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Journal of Luminescence 92 (2001) 311–316

JOURNAL OF
LUMINESCENCE

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Anomalous decay of the slow emission component in doped alkali halides

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Received 21 February 2000; received in revised form 9 August 2000; accepted 21 September 2000

Abstract

We provide a wide class of experimental fits in support of a model previously proposed to explain anomalous non-exponential decay of the slow luminescence component of Pb^{2+} centers in alkali halide crystals. The model was based on the assumption that the lattice relaxes on the same time scale as the slow-component decay time. This relaxation is a response to the Jahn–Teller local distortion of the Pb^{2+} luminescence centers. The original work studied $\text{KBr}:\text{Pb}^{2+}$ centers (at LHe temperature). We now apply the method to fit experimental data for the slow-component decay of $\text{KX}:\text{Pb}^{2+}$ and $\text{KX}:\text{Tl}^+$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$). An essential feature of the model is that lattice relaxation causes a time-dependent coupling of the Jahn–Teller levels. In the first place, the present successful fits provide evidence for the mechanism earlier proposed. Moreover, the dependence of the fitting parameters on lattice and impurity features allow systematic physical interpretation. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 31.70.Hq; 71.55.–i; 78.55.Fv; 78.55.–m; 83.85.Ns

Keywords: Alkali halides; Jahn–Teller effect

1. Introduction

Detailed experimental study of the decay kinetics of isolated Pb^{2+} and Tl^+ ions in KX crystal matrices ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) in Refs. [1–5] showed that the slow luminescence component under excitation in the A-absorption band (A-luminescence) does not decay exponentially as one

might have expected. Any single exponential that describes the *tail* of the decay deviates from the experimental curve in its initial part (i.e., the first few ms). Furthermore, if one, nevertheless, tries to fit the decay by a sum of several exponentials it is found that independent microsecond decay rates are needed (in addition to the natural electronic rates of nanoseconds and milliseconds). This anomalous decay pattern is believed to be an intrinsic property of the isolated luminescent center itself rather than a macroscopic average of different contributions coming from unperturbed

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and possibly perturbed centers. As mentioned in Ref. [6], there are several arguments supporting this assertion:

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 [7]).
2. Measurements of decay using crystals of varying quality (different growth techniques, different purity of growing material), nevertheless provide reproducible results. In particular, at the qualitative level, the slow decay shows the same non-exponential character for different samples and at the quantitative level the actual decay curves are very similar.
3. As indicated, to properly fit the initial part of the *slow* decay one would need to use the sum of several exponentials with lifetimes ranging from μs to ms. The presence of defects that would reduce the metastable level lifetime (order of ms) by two to three orders of magnitude (i.e., to μs) would be very hard to explain.

It was suggested [1] that there is a time on the order of ms during which the lattice surrounding the $(\text{AX}_6)^{i-}$ (for $\text{A}=\text{Pb}, \text{Tl}$, $i=4, 5$, respectively) centers relaxes. Such slow relaxation could be a response of the lattice to the Jahn–Teller (JT) local distortion of $(\text{AX}_6)^{i-}$ centers, and affects the slow-component decay of $\text{KX}:\text{Pb}^{2+}(\text{Tl}^+)$ emission. In fact, the JT-effect and the spin–orbit (SO) interaction were found to play a crucial role in the explanation of the presence of the slow as well as of the fast luminescence component [8,9]. In Ref. [6] a model based on the assumption of slow-lattice relaxation was constructed and a successful fit of experimental data of the $\text{KBr}:\text{Pb}^{2+}$ slow-component decay was obtained. In the present work, we apply that model to a larger set of experimental data obtained for slow component decays of potassium halides (FCC crystal structure) doped by Tl^+ and Pb^{2+} ions. In all cases a successful fit was obtained. Of particular interest is the systematic dependence of the values of the fitting parameters in relation to other lattice and impurity properties.

We remark that the extremely slow crystal relaxation times postulated in our earlier work had not been noted previously, so that the additional (successful) fits described in the present article provide further evidence for this proposal. This work explains the slow-emission-component behavior in lattices with FCC crystal structure. Recently, more work was devoted to the study of optical properties of isolated emission centers in lattices with BCC structure as well Refs. [10–20]. Similar “anomalous” non-exponential decay of the slow-emission component already reported in $\text{CsI}:\text{Tl}$ crystals [12] thus suggests that the proposed model may prove applicable in a wider class of materials with different lattice structures.

