

Interpretation of self-trapped excitons in rock salt halides from a vibronic coupling perspective: A first step to simulate real time diffusion

Toraya Fernández-Ruiz¹, Juan María García-Lastra², Pablo García-Fernández¹

¹*Departamento de Ciencias de la Tierra y Física de la Materia Condensada, Universidad de Cantabria, Cantabria, Avenida de los Castros s/n, 39005 Santander, Spain*

²*Department of Energy Conversion and Storage, Technical University of Denmark, Anker Engélunds Vej. Building 301, 2800 Kgs. Lyngby, Denmark*

Localized charge carriers in a solid state system play a fundamental role in the understanding of multiple attractive phenomena such as high-temperature superconductivity in the cuprates, colossal magnetoresistance in manganites [1], the performance of Li-air batteries [2] or the Stokes shift between absorption and emission in rock salt halides [3]. This last example has its origin in the formation of self-trapped excitons (STE), a bound state between an excited electron and a hole, where one or both of them are highly localized in space due to a large lattice distortion, where atoms move $\approx 0.5\text{\AA}$ from their original position. Our proposal in this work is to perform a detailed description of the nature of this lattice distortion from a vibronic-coupling formalism, analyzing the chemical particularities of each system. This procedure let us explain the different nature of STE in transition silver halides such as AgCl (hole localized in an elongated D_{4h} Jahn-Teller complex with a delocalized electron bound to it) versus alkaline halides, where the hole is localized in a V_k center (X_2^- dimer, with X a halide atom) linked to a localized electron.

This information is used as a first step to study the diffusion of STE, a topic with potential applications in the development of modern optoelectronic devices such as solar cells, where the charge transport is carried out by a neutral charge particle (the exciton) that is well-localized in space. In order to do it, we use Second Principles (SP) [4], based on the construction of rigorous models including parameters obtained from DFT that measure, in real space, the electron-hole and vibronic coupling [5] needed to account the physics of STE.

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[1] Emin, D. Polarons; Cambridge University Press: New York, 2013

[2] Garcia-Lastra, J. M.; Myrdal, J. S. G.; Christensen, R.; Thygesen, K. S.; Vegge, T. J. Phys. Chem. C 2013, 117, 5568–5577

[3] K. S. Song et al., Self-Trapped Excitons. Springer-Verlag Berlin Heidelberg 1993

[4] P. García-Fernández, J. C. Wojdeł, J. Iñiguez and J. Junquera, Phys. Rev. B 93, 195137 (2016).

[5] I. B. Bersuker, The Jahn-Teller Effect: Cambridge University Press, Cambridge, 2006