WEIZMANN INSTITUTE OF SCIENCE

Low charge-mobility and defect-tolerance in *Soft* polar crystals is *Fundamental*! *The case of halide perovskites*

Yevgeny Rakita*, *Gary Hodes, David Cahen*

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel ; yevgeny.rakita@weizmann.ac.il

The combination of properties halide perovskites (HaPs) possess (e.g., high absorption coefficient, low defect density, long carrier lifetimes, etc.) should (and does) allow high-performing optoelectronic devices. Their relatively low carrier mobility, however, is one fundamental property that does not fit the expected prognosis. When comparing mobility values of HaP (1-100 $cm^2V^{-1}s^{-1}$) with high-quality heteropolar semiconductors, such as GaAs or CdTe (10^3-10^5 $cm^2V^{-1}s^{-1}$),[1] a significant difference is revealed. **Here we show that mobility temperature dependence of HaPs, as well as other low-defect density heteropolar semiconductors, is found to exhibit scattering by 'polar optical phonons' (POP), or *dipoles formed during thermal fluctuations*. We explain why the mobility in *soft* heteropolar materials, like HaPs, will never be as high as for other, more rigid, heteropolar semiconductors, but also show that their softness is responsible for the potential to be more defect-tolerant that more rigid systems.**

1 Charge mobility temperature dependence

Charge mobility : $\mu_q = \frac{q \cdot \tau_s}{m^*}$; Scattering frequency : $\frac{1}{\tau_{total}} = \frac{1}{\tau_{s1}} + \frac{1}{\tau_{s2}} + \cdots$

$$\frac{1}{\mu_{total}} = \frac{1}{\mu_{II}} + \frac{1}{\mu_{NI}} + \frac{1}{\mu_{ADP}} + \frac{1}{\mu_{ODP}} + \frac{1}{\mu_{PZ}} + \frac{1}{\mu_{POP}}$$

Ionized impurities	$\mu_{II} \propto \frac{T^{+3/2}}{N_I}$	$N_I \equiv$ Ionized impurity density
Neutral impurities	$\mu_{NI} \propto \frac{T^0}{N_N}$	$N_N \equiv$ Neutral impurity density (relevant mostly at low temperatures)
Acoustic phonons	$\mu_{ADP} \propto \frac{T^{-3/2}}{d'^2}$	$d' \equiv$ deformation potential (2)
Polar acoustic phonons	$\mu_{PZ} \propto \frac{T^{-1/2}}{e_{pz}^2}$	$e_{pz} \equiv$ piezoelectricity constant
Polar optical phonons*	$\mu_{POP} \propto \varepsilon^* \cdot \frac{T^{1/2}}{\theta} \cdot \left(\exp\left(\frac{\theta}{T}\right) - 1\right)$ (3)	$\theta \equiv$ Debye temperature $= \frac{\hbar \cdot \omega_{LO}}{k_B}$; $\omega_{LO} \equiv$ longitudial optical phonon ; $\varepsilon^* \equiv$ effective dielectric constant (4)

* *[Also known as Fröhlich interactions]*

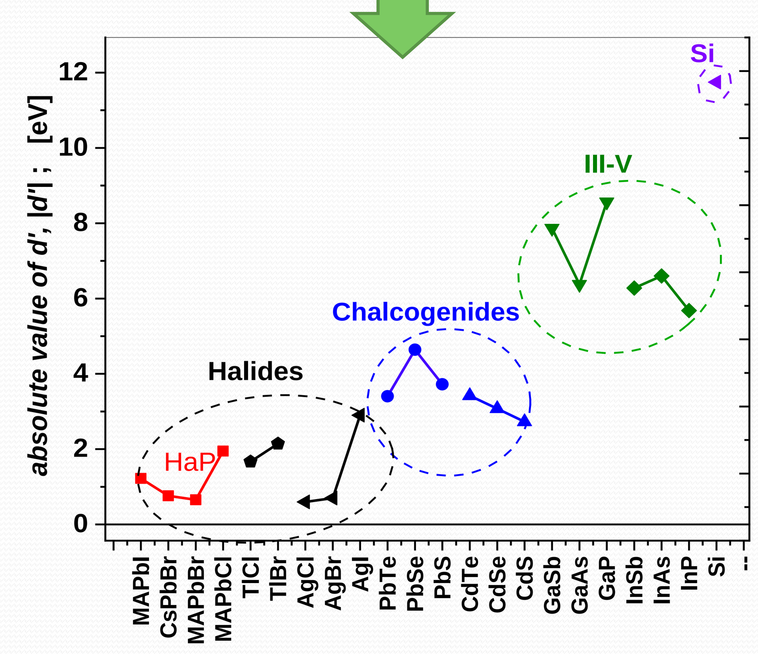
Theory and explicit equations can be found in:

