Extremely Slow Spin Relaxation in Cu-doped Colloidal CdSe Quantum Dots

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Motivation

❑ copper dopants have been exploited as phosphors in early display technologies

❑ remember your old TV set? chances are the image was created thanks to donor-acceptor pair emission from Cu,Al.:ZnS

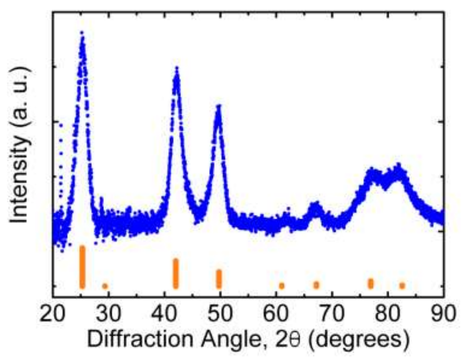
❑ **what about newer technologies?**

❑ **what is the role played by Cu dopants in the emission of Cu:CdSe colloidal QDs?**

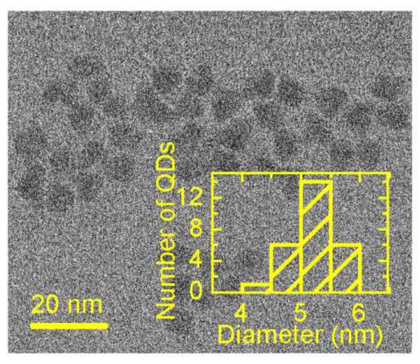
❑ **what are the time scales of spin relaxation?**

The dots

❑ synthesis as in: Yang *et al. Chem. Mater.* **28**, 7375 (2016).



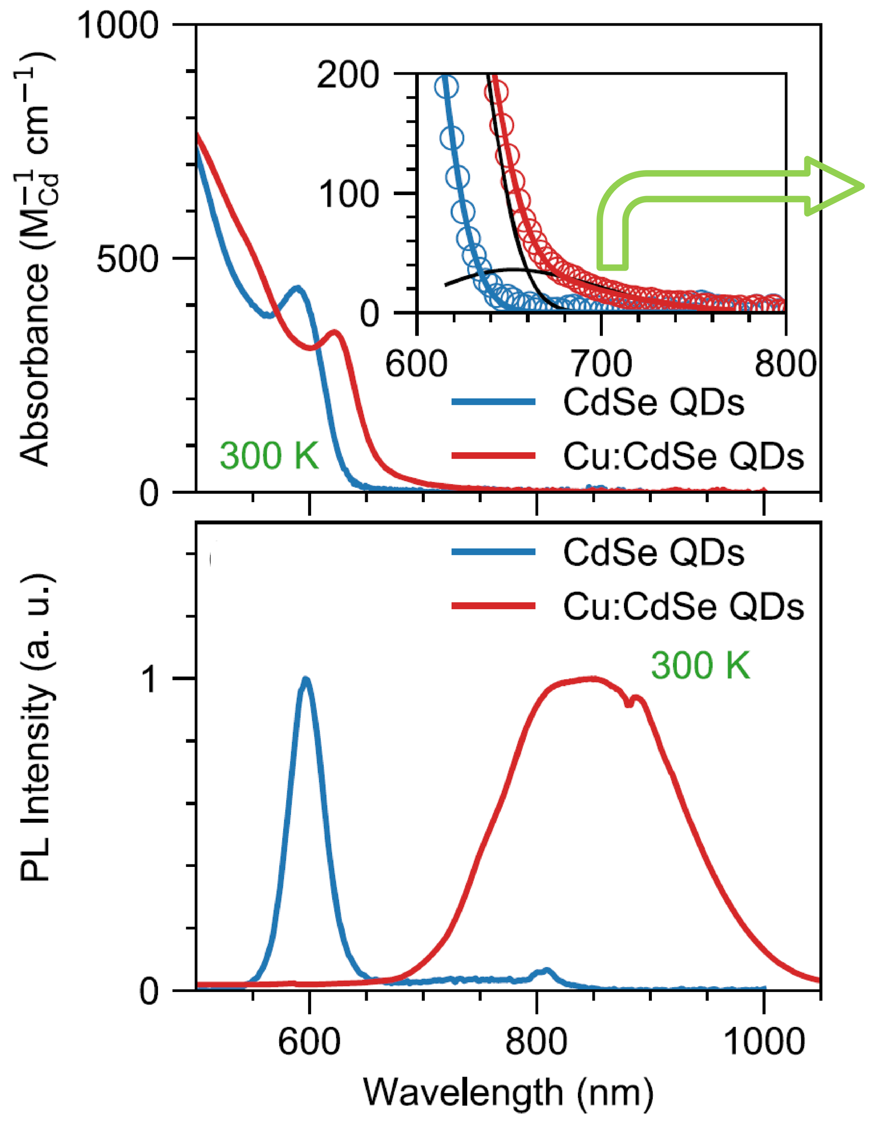
❑ zinc blende CdSe QDs



❑ average diameter of 5.2 nm

Room temperature characterization

Knowles *et al. Chem. Rev.* **116**, 10820 (2016).



Cu:CdSe QDs:

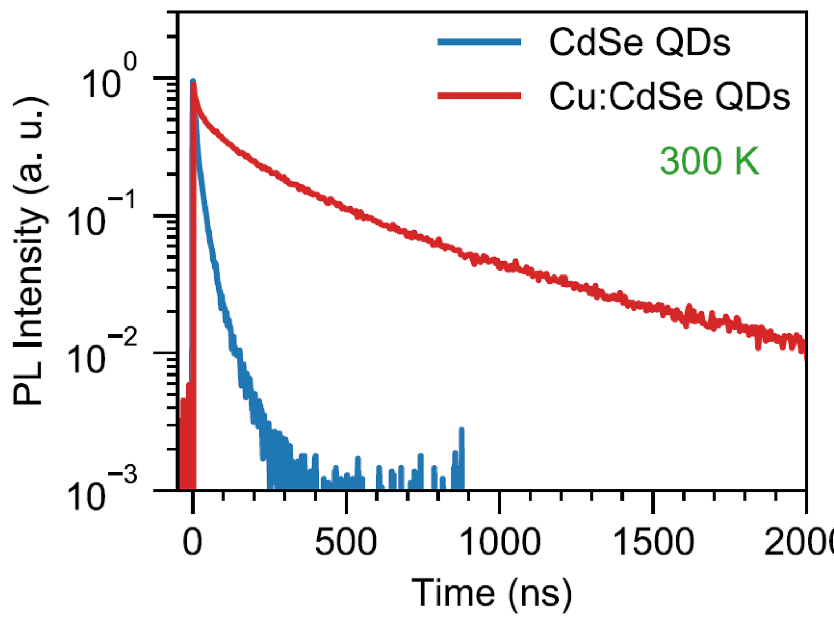
❑ long wavelength absorption tail

❑ average number of Cu dopants per dot $\bar{N}_{Cu} = 13$

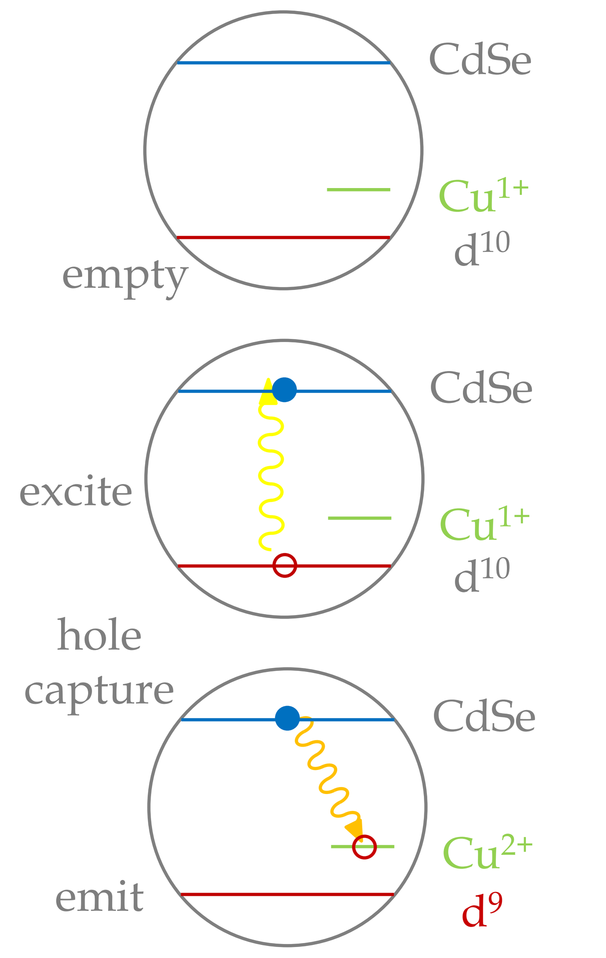
❑ giant apparent Stokes shift of ~ 0.6 eV

❑ extremely long PL lifetimes of ~ 0.5 s

(vs. 20 ns for **CdSe QDs**)



PL mechanism

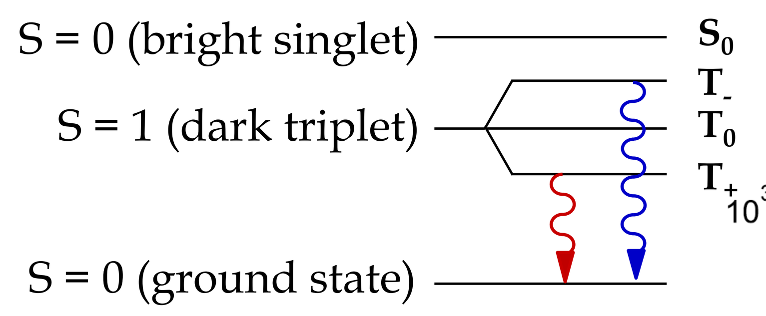


❑ PL and absorption tail: a free-to-bound transition

Spin dynamics

❑ exchange interaction between the = ½ electron and the s = ½ copper ion gives rise to the spin structure of the luminescent excited state

Knowles *et al. JACS* **137**, 13138 (2015).



❑ circular PL polarization reflects the spin dynamics

❑ for undoped **CdSe QDs**, polarization rise times shorter than temporal resolution of ~ 1ns

❑ for **Cu:CdSe QDs** at 2 K and below 1 T, rise times on the order of microseconds

