Stability and Polaronic Motion of Self-Trapped Holes in Silver Halides - DTU Orbit (09/11/2017)

Stability and Polaronic Motion of Self-Trapped Holes in Silver Halides: Insight through DFT plus U Calculations

Polarons and their associated transport properties are a field of great current interest both in chemistry and physics. To further our understanding of these quasi-particles, we have carried out first-principles calculations of self-trapped holes (STHs) in the model compounds AgCl and AgBr, for which extensive experimental information exists. Our calculations confirm that the STH solely stabilizes in AgCl but with a binding energy of only 165 meV, an order of magnitude smaller than that found for the V_k center in KCl. Key contributions to this stabilization energy come from the local relaxation along breathing (a_{1g}) and Jahn Teller (e_g) modes in the $AgCl_6^{4-}$ unit. To study the transfer of the STH among silver sites, we (i) use first-principles calculations to obtain the hopping barrier of the STH to first and second neighbors, involving eight distinct paths, using first-principles and (ii) construct a simple model, based on Slater-Koster parameters, that highlights the similarity of polaron transfer with magnetic superexchange. This allows one understanding of why the movement of STHs to second neighbors is highly enhanced with respect to closer ones. In agreement with experimental data and the model, the present calculations prove the existence of a dominant mechanism of polaronic motion that corresponds to the displacement of the STHs to the next-nearest sites in the <100 > direction and a small barrier of 37 meV. This mechanism is dominated by the covalency inside a AgX_6^{4-} complex (X:Cl;Br), thus explaining why the STH is not stabilized in AgBr following the increase of covalent/due to the Cl -> Br substitution. The present calculations confirm that, similar to 10% of the charge associated with the STH in AgCl is outside the $AgCl_6^{4-}$ complex. This fact is behind the differences between optical: and magnetic properties of the STH in AgCl and those observed in KCl:Ag^{2+}.

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