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Relaxation dynamics, dissipative tunneling, solitons, and anomalous decay

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An anomalous behavior of the emission properties of alkali halides doped with heavy impurities, stimulated new efforts for its interpretation, invoking delicate and sophisticated mechanisms whose interest transcends the considered specific case. Of crucial importance is the evolution of the lattice reaction time. This gives strong support to a Jahn-Teller model which is able to interpret the slow (complex) decay of the emissions in the *A* band. The mechanism adopted is borrowed from the dissipative-tunneling approach, previously developed for loaded superconducting Josephson junctions, and suitably modified. Moreover, an attempt is made for a modification of the model by considering a mechanism based on soliton confinement.

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The interpretation of the optical properties of impurity centers in alkali-halide crystals, a classical problem in solid-state physics, could be considered as basically resolved in the early 1980s,[1] even if new contributions to the subject continued to appear in the subsequent literature. More recently, however, the problem of the emission of phosphors of the type $KX:Tl^+$ ($X=Cl,Br,I$) has become topical again, following the discovery of an anomalous and complex behavior of their emission decay times.[2] The anomaly consists of a gradual change in the decay time, from the faster component (at ns) to the slower (at ms) by assuming all the intermediate values. This finding stimulated new efforts of investigation, which led to much more sophisticated interpretation models, involving concepts and mechanisms whose field of applicability is of broad interest. A mechanism based on soliton confinement (obtainable with a suitable selection of the interatomic potential), was adopted in Ref. 3 in order to interpret the anomalous slow relaxation, under the assumption that the slow emission and the lattice reaction are on the same time scale. This, however, implies an unrealistic elongation of the characteristic time: in fact, a factor of the order of 10^9 is required for passing from the scale of picoseconds (crystal time) to that of milliseconds (emission time). The numerical simulations reported, although based on a reasonable selection of the damping parameter, exhibit a time scale that does not exceed nanoseconds. Independently, a different mechanism was proposed[4] based on a tunneling process, the duration of which (assumed to be given by the inverse of the decay rate, which also characterizes the emission time) strongly depends on the features of the barrier and presents a magnification of the decay time. Even a small variation in the equilibrium coordinate of the optically excited state, causes an appreciable change of the barrier, and very large variations of the delay time (in principle, from picoseconds to seconds) are admissible. Although the assumption of the existence of a delay in reaching the equilibrium configuration (due to the lattice reaction) appears plausible, its time scale remained completely indeterminate,[4] but presumably located around that of nanoseconds.[5]

In this work we first analyze the tunneling mechanism with inclusion of dissipation. Subsequently, the analysis is devoted to the evaluation of the lattice reaction time according to two different mechanisms, namely, the tunneling and the soliton confinement. On this basis an attempt is made for a unification of the two models.

Dissipative tunneling. A marked improvement of the model of Ref. 4 is here proposed, based on dissipative effects which accompany the tunneling processes, a topic which has been considered in several studies, especially in relation to tunneling in Josephson junctions.[6,7] For this reason, the interest in this approach transcends the problem of phosphor emission. A crucial quantity in these problems is the duration of the tunneling process, a quantity that has been interpreted in a variety of manners and that will be here briefly reconsidered in a preliminary way: this aspect deserves, however, to be analyzed in a more rigorous way for its broad relevance. The analogy between the potential shape for the junctions, and that of the excited state of luminescence centers, allows the application of the same analysis to the physical systems under study. In particular, the approach of Refs. 8 and 9, where tunneling in junctions coupled to electrical lines is considered, can be adapted to the present case. In fact, as will be described in the following, the absorption of light is followed by a local Jahn-Teller distortion of the lattice surrounding the heavy ion, along one of the *X*-Tl-*X* bonds, in the local *x* direction, say. This selects a preferential linear chain of the type -K-*X*-Tl-*X*-K-, along which the vibrational excitation initially propagates. Although in the course of the evolution vibrational energy will also diffuse in transverse directions, it seems reasonable to model for some time the process by a linear chain. This assumption is essentially the same as the one made in Ref. 3. This ionic chain of the lattice, stressed by the Jahn-Teller deformation in the excited state of the cluster $(TlX_6)^{5-}$, consists of a bilateral sequence of springs and masses, and can be considered as the analogue of a chain of inductances and capacitances ("Cauer form" network), which constitutes an artificial electrical line.[10] This analogy is based on the fact that the wave equations for both electrical and mechanical situations have the same structure, i.e., that of the D'Alembert equation