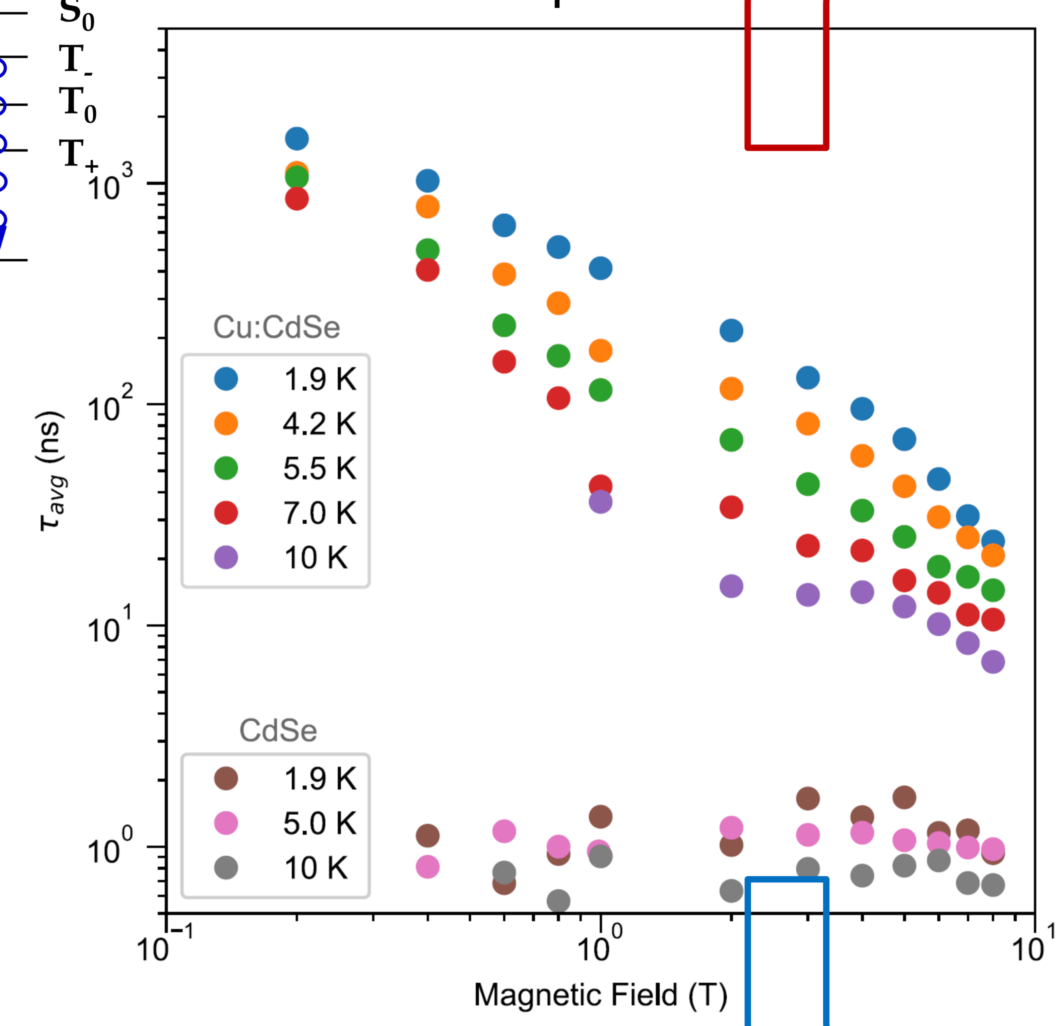
❑ the dynamics sensitive to field and temperature

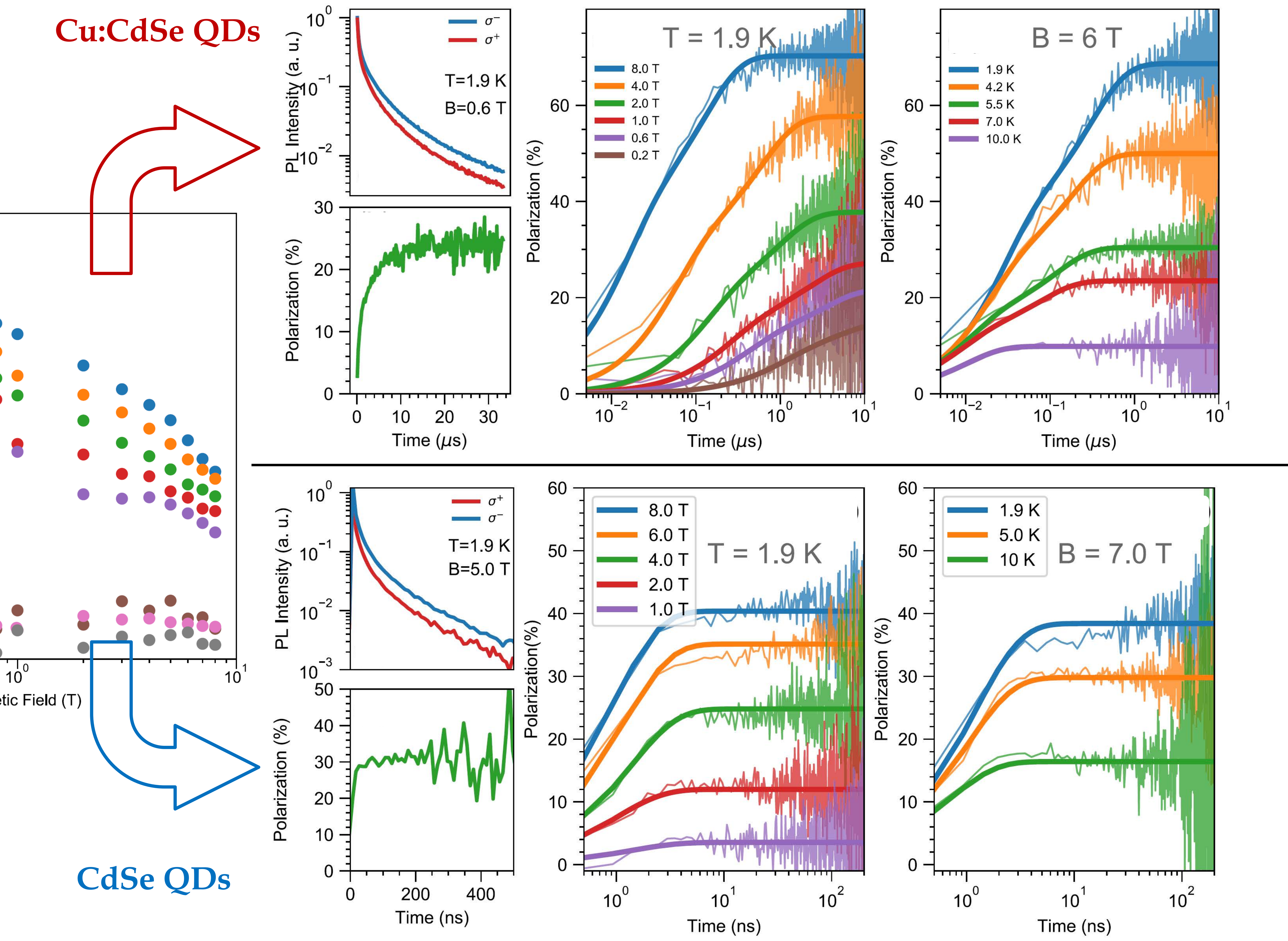
❑ fitting polarization dynamics with two relaxation times:

