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Anomalous decay of the slow component of Pb^{2+} emission

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A theoretical model is introduced for the experimentally observed nonexponential slow-component decay of Pb^{2+} ions in potassium halide crystal hosts. It is based on the assumption that the adiabatic approximation is violated for the slow emission process. The Hamiltonian of the model describes the lowest excited state of the system as two energy levels resulting from the Jahn-Teller effect and from spin-orbit coupling. It is parametrized by the lattice relaxation time scale and by lattice-induced coupling and energy values for those levels. Using the model, a successful fit of the experimental data was obtained. [S0163-1829(98)00535-9]

I. INTRODUCTION

Optical properties of alkali halide crystals doped with ions that have ns^2 configurations in their ground state have been studied extensively, beginning in 1927 with the work of Hilsch.[1] There are several review articles on the subject.[2–4] Until recently experimental and theoretical work concentrated on ns^2 ions built in alkali halide lattices with fcc crystal structure. Recent work (see, e.g., Refs. 5–12) provides more detailed information on heavy ns^2 ions (Tl^+,Pb^{2+}) built in lattices with bcc crystal structure as well. Actually, more complicated spectra with respect to fcc host matrices are obtained. Their complex structure is explained by the coexistence of ns^2 ion states and perturbed exciton states.[8]

Experimental studies of luminescence decay kinetics under excitation in the A absorption band (A luminescence) have revealed at least two luminescence components: a fast one with a lifetime on the order of nanoseconds and a slow one with a lifetime on the order of milliseconds. The existence of these two emission components is explained as a consequence of the Jahn-Teller (JT) effect and a spin-orbit (SO) interaction.[3,13] Detailed experimental study of the decay kinetics of Pb^{2+} ions in KX crystal matrices ($X = \mathrm{Cl, Br, I}$) in Ref. 14 showed that the slow luminescence component does not decay exponentially as one would expect. Any single exponential that properly describes the tail of the decay deviates from the experimental curve in its initial part (up to about a few ms). This effect probably has a more general character, as has been observed in the Tl^+ center in KCl, KBr, KI, and CsI as well (see Refs. 7,15–18).

The observed nonexponential decay under excitation in the A absorption band cannot be explained as the result of a macroscopic average of contributions coming from many (slightly different) emission centers, as is the case, for example, in isolated centers embedded in glassy matrices.[19,20] Similar effects coming from unwanted impurities and/or structural defects cannot be excluded a priori even in single crystal hosts. However, there are several arguments supporting the idea that the observed nonexponential decay is an intrinsic property of the emission centers in KX:Pb crystals, such as the following.

(1) In our work dealing with *isolated* Pb^{2+} centers in KX hosts, the possible presence of defects was significantly reduced by the crystal growth technology used (Brigdman technique using very pure zone-refined starting materials[21]).

(2) Reproducibility of the nonexponential character of the slow decay in crystals of varying quality (different growing techniques, different purity of growing material) used in Refs. 14 and 18.

(3) To properly fit the initial part of the slow decay one would need to use the sum of several exponentials with lifetimes ranging from microseconds to milliseconds. The presence of defects that would reduce the metastable level lifetime (order of milliseconds) by 2–3 orders of magnitude (microseconds) would be very hard to explain.

In this article we provide a theoretical framework for studying the nonexponential decay of the luminescence of Pb^{2+} ions in alkali halide crystal matrices KX ($X = \mathrm{Cl}$, Br, and I), with reference to the work 14. See also another theoretical study.[22]

The physical idea suggested in Ref. 14 is that there is a time on the order of milliseconds during which the lattice surrounding the $(PbX_6)^{4-}$ centers relaxes. Such a slow relaxation could be a response of the lattice to the Jahn-Teller local distortion of $(PbX_6)^{4-}$ centers, and affects the slow decay component of KX:Pb^{2+} emission.

