Relaxation dynamics in the excited state of impurity centers in alkali halides

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A Jahn-Teller model, recently re-proposed in order to explain the anomalous slow emission of impurity centers in alkali halides, can be supported on the basis of an analogy with the behavior under hydrostatic pressure. An improvement in the model, aimed at obtaining a more precise evaluation of relaxation times, is then introduced.

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A Jahn-Teller model for explaining the emission properties of impurity centers in alkali halide crystals, which has been proposed ever since the 1970's,[1,2] has been shown to be capable of interpreting new experimental results, to the understanding of which recent efforts have been devoted.[3]

In a previous paper,[4] we demonstrated that this Jahn-Teller model is suitable for explaining the anomalous decay in the slow-emission component of Tl^+ luminescence. Subsequently, it was successfully applied to the low-energy emission of KCl:Tl.[5] In this particular model, a crucial role is played by tunneling between different kinds of minima in the excited-state potential surface, from which the two (high-energy A_T and low-energy A_X) emission bands originate. The gradual increase in the decay time can be interpreted as being due to a variation of the equilibrium configuration coordinate of the excited state in the subspace of the tetragonal coordinates, a variation which modifies the potential barrier between minima.

During the same lapse of time, a different interpretation of the above-mentioned anomalous decay, based on a mechanism of soliton (or breather) confinement, has been proposed.[3,6] Our approach to this problem, although similar in some respects to the first explanation proposed,[7] was aimed at giving a simpler alternative. Moreover, while the model of Refs. 3, 6, and 7 is based on the assumption that the host lattice relaxes at the same, extremely long, time scale as the slow-component decay time (ms), in our model a much shorter time scale is sufficient (order of μs or less), since even a small change in the equilibrium coordinate can produce a variation of orders of magnitude in the decay time.[4,5]

The purpose of the present work is to better explain the advantages of this alternative interpretation, by supporting it on the basis of an analogy with hydrostatic pressure effects, and to make an improvement in the theoretical model so as to have a more precise determination of the relaxation between different minima.

A section of the excited-state potential surface along the reaction path (in the subspace of tetragonal coordinates) from T to X minima is sketched in Fig. 1(a). It shows that, when the parameter $A=12(1-\beta)\xi/b^2$ (β accounts for the difference in curvature between the ground and excited states, ξ is the spin-orbit coupling constant, and b is the electron-lattice coupling constant) is varied from A_i to $A_f<A_i$, the barrier height is modified from E_{bi} to $E_{bf}>E_{bi}$, and the minimum coordinate Q_0 is slightly augmented.[4] In Fig. 1(b), the Jahn-Teller distortion of the luminescence center—say the $Tl^+(Cl^-)_6$ quasi-molecule, or cluster—for the Q_3-tetragonal coordinate is represented. The reaction path of Fig. 1(a) mainly concerns the Q_3 coordinate:[9] we note that the Δz elongations along the z axis are twice as large as the shortenings along the x and y axes; moreover, these coordinate variations are expected to be rather important (say of the order of 10% of the unperturbed nearest-neighbor separation d in the lattice; see below). In such situations, in principle one should also include in the analysis the quadratic and higher order Jahn-Teller interactions, besides the only one considered here (parameter β). However, in the case of heavy impurities like Tl^+ and Pb^{2+}, the spin-orbit interaction is strong enough to assure the coexistence of different kinds of minima, and this scheme turns out to be the most adequate. The advantage of this scheme lies in its semplicity because it requires only few parameters (included in A and g) for an analytical though approximate description of the potential surfaces.[4]