$$\frac{\partial^2\phi}{\partial x^2} - \frac{1}{v^2}\frac{\partial^2\phi}{\partial t^2} = 0, \tag{1}$$

where ϕ is the wave amplitude and v the propagation velocity. Such an analogy allows us to perform an estimate of the lattice reaction time, provided that a reliable estimate of the involved quantities (or at least of their orders of magnitude) is obtained. In this way, a robust support of plausibility is given to a model which represents an alternative (or a complementary) interpretation of a complex phenomenology to the one based on the mechanism of soliton confinement.

Let us now briefly summarize the essential features of the model,[4] which is based on the coexistence of two kinds of minima on the $^3T_{1u}$ excited-state potential surface, in the space of the normal coordinates of the quasimolecule $(\mathrm{Tl}X_6)^{5-}$; from these minima, two emission bands (A_T and A_X) originate by transitions to the ground state $^1A_{1g}$. For heavy impurities (like Tl^+), the coexistence of minima is ensured by the strong spin-orbit interaction. The minima from which the A_T emission originates, have tetragonal symmetry and are the ones mainly populated after absorption and vibrational relaxation. The A_X emission originates from minima of different symmetry, which become populated by nonradiative transitions from the A_T ones. At sufficiently low temperature,[11] the A_X minima can only be populated by tunneling through the potential-energy barrier that separates them from the A_T ones, and it is just such tunneling mechanism which induces more or less pronounced delay in these transitions. This delay, in turn, is reflected in the emission: not only A_X, but also A_T itself, due to contributions of back-tunneling (that is from A_X back to A_T), and to the role played by the underlying $^3A_{1u}$ trap level, as tentatively explained in Ref. 4(a) (see below however).

The potential barrier that separates A_T and A_X minima has a shape that critically depends on the dimensionless parameters A and g: $A=12(1-\beta)\zeta/b^2$ is a function of the curvature β of the potential (assumed harmonic near the minimum), of the electron-lattice coupling constant b^2, and of the spin-orbit coupling constant ζ; $g=G/\zeta$ is the ratio of the exchange integral G to ζ. The potential shape, of the cubic type $\epsilon x^2-\rho x^3$ in the barrier region, is depicted in the inset of Fig. 1, where x is a dimensionless variable given by $(-b/2\sqrt{3}\zeta)Q_3$, with Q_3 being the tetragonal interaction-mode coordinate.[1] Taking $g=0.4$ as a typical value, from the analytical expression of the potential in Ref. 4(a) we determine the normalized height of the potential barrier V_b/ζ as a function of A, as well as the values of the abscissae of the A_T minimum (x_0), and of the bounce coordinate (x_B), as reported in Fig. 1.

We note that the height of the potential barrier V_b and the difference of abscissae $\Delta x_B=x_0-x_B$ strongly depend on A: they decrease with increasing A and vanish for $A=3.6$. As anticipated above, the analogy between this potential shape and that of the Josephson junctions, allows a direct evaluation of the action integral for the bounce trajectory; in the case of the above-mentioned cubic potential, the action is exactly given by $S_b/\hbar=7.2V_b/\hbar\Omega$, where $\Omega=2\pi\nu$ is the angular frequency of small oscillations inside the initial potential well.[6] Within this framework, the tunneling transition probability (decay rate), at low temperature, can be expressed as[12]

