \frac{d}{d\xi} \left[\frac{1}{k_B T} \frac{dV(\xi)}{d\xi} P_n(\xi) \right] + D^{-1} \lambda_n P_n(\xi) = 0. \quad (4)$$

To obtain Eq. (4), it has been assumed that the viscosity of the medium, and thus D , is constant with respect to ξ and fairly high. The change of function

$$P_n(\xi) = e^{-V(\xi)/2k_B T} \phi_n(\xi) \quad (5)$$

into Eq. (4) yields a Schrödinger-like time-independent equation written as

$$\frac{d^2 \phi_n(\xi)}{d\xi^2} + [\lambda_n D^{-1} - V^*(\xi)(k_B T)^{-1}] \phi_n(\xi) = 0 \quad (6)$$

with an effective potential $V^*(\xi)$ given by

$$V^*(\xi) = \frac{1}{2} \left[-\frac{1}{k_B T} \frac{d^2 V(\xi)}{d\xi^2} + \frac{1}{2k_B T} \left[\frac{dV(\xi)}{d\xi} \right]^2 \right]. \quad (6')$$

The set of functions $\phi_n(\xi)$ in Eq. (6) obeys the orthogonality condition. The eigenfunction $\phi_0(\xi)$ connected to the lower eigenvalue $\lambda_0=0$ corresponds to the stationary state [Eq. (3)]; it is related to $V(\xi)$ by the relation¹⁵

$$\phi_0(\xi) = e^{-V(\xi)/2k_B T}. \quad (7)$$

The coefficient A_n is then obtained by specifying the initial position ξ_0 of the ion as

$$P(\xi, t=0) = \delta(\xi - \xi_0). \quad (8)$$

This gives finally the expression for $P(\xi, t)$ as

$$P(\xi, t) = \sum_{n=0}^{\infty} \frac{\phi_n(\xi_0)}{\phi_0(\xi_0)} e^{-\lambda_n t} \phi_0(\xi) \phi_n(\xi), \quad (9)$$

where the first term of the series ($n=0$) is simply the Boltzmann probability for the equilibrium distribution.

Equation (9) is, with intermediate Eqs. (6) and (7), the key equation for solving the diffusion mechanism of an alkali-metal ion or of a proton in a quartz channel.

III. DYNAMICAL DEACTIVATION OF Al-M⁺ AND Al-OH⁻ IN QUARTZ

The probability $P(\xi, t)$ [Eq. (9)] is a continuous function of the ion location and of time. It therefore gives statistical information on the instantaneous position of any ion in a quartz channel when the initial location, the interaction potential of the ion with the ambient medium, and the viscosity are known. It has been shown elsewhere^{6,7} that the ionic current density due to the M⁺-ion migration and to the subsequent compensation of Al centers by protons is characterized by two quantities. The first quantity is connected to the time required for the M⁺ migration in clean crystal parts (parts of the channel without impurity Al centers). The second one characterizes the time spent by M⁺ ions in the close vicinity of the Al centers. These two times do not contribute similarly to the current, but the second time, also called deactivation time for the Al-M* centers, generally provides the main contribution. This deactivation time is connected, in the discrete transport theory,⁶ to the jump frequency k'_0 which is generally calculated for the experimental electrodiffusion temperature $T \simeq 750$ K. It is consequently the value connected to the jump probability of M⁺ or H⁺ from a well containing an Al center to the adjacent well which can be calculated from the Smoluchowski equation, or, equivalently, from Eq. (6).