2. Model Hamiltonian

Justification of the model is extensively discussed in Ref. [6]. We summarize this development here. The lowest excited state of the $(\text{AX}_6)^{i-}$ center consists of two electronic levels, one with slow decay, the other with fast decay. The Hamiltonian describing the system has the form

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

where $E(R)$ is the energy difference between levels, the imaginary parts of the energies represent the (radiative) instability, and α is the interaction between the levels. This interaction can vary with R (R is the collective coordinate for the configuration of the nuclei of the $(\text{AX}_6)^{i-}$ complex), based on the assumption that this coupling of electronic levels is a consequence of their interaction with the neighboring atoms. The quantities γ_s and γ_f correspond to the slow and fast decay, respectively, i.e., $\gamma_f \gg \gamma_s$. The collective coordinate R is treated as quasiclassical, namely, as a parameter that finds its preferred value quickly as the lattice adjusts. As a function of time it is taken to be

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

Consequently the energy difference between the levels can be taken to be

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

and the variation of the coupling strength becomes

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

where E_0, α_0 and E_f, α_f are the initial and asymptotic values, respectively.

We comment that the ability to use a Hamiltonian formalism in this context was an unusual feature of Ref. [6], a feature which does not persist for calculations at higher temperatures where decoherence is introduced by phonon interactions. In principle, one should use a density matrix, which for a Hamiltonian subjected to radiative decay (hence not Hermitian) satisfies the equation $i\hbar\dot{\rho} = [H', \rho] + i\{H'', \rho\}$ (5)

with $H = H' + iH''$ (H' and H'' are Hermitian). The reason a Hamiltonian formalism is sufficient in this context is that even under the full evolution equation (5), with the Hamiltonian (1), ρ remains unentangled, that is, it continues to have the form of a pure state, albeit one of declining norm. We emphasize though that both approaches give the same results. (This has been checked numerically as well.)

3. Results and discussion

Time evolution governed by the Hamiltonian (1) was used to predict decay curves for the millisecond regime and the results compared to experimental data for $\text{KX}:\text{Pb}^{2+}(\text{TI}^+)$. Six para-

meters enter the model. Three are known from experiment. The values of the fast (τ_f) and slow (τ_s) decay times at liquid Helium (LHe) temperature give (the reciprocals of) γ_f and γ_s . The value of the asymptotic energy difference E_f is estimated from the temperature dependence of the decay times, also obtained from experiment. The three remaining parameters (E_0, Γ , and α_0) were used to fit the experimental data. All parameters are listed in Table 1. The most remarkable feature of our model is the long lattice relaxation time and indeed, were it not for the consistent fit of experimental data based on this ansatz, our proposal would seem highly unlikely. Below we will discuss the possible explanations for this phenomenon.

Fig. 1 presents a fit of $\text{KX}:\text{Pb}^{2+}$ decay curves, while Fig. 2 shows a fit of the $\text{KX}:\text{TI}^+$ data. As one can see from the experimental data for both TI^+ and Pb^{2+} centers (which was also pointed out in Ref. [1]) the decay curve tends to deviate more from a single exponential as one progresses through the sequence of crystal lattices $\text{KCl} \rightarrow \text{KBr} \rightarrow \text{KI}$. The best reflection of this tendency is given by the parameter α which is the coupling between the energy levels of the excited state induced by the lattice. In the sequence $\text{KCl} \rightarrow \text{KBr} \rightarrow \text{KI}$ its value increases (with the same trend as the value of the halogen spin-orbit coupling parameter), indicating that the coupling between the levels becomes stronger. This is consistent with the idea that the larger and more massive lattice anions induce a stronger coupling.

On the other hand if one looks at decay curves obtained for different centers embedded in the

Table 1
Parameter values of K-halide systems

System	From experiment			From fit		
	γ_f (ms^{-1})	γ_s (ms^{-1})	E_f (meV)	E_0 (meV)	α_0 (meV)	Γ (ms^{-1})
$\text{KCl}:\text{Pb}^{2+}$	7×10^4	0.25	65	≥ 10	≤ 0.001	0.08
$\text{KBr}:\text{Pb}^{2+}$ (Ref. [6])	4×10^4	0.13	45	3	0.0075	0.077
$\text{KI}:\text{Pb}^{2+}$	5×10^4	0.11	55	3	0.014	0.075
$\text{KCl}:\text{TI}^+$	10×10^4	0.40	56	4	0.005	0.7
$\text{KBr}:\text{TI}^+$	4×10^4	0.34	60	3.5	0.025	0.6
$\text{KI}:\text{TI}^+$	4×10^4	0.30	55	5.5	0.035	0.2