Prior to the UV flash, the Pb^{2+} sits in a symmetric but displaced array of the six nearest-neighboring X anions (displaced because of the large size of the Pb^{2+}). Let R be a collective coordinate for the configuration of the nuclei of the $(PbX_6)^{4-}$ complex. This could be a displacement with octahedral or other symmetry (but generally not preserving the original full symmetry). The value of R in the initial state is taken to be 0. In terms of an adiabatic (Born-Oppenheimer) analysis, the electronic energy levels as a function of R have a roughly parabolic shape, with $R=0$ the

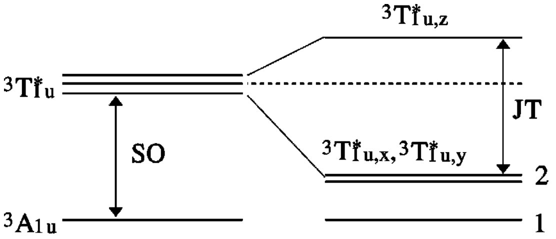

FIG. 1. Energy-level scheme for the relaxed excited states of the PbX_6^{4-} molecular complex with O$_h$ symmetry in its ground state. Splitting of the levels is due to SO and JT interactions. The JT axis is parallel to the [001] direction. The asterisk on ^{3}T$^*_{1u}$ is to remind the reader that the level is not the pure triplet state, but is the state resulting from the SO mixing of ^{3}T$_{1u}$ with an upper lying singlet ^{1}T$_{1u}$ state. For more details see also Ref. 4.

minimum (note that this applies while the $(\mathrm{Pb}X_6)^{4-}$ remains in its ground state).

After the UV flash the $(\mathrm{Pb}X_6)^{4-}$ system goes into an excited state. The lowest excited state is sketched in Fig. 1. The splitting of the levels is a result of a SO interaction and the JT effect. The emitting states in the potential well consist of the lower level 1, corresponding to the ^{3}A$_{1u}$ state, and the upper level 2, corresponding to the lower doublet of the split ^{3}T$^*_{1u}$ state. (This scheme is generally accepted; see, e.g., Refs. 4,13, and 23.) In both cases the $(\mathrm{Pb}X_6)^{4-}$ system quickly relaxes to the minimum on the adiabatic potential energy surface (APES) which is a Jahn-Teller minimum with lowered symmetry relative to the original octahedral symmetry of the ground state. From this minimum it can decay radiatively (or otherwise). In the case of a frozen (or absent) lattice[24] an adiabatic calculation of the electronic levels would yield something like Fig. 2. (For simplicity we consider only one JT state and therefore both upper energy levels of the excited state belong to the same JT state.) Note that levels in the figure are labeled in ascending order. Relaxation to the minimum of the JT state occurs by virtue of the passage from $R=0$ to a nonzero value of R, which is the same process as the loss of vibrational phonons prior to emission.

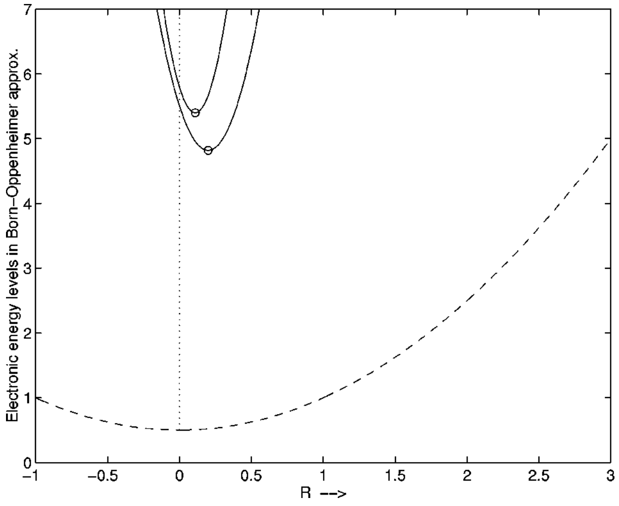

FIG. 2. Adiabatic electronic energy levels as a function of the coordinate R. The upper two levels (numbers 1 and 2) represent energies for ^{3}A$_{1u}$ and ^{3}T$_{1u}$ states. Scales are exaggerated. Arbitrary units.

