Muonium Formation and Dynamics in Double Perovskites Cs_2AgBiX_6 (X = Cl, Br)

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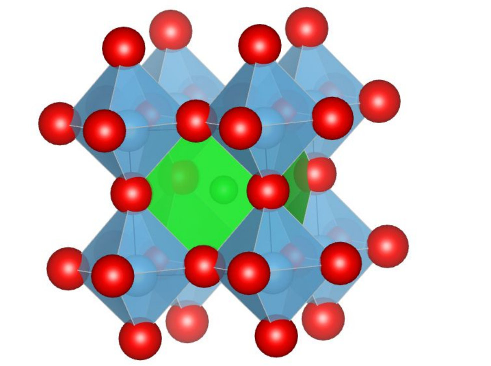
Perovskite Structure

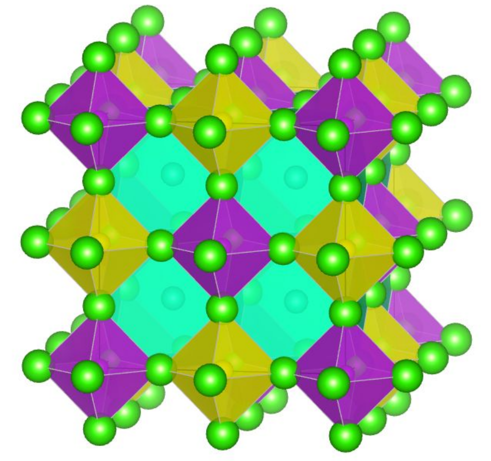
- Perovskites are based on octahedral oxygen cages
- Perovskite structure: ABO_3
  - A = Rare or alkaline earth metals
  - B = First-row transition metals
  - O = Oxygen
- Double perovskites structure: $A_2B'B''X_6$
  - A, B′ = Monovalent cations
  - B″ = Trivalent cations
  - X = Halide
- Samples studied – $Cs_2AgBiCl_6$ $Cs_2AgBiBr_6$

(Yasuda et al., J Synchrotron Rad 2009, 16 (3), 352–357.)

Example of general perovskite $BaTiO_3$

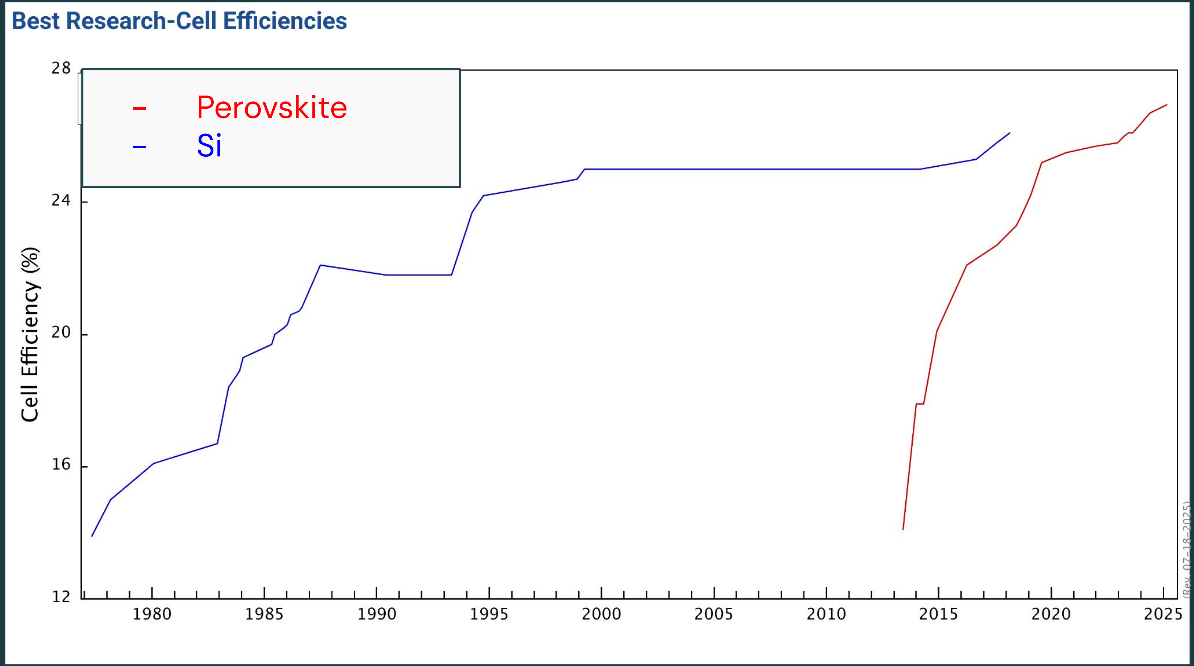


Structure of $Cs_2AgBiCl_6$



(Gao, Wang, Shen, Zhou, & Zhang, RSC Adv. 2024, 14 (50), 37322–37329.)

Why Study Perovskites?