In principle, numerical solutions of Eq. (6) could be obtained for the potential form defined in Ref. 5. This potential explicitly takes into account the presence of the Al centers in a quartz channel and of the crystal surrounding. In practice, analytical solutions of Eq. (6) are available only for special forms of the potential. We therefore propose to replace the effective potential $V^*(\xi)$ by an analytically solvable trial potential $V_T^*(\xi)$. When substituted into the Schrödinger equation, $V_T^*(\xi)$ leads to a ground-state wave function $\phi_0(\xi)$ which gives, with Eq. (7), a physically convenient potential $V(\xi)$. A minimum set of parameters for the trial potential $V_T^*(\xi)$ must thus be chosen with the condition that the shapes of the computed potential and of the physical potential look similar: the criteria for this similarity are the barrier height and the distance between well minima. An iterative process must then be performed to determine the values of the parameters characterizing this trial potential. The selected potential form is represented, in Fig. 1, by a square well with length equal to $3d+4l$, two barriers with height V_{T0}^* and length $2l$, and three wells with length d . We give in Fig. 1, as an example, the potentials experienced by Li⁺ and H⁺ in a channel containing an Al center located at $\xi=0$, and, in Table I, the corresponding values of the parameters V_{T0}^* , l and d .

Beside the interaction potential, a second quantity D must be evaluated. This quantity, which depends on the coupled dynamics of the ion and of the remaining crystal atoms, is assumed to be constant in space and equal everywhere in the channel, whatever the location of the Al centers. Within this assumption, the viscosity γ , and thus D , can be determined as if the channel does not contain impurity centers. The values obtained from Refs. 6 and 7 are given in Table II for Li⁺ and H⁺. We also give

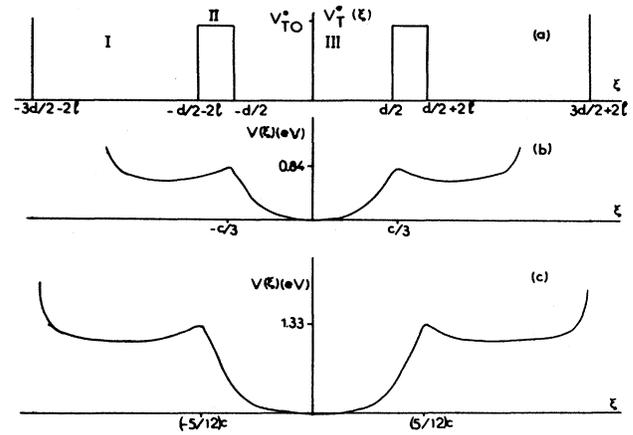


FIG. 1. Interaction potential experienced by M⁺ or H⁺ trapped by an Al impurity (located at $\xi=0$) in a quartz channel parallel to the c axis. (a) Trial square potential used for the analytical calculation of eigensolutions. (b) Effective potential V for M⁺=Li⁺ obtained for $V_{T0}^*/k_B T$, l and d values given in Table I. (c) Effective potential for H⁺ (cf. Table I). $c/3$ characterizes the distance between Si planes perpendicular to the axis c (cf. Ref. 5).

in this table the characteristic frequency ω for the motion of the ion in the physical potential experienced near the Al impurity, and show that $\gamma \gg \omega$, which is consistent with the assumption of the high-viscosity regime for the Smoluchowski equation.

The solutions of Eq. (6) with the square potential drawn in Fig. 1 are either symmetric or antisymmetric with respect to reflection through $\xi=0$ and they are determined according to the usual technique of quantum mechanics, in the different regions of constant potential. Let $\phi_{n,s}(\xi)$ and $\phi_{n,A}(\xi)$ be the symmetric and antisymmetric eigenfunctions connected to the eigenvalues $\lambda_{n,s}$ and $\lambda_{n,A}$; the eigensolutions are written as

$$\phi_{n,s}(\xi) = A_{n,s} \sin[K_{n,s}^{1/2}(\xi + \frac{3}{2}d + 2l)],$$

$$\phi_{n,A}(\xi) = A_{n,A} \sin[K_{n,A}^{1/2}(\xi + \frac{3}{2}d + 2l)],$$

$$\text{for } -\frac{3}{2}d - 2l \leq \xi \leq -\frac{1}{2}d - 2l;$$

$$\phi_{n,s}(\xi) = B_{n,s} e^{-\gamma_{n,s}(\xi + d/2 + 2l)} + C_{n,s} e^{\gamma_{n,s}(\xi + d/2 + 2l)},$$