Note that we have only pictured two excited levels. In fact the upper level 2 has an additional splitting due to the occurrence of a cation vacancy in the neighborhood of the Pb^{2+} ion. But this splitting is small compared to the energy spacing related to level 1, so that in the first approximation we can neglect this splitting and consider the upper level, 2, to be merely twofold degenerate.

We thus confine attention to two levels: level 1, the ''metastable'' level, with a decay time on the order of milliseconds and level 2, the ''radiative'' level, with a decay time on the order of nanoseconds. Following the excitation (the light flash) both levels are populated. In our present discussion we do not attempt to explain the initial relative population of the levels. As such we provide no explanation for fast/slow relative intensities. In each of the levels the system rapidly relaxes to the minimum of the curve of adiabatic energy levels. For the upper level, with its ns radiative decay time, this is the end of the story and emission is immediate (i.e., ns).

For the lower level the radiative decay is much slower, giving the lattice an opportunity to relax, thereby changing the adiabatic energy levels themselves. Of course since the time scales for emission and for adjustment of the lattice are competing it is not correct to assume the validity of the adiabatic approximation. That is, the eigenstates obtained in this approximation may differ significantly from true eigenstates of the full Hamiltonian. Nevertheless, we will use the moving values of the adiabatic energy levels in the following way: for any particular lattice configuration there is some such set of states and levels (if the lattice could be frozen), and we will use them as our basis vectors. Note that the time dependence of the Hamiltonian refers to the changes in energies and interstate couplings due to changes in the lattice. The electronic states themselves do not change appreciably during the course of the late lattice relaxation; that is, the relaxation on the millisecond time scale on which we now focus. In particular, their natural radiative decay rates can be taken to be constant in our work.

We concentrate on the lower level, 1, that having the slow decay. As the lattice adjusts to the distortion of the $(\mathrm{Pb}X_6)^{4-}$ complex in its excited state (due to the Jahn-Teller effect) the entire pattern of adiabatic energy levels shifts.[25] This is illustrated in Fig. 3, where a number of curves of adiabatic energy levels are drawn, each corresponding to a different lattice configuration. As far as emission is concerned the only point of interest (on each such curve) is the lowest one (with a circle round it in Fig. 3) and we can plot the locus of these circles. This is done in Fig. 4, and represents the energies of the (vibrational) ground states for the metastable level 1. Correspondingly there is a collection of distorted-lattice levels for the radiative level 2 and these too are illustrated in Fig. 4. Note that those upper levels are, at the moment, theoretical constructs. No upper level states survive from the initial flash and those pictured can only be entered from the lower state by the process described in the present article.

We focus on decay from the lower level. First it can decay radiatively. In Ref. 14 its lifetime was estimated to be several ms. The complicating feature is the ability to make a transition to the upper level and from there to decay quickly. This transition results from electron-lattice interactions.

The physically significant assumption is that the lattice

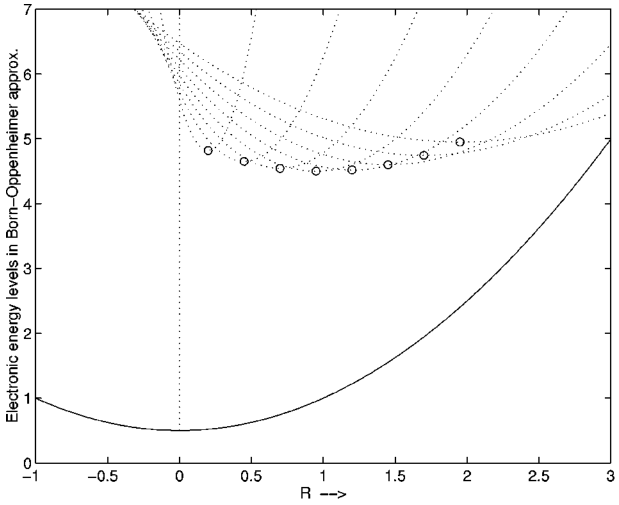

FIG. 3. Adiabatic electronic energy levels of the slowly decaying state 1 as a function of the coordinate R. The many curves correspond to different lattice configurations, for each of which a separate adiabatic calculation is undertaken. The circle at the bottom of each of these curves represents the zero-vibrational state. This is the state from which emission takes place and the system relaxes to this state on a time scale less than those of interest in the present article.

relaxation is on the order of ms. In this article we show that this assumption can lead to the observed decay curves. Naturally this will motivate further exploration of physical justifications, such as those alluded to in Ref. 14. We remark that such slow relaxation could have escaped previous notice. In particular, optical experimental evidence is possible only under special conditions related to the arrangement of the excited energy levels. First, in order to be able to follow relaxation effects on the proposed ms time scale, the excited state needs to be composed of (at least) two levels—a radiative level with a fast decay and a metastable trap whose decay is on the same order as the slow lattice relaxation. Second, the energy separation of these levels immediately after excitation must be small enough to allow the effective trap-radiation level transfer. In many other cases the final decay could be composed of either one or two exponentials without observable distortion.

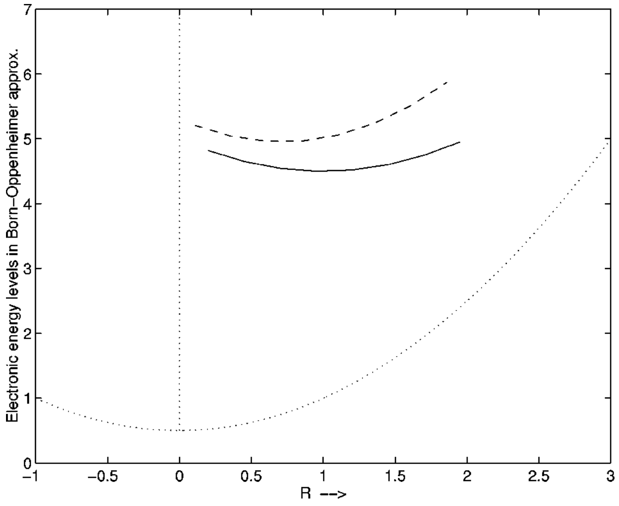

FIG. 4. Locus of minima of adiabatic electronic energy levels (circles of the previous figure). Each of these corresponds to a particular lattice distortion. The functional dependence on R (which is what is displayed in the figure) is indirect in the following sense. First the lattice distortion is given (not indicated in the graph) and then the corresponding optimal R value found, namely, that minimizing the corresponding adiabatic energy levels. Curves are shown for both the slow levels (solid line, related to the previous figure) and fast levels (dashed line, not indicated in the previous figure).

We reiterate that part of the phenomenon is outside the scope of our explanation. This is the ratio of fast to slow decay intensity. We assume that this ratio is the result of responses on the order of ns (or less), while our theoretical description applies to longer time scales. Thus we take it as given that (a few ns) after the flash the upper and lower states have a particular relative occupation. This may be the result of their being populated via a third state or having a fast phononic response kick systems from the upper to the lower state. From the perspective of our explanation of the nonexponential decay, those systems in the upper level at this point simply decay. Those in the lower level, decay more slowly, but not yet with the asymptotic characteristic lifetime found in Ref. 14. Rather (as we describe quantitatively below) they continue to interact strongly with the upper level and amplitude leaks out of the lower level due to transitions to the upper level. This continues until lattice relaxation weakens the coupling between the levels. At this point the basic lower-level lifetime can be used to describe the exponential decay of the system. This description applies to experiments performed at low (liquid He) temperatures—at higher temperatures there may be back transfer to the upper level, induced perhaps by phonons.

II. MODEL AND METHOD

We confine attention to two electronic levels, one with slow decay and one with fast decay. The fact that the fast level is in fact two closely spaced but not degenerate levels should make no difference to this calculation.

Our basis consists of the two electronic levels, which in the absence of interactions, etc., have energies 0 and $E(R)$. (In practice there is an overall variation of energy, but for our purposes, and without loss of generality, we can set the lower energy to zero, so that the function $E(R)$ is the energy *difference* of the levels.) We also incorporate within the Hamiltonian the fact of their (radiative) instability, assigning imaginary parts to the energies. Finally we include an interaction ''α'' between the levels, which can vary with R, based on the assumption that this coupling of electronic levels is a consequence of their interaction with the neighboring atoms. The Hamiltonian reflecting these assumptions has the form

$$H=\begin{pmatrix} E(R)-\frac{i}{2}\hbar\gamma_f & \alpha(R) \\ \\ \alpha(R) & -\frac{i}{2}\hbar\gamma_s \end{pmatrix}. \tag{1}$$

The quantity γ_s ($s\sim$''slow'') corresponds to the slow decay, so that $\gamma_f \gg \gamma_s$ ($f\sim$''fast''). We will treat the collective coordinate R as quasiclassical, that is, not as a quantum-mechanical degree of freedom, but rather as a parameter that finds its preferred value quickly as the lattice adjusts. This adjustment of the lattice is a reaction to the force that the local region (Pb and its immediate neighbors—the system described by our quantum formalism) exerts on the lattice. The change in the electronic state of the $\mathrm{Pb}X_6^{4-}$ complex (due the UV illumination in the experiment) leads to its tendency to reach the new equilibrium intramolecular position due to the electron redistribution. This tendency results in a distortion of the already stretched lattice (recall the Pb is big compared to the K it replaces). So the molecular complex pushes out and the lattice pushes back. When the system reaches structural equilibrium these forces balance. If one had full knowledge of the derivative of the energy of the levels with respect to R it could provide information about this force. However, the present paper uses less comprehensive information, namely, the energy difference of the two levels of interest.

The above-mentioned adjustment of the lattice, the configuration of which is also treated quasiclassically, is slow, i.e., it occurs on a ms scale. Thus while the system is in the state 1 (which is the lower state in Fig. 4) the lattice adjusts and the value of R is some function of time. We take that function to be

$$R(t)=R_0+(R_\infty-R_0)(1-e^{-\Gamma t}) \tag{2}$$

so that R_0 is the value of R taken just after the light flash (the first minimum in Fig. 3). It is by assuming that $1/\Gamma$ is on the order of ms that we will produce nonexponential decay on this time scale.

When the system is fully relaxed the splitting between the levels reaches an asymptotic value, E_f, but during the initial phases of lattice relaxation the levels should be closer, perhaps nearly degenerate. We express this change, with R, in the following way: $E(R)$ is assumed to go from some value E_0 at the earliest time, to an asymptotic value E_f. Since R is in turn a function of t, the form we assume for E is

$$E=E_0+(E_f-E_0)(1-e^{-\Gamma t}). \tag{3}$$

As indicated, we further assume that the strength of the coupling α varies. When the configuration of the neighbors of the Pb^{2+} ion and of the lattice for the two states are similar, the coupling of the electronic states is strong. However, as the lattice relaxes the overall states bear less and less resemblance. Our prescription is then, as above,

$$\alpha=\alpha_0+(\alpha_f-\alpha_0)(1-e^{-\Gamma t}). \tag{4}$$

Integration method and units

The evolution of the system is calculated by assuming an initial wave function of the form $\psi(0)=\binom{\rho}{\sigma}$ and evaluating the time-ordered product ($\mathcal{T}$),

$$\psi(t)=\mathcal{T}\prod_{j=1}^{j=N}\exp[-iH(t_j)\delta t/\hbar]\psi(0) \tag{5}$$

with $t_j=jt/N$ and $\delta t=t/N$. This is done numerically for N sufficiently large that there is little change in H during the interval δt. From $\{\psi(t_j)\}$ the physically important quantities can be obtained. For example the radiation rate at time t_j is $[\|\psi(t_j)\|^2-\|\psi(t_{j+1})\|^2]/\delta t$. (N.B. This does not distinguish between radiation from the upper or lower level, reflecting the experimental situation.)