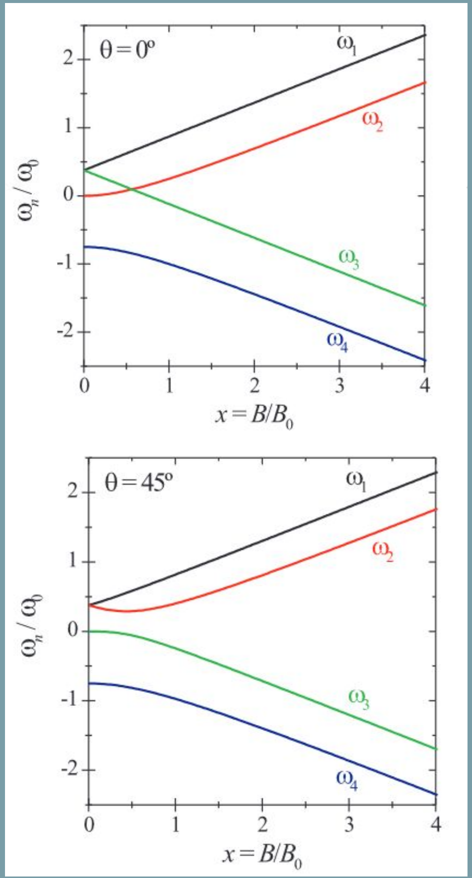


Comparing solar cell efficiencies over time. Retrieved from https://www.nrel.gov/pv/cell-efficiency

- Highly tunable
- Defect tolerance
- Photovoltaic applications
- Light emission
- Radiation detection

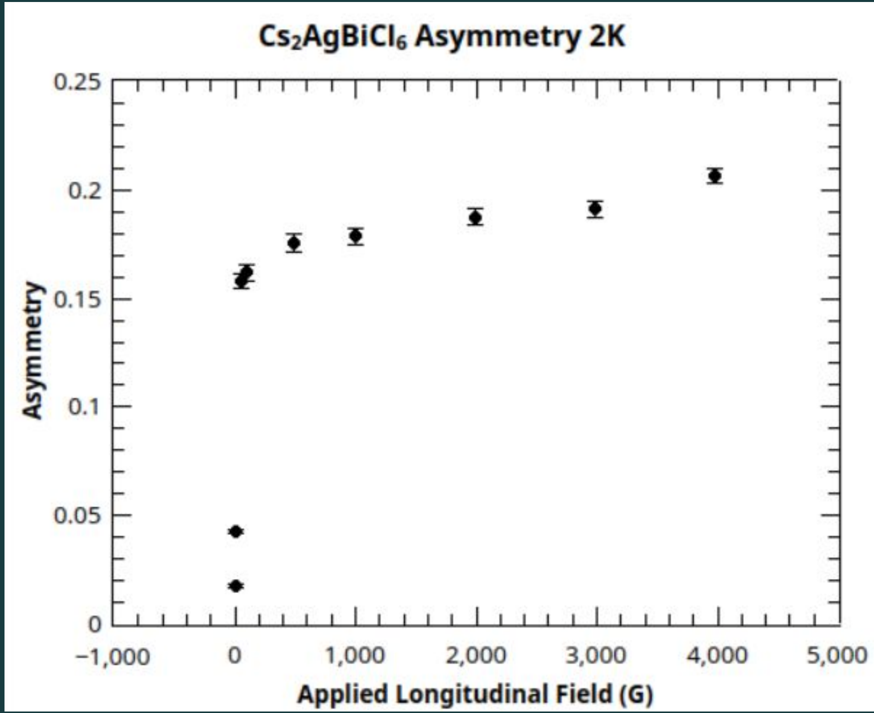
Muonium

- Hydrogen analogue, often forms in semiconductors
- Electron and muon interact through hyperfine coupling
- Hyperfine interaction may be isotropic or anisotropic
- Combining Zeeman and hyperfine interactions results in triplet and singlet states



Duarte, Joao Pedro Piroto Pereira., Diss. Universidade de Coimbra (Portugal), 2006.

Experimental Evidence For Muonium



- Unpolarized electrons means equal chance electron spin is aligned versus anti-aligned with muon spin
- Spins aligned is an eigenstate, will not change
- Spins anti-aligned leads to very fast precession
- Increased fields change asymmetry due to Zeeman interaction

Dynamics of Muonium

Charge exchange, muon gaining and losing electron cyclically

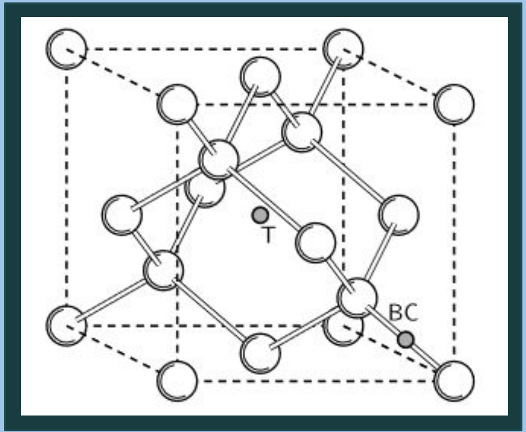
$$Mu^0 \rightleftharpoons Mu^+$$

Diffusing between sