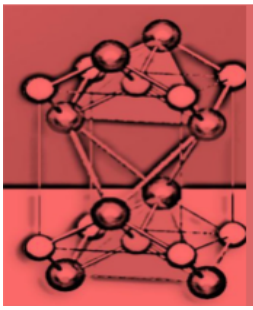

IX Workshop on Novel Methods for Electronic Structure Calculations

10th – 19th November 2021
La Plata – Argentina

Understanding the Temperature & Pressure Dependence of Hybrid Perovskite Band Gaps

Adrián Francisco-López [a], Kai Xu [a], Bethan Charles [b], M. Isabel Alonso [a], Miquel Garriga [a], Mariano Campoy-Quiles [a], Mark T. Weller [b,c], Jarvist M. Frost [d], Alejandro R. Goñi [a,e]

[a] *Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellatera, Spain.*
[b] *Dept. of Chemistry & Centre for Sustainable Chemical Technologies, University of Bath, Claverton Down, Bath BA2 7AY, UK.*
[c] *Dept. of Chemistry, Cardiff University, Wales CF10 3AT, UK.*
[d] *Dept. of Physics, Imperial College London, Exhibition Road, London SW7 2AZ, UK.*
[e] *ICREA, Passeig Lluís Company 23, 08010 Barcelona, Spain.*

email: goni@icmab.es

Hybrid lead halide perovskites exhibit an atypical temperature dependence of the fundamental gap for the phases stable at ambient conditions: it decreases in energy with decreasing temperature. Reports ascribe this behavior to a strong electron-phonon renormalization, neglecting contributions from thermal expansion. However, high pressure experiments performed on the archetypal perovskite $MAPbI_3$ (MA stands for methylammonium) yield a negative pressure coefficient for the gap of the tetragonal room- temperature phase [1], which speaks against the assumption of negligible thermal expansion effects. I will show that for $MAPbI_3$ the temperature-induced gap renormalization due to thermal expansion is as important as that caused by electron-phonon coupling [2]. This result holds also for phases, stable at ambient conditions, of most halide perovskite counterparts. As an example, results obtained for a series of $FA_xMA_{1-x}PbI_3$ solid solutions, where FA stands for formamidinium [3], will be also presented. Strikingly, the temperature dependence of the gap of a presumably tetragonal but disordered phase, which is stable in a wide range of intermediate compositions and temperatures lower than ca. 250 K, exhibits a quadratic *bowing* of the gap with temperature. This is again interpreted in terms of the combined effects of thermal expansion and electron-phonon interaction. Ab-initio band-structure and lattice-dynamics calculations provide crucial insights into this intriguing behavior of the gap with temperature.

[1]. A. Francisco-López et al., J. Phys. Chem. C **122** (2018) 22073-2208.

[2]. A. Francisco-López et al., J. Phys. Chem. Lett. **10** (2019) 2971-2977.

[3]. A. Francisco-López et al., J. Phys. Chem. C **124** (2020) 3448-3458.