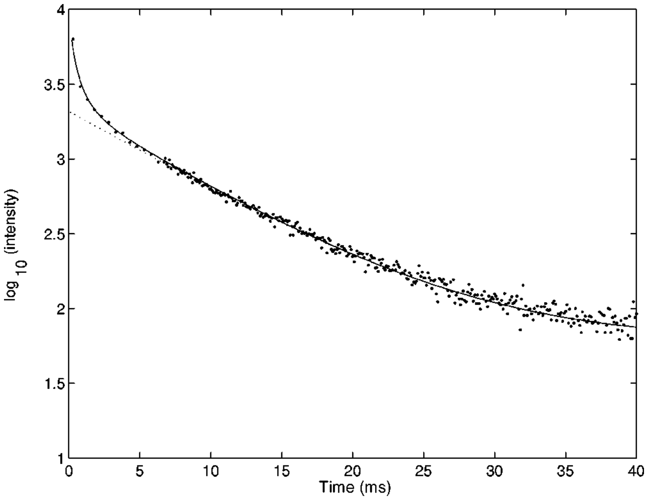

FIG. 5. Decay curve ($\log_{10}$ of radiation intensity) calculated from the model. Dots represent experimental data for the decay of KBr:Pb^{2+} at LHe temperature. [The data set is the same as pictured in Fig. 3(a) of Ref. 14.] Values of the calculated curve are normalized to the experimental data. For this run only the lower level is initially populated. The parameters used are $\alpha_0=0.0075$, $\gamma_f=4\times10^4$, $\gamma_s=1/8$, $E_0=3$, $E_f=45$, and $\Gamma=0.077$, where rates are "per ms" and energies are in meV. The dashed curve superimposed is the same as the solid line in the referenced figure in Ref. 14 [$I=2019\times\exp(-t/8.06)+61$], where the additive constant represents the background. This last curve represents an exponential fit to the late-arriving data.

III. RESULTS AND DISCUSSION

For now we concentrate on the case Pb^{2+} in a KBr crystal matrix at liquid-helium temperature. The parameters entering the theory are

E_0 (E_f): initial (final) energy split,
α_0 (α_f): initial (final) coupling strength,
$\gamma_s(\gamma_f)$: decay rate of slow (fast) level,
Γ: lattice relaxation rate.

Some of these can be assigned values with reasonable confidence. They are (1) E_f, about 45 meV; (2) α_f, reasonably assumed to be zero; (3) γ_f^{-1}, known to be about 25 ns; (4) γ_s^{-1}, which can be taken to be 8 ms, based on the fit to the slow mode given in Fig. 3(a) of Ref. 14. The last assumption could prove incorrect if it turns out that more than one independent process contributes to the slow decay.

With the above values, there remain α_0, E_0, and Γ as the significant parameters for the fit. As we demonstrate, the decay curve does not uniquely pin these down. Given a physical understanding of these parameters and a variety of experimental substances and temperatures, further progress could be made.

In Fig. 5 we show a successful fit with the parameter values indicated in the figure caption. Figure 6 shows four successful fits superimposed. Because they are nearly indistinguishable we only show the first few ms, where slight differences exist. Finally in Fig. 7 we show the consequences of excess and insufficient values of α_0. The reason that small α_0 is bad is obvious: the levels are not sufficiently coupled and no transfer from the slow to the fast mode can give the desired faster-than-slow-exponential decay that is observed. The reason that large α_0 fails is more subtle. Large α_0 also