It is reasonable to assume that the lattice will react, especially along the z axis, so that attainment of the equilibrium coordinate will be reached in some finite time.[10] Moreover, the $\Delta z=2\Delta x$ (or $2\Delta y$) variation will suffer a more important slowing down before reaching the expected equilibrium value. This means that, during the course of the relaxation to the Q_0 value, the complete deformation cannot be represented only by the Q_3 coordinate, but the Q_1 (totally symmetrical) coordinate is also involved. More precisely, let ions (Cl^-) 1,2,3 be located on the positive x,y,z coordinate axes, respectively, and ions 4,5,6 on the opposite sides. Denoting by X_i,Y_i,Z_i the displacements (all of the same entity) of an ion from the ideal octahedral arrangement (x_i^0,y_i^0,z_i^0), so that $X_i=x_i-x_i^0$, etc., we have that the Q_1 and Q_3 coordinates are expressed as[11]

$$Q_1=(X_1-X_4+Y_2-Y_5+Z_3-Z_6)/\sqrt{6},$$

$$Q_3=\left[\tfrac{1}{2}(X_1-X_4+Y_2-Y_5)-Z_3+Z_6\right]/\sqrt{3}. \qquad (1)$$

We note that in both expressions, the displacements in the x-y plane have the same sign, while those along the z axis

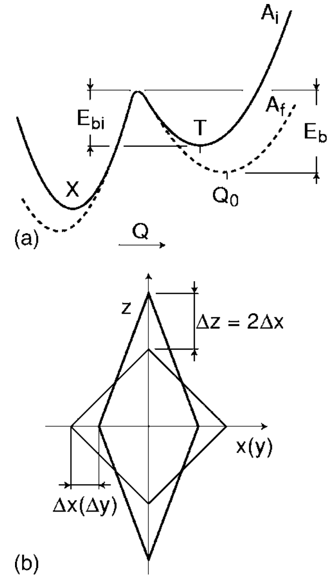

FIG. 1. (a) The cross section of the excited-state potential surface along the transition path from T to X minima, for two values of the parameter A which cause different barrier heights E_b. (b) The variation of the quasi-molecule geometry from the initial octahedral configuration to the final one according to pure-tetragonal Q_3-coordinate distorsion.

have opposite sign; so, the above assertion can be easily verified. In fact, a cluster deformation Q in which the $Z_{3,6}$ displacements do not satisfy the condition required for a pure Q_3 coordinate, that is (in absolute values) $Z_{3,6}=2X_{1,4}$ or $(2Y_{2,5})$, will be described by adding (algebrically) a suitable amount α of the Q_1 coordinate. For the case here considered, an elongation along the z axis, with $Z_{3,6}<2X_{1,4}$ or $(2Y_{2,5})$, we will have $Q=\alpha Q_1-Q_3$. In other words, the mean value of d in the quasi-molecule during relaxation is found to be slightly lowered (while for a pure Q_3 coordinate it would be maintained exactly).

Now, we should recall that the Jahn-Teller model described above was successfully adopted for interpreting the behavior of A_T and A_X emission bands under hydrostatic pressure.[12] The change in the balance of intensities under pressure—A_T emission increases while A_X emission decreases—was attributed to an increase in the barrier height [E_b in Fig. 1(a)] due to a lowering of the $gA=12(1-\beta)G/b^2$ product, where $g=G/\xi$ is the ratio of the exchange integral G to the spin-orbit coupling constant. While G and β are expected to be rather insensitive to the pressure, the electron-lattice coupling constant b^2 strongly depends on it, since it is inversely proportional to the ninth power of d, $gA \propto d^9$ and, typically, can undergo, under pressure, a decrease of up to 35%, which corresponds to an increase in the barrier height.[12] A similar, though less pronounced, effect is expected to occur also during the course of relaxation since, as previously noted, the mean value of d is slightly lowered, analogously to what happens under hydrostatic pressure. Therefore, we can conclude that the lattice reaction tends to lower A which, in a given time, will reach the final value A_f at its proper equilibrium coordinate Q_0. It is difficult to evaluate the time scale required to reach equilibrium. However, on the basis of previous analysis,[4,5] the following points can be well established:

(i) A relatively small variation in Q_0 (in tetragonal space) of the order of $\Delta Q_0/Q_0 \simeq -\Delta A/A \lesssim 10\%$ is sufficient to produce, in temporal succession, the required increase in the time constant (from μs to ms) needed to fit the experimental data.

(ii) In our model, the time scale for the relaxation process of the lattice is considerably shorter than the one required in the model of Refs. 6 and 7 where this time scale is the same as the optical relaxation time (ms). Our model benefits from a sort of delay amplification, so that the lattice relaxation time scale can be limited within a range of μs or less.

