Anomalous decay and breather formation in doped alkali halides

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Abstract

Anomalous decay of doped alkali halides has been ascribed to breather formation in the immediate neighborhood of the impurity. New results support this connection. We report experimental data for NaBr and RbBr crystals showing anomalies in their slow emission decay. These data complete the earlier picture, confirming that the decay anomaly becomes bigger as the host-lattice-anion/cation mass ratio increases. We show the correlation between the decay anomaly and the breather formation as a function of this ratio. By simulating finite-temperature effects (which do not just involve white noise) in the lattice dynamics, we demonstrate that with increasing temperature the breather weakens, as is experimentally observed for the decay anomaly.

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1. Introduction

Luminescence of alkali halides doped by heavy ns2 ions excited into the A-absorption band shows two decay components that are due to the Jahn–Teller (JT) and spin-orbit splitting of their lowest excited states. The slow component decay displays an anomaly. For up to several ms the decay is nonexponential, ultimately attaining the character of a single exponential [1]. This anomaly was explained by postulating extremely slow lattice relaxation [2] as a response to the JT deformation of the isolated emission center—the impurity ion and its nearest neighbors—in its excited state. The lattice relaxation is on the same time scale as the asymptotic exponential slow-component decay. Based on this assumption, a model of the zero-temperature dynamics of the lowest excited state was set up, and experimental data of various substances obtained at the liquid
helium temperatures (LHeT) were satisfactorily fit [2,3]. Later, the model was extended to fit experimental data at higher temperatures, showing that with increasing temperature the anomaly gradually fades, and is completely extinguished above 100 K [4]. The biggest puzzle was to explain the remarkable slowdown of lattice relaxation. Simulation of the dynamics of a chain of atoms along the JT axis showed that at zero-temperature the energy of the chain becomes confined within the immediate neighborhood of the impurity. A connection between energy confinement and Fermi–Pasta–Ulam type solitons or breathers was established [5]. Lattice-relaxation slowdown was therefore ascribed to breather formation. The presence of FPU solitons or breathers in alkali halides was previously proposed [6]. Breathers themselves have been extensively studied in recent years both experimentally and theoretically (see e.g. review articles [7,8] and references therein). Experiments on Pb\(^{2+}\)-doped and Tl\(^{+}\)-doped KCl, KBr, and KI showed that the decay anomaly gets bigger (the deviation from the single exponential is steeper and/or survives to longer times) as the lattice anion gets bigger and heavier.

We now provide new experimental and theoretical support for the relation between the decay anomaly and breather formation. In particular, we report new experimental data of slow-component decay in Pb\(^{2+}\)-doped RbBr and NaBr to demonstrate how the anomaly responds to changes of the lattice cation. We show the correlation between breather formation and decay anomaly in various alkali halides as a function of anion/cation ratio. We also model finite-temperature effects on the lattice chain dynamics demonstrating that with increasing temperature, as the decay anomaly gets weaker, the breather also becomes “weaker” (the kinetic energy is drawn off the breather and travels away).

2. Decay anomaly and breather as a function of anion/cation mass ratio

In Ref. [1], we studied the slow-emission decay of the Pb\(^{2+}\)-doped potassium halides, KCl, KBr, and KI. This range of samples demonstrated that the decay anomaly grows with increasing size and mass of the lattice anion. There was practically no decay anomaly for KCl, a fairly big anomaly for KBr and a very big anomaly for KI. Here we show a similar progression for the decay anomaly with changing lattice cation. In Fig. 1, we report new experimental data on NaBr and RbBr crystals. The decay also manifests significant deviation from exponential. We also show an already published data set for KBr so as to have the

![Fig. 1](image)