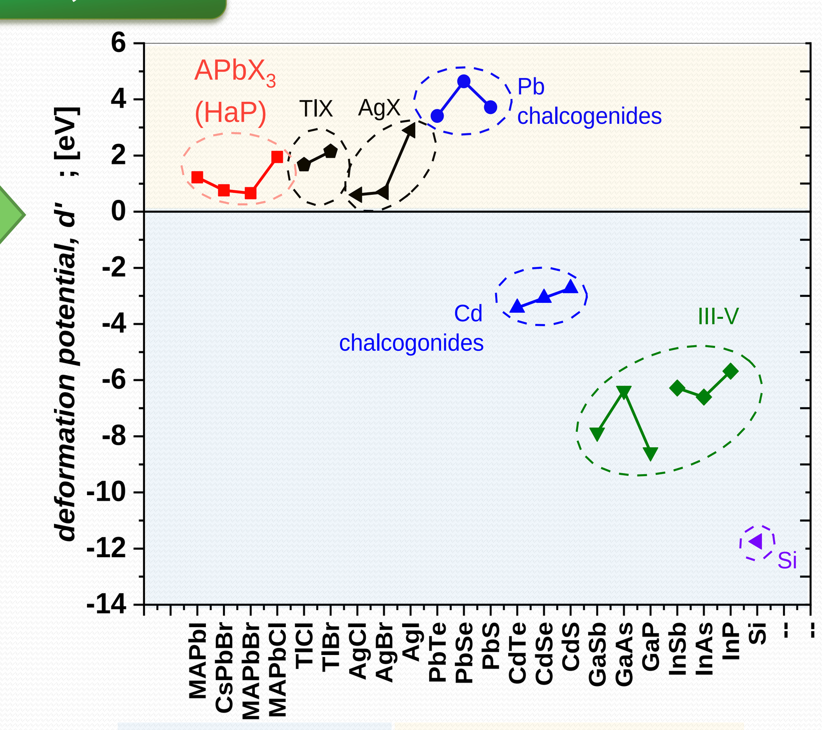
- Li, S. S. *Semiconductor Physical Electronics*. (Springer-Verlag, 2006), Chapter 8
- Lundstrom, M. Fundamentals of Carrier Transport,2nd edn. Meas. Sci. Technol. 13, 230 (2002).

2 Deformation potential, d'

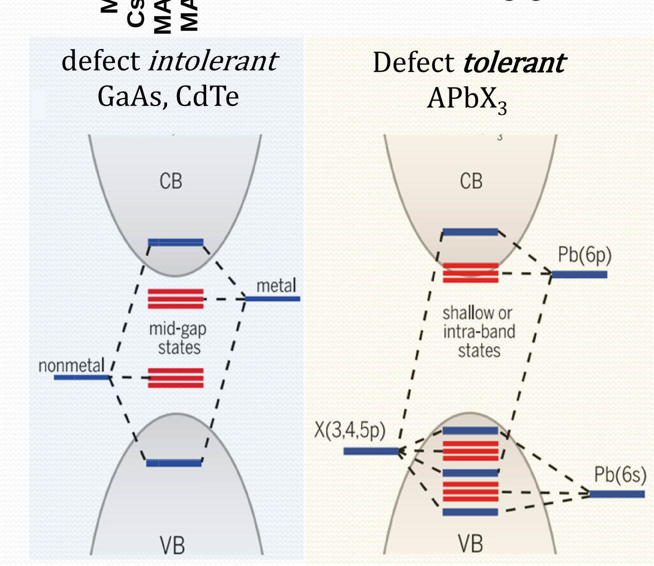
$$d' \equiv -B \cdot \frac{\Delta E_g}{\Delta P}$$