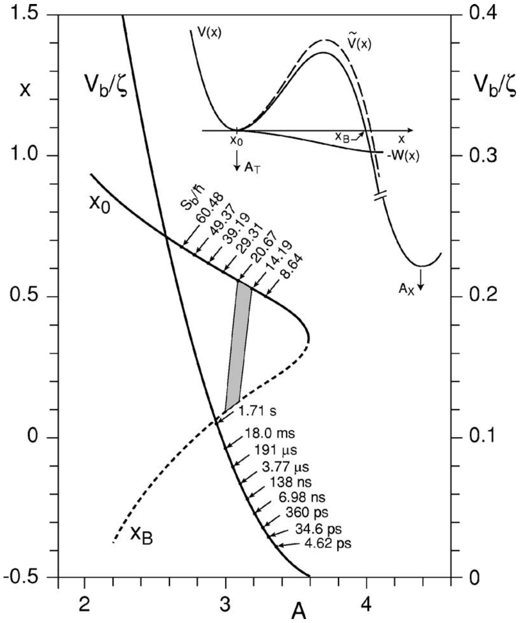

FIG. 1. Potential barrier V_b, normalized to the spin-orbit coupling constant ζ, and curve of the abscissae value x_0 and x_B, evaluated as a function of the parameter A and for $g=0.4$. On the curve of x_0, some values of the bounce action integral $S_b/\hbar$ are reported, while on the curve of V_b/ζ the corresponding delay-time values, evaluated as the inverse of Γ as given by Eq. (2), are indicated. The shape of the potential in the barrier region, $V(x)$, is depicted in the inset, where the dashed line represents the potential $\tilde{V}(x)=V(x)+W(x)$ as modified by dissipative effects. The latter cause tunneling paths situated in the shaded area connecting x_0 with x_B.

$$\Gamma = \Omega\left(\frac{30S_b}{\pi\hbar}\right)^{1/2} e^{-S_b/\hbar} \tag{2}$$

and the corresponding time delay is given by $\tau_d=\Gamma^{-1}$. The assumption that this quantity is representative of the duration of the tunneling process, depends on the parameter values that characterize the physical system under consideration. According to the results of Ref. 4(b), the relaxation trajectories, as given by the mean coordinate $\langle x(t)\rangle$, follow on average an exponential irreversible decay (sometime named *incoherent tunneling*), whose time constant can be identified with Γ^{-1}. Superimposed to the average coordinate, see Fig. 3 in Ref. 4(b), there is a damped fast oscillation (*coherent tunneling*) whose period $T_0=h/(2\delta_s+\sigma)$ (where δ_s is the energy shift due to tunneling and σ the mismatching of the levels), can become comparable to that of oscillations inside the initial well, namely $2\pi/\Omega$. In the present case, with $\sigma\gg\delta_s$, it is natural to assume the time delay due to tunneling as given by Γ^{-1} in Ref. 13. The numerical results for τ_d quoted in Fig. 1 are obtained from Eq. (2) by assuming typical values for the involved quantities, namely $\zeta \simeq 0.5$ eV and $\hbar\Omega \simeq 12$ meV.[4(a)] We note that, in the neighborhood of $A \simeq 3-3.2$, a small variation of Δx_B causes a strong variation of the order of magnitude of the decay time in the expected range of values (from ns to ms).

Now we want to consider the effect of the diatomic chain of ions stimulated by the Jahn-Teller effect. Considering, for simplicity, a homogeneous one-dimensional chain of masses M, elastic constant k and lattice constant a, the phase velocity has a limiting value given by $v_0 = a(k/M)^{1/2} = a\omega_0$, with $k = M\omega_0^2$.[14] For an artificial electrical line consisting of a large number of cells with inductance L and capacitance C at each site, the characteristic impedance is $Z_0 = (L/C)^{1/2}$ and the wave velocity is $v \propto (LC)^{-1/2}$. The Euclidean-Lagrangian components in this case are of the type $\frac{1}{2}CV_i^2 = \frac{1}{2}C\dot{\psi}_i^2$ and $\frac{1}{2}LI_i^2 = \frac{1}{2L}(\Delta\psi_i)^2$, where V_i and I_i are the voltage and the current relative to the ith cell, and $\Delta\psi_i = LI_i$ is the magnetic flux.[9] The corresponding mechanical components are of the type $\frac{1}{2}M\dot{x}_i^2$ and $\frac{1}{2}k(\Delta x_i)^2$.[14]