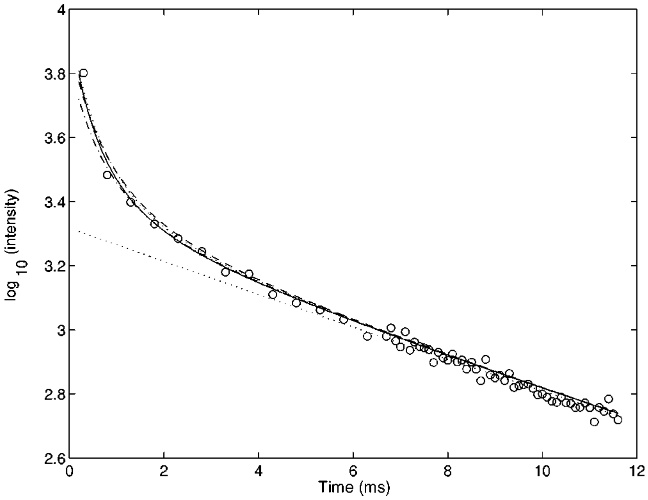

FIG. 6. Results for several combinations of parameter values are displayed. To emphasize the slight differences in intensity predictions, only the first few ms are shown. Parameter values for the solid line are the same as in Fig. 5 ($\alpha_0 = 0.0075$, $\gamma_f = 4\times 10^4$, $\gamma_s = 1/8$, $E_0 = 3$, $E_f = 45$, and $\Gamma = 0.077$). For the other curves the values are the same except as follows. For the dashed line $E_0 = 3.7$, $\alpha_0 = 0.0085$, and $\Gamma = 0.072$. For the dot-dashed line $E_0 = 4$, $\alpha_0 = 0.0085$, and $\Gamma = 0.08$. Finally for the dotted line $E_0 = 3$, $\alpha_0 = 0.0075$, and $\Gamma = 0.07$. The dotted line beneath these is, as in Fig. 5, the late-time exponential (plus constant) fit to the data. Empty circles represent experimental data.

causes mixing of the *decay rates*, leading the formerly observed slow component to decay much more quickly. There is then essentially nothing left to decay by the time 2 ms have passed. This remark is elaborated in the Appendix. For all these figures (5–7), only the lower level has been populated initially, in keeping with our not attempting to explain the slow/fast distribution. For a mix of occupancies the (incoherent) results should be added. Note that by our mechanism, during the first hundred or so ns (‘‘fast decay’’ interval) very little amplitude is transferred from the upper to the lower level.

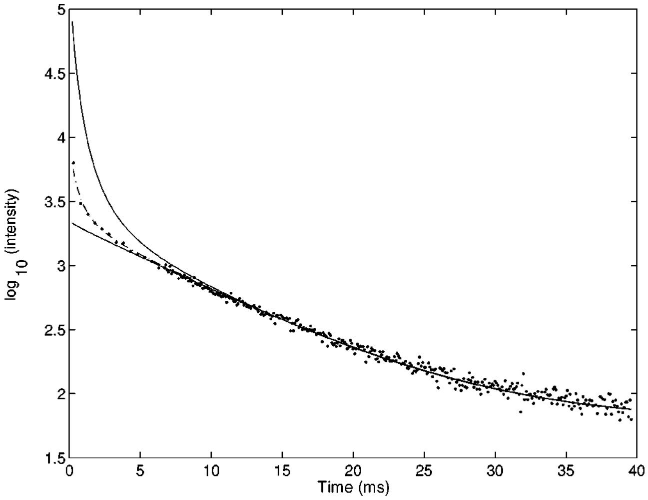

FIG. 7. As in Fig. 5, except that the parameter α_0 is varied to the point where the data are no longer well represented. All parameters are the same as in Fig. 5, except that for the solid line $\alpha_0 = 0.001$ and for the dotted line $\alpha_0 = 0.02$. The experimental data are also presented and it can be seen that neither of these curves is a candidate for a successful fit.