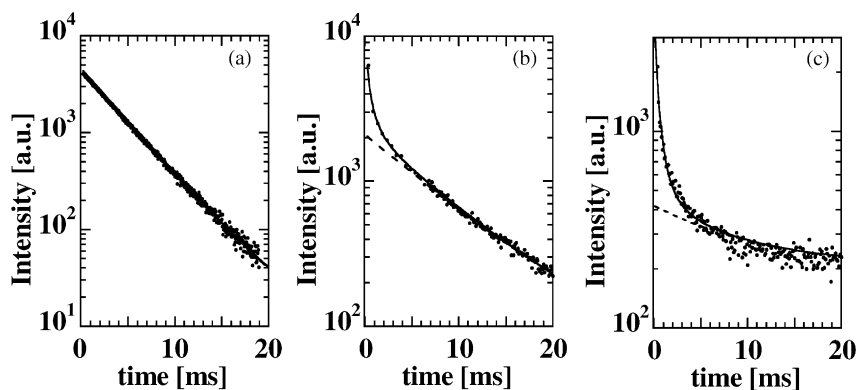


Fig. 1. Decay curves calculated from the model. Marks represent experimental data for the decay of (a) KCl:Pb²⁺, (b) KBr:Pb²⁺ and (c) KI:Pb²⁺ at LHe temperature. Values of the calculated curves are normalized to the experimental data. Only the lower level is initially populated. Dashed lines represent exponential fits to the late-arriving data. In (a), the fit is $I = 4434 \times \exp(-t/4) + 10$; in (b), $I = 2019 \times \exp(-t/8.06) + 61$; in (c) $I = 209 \times \exp(-t/9) + 209$. The additive constant represents the background.

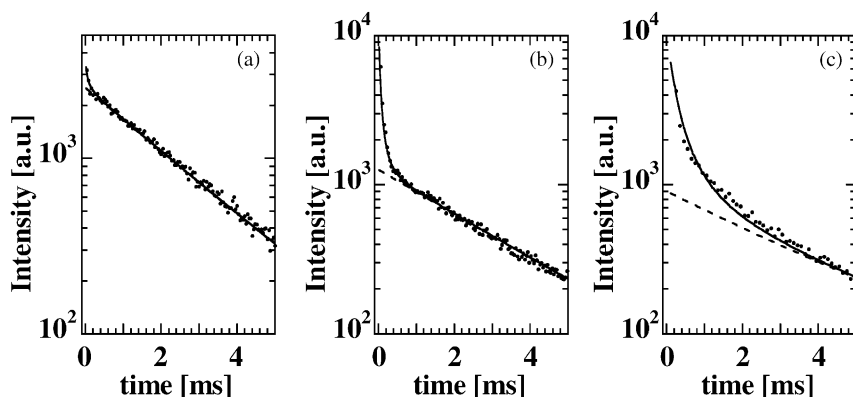


Fig. 2. Decay curves calculated from the model. Marks represent experimental data for the decay of (a) KCl:Tl⁺, (b) KBr:Tl⁺ and (c) KI:Tl⁺ at LHe temperature. Values of the calculated curves are normalized to the experimental data. Only the lower level is initially populated. Dashed curves represent exponential fits to the late-arriving data: (a) $I = 2500 \times \exp(-t/2.37) + 22.5$, (b) $I = 1250 \times \exp(-t/2.87) + 15$, (c) $I = 850 \times \exp(-t/3.3) + 51$. The additive constant represents the background.

lattice, it is evident that the deviation from a single exponential lasts longer for the (PbX₆)⁴⁻ center compared to the (TlX₆)⁵⁻ center. This tendency is reflected in the parameter Γ . In our model Γ is connected with the speed of lattice relaxation in response to the JT distortion, and it is significantly larger for the (TlX₆)⁵⁻ center in all crystal hosts. We suggest that the speed of a lattice response is connected to the number of lattice ions (surrounding the luminescence center) involved in the overall relaxation process. In other words, this relaxation rate depends on how far from the luminescence

center the surrounding lattice is still affected by the JT distortion of a center and vice versa. The results obtained indicate that the lattice response is faster for the (TlX₆)⁵⁻ center relative to that of the (PbX₆)⁴⁻ center. Thus in the case of the (PbX₆)⁴⁻ center a larger volume of the surrounding lattice (more mass) is affected and responds back. This idea is supported by two facts. First, because of the larger ionic radius (1.49 Å for Tl⁺ and 1.32 Å for Pb²⁺ – see Ref. [21]), the character of the bond between the Tl⁺ and the lattice anions is shifted toward a covalent type more than it is for Pb²⁺. As