This suggests us to establish the following correspondence between electrical and mechanical systems, $\psi \to x$, $C \to M$, and $L \to k^{-1}$, see Ref. 15. In such a way, the quantity corresponding to Z_0 is $Z_0' = (kM)^{-1/2} = 1/M\omega_0$. In the electrical case, the damping coefficient is $\eta \propto Z_0^{-1}$, so the corresponding mechanical quantity will be given by $\eta' \propto M\omega_0$. Still in the electrical case, the increase of the bounce action is given by $\Delta S_b = \eta\phi_B^2 f$, ϕ_B being the bounce amplitude and f a numerical function of the order of unity, which depends on the frequency Ω and on the line delay τ_0. Therefore, in the mechanical case we obtain an expression for the action variation given, for $f \approx 1$, by $\Delta S_b = M\omega_0(\Delta x_B)^2$, with $\Delta x_B = a\Delta Q_0/Q_0$, where $\Delta Q_0/Q_0$ is of the order of 10%, and Q_0 is the position of the minimum in the normal coordinate space.[4(b)] A result is the latter, which is also supported by numerical integration of classical equations of motion describing the lattice dynamics.[3,14] Taking for M the mass of Cl (which is the lightest ion in the considered cases), $M \simeq 35$ amu $\simeq 58 \times 10^{-24}$ g, $\omega_0 = 2\pi\nu$ with $\nu \simeq 3 \times 10^{12}$ s^{-1} and $a \simeq 3 \times 10^{-8}$ cm, we have that $\Delta S_b/\hbar \approx 10$, which is just the order of magnitude required for producing the delay-time variation suitable for fitting the experimental results, with a change of several orders of magnitude. The shaded area in Fig. 1 shows that when the bounce action changes from $14.19\hbar$ to $29.31\hbar$, the decay-time varies from 6.98 ns to 18 ms. It seems, therefore, that the "load" due to propagation of the mechanical deformation along the ionic chain turns out to be of the right order of magnitude for interpreting the luminescence behavior.

Lattice reaction time. The problem we are faced with now, is the evaluation of the time dependence of the lattice reaction, which is determined, in the previous model, by the a-dimensional function f introduced above. To this purpose, we follow the (elegant) approach of Ref. 8, as subsequently developed in Ref. 9, obtaining the following expression for the action variation due to the line:

$$\Delta S_b = \int_{-\infty}^{+\infty} d\omega F(\omega, \tau_0)|\xi(\omega)|^2, \tag{3}$$

where $F(\omega, \tau_0) = \omega^2 \mathcal{L}(i\omega, \tau_0)$, $\mathcal{L}(i\omega, \tau_0)$ being the Laplace transform of the Lagrangian of the line, and

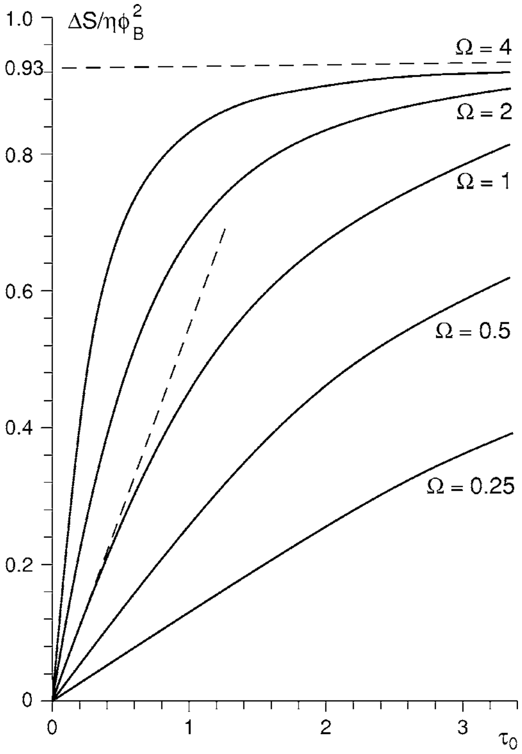

FIG. 2. Curves of the function $f(\Omega, \tau_0) = \Delta S_b/\eta\phi_B^2$, calculated by Eq. (6) as a function of the chain delay τ_0 for some values of the frequency Ω, which allow for an evaluation of the lattice reaction time.