(iii) The proposed model had already demonstrated its capability to explain the intensity balance of the two emissions, A_T and A_X, versus temperature, as well as to provide a preliminary interpretation of multiple decay time.[13] These characteristics are still preserved if it is considered that longer time constants (from tens of μs to tens of ms) are required when the intensity is reduced up to $\lesssim 10^{-3}$ of its initial value.[5]

The relaxation time (tunneling delay) corresponding to different parameter values of the luminescence center, mainly the values of A, were evaluated in Refs. 4 and 5 in accordance with a simplified Wentzel-Kramers-Brillouin (WKB) analysis. Our intention is to plan a more sophisticated way of determining this relaxation time, through an evaluation of the tunneling relaxation trajectories. Approaches of this kind, which are distinctly different from the WKB method,[14] have been used for the study of squeezed states in symmetrical[15] and asymmetrical[16,17] double-well potentials. What emerged from these works was a chaotic character of the expectation value of the coordinate versus time, and the result was that a fractal dimension could be assigned to the trajectory because of its irregular behavior (a result that calls to mind the shape of quantum-mechanical paths as predicted by Feynman[18]). More precisely, a sort of "noise," due to the squeezing, is superimposed on a more regular behavior which, in the presence of dissipative effects, becomes a decay overimposed with a more or less damped oscillation.

The results of the analysis reported in Ref. 17 can be used for an evaluation of the tunneling relaxation trajectory. Without considering the effects of squeezing in the initial state, the shape of the trajectory is given by Eq. (15) in Ref. 17, which can be written in simplified form as

$$\frac{\langle x(t)\rangle}{\langle x(0)\rangle} = G_1(t) - G_2(t)\tanh\left(\frac{\sigma}{2kT}\right) + 4\frac{\delta}{\sigma}G_3(t), \tag{2}$$

where $\langle x(0)\rangle$ is the initial coordinate, k is the Boltzman constant, T is the temperature, and

$$G_1(t) = \exp\left(-\frac{2\varepsilon_1}{\hbar}t\right) - \frac{\delta}{\sigma}\exp\left(-\frac{2\varepsilon_0}{\hbar}t\right),$$

$$G_2(t) = 1 - \exp\left(-\frac{2\varepsilon_1}{\hbar}t\right) - \frac{\delta}{\sigma}\exp\left(-\frac{2\varepsilon_0}{\hbar}t\right),$$

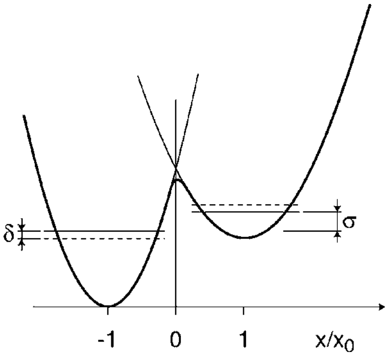

FIG. 2. The same as Fig. 1(a), with the normalized coordinate Q/Q_0 denoted as x/x_0, showing the energy shift δ and the mismatching σ of the levels.

$$G_3(t) = \exp\left(-\frac{\varepsilon_0+\varepsilon_1}{\hbar}t\right)\cos\left(\frac{2\delta+\sigma}{\hbar}t\right).$$