a result, the response to the JT distortion is constrained to a much closer lattice environment of the $(\text{TlX}_6)^{5-}$ central quasimolecule than it is in the case of $(\text{PbX}_6)^{4-}$. Second, Tl^+ substitutes for K^+ in the lattice with the same charge, i.e., the charge distribution in the lattice remains unchanged. By contrast, Pb^{2+} substitutes for the lattice cation with an excess of a positive charge and needs a cation vacancy (v_c^-) nearby to locally compensate the charge imbalance. Nevertheless, the $\text{Pb}^{2+}-v_c^-$ pair is an electric dipole with its own electric field. This field has long range effects and creates charge redistribution in the lattice. Therefore, it may be expected that any change in the luminescence center itself (JT distortion after an excitation) affects a much larger region of the lattice than in the Tl case.

We now consider possible causes for the remarkable slowdown in relaxation experienced by alkali halide lattices at low temperatures. The first idea is that barrier penetration could be involved. Due to the JT effect, the nearest neighbors of the Pb (or Tl) ion after excitation are being forced significantly ($\sim 10\%$) away from their previous (equilibrium) positions. A cold and sufficiently rigid lattice could resist this push until fortuitously small random thermal motions allow a *relatively* easier tunneling breakthrough. As with all tunneling processes, long time scales are possible. We tested this hypothesis by trying to fit the data with a variant of the program described earlier. Instead of allowing the Hamiltonian H to vary continuously in time, we took it to be constant up until a random time, after which it changed to the final form of H , thereby simulating a jump process. The random time was selected from a distribution that depended on N independent, exponentially distributed events, with $1 \leq N \leq 6$. This modeled a breakthrough depending on one or more ions in the neighborhood of the center. In all cases the fits were reasonable, but not as good as those presented above. The discrepancy was largest in the first 1–2 ms.

A second proposed mechanism involves confinement of the excitation due to nonlinear effects and to the stiffness of the lattice. The intensity of the outward push causes a traffic jam of sorts, confining the energy to a small region around the

center. Perhaps a better analogy is a bad dive, in which the diver hits the water obliquely and the inertia of the water obstructs his entry. As we shall see, our modeling suggests that in the crystal this obstruction can last a long time. Another way to think of this is to note that nonlinearity of the lattice (when significantly stressed) implies phonon–phonon scattering. Extensive scattering prevents ballistic motion of the phonons and they escape the center only diffusively. In an extreme situation this would give the escape from confinement a power law behavior. In effect the system cannot dissipate the energy introduced by the sudden mechanical deformation. This idea was tested by modeling a classical chain of two sorts of atoms with a nonlinear force between pairs. Besides the nearest neighbor coupling of atoms on the one-dimensional chain, the effect of atoms off the chain was modeled by assuming that the rest of the lattice created an equilibrium position to which the atom would be attracted even though it was stressed (there is no evidence that bonds are broken in the post-JT excitation relaxation). At one end of the chain a displacement was imposed. When this displacement was small, or when the nonlinearity was small, the results of the displacement propagated freely away at the speed of sound. However, with large displacement (and nonlinearity) the excitation remained substantially confined. With the first displacement-induced expansion, a small wave propagated outward, but most of the energy remained within a few atomic distances for extremely long times. (Our numerical integration lasted several times the size of the lattice (speed of sound ~ 1), during which confinement persisted. Lattice sizes of about 60 atoms were used.) The initial displacement in this case could be scaled to the mechanical (but not electronic) energy expected to be deposited by the JT excitation (~ 0.1 eV) and, if anything, the displacements we used were conservative. From a general perspective, there appears to be a phenomenon in which, due to nonlinear effects, an excitation fails to disperse, analogous to the soliton (but not literally a soliton, for example because the speed of those excitations is amplitude-dependent while in our case the essential feature is the absence of speed).

We tend to favor the second approach. Nevertheless, we emphasize that we consider these mechanisms as objects of investigation rather than fully formulated theories.

4. Conclusion

The results presented in this article show that the theory previously used to describe a single system can be extended to a variety of systems. The fitting parameters, which for a single example could not show any systematic behavior, have, for the range of experiments now described, demonstrated that our model explains the data in a way consistent with general knowledge of the lattices and impurities.

Acknowledgements

We thank the referees for their thoughtful responses and in particular for urging us to offer theoretical proposals for the slow relaxation phenomenon. This work was supported by the United States National Science Foundation Grant PHY 97 21459, ASCR Grant B1010901 and the Grant ME 382. A preliminary version of these results was presented at EURODIM '98, Ref. [22].

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