B – bulk modulus
ΔE_g - change in bandgap
ΔP – change in pressure

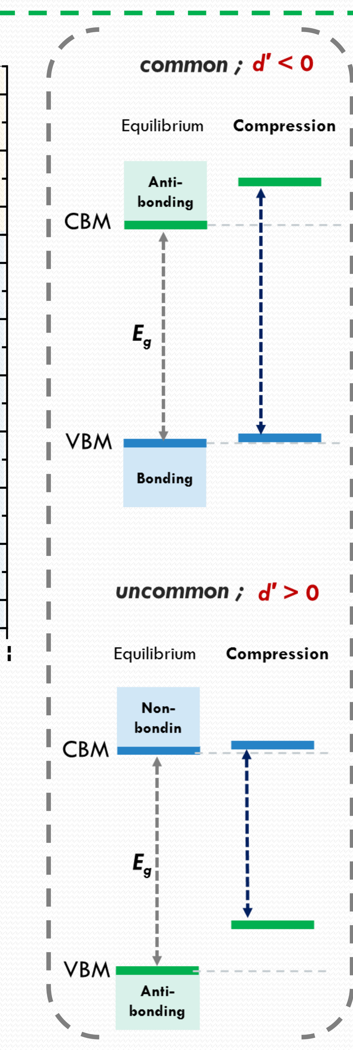




Halide-based materials have relatively **low** absolute deformation potential



Adopted from: Kovalenko et al., Science 358, 745–750 (2017)



Defect states in the bands = **defect tolerance**

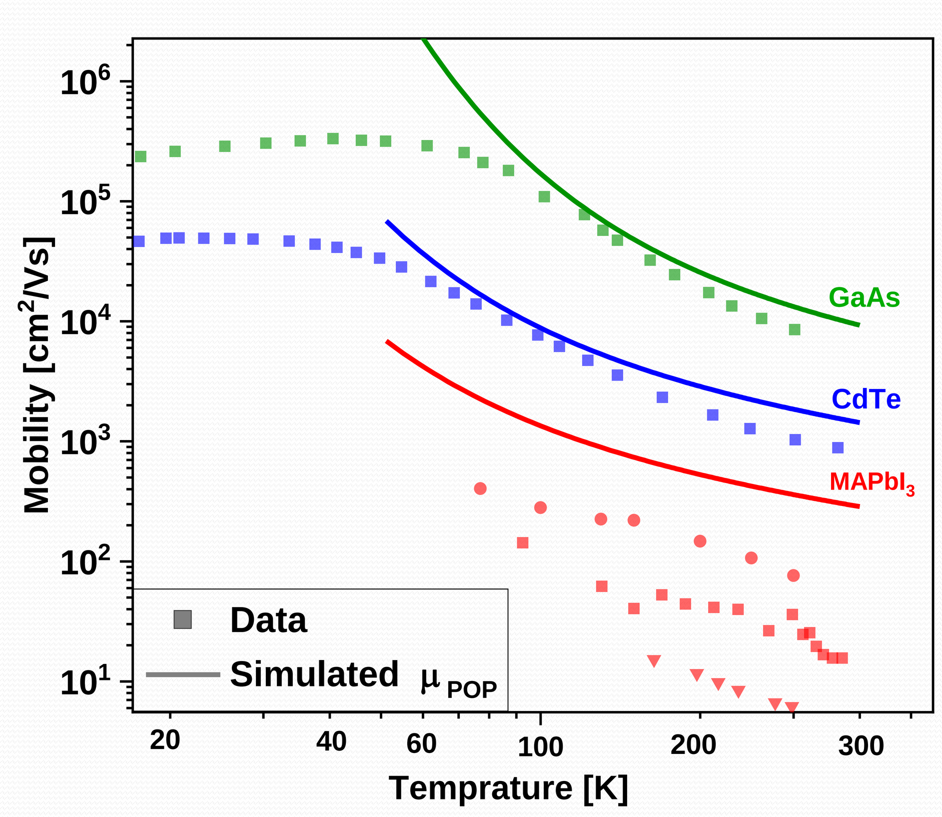
Results

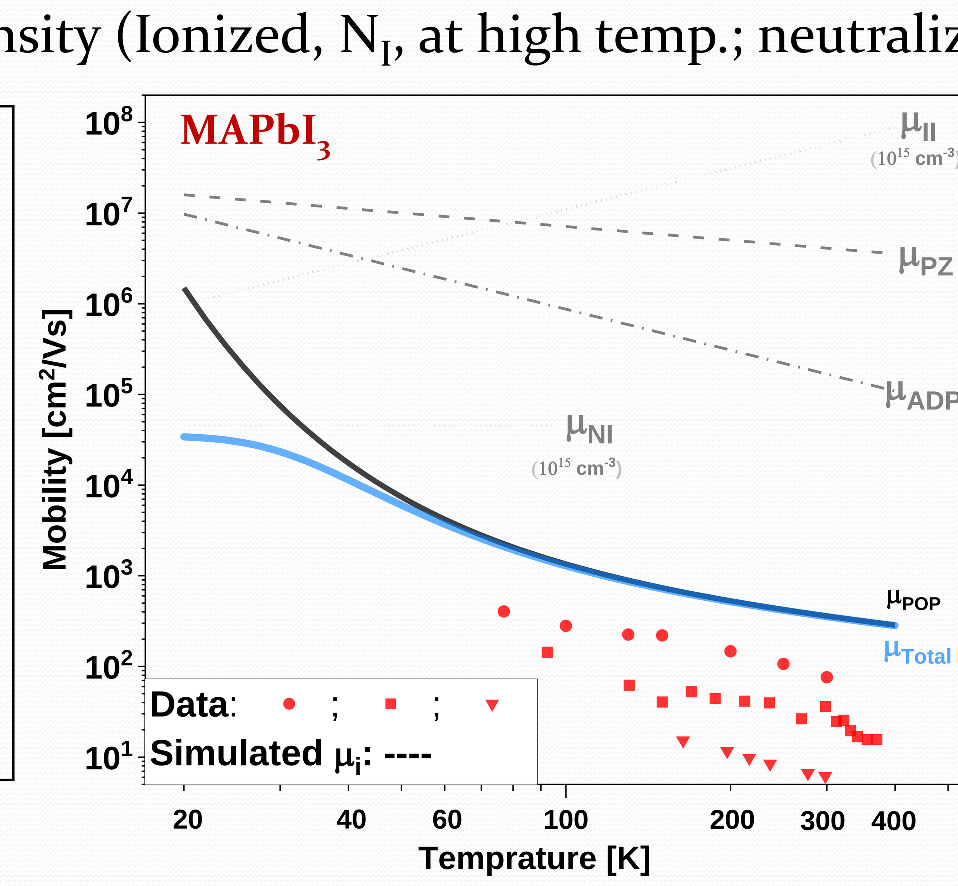
3 Temperature dependence

Using experimentally-based relevant parameters (from literature) such as: effective mass (m*), lowest longitudinal optical phonon frequency (ω_{LO}), the dielectric constant at optical (ε_∞) and static/low (ε_s) frequencies and defect density (Ionized, N_I, at high temp.; neutralized, N_N, at low temp.) of 10^{15} cm^{-3}:

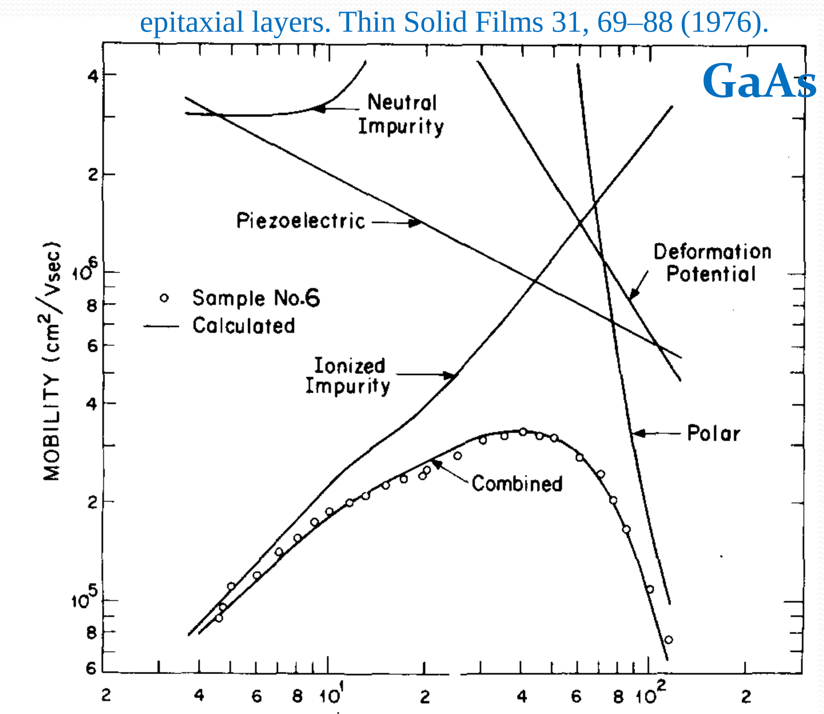
POP dominates scattering in heteropolar materials