Here, it is assumed that the energy shift δ must be much smaller than the asymmetry parameter σ that measures the mismatching of the levels (see Fig. 2). In Eq. (2), ε_1 and ε_0 are related to the forward (Γ_1) and backward (Γ_0) tunneling rates from the upper minimum (where the system is initially prepared) towards the lower one. In Fig. 3 we show some examples of relaxation trajectories, evaluated for typical values of the parameters involved. We note that the damped oscillation [due to the last term in Eq. (2), which represents the coherent part of the tunneling] strongly depends on the δ value. The average relaxation roughly follows an exponential decay [due to the second term in Eq. (2), which represents the incoherent tunneling], whose time constant is given by $\hbar/2\varepsilon_1$. Therefore, the crucial quantity for evaluating the decay time, or, according to our model, the delay time, is ε_1 [ε_0 is negligible at low temperature and for large σ (Ref. 17)]. Still, for large σ, ε_1 represents the decay rate (Γ_1) from the upper to the lower minimum, while ε_0 is the rate (Γ_0) of the back tunneling; the total decay rate will be given by $\Gamma=\varepsilon_0+\varepsilon_1$. Indeed, the quantities ε_1 and δ are not independent but are related to the tunneling rates $\Gamma_i(i=0,1)$: in our case only Γ_1 is very important, as $\Gamma_0=\Gamma_1\exp(-\sigma/kT)$. For a high asymmetric situation, for Γ_1 we can adopt an expression which is strictly valid only for cubic potentials, namely[19]

$$\Gamma_1 = 2\frac{|\mathrm{Im}\,\delta|}{\hbar} = \omega\left(\frac{30S_b}{\pi\hbar}\right)^{1/2} e^{-S_b/\hbar} \tag{3}$$

where ω is the angular frequency inside the initial well and S_b is the action integral of the bounce trajectory. Equation (3) can be written in a different form: $\Gamma_1=\bar{\omega}\exp(-2S_0/\hbar)$, where $\bar{\omega}$ is an effective frequency and S_0 is the action integral across the barrier (that is, $2S_0 \sim S_b$). In this way, we recover an expression which is comparable to the WKB form adopted in Refs. 4 and 5. It is therefore expected that, even if more accurate results of time delay can be obtained by using Eqs. (2) and (3), the general trend will be confirmed.[20] In particular, for the cases of Tl$^+$ luminescence, parameter A tends to increase slightly (say from 3 to 3.2) in passing from KCl to KBr and KI host lattices. The consequence of this