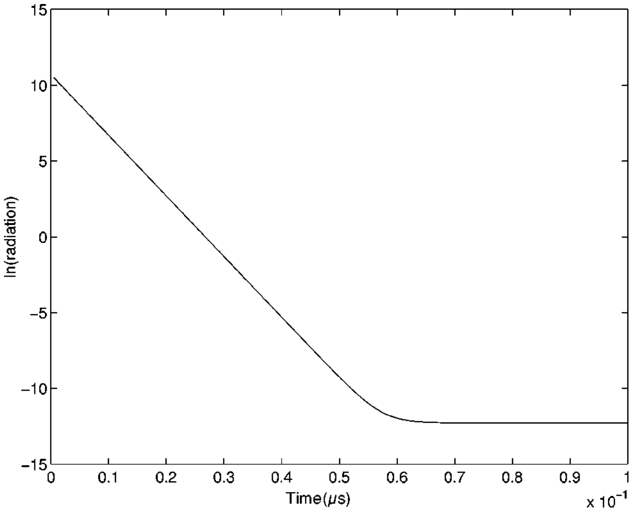

FIG. 8. As in Fig. 5. Only the first 100 μs are shown. Only the upper level is initially populated.

In Fig. 8 we show the first 1 μs of decay for parameter values that fit the later nonexponential decay rather well. Note that for a period pure fast exponential decay prevails, until at some point the amplitude transferred to the slow level by the coupling is all that remains, and the process goes over to the slow rate. Note that the amplitude remaining does not significantly affect the fast/slow intensity.

We summarize. By introducing a simple model we provide an explanation for the experimentally observed nonexponential decay of the slow emission of a Pb^{2+} center in alkali halide crystal hosts. For the case of the $\mathrm{KBr{:}Pb}^{2+}$ system we found parameters for our model that satisfactorily fit the experimental data. We hope to make further progress by including temperature dependence into the model.

ACKNOWLEDGMENTS

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APPENDIX: COUPLED LEVELS

Given the proposed time scale of Γ (on the order of inverse ms), for the first 100 μs one can treat the Hamiltonian as time independent. Therefore to get a qualitative idea of the initial decay one can look to the eigenvalues of $H/\hbar$. For a general matrix

$$M=\begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

the eigenvalues are

$$\lambda = \frac{a+d}{2} \pm \frac{1}{2}\sqrt{(a-d)^2+4bc}. \tag{A1}$$

With $a = E/\hbar - \frac{i}{2}\gamma_f$, $b = c = \alpha/\hbar$, and $d = -\frac{i}{2}\gamma_s$, we get

$$2\lambda = \frac{E}{\hbar} - \frac{i}{2}\gamma_f - \frac{i}{2}\gamma_s \pm \sqrt{\left(\frac{E}{\hbar} - \frac{i}{2}\gamma_f + \frac{i}{2}\gamma_s\right)^2 + \frac{4\alpha^2}{\hbar^2}}. \tag{A2}$$

Typical values found from our curve fitting are $E_0 \sim 1$ and $\alpha_0 \sim 0.01$ (units for E and α are meV (see Ref. 25). Then $E/\hbar \sim 10^9$ is the largest quantity in the expression for the eigenvalue ($\gamma_f \sim 4 \times 10^4$ in units of ms). From Eq. (A2), so long as $\alpha \ll E$ the imaginary parts of the two values of λ will be essentially γ_s and γ_f. However, once α is large enough to make the expansion of the square root a bit more complicated, then for both eigenvalues the imaginary part is essentially $\gamma_f/2$. This slows the fast decay, but speeds the slower one to the point where there is nothing left in the system by the time 2 ms have elapsed.

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[24] In this article, the term ''lattice'' means the next (higher than first) coordination spheres of the Pb^{2+} ion.

[25] In principle, we could here define lattice variables and extend our energy-level structure (by means of the Born-Oppenheimer approximation) so as to depend on those coordinates as well. However, in practice the relaxation of R to its optimum value for each lattice variable value is extremely fast and the additional dynamical process is subsumed into the R dependence.