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Long lifetimes and small phonon energies in metal-halide perovskite solar cells

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Lead-halide perovskite solar cells have remarkably high open-circuit voltages and relatively long lifetimes as determined from e.g. transient photoluminescence or transient microwave photoconductivity.[1] These long lifetimes[2;3] lead to fairly good charge carrier collection properties and in addition a high internal luminescence yield[4;5] that makes these materials suitable for photovoltaics and other optoelectronic applications. Calculations of defect positions and formation energies have suggested that most intrinsic defects are either shallow donors or shallow acceptors while few are deep defects.[6] Those that are deep have high formation energies implying that lead-halide perovskites should be defect tolerant,[7] i.e. even if the defect density is high, the material should still be functional for electronic and optoelectronic applications. In order to better understand the relation between defect positions and defect densities, it is important to remember the theories on non-radiative recombination via localized states that were derived mostly in the late 70s and early 80s.[8-10]

Markvart[11] derives the multiphonon transition rate k of a single defect as being proportional to

$$k \propto \frac{\sqrt{2\pi}}{\hbar^2\omega\sqrt{p\sqrt{1+x^2}}}\exp\left[p\left(\frac{\hbar\omega}{2kT}+\sqrt{1+x^2}-x\cosh\left(\frac{\hbar\omega}{2kT}\right)-\ln\left(\frac{1+\sqrt{1+x^2}}{x}\right)\right)\right] . \quad (1)$$

Here, T is temperature, k the Boltzmann, $\hbar$ the reduced Planck constant ω the angular frequency of the phonon mode considered and p is the number of phonons needed for the transition to happen.The parameter x includes the dependence of the recombination rate on the ratio p/S_{HR} and is defined as[11]

$$x = \begin{cases} \dfrac{S_{\mathrm{HR}}}{p\sinh(\hbar\omega/2kT)} & \text{for } S_{\mathrm{HR}} < p \\ \dfrac{p}{S_{\mathrm{HR}}\sinh(\hbar\omega/2kT)} & \text{for } S_{\mathrm{HR}} > p \end{cases} . \quad (2)$$

Following the derivations outlined by Ridley[8;12], the Huang-Rhys factor for polar coupling can be written as

$$S_{\mathrm{HR}} = \frac{3}{2(\hbar\omega)^2}\left\{\frac{q^2(M_r/V_0)\hbar\omega^2}{M_r\omega q_D^2}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon}\right)\right\}I(-2,2\mu,q_D a^*\nu/2) \quad (3)$$

where M_r is the reduced mass of the atomic oscillator (Pb and I for $MAPbI_3$), q_D is the radius of a sphere with the Brillouin-zone volume, ε_∞ and ε are the high- and low-frequency limit of the dielectric function, and $a^*\nu/2$ is a rough estimate for the radius of the defect wavefunction in the 'quantum defect model'. The function I is given by

$$I(a,b,c) = \frac{1}{(bc)^2}\int_0^1 \frac{x^a\sin^2\left(b\tan^{-1}(cx)\right)}{\left[1+(cx)^2\right]^b} . \quad (4)$$

The trap depth ΔE enters the parameter $\nu = q(8\pi\varepsilon a^*\Delta E)^{-1/2}$ through which it affects the function I, and subsequently S_{HR}. The charge state of the trap also enters the calculation via the parameter μ: where $\mu = \nu$ holds for positively charged defects, $\mu = 0$ for neutral defects, and $\mu = -\nu$ for negatively charged defects.

Figure 1 illustrates the meaning of Eq. (1) for the Shockley-Read-Hall (SRH) lifetime τ for an arbitrary trap density $N_t = 10^{15}$ cm^{-3}. For a constant value of S_{HR}, the lifetime τ strongly increases for smaller phonon energies (see Fig. 1a). The same holds for increasing values of S_{HR} for constant phonon energies (see Fig. 1b). Thus, low phonon energies seem to slow down recombination. However, if we consider that the Huang-Rhys factor itself depends on phonon energy as well, we observe a different picture. Figure 2 shows the resulting effect when only considering polar coupling. Figure 2a shows the Huang-Rhys factor using Eqs. (3) and (4) as a function of the trap depth and the phonon energy. Shallower traps lead to lower Huang-Rhys factors. Figure 2b now shows the trap densities that would be needed to achieve a SRH lifetime of 1 µs. For the lower phonon energies and higher Huang-Rhys factors observed in $MAPbI_3$, we find that only rather deep traps would yield a lifetime of a µs at trap densities in the 10^{15} cm^{-3} range (as has been observed)[13] while for shallower traps the necessary trap density quite rapidly increases. This increase is much slower for higher phonon energies and suggests that the relation between the position of the traps and their impact on recombination is a strong function of phonon energy. Because optical phonon energies themselves are a function of the reduced mass of the atomic oscillator (higher mass → lower phonon energy), polar semiconductors based on heavier elements would have a tendency to be quite tolerant to rather shallow defects when it comes to recombination and open-circuit voltage. However, the shallow defects may still lead to hysteresis effects, device degradation and spatially inhomogeneous properties.

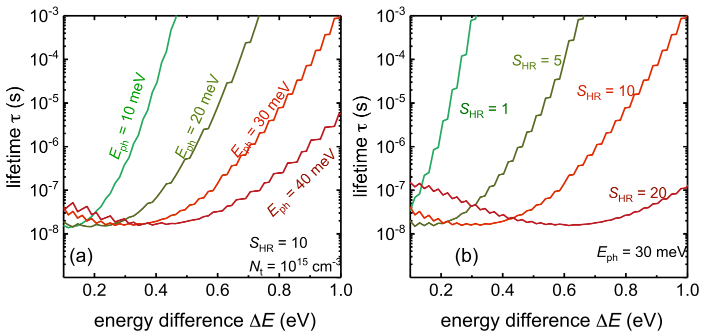

Figure 1: Lifetime for multiphonon recombination as a function of (a, b) the energy difference between a localized and a non-localized state (i.e. trap and band) with (a) a constant Huang-Rhys factor (S_{HR} = 10) and varying phonon energy and (b) constant phonon energy (E_{ph} = 30 meV) and a variable Huang Rhys factor. For all panels we assume a trap density N_t = 10^{15} cm^{-3}. Figure is redrawn after ref. 14.

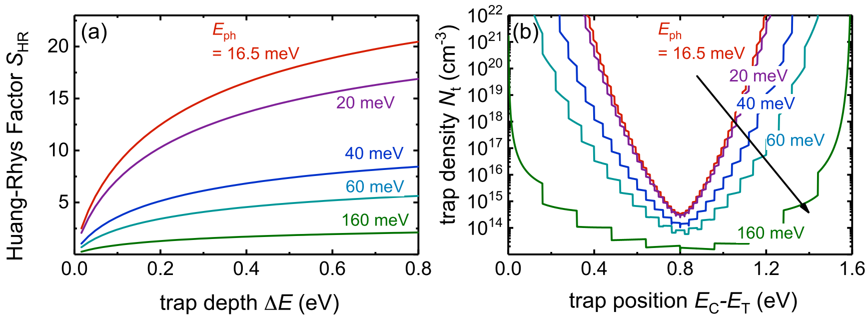

Figure 2: (a) Huang-Rhys factor for a positively charged trap as a function of trap depth and phonon energy. (b) Trap density needed to achieve a SRH lifetime of 1 µs, for phonon energies ranging from 16.5 meV to 160 meV, showing that larger phonon energies make the exact position of the trap less important with midgap energy always remaining the worst-case scenario. Redrawn after ref. 15.

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