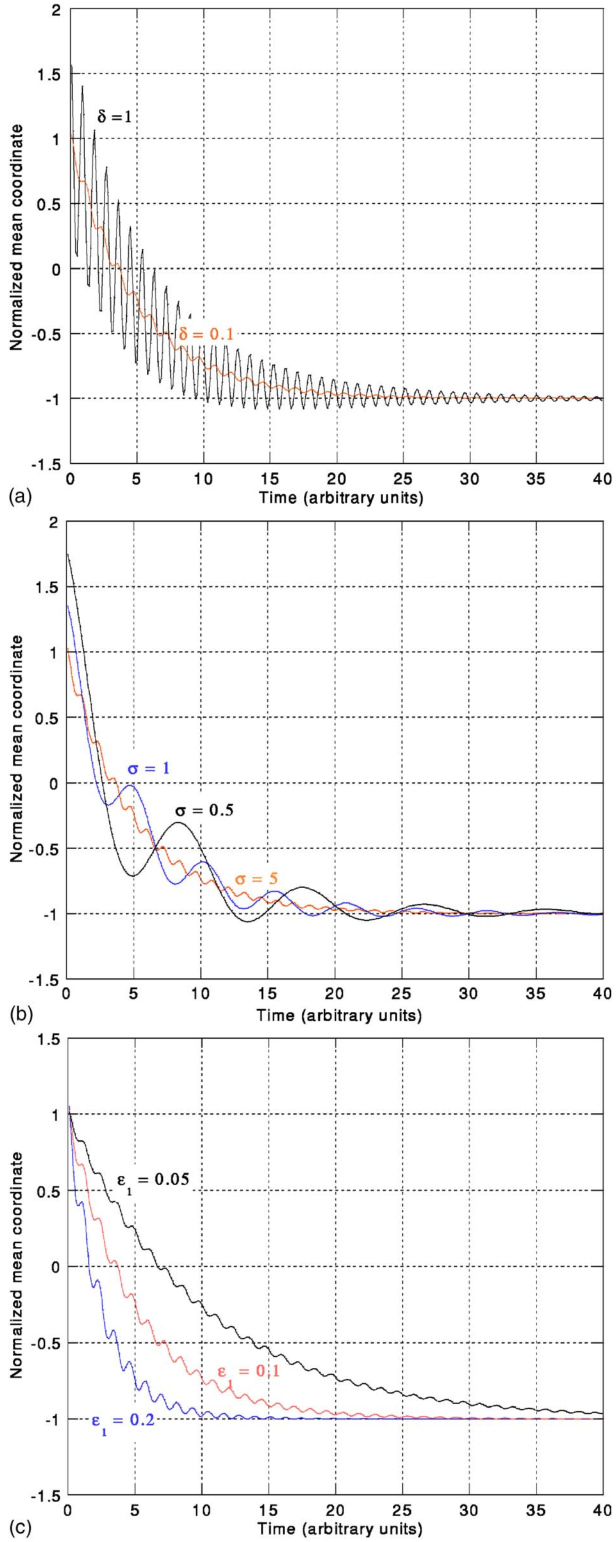

FIG. 3. (Color online) The mean relaxation trajectories $\langle x(t)\rangle/\langle x(0)\rangle$ versus time for a system initially prepared in the upper minumum $(x/x_0=1)$ towards the lower minimum $(x/x_0=-1)$, calculated according to Eq. (1), where $\varepsilon_0=\varepsilon_1\exp(-\sigma/kT)$, for parameter values as follows (assuming $\hbar=1$): (a) $\varepsilon_1=0.1$, $\sigma=5$, $kT=0.1$, and $\delta=0.1$, 1; (b) $\varepsilon_1=\delta=0.1$, $\sigma=0.5$, 1, 5, and $kT=0.1$; and (c) $\varepsilon_1=\delta=0.05$, 0.1, 0.2, $\sigma=5$, and $kT=0.1$. Increasing the temperature only slightly modifies the coordinate value of arrival.

tendency is that the barrier height, E_b in Fig. 1(a), tends to decrease appreciably [say from 69.0 to 38.5 meV (Ref. 4)], while the variation range of the delay time is augmented (see Fig. 3 in Ref. 4). This fact agrees with the experimental evidence that the anomaly in the slow component of the emission becomes more and more evident in passing from KCl:Tl to KI:Tl.

A similar, and even more evident, behavior was also evidenced in the cases of Pb^{2+} as an impurity center,[8] for which the model of Refs. 3 and 6–8 was originally proposed.[7] Our approach so far has concerned only Tl^+ luminescence, which is characterized by the presence of two —A_T and A_X— emission bands, offering a model interpretation based on tunneling between the relative minima. This model therefore seems to be inadequate for treating the Pb^{2+} luminescence, due to the presence of only one emission band (presumably the A_T one). This situation is, in a sense, similar to the case of KCl:Tl which, for a long time, was considered to have only one emission band (the leading one at 305 nm), ignoring the minor emission at 475 nm which is the subject of study in Ref. 5.

In an attempt to apply our model to cases of Pb^{2+} luminescence, we have to keep in mind that a further reduction in the barrier height could lower the temperature range for the emission (considered to be A_X in type) with strong evidence, due to a very small potential barrier, of its anomalous behavior. In this hypothesis, the A_T emission should not be observable, because it is prevented by some unknown nonradiative mechanism,[21] or confined to an extremely low temperature range.

The temperature dependence of the anomalous behavior deserves to be mentioned. In the case of Pb^{2+} impurity, the results already reported[22] demonstrated that with increasing temperature the anomaly of the slow decay gradually becomes less evident with an increase of the decay constants, that is with a lowering of the time constants. Something similar was also observed for the time constants of the low-energy emission of KCl:Tl,[5] although starting from higher values of temperature. However, for the weakness of the anomalous effect, it is difficult to draw in this case a precise indication about the more or less evidence of temperature effect on the entity of the anomaly itself.

We can therefore conclude that our approach to an interpretation of the anomalous behavior in the slow emission appears to be particularly suitable for the case of Tl^+ impurity. However, we might argue that a similar conclusion cannot be excluded also for other cases, provided that these are characterized by strong spin-orbit interaction, which, together with the A parameter, has a decisive role in shaping the potential surface.

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[20] More accurate results, considering the parameter values which characterized the several cases (see Table II in Ref. 4), will be reported elsewhere.

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