$$\phi_{n,A}(\xi) = B_{n,A} e^{-\gamma_{n,A}(\xi + d/2 + 2l)} + C_{n,A} e^{\gamma_{n,A}(\xi + d/2 + 2l)}, \quad (10)$$

$$\text{for } -\frac{1}{2}d - 2l \leq \xi \leq -\frac{1}{2}d; \text{ and}$$

$$\phi_{n,s}(\xi) = D_{n,s} \cos(K_{n,s}^{1/2}\xi),$$

$$\phi_{n,A}(\xi) = D_{n,A} \sin(K_{n,A}^{1/2}\xi),$$

for $-\frac{1}{2}d \leq \xi \leq \frac{1}{2}d$. K_n and γ_n are reduced energies defined by

$$K_n = \lambda_n D^{-1},$$

$$\gamma_n = (V_{T0}^*/k_B T - K_n)^{1/2}. \quad (11)$$

The solutions for the region $\frac{1}{2}d \leq \xi \leq \frac{3}{2}d + 2l$ can be ob-

TABLE I. Parameters for the square potential ($T \approx 750$ K).

M^+	$V_{T0}^*/k_B T$ (\AA^{-2})	l (\AA)	d (\AA)
Li ⁺	43.57	0.424	3.636
H ⁺	7.41	0.512	4.548

tained from those given by Eq. (10) and the following symmetry rules:

$$\begin{aligned}\phi_{n,s}(\xi) &= \phi_{n,s}(-\xi), \\ \phi_{n,A}(\xi) &= -\phi_{n,A}(-\xi).\end{aligned}\quad (12)$$

The corresponding eigenvalue equations are

$$\begin{aligned}\frac{K_{n,s}^{1/2}}{\gamma_{n,s}} [\cot(K_{n,s}^{1/2}d)\cot(K_{n,s}^{1/2}d/2) - 1] \coth(2\gamma_{n,s}l) \\ - \frac{K_{n,s}}{\gamma_{n,s}^2} \coth(K_{n,s}^{1/2}d) + \cot(K_{n,s}^{1/2}d/2) = 0\end{aligned}\quad (13)$$

and

$$\begin{aligned}\frac{K_{n,A}^{1/2}}{\gamma_{n,A}} [\cot(K_{n,A}^{1/2}d) + \cot(K_{n,A}^{1/2}d/2)] \coth(2\gamma_{n,A}l) \\ + \frac{K_{n,A}}{\gamma_{n,A}^2} \cot(K_{n,A}^{1/2}d)\cot(K_{n,A}^{1/2}d/2) + 1 = 0.\end{aligned}\quad (13')$$

The data of Tables I and II have been used to perform numerical calculations in Eqs. (13) and (13'); the first ten symmetric and antisymmetric reduced eigenvalues are given in Table III for the Li⁺ ion and the proton. The eigenvalue $K_{0,S}$ corresponds to the stationary state. Many eigenstates are nearly degenerated as can be seen in Table III; this is due to the special form of the square potential. Moreover, the first nonzero eigenvalue K_1 appears, for Li⁺ and H⁺, very different from and smaller than the other eigenvalues. These other eigenvalues, K_n ($n > 1$), rapidly increase with the quantum number n .

The eigenvalues, with the corresponding eigenfunctions, can then be introduced into Eq. (9) to calculate the probability for finding the ion Li⁺ or the proton at a position ξ at time t , with the initial condition $\xi_0 = 0$ at $t = 0$. Recall that $\xi_0 = 0$ corresponds to the bottom of the Al well for the ion location. $P(\xi, t)$ is drawn in Fig. 2 for some characteristic times. Note that the condition $\xi_0 = 0$ leads to the vanishing of the antisymmetric solutions. In the long-time regime, the series expansion in Eq. (9) can be truncated at the first-order term $\lambda_{1,S}$ as discussed before.