$$P(t) = P_0\left(1 - \frac{1}{2}e^{-t/t_1} - \frac{1}{2}e^{-t/t_2}\right)$$

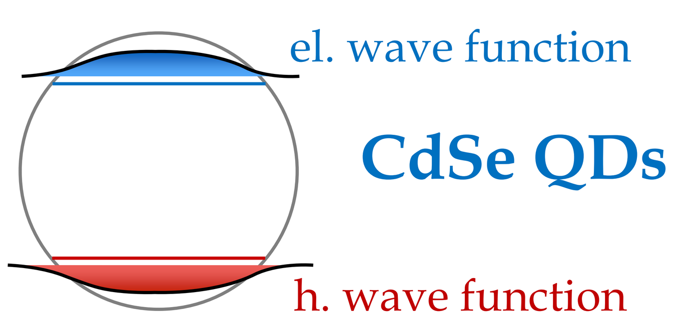
❑ average relaxation time accounting for non-exponential dynamics

$$\frac{1}{\tau_{avg}} = \frac{1}{t_1} + \frac{1}{t_2}$$





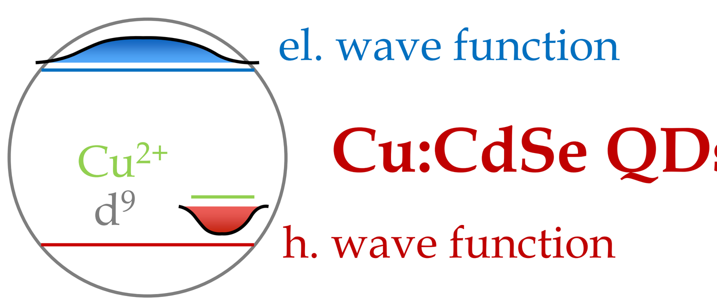
The role of hole trapping



❑ carrier interaction with surface spins due to dangling bonds

❑ efficient spin relaxation

Rodina and Efros *Nano Lett.* **15**, 4214 (2015).