$$\xi(\omega) = \phi_B \frac{2\sqrt{2}}{\sqrt{\pi}\Omega}\left(\frac{\pi\omega}{\Omega}\right)\operatorname{csech}\left(\frac{\pi\omega}{\Omega}\right) \tag{4}$$

is the Fourier transform of the bounce trajectory $\phi(\tau) = \phi_B \operatorname{sech}^2(\Omega\tau/2)$.

The results obtained by numerical analysis, according to the simplified procedure of Ref. 9, are comparable with those obtained by the functional integration adopted in Ref. 8. This is based on the solution of the Fourier transform of the wave equation (1), according to the Green's function method, which supplies the analytical result $F(\omega, \tau_0) = \eta\omega \tanh(\omega\tau_0)$. Therefore, Eq. (3) becomes

$$\Delta S_b = \eta \int_{-\infty}^{+\infty} |\xi(\omega)|^2 \omega \tanh(\omega\tau_0) d\omega. \tag{5}$$

By substituting (4) into (5) we obtain the following expression for the numerical function $f = \Delta S_b/\eta\phi_B^2$,

$$f(\Omega, \tau_0) = \frac{16\pi}{\Omega^4} \int_0^{\infty} \frac{\omega^3 \tanh(\omega\tau_0)}{\sinh^2\left(\frac{\pi\omega}{\Omega}\right)} d\omega. \tag{6}$$

In the limit of $\omega\tau_0 \gg 1$, $f \to 0.93$ while, in the opposite limit of $\omega\tau_0 \ll 1$, $f \to 0.534\Omega\tau_0$.[16] In the general case, Eq. (6) has been integrated numerically and the results are shown in Fig. 2 as a function of τ_0, and for some values of Ω, both quantities being given in arbitrary units. In our physical systems, where ω_0 is of the order of 10^{12} s^{-1}, the chain delay, as given by $\tau_0 = Na/v_0 = N\omega_0^{-1}$, can reach values of the order of hundreds of ps and even more, since the number N of cells can be assumed as arbitrarily large. Depending on the value of Ω, see Fig. 2, the reaction of the lattice will be more or less gradual before reaching the saturation at $f = 0.93$. In such a way the tunneling decay time, see Fig. 1, will be gradually varied from the smallest to the largest values. Therefore, the selection of a suitable compromise between Ω and τ_0 can provide the required time constants which characterize the different cases.[3,4]

The "hydrostatic-effect" mechanism, introduced in the Ref. 4(b) was found to be capable of varying the product $gA \propto d^9$, where d is the unperturbed nearest-neighbor separation in the quasimolecule $(\mathrm{Tl}^{+}X_6)^{5-}$, and therefore was suitable to enhance the tunneling decay-time variation; this mechanism can be considered as concomitant with the dissipative mechanism considered here, reinforcing its effect. The latter has been interpreted here as being due to a progressive wave traveling along the ionic chain of the lattice. However, any confinement mechanism of lattice excitation can also contribute to the decay-time variation in the slow luminescence up to a time scale that, in the model of Ref. 3, should be of the order of milliseconds. This is indeed a controversial point since, according to some works reported in literature[17] this time scale should not exceed that one of nanoseconds. However, a different conclusion about the stability of confined solitons (or breathers) has been recently given in Ref. 18 which holds the possibility of extremely long time values.