Fig. 1. Liquid He temperature time decay of the slow component of the emission excited in the A-absorption band, \(\lambda_{\text{exc}} = 298\) nm for all samples, \(\lambda_{\text{em}} = 380(360, 335)\) nm for Pb-doped RbBr (KBr, NaBr) samples. Data for KBr:Pb\(^{2+}\) are taken from Ref. [4]. Dots represent experimental data, solid line is an exponential fit to the late-arriving data.
complete set of alkali bromides and study the
dependence of the anomaly on the change of
lattice cation. The RbBr crystal displays a fairly
weak anomaly, while KBr and NaBr crystals show
rather strong anomalies. A quantity that certainly
affects the character of the decay anomaly is \( r \), the
ratio of the mass of the lattice anion to that of the
lattice cation. The anion/cation mass ratio \( r \) in the
sequence KCl → KBr → KI goes as: \( r \sim 1 \rightarrow \sim 2 \rightarrow \sim 3.3 \). In the sequence RbBr → KBr → NaBr, the
mass ratio goes as: \( r \sim 1 \rightarrow \sim 2 \rightarrow \sim 4 \). To summarize,
from the experimental point of view, a very slight
anomaly is observed—or none at all—for mass
ratios close to 1, while for ratios of 2 or more the
anomaly is large. To study the relation between
this decay-anomaly behavior and the breather we
modelled the chain dynamics, as in Ref. [5], as a
function of \( r \). The simulations were made for a
chain of 40 atoms. We used a polynomial potential
as in Ref. [5]; for details refer to this work. It turns
that different mass ratios can be more or less
favorable for forming the breather. In Fig. 2, we
show a plot of a kinetic energy as a function of
time and atom number. The picture shows that
breather—kinetic energy is confined within the
first two atoms of the system. As a measure of how
“good” the breather is, which is to say, how good
is the confinement of the energy to the region of
the impurity, we calculated a kinetic energy-
weighted position. That is, let \( k \) be the atom
number. Let \( w_{KE}(k) \) be the average kinetic energy
of the \( k \)th atom. Then
\[
k_{KE} = \langle k \rangle = \frac{\sum_k k w_{KE}(k)}{\sum_k w_{KE}(k)}.
\]

The smaller this quantity is, the more the energy
is concentrated in the breather, and therefore the
bigger the expected decay anomaly. The result
of a systematic study of \( k_{KE} \) as a function of \( r \) is
shown in Fig. 3. This graph is perfectly coherent.

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Fig. 2. Kinetic energy of the system as a function of time and atom number. The inset shows positions of the atoms of the lattice chain
vs. time. The simulation was made with a quartic polynomial potential having parameters \( N = 20, q_0 = 1, r = 2, v = 4, \lambda = 1 \); for
details see Refs. [5,11]. The time unit is about 0.1 ps and the energy unit about 0.839 eV. The Hamiltonian for the system and further
details concerning our units can be found in Ref. [12].
with experimental observations concerning decay anomaly.

3. Decay anomaly and breather at finite temperatures

It was experimentally observed that with rising temperature the decay anomaly becomes less pronounced, finally disappearing in the range 100–150 K (depending on the substance). In view of our breather explanation of slow lattice relaxation, this temperature dependence should be a consequence of the effect of temperature on breathers. That effect is in fact a topic of current research [9,10], where the emphasis is on the formation of breathers. It is thus evident that heat, or noise, in and of itself, need not destroy breathers. This was confirmed in our own simulations. We found that both white noise and a temperature-dependent noise-frequency-spectrum either failed to dislodge the breather in the impurity neighborhood, or at very high temperature, swamped the entire system in a high level of excitation (including breathers throughout the chain).

The speedup in crystal relaxation with temperature depends on more subtle effects. We are currently exploring a model in which there are dissipative effects on the breather due to transverse waves, i.e., phonons representing motion of off-chain ions, which draw off energy in roughly the same pattern (i.e., exponentially) seen in low temperature decay, but at an accelerated rate. In Fig. 4, we display how, induced by a phonon kick, the kinetic energy travels away from the breather. At low temperatures there are few transverse phonons that could cause this effect. At higher temperatures, many more phonons can draw energy away. This corresponds to weakening of the breather as the temperature increases, directly parallel to the observed temperature evolution of the decay anomaly.

4. Conclusions

Present work provides additional support to previously suggested hypothesis that experimentally observed anomaly in the luminescence decay of ns²-doped alkali halides is a consequence of a lattice relaxation slowdown due to breather formation in the close neighborhood of the impurity. Correlation between the decay anomaly and breather formation presented here concerns two features. First is a dependence on the lattice anion/cation mass ratio. As this parameter increases the decay anomaly gets stronger as well as “better” breather is formed. The second feature is related to a temperature dependence. With increasing temperature the decay anomaly is fading. The breather...
also gets weaker with increasing temperature modelled as an interaction with transverse phonons.

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References