❑ hole trapping at the Cu dopant site

❑ shrinkage of carrier wave functions

❑ limited interaction with the surface

❑ slow spin relaxation

Spin relaxation rates

❑ temperature dependence of τ_{avg}

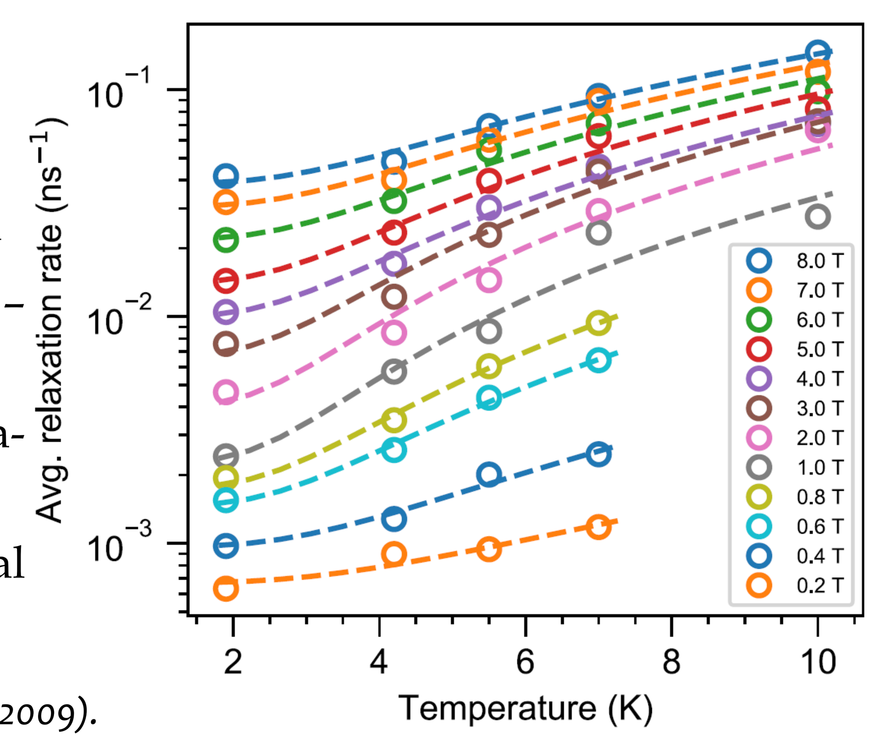
❑ role of phonons in spin relaxation

❑ phonon bottleneck regime – second order process

❑ relaxation between $T_\pm$ states, separated by ΔE, produces polarization

❑ carrier interaction with spheroidal phonon modes, $E_{ph} \approx 1$ meV, $l \approx 2$

Oron *et al. Phys. Rev. Lett.* **102**, 177402 (2009).



spin relax. rate | surface contribution | phonon contribution → 2nd order Orbach process

$$k_{spin}(B,T) = k_{surface} + A(B)\, n_B(E_{ph},T)\,\left(n_B(E_{ph}+\Delta E,T)+1\right)$$

A(B): related to mixing of spin states | $n_B(E_{ph},T)$: phonon absorption | $(n_B(E_{ph}+\Delta E,T)+1)$: phonon emission

❑ the combined carrier interaction with dangling bond spins at the QD surface and with phonons determine the relaxation rates

Conclusions and Outlook

❑ spin polarization in **Cu:CdSe QDs** develops 2 orders of magnitudes more slowly than in undoped **CdSe QDs**

❑ this extremely slow spin relaxation underlines the nature of the luminescent excited state composed of a hole trapped at the Cu site and a delocalized electron

! ❑ shrinkage of the exciton wave function limits the interaction with dangling bond spins at the surface and, hence, suppresses spin relaxation

❑ non-exponential PL decays due to contributions from different ion positions (electron-hole overlaps), QD morphology, and the vibronic structure

❑ analogous conclusions expected for other copper- and silver-doped II-VI and III-V QDs

❑ comparison with **$CuInS_2$ QDs** will reveal the (contested!) nature of the luminescent state in these nanostructures

Kłopotowski *et al.* *J. Phys. Chem. C* 124, 1042 (2020).

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