A basic feature of such a model[2,3] lies in the assumption that the energy separation between transition-allowed excited state (decay time of nanoseconds) and underlying trap level (decay time of milliseconds), that is δ in the inset of Fig. 3, increases with the Jahn-Teller parameter, or configuration coordinate x_0, for explaining the augment of the decay time up to ms. This tendency, however, is indeed just the opposite with the respect to the one derived according to the Jahn-Teller theory.[4,19] On the contrary, assuming that the A_T emission originates from T^* tetragonal minima, whose depth is E_T in Fig. 3, we have that the energy separation between them and the underlying trap level, that is $\Delta E + \delta$ in Fig. 3, actually increases with x_0, and the entity of this separation, for small values of parameter g, is found to be of the order of tens of meV.[20] In this way, a level scheme is obtained which, at least qualitatively, is just the one required in the model of Refs. 2 and 3.

As for the time duration of the lattice reaction acting directly on the E_T minimum, we shall assume (in the hypothesis of a soliton confinement situation) that the Jahn-Teller active luminescence cluster is loaded by a finite bilateral section of ionic chain (something similar to what was done in Ref. 18), which becomes seat of standing waves and can be considered as the analog of a resonant circuit. The analysis of this system can be performed according to the telegrapher's equation, that is Eq. (1) with inclusion of the term $-(2\alpha/v^2)\partial\phi/\partial t$, where α is a positive constant which accounts for dissipative effect.[21] By considering the Jahn-Teller excitation as a step-function pushing, at $t=0$, on the ionic chain assimilated to a damped oscillator, we have that the lattice reaction can be expressed for $t \geq 0$, as[22]

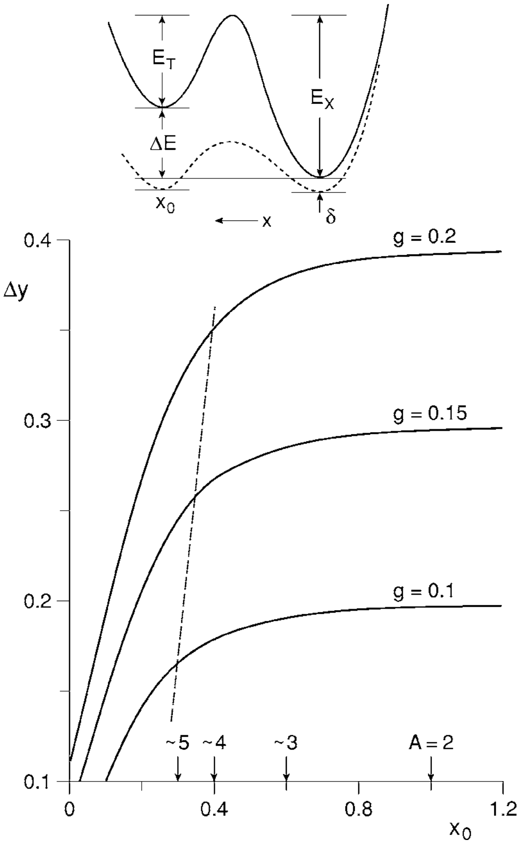

FIG. 3. Energy separation $\Delta E + \delta$, between T^* (E_T) minimum and underlying trap level, normalized to the spin-orbit coupling constant ζ, calculated as function of the coordinate x_0 of the T^* minimum and for some values of the parameter g (after Ref. 20). The dashed line delimits the parameter space (on the right-hand side) for which the minimum T^* is stabilized. The inset shows a sketch of the double minimum excited-state potential function along the reaction path from E_T to E_X minimum.

$$x(t) = \Delta x_B\{1 - e^{-\alpha t}[\cos(wt) + (\alpha/w)\sin(wt)]\} \tag{7}$$

where $w = (w^2 - \alpha^2)^{1/2}$ is an "effective velocity," having dimension of $(\mathrm{time})^{-1}$, and (as before) $\Delta x_B = a\Delta Q_0/Q_0$. The action variation will be of the order of $Mw(\Delta x_B)^2(w/a)$, therefore (w/a) times the estimate made before, $\Delta S \simeq 10\hbar$. The duration of the process, or better the time required to reach the equilibrium displacement, turns out to be of the order of α^{-1} and for α sufficiently small can reach even very long values.