The *softer* the materials (i.e., lower $|d'|$), the **higher the probability that the scattering will be due to POP**, rather than by deformation potential or impurities.



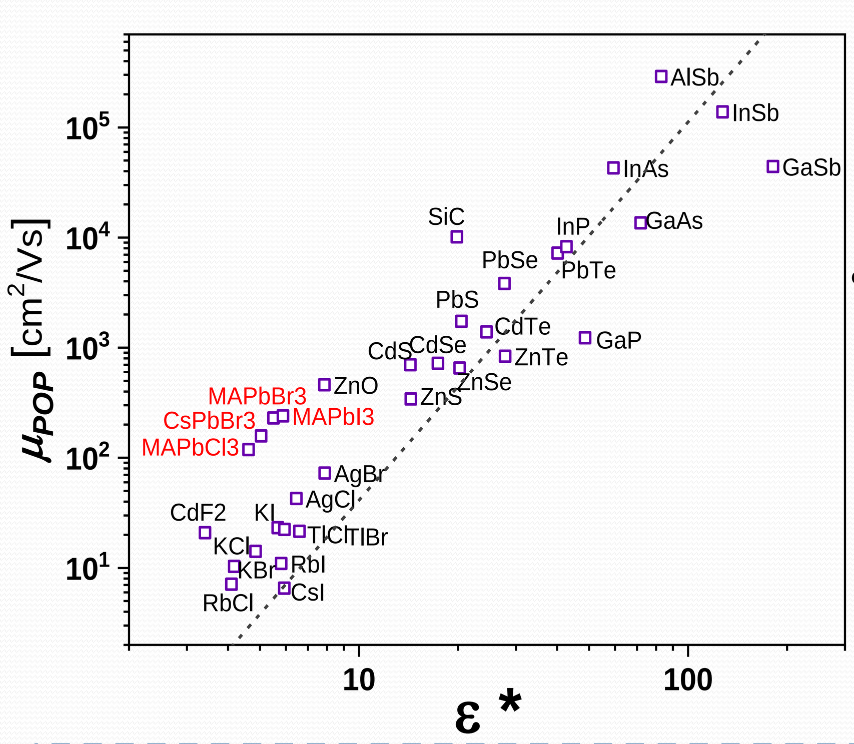


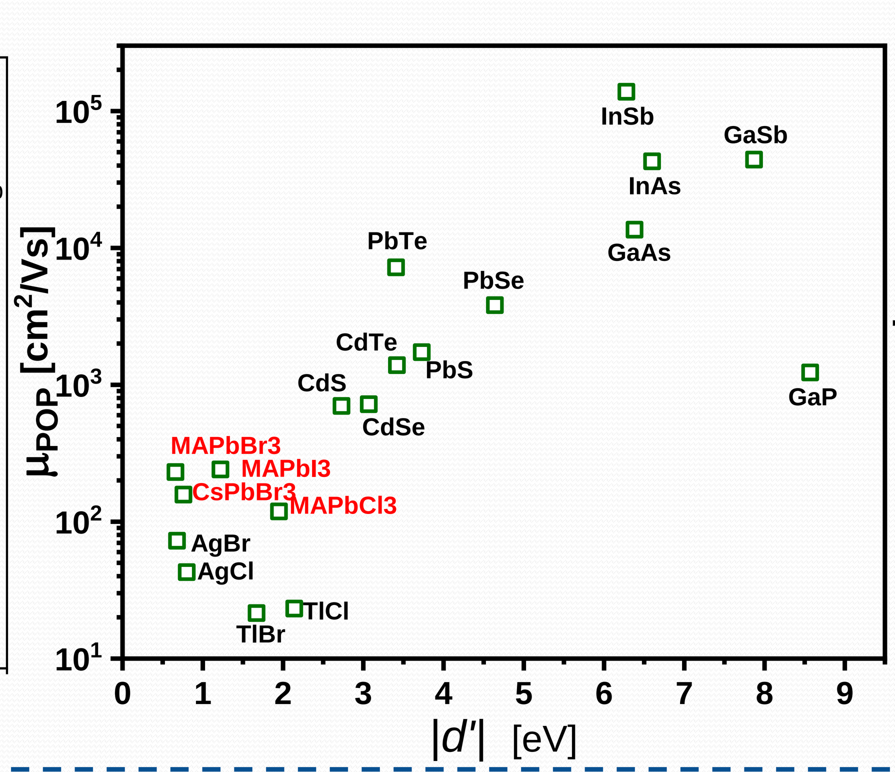
Stillman, G. E. & Wolfe, C. M. Electrical characterization of epitaxial layers. Thin Solid Films 31, 69–88 (1976).

