Exciton-phonon coupling - the Driving Force Behind Metal-Halide Perovskite Optical Response

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Metal-halide perovskites have emerged in recent decades as revolutionary semiconductor materials for energy harvesting and light emissions. The characteristic structure of bulk and low dimensional perovskite materials comprises corner-sharing octahedra BX_6, composed of metal cation and halide anions with the voids between the octahedra filed with organic or inorganic cation. The soft and ionic lattice form a complex background for electronic excitation where polaronic effects cannot be neglected. While this feature of perovskites has been already used to explain some of the puzzling aspects of carrier transport in these materials, the impact of polaronic effects on the optical response, especially excitonic properties, is much less explored.

Here we show that the excitonic properties of these materials are strongly affected by the interaction of carriers with the lattice which has a profound impact on their optical response. First, with the use of magneto-optical spectroscopy, we show the non-hydrogenic character of the excitons in 3D metal halide perovskites, resulting from non-negligible Frohlich coupling. These results can be well described by the polaronic-exciton picture where electron and hole interaction are no longer described by a Coulomb potential. Furthermore, we show experimental evidence that the carrier-phonon interaction leads to the enhancement of the carrier's effective mass. Notably, we reveal a pronounced temperature dependence of the carrier's effective mass, which we attribute to a band structure renormalization induced by the population of low-energy phonon modes.

Further, we show that the particular interplay between phonons and excitons energy structure in the 2D perovskites is responsible for their superior brightness. In these natural quantum wells excitons exhibit a characteristic fine structure comprising bright triplet and dark singlet states. Recent studies have shown that the dark state is situated several to tens of meV below the bright states in 2D perovskites [1]. Despite this significant splitting, these materials exhibit surprisingly intense PL emission even at cryogenic temperatures, pointing to the non-Boltzmann distribution of excitons. However, the origin of this high bright-state occupation has remained elusive. Using magneto-optical spectroscopy we show that indeed exciton population is characterized by higher temperature than the crystal lattice [2]. To explain this observation we used detailed microscopic and material-specific many-particle theory, exploring the formation, relaxation and decay dynamics of excitons. Our modelling shows that the energy mismatch between the fine structure of exciton and phonons leads to a pronounced phonon-bottleneck effect highlighting the importance of carrier phonon interaction for the optical response of metal halide perovskites

References

[1] M. Dyksik et al. Sci. Adv.7,eabk0904 (2021)

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