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Plastic crystal behavior, tight-binding modelling and low energy phonon spectroscopy in hybrid perovskites crystals

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In this paper, we examine recent theoretical investigations on 3D hybrid perovskites (HOP) that combine concepts developed for classical bulk solid-state physics and empirical simulations of their optoelectronic properties. In fact, the complexity of HOP calls for a coherent global view that combines usually disconnected concepts, related to classical semiconductors, perovskites and plastic crystals[1]. For the pseudocubic high temperature reference perovskite structure that plays a central role for 3D HOP, we introduce a new tight-binding Hamiltonian, which specifically includes spin-orbit coupling. The resultant electronic band structure is compared to that obtained using state of the art density functional theory (DFT). Possible plastic crystal and orientational glass behaviors of HOP will be discussed, building on Car-Parrinello molecular dynamics simulations and symmetry analyses of the cation stochastic reorientations. As available experimental or simulated data on low energy structural excitations are limited, large single crystals of $MAPbBr_3$ have been grown and used to perform neutron and Brillouin scattering and ultrasonic characterization of low frequency acoustic phonons, as well as relaxation modes in different energy ranges. Neutron scattering experiments further reveal that the $MAPbBr_3$ crystal presents a coexistence of crystalline domains below the cubic to tetragonal phase transition at T_c=225K. This observation is consistent with the improper ferroelastic character of the phase transition as predicted from the symmetry analysis of phonon and molecular relaxational modes.

[1] Even, J., Carignano, M. & Katan, C. “Molecular disorder and translation/rotation coupling in the plastic crystal phase of hybrid perovskites.” Nanoscale DOI: 10.1039/C5NR06386H, (2016)

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