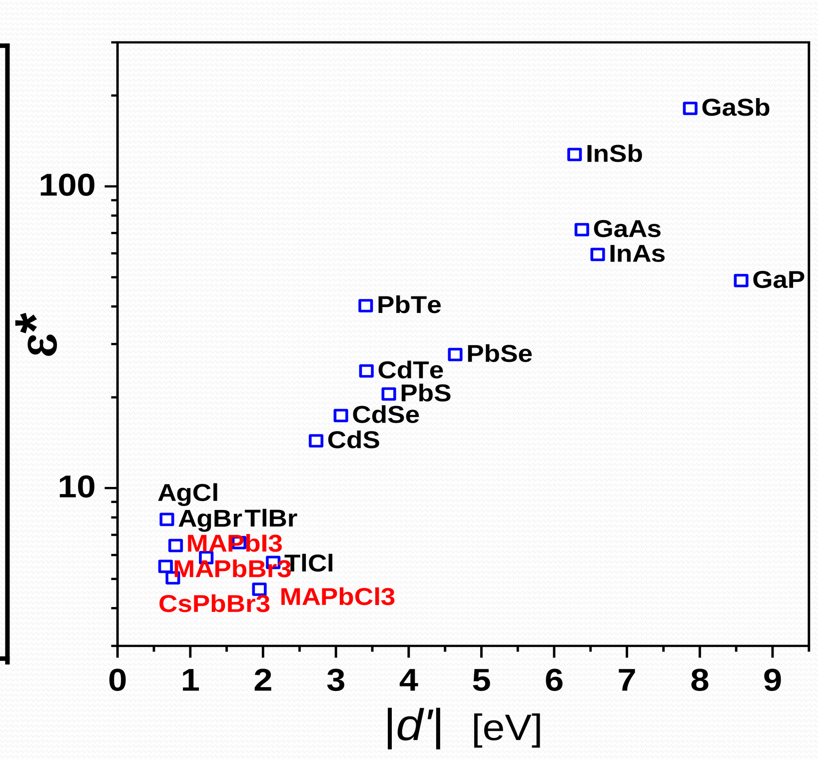


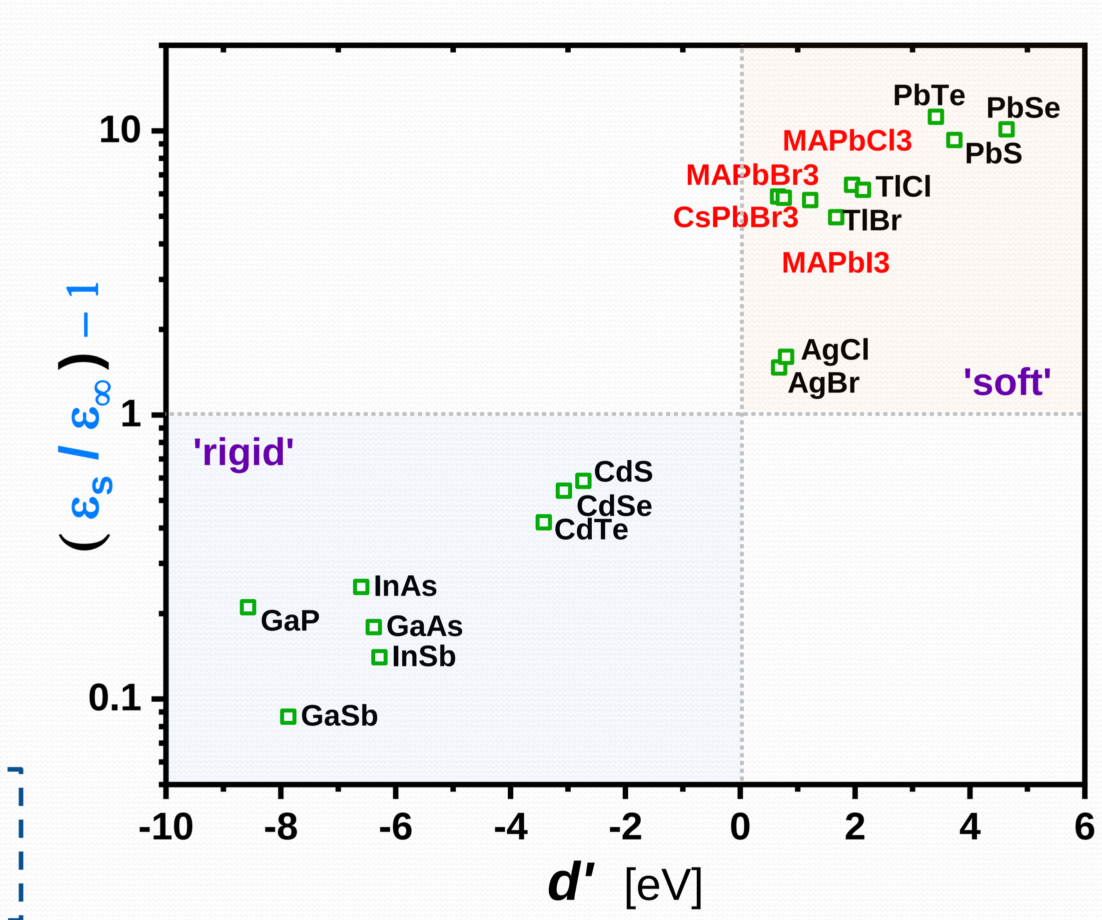
4 Exploring scattering by POP

Scattering potential : $U_{POP}(r) \propto \frac{q^*}{V_u}$; $\frac{q^*}{V_u} \equiv$ Effective charge density during vibration in a heteropolar system ; $\left(\frac{q^*}{V_u}\right)^2 \propto \frac{\omega_{LO}^2}{\varepsilon_s}\left(\frac{\varepsilon_s}{\varepsilon_\infty} - 1\right) = \omega_{LO}^2\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s}\right) = \frac{\omega_{LO}^2}{\varepsilon^*}$









- Plotting μ_{POP} for T=300K as a function of ε^* and $|d'|$ shows that **mobility increase with higher ε^* and $|d'|$.**
- ε^* increase as $\varepsilon_s \rightarrow \varepsilon_\infty$, while at the limit where $\varepsilon_s \gg \varepsilon_\infty$, $\varepsilon^* \rightarrow \varepsilon_\infty$

- Lower $|d'|$ results in increasing ε_s w.r.t. ε_∞. ➔ the energy-cost to spatial distortion to screen electric-fields is smaller ➔ tolerant to charged defects.

__We conclude__ that 'soft' materials are regarded as such with highly-polarizable bonds (i.e., $\varepsilon_s \sim 2 \cdot \varepsilon_\infty$), where *d'* is expected to be *positive*, suggested to possess in-band berried defect states, and therefore, defect tolerant (see 2)

YR thanks Dr. Omer Yaffe and Dr. David Egger for fruitful discussions.