TABLE II. Viscosity coefficient γ and characteristic frequency ω .

M^+	γ (s^{-1})	ω (s^{-1})
Li ⁺	1.857×10^{15}	1.642×10^{13}
H ⁺	4.435×10^{15}	5.329×10^{13}

TABLE III. Reduced eigenvalues of Eq. (6) obtained from Eqs. (13) and (13').

n	$K_{n,s}$		$K_{n,A}$	
	Li ⁺	H ⁺	Li ⁺	H ⁺
0	0.0	0.0		
1	0.0764	0.0276	0.0764	0.0276
2	3.1050	1.7886	2.7978	1.6775
3	7.4454	4.4319	3.1051	1.7886
4	8.1435	4.7224	8.1434	4.7224
5	15.1749	8.8271	13.9166	8.3793
6	22.1656	13.3950	15.1753	8.8271
7	24.1712	14.1000	24.1697	14.1000
8	35.0708	20.5370	32.1106	19.5120
9			35.0768	20.5370

Of course, for $t \rightarrow \infty$, the Boltzmann equilibrium distribution is recovered since only the zeroth-order term in the series contributes to $P(\xi)$. We can then define a characteristic Boltzmann time t_B as

$$t_B \approx \lambda_{1,S}^{-1}. \quad (14)$$

The value of t_B is around 100 ps (4×10^{-10} s for Li⁺ and 3.6×10^{-10} s for H⁺). In contrast, in the short-time regime, all the terms in the series contribute to $P(\xi, t)$. In

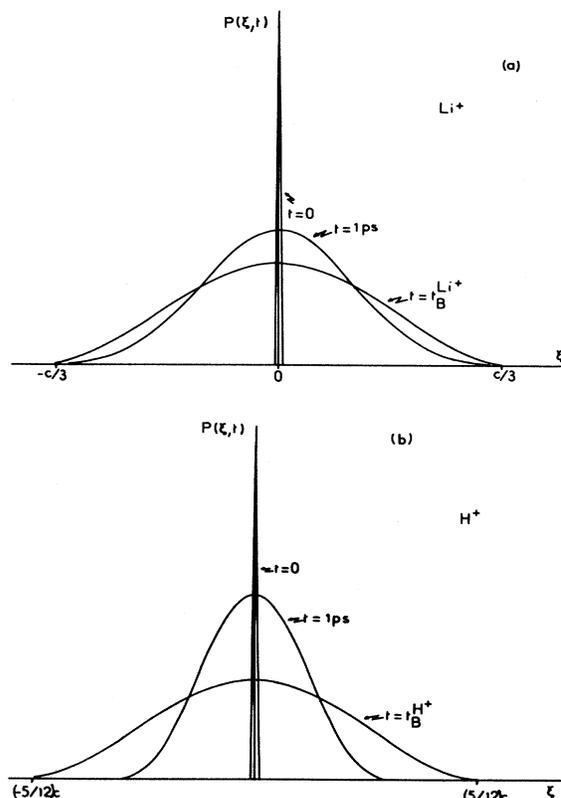


FIG. 2. Distribution function $P(\xi, t)$ vs the position of the ion with respect to the Al center at $\xi = 0$, and for three characteristic times— $t = 0$, $t = 1$ ps, and $t = t_B$ —(a) for Li⁺ and (b) for H⁺.

spite of the truncation for $n = 8$, the series expansion will be regarded as accurate for times longer than 1 ps. The curves $P(\xi, t)$ versus ξ in Fig. 2 are obviously very sensitive to the selected values of the characteristic times, due to the exponential behavior with t .