It seems therefore, that a suitable combination of the two above-mentioned models could offer a complete interpretational scheme for explaining the complex phenomenology of the slow emission in doped alkali-halide phosphors. Specifically, the model based on tunneling between different kinds of minima turns out to be particularly suited for the cases of two emission bands (high-energy A_T and low-energy A_X) as typically shown by the Tl^{+} impurity. The mechanism adopted, however, can easily explain the anomaly of the slow component of the A_X emission, while the anomaly observed in the A_T emission remains in this framework more problematic. In addition, the cases in which we have only one emission band (presumably of A_T type), as for most cases of the Pb^{2+} impurity, appear rather difficult to explain since the A_X emission seems to be nonexistent. However, an overlapping of the two emissions, A_T and A_X, cannot be excluded because of the strong reduction of the g parameter down to values (say $g \leqslant 0.1$) that actually could make the two emissions rather undistinguished, the energy difference between their peaks being given by $\Delta E \simeq 2g\zeta$.

On the contrary, the mechanism based on soliton confinement, revisited in the light of a correct energy-separation behavior as in Fig. 3, appears as more suited for interpreting the anomaly of the A_T emission. However, the elongation of the lattice reaction time (up to ms in Refs. 2 and 3) remains difficult to be a-critically accepted and requires further consideration. A crucial point in the analysis in Ref. 18 is the neglecting of quantum-tunneling delocalization, so that an initially localized pulse can be trapped "indefinitely" as a quantum excitation.

In the approach to the problem outlined here, Eq. (7), the evaluation of the time duration ultimately rests on a reasonable estimate of the constant α; estimate that, even for small values as $\alpha \simeq 10^{-4}-10^{-3}$, supplies decay times of the order of thousands of vibrational periods,[17] that is again in the range of nanoseconds. However, the load due to the ionic chain contrasts the reaching of the equilibrium coordinate (analogously to the role played by the "hydrostatic effect" mentioned above), thus producing an appreciable variation (a decrease) of the parameter A (see Fig. 3) which, in turn, causes the required increasing energy-level separation. In such way, a delay amplification, similar to the one considered before for the tunneling mechanism (mainly acting on the A_X emission), can be considered as operating even for the A_T emission itself; so that its emission times, as depending on the level characteristics, can result to be distinctly different from the lattice reaction time, thus avoiding the heavy assumption of Refs. 2 and 3.

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[5] Nanosecond time scale, which corresponds to the fast component of the emission, followed by the components at μs and ms.

[6] See, for example, the pioneering work by A. O. Caldeira and A. J. Leggett, Phys. Rev. Lett. **46**, 211 (1981); Ann. Phys. **149**, 374 (1983).

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[10] E. A. Guillemin, *Synthesis of Passive Networks* (Wiley, New York, 1957), Chap. 3.

[11] By increasing temperature, the tunneling transition probability constantly grows due to the increase of the transmission coefficient through the barrier, and ultimately will be dominated by the thermal overcoming of the barrier. For the systems of our interest, this occurs at temperature values around 40–80 K [Ref. 4(a)].

[12] In the present case of an asymmetric double-well potential, the use of Eq. (2) (which exactly holds for a cubic potential) might appear questionable. However, in the presence of a large asymmetry parameter σ, the cubic form is certainly acceptable in the neighborhood of the barrier, while irreversible behavior will be produced by coupling to the thermal bath [see J. P. Sethna, Phys. Rev. B **25**, 5050 (1982)].

[13] See also, A. Ranfagni, I. Cacciari, M. A. Vitali, G. Viliani, P. Moretti, and R. Ruggeri, Phys. Rev. A **74**, 014102 (2006).

[14] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1957), Chap. 5. For $\omega_0 = 1$, and space in unity of lattice constant, we have $v_0 = 1$, as shown in the upper panel of Fig. 1 in Ref. 3(a) with time unity $1/\omega_0$.

[15] A correspondence which is similar to that usually made for the resistively shunted junction model, of current biased Josephson junctions, where the electrical equation of motion is related to a mechanical analog.

[16] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integral, Series, and Products* (Academic, New York, 1980), p. 352.

[17] See, for example, V. Hizhnyakov and D. Nevedrov, Phys. Rev. B **56**, R2908 (1997).

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