As mentioned before, it is interesting to connect the results obtained here to the jumping frequency obtained in the transit-time-concept approach of the transport theory. We therefore define a residence time t_c in the central well containing the Al impurity, which gives an idea of the deactivation time (time for the ion M^+ or the proton to escape from the Al well and jump in the adjacent well) as

$$t_c = \frac{t_B}{\int_{\text{adjacent well}} \phi_0^2(\xi) d\xi} \approx \left[\lambda_{1,s} \int \phi_0^2(\xi) d\xi \right]^{-1}. \quad (15)$$

The corresponding jumping frequency k'_0 is then defined as

$$k'_0 = t_c^{-1}, \quad (16)$$

leading to the values given in the first column of Table IV.

In a similar way, we define the residence time t_L for the ion or the proton in a lateral well (adjacent to the Al well) as

$$t_L = \frac{t_B}{\int_{\text{Al well}} \phi_0^2(\xi) d\xi} \approx t_B \quad (15')$$

since the integral in Eq. (15') is nearly equal to 1, due to the structure of the potential (deep and wide wells). The corresponding jumping frequency is, in this case, equal to

$$k''_0 = t_B^{-1} \approx \lambda_{1,s}. \quad (16')$$

The calculated values are given in the third column of Table IV.

IV. DISCUSSION

The values of the jumping frequencies (Table IV) calculated from the present approach are different by 1 order of magnitude from those obtained in the transit-time-concept method. Given the sensitivity of these values with the potential parameters, such results are relatively gratifying. The difference between the two approaches stands in a better description of the dynamics of the ion (or proton) in the continuous model, although the interaction potential is slightly modeled. The use of the effective potential in the Smoluchowski equation would

TABLE IV. Jumping frequencies for the various transport models.

M^+	k'_0 (s ⁻¹)		k''_0 (s ⁻¹)	
	Eq. (16)	Refs. 6 and 7	Eq. (16')	Ref. 13
Li ⁺	1.4×10^5	10^6	2.5×10^9	1.6×10^9
H ⁺	177	17	2.8×10^9	2.0×10^9

be possible but would require numerical time-consuming solutions. The values of k'_0 are about 1000 times greater for the alkali metal than for the proton, leading to the conclusion that the Al-OH⁻ centers are much more stable than the Al-Li⁺ ones, in agreement with the results of the discrete transport theory and with experiments.

Moreover, the jumping frequencies k''_0 for the ions in the lateral wells can be compared to the values obtained by using the Kramers model (Table IV). Here again, the agreement is good. These values of k''_0 are 10^3 – 10^4 times greater (for Li⁺) and 10^6 – 10^7 times greater (for H⁺) than the frequencies k'_0 and they exhibit the strong attractive character of the Al³⁺ impurity center.

A direct comparison with the available experimental data is possible if we know the behavior with time of the ionic current density during electrodiffusion of a quartz sample at $T \approx 750$ K, submitted to an external electric field equal to 1000 V cm^{-1} . Within the framework of the diffusion-compensation model, developed in Ref. 7, which rests on the assumption that the motions of the diffusing ion M^+ and of the compensating proton are independent, the ionic current density j_{n*} can be drawn for the values obtained for k'_0 in the present paper. The curve $j_{n*}(t)$ is shown in Fig. 3. Since the value of $k'_0(\text{Li})$, obtained from Eq. (16), is smaller than the value of Ref. 7, the initial ionic current is about seven times smaller. On the contrary, the asymptotic current which characterizes the proton diffusion appears to be two times greater, for the opposite reason. The overall behavior of the curve $j_{n*}(t)$ and the characteristic values of j_{n*} at long and short electrodiffusion times reflect the experimental trends, as do the results obtained in the discrete transport theory.

Note, however, that the present model also has some drawbacks. Beside the fact that the interaction potential is modeled, the results obtained for $j_{n*}(t)$ do not contain the modification induced by the external electric field. As mentioned in Refs. 6 and 7, this field is responsible (i) for a slight drift of the interaction potential $V(\xi)$ as the ion (or the proton) moves in the quartz channel and (ii) for an additional gradient due to the motion of the

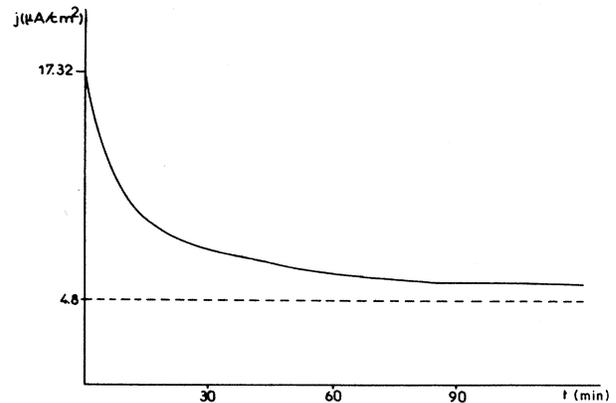


FIG. 3. Ionic current density j_{n*} ($\mu\text{A cm}^{-2}$) vs time (min) for the diffusion-compensation model of Ref. 7 and using the quantities calculated in the present method.

charged particles in the polarized medium. These effects, which are macroscopic in essence, can be considered to remain small at the microscopic scale. In the present calculation, we have thus assumed that the electric field gradient vanishes. The use of the simplified diffusion-compensation model appears to introduce more severe limitations in the accuracy of the results. Indeed, several species of alkali-metal ions (Li^+ , Na^+) can simultaneously exist in a quartz channel and interact through long-range ionic forces, as M^+ ions and protons can interact in the diffusion-compensation mechanism. The inclusion of this coupling between M^+ and M'^+ or H^+ , which was tedious in the discrete method, though not discussed here, could be done without difficulty in the present method, where $P(\xi, t)$ is considered as a continuous func-

tion of ξ .

To conclude, the present method is another way to calculate the jumping frequency of diffusing ions in crystals, in the sense that it gives similar results to those obtained from the transit-time concept in the transport theory. One of its advantages is the use of more complete information on the ion (proton) dynamics than the discrete method, and it appears potentially much more interesting for further improvements of the electrodiffusion model.

ACKNOWLEDGMENTS

The authors gratefully acknowledge partial support for the numerical computational procedure from the Gobierno Autónomo de Canarias.

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¹J. C. Brice, *Rev. Mod. Phys.* **57**, 105 (1985).

²J. Plata, J. Breton, and C. Girardet, *Phys. Rev. B* **38**, 3482 (1988), and especially Refs. 2–18 therein.

³M. J. Mombourquette, J. A. Weil, and P. G. Mezey, *Can. J. Phys.* **62**, 21 (1984); **63**, 1282 (1985).

⁴T. M. Wilson, L. E. Halliburton, M. G. Jani, and J. J. Martin, in *Proceedings of the 40th Annual Frequency Control Symposium, Ft. Monmouth, 1986* (IEEE, Piscataway, 1986), p. 26.

⁵J. Bretón and C. Girardet, *Phys. Rev. B* **33**, 8748 (1986).

⁶J. Plata, J. Bretón, and C. Girardet, *Phys. Rev. B* **38**, 3482 (1988).

⁷C. Girardet, J. Plata, J. Bretón, and A. Hardisson, *Phys. Rev.*

B **38**, 5648 (1988).

⁸N. G. Van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).

⁹H. Dieterich, P. Fulde, and J. Peschel, *Adv. Phys.* **29**, 527 (1980).

¹⁰T. Munakata, *Phys. Rev. B* **33**, 8016 (1986), and references therein.

¹¹M. A. Olson and S. A. Adelman, *J. Chem. Phys.* **83**, 1865 (1985).

¹²S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943).

¹³H. A. Kramers, *Physica* **7**, 284 (1940).

¹⁴N. G. Van Kampen, *J. Stat. Phys.* **17**, 71 (1977).

¹⁵L. E. Reichl, *J. Chem. Phys.* **77**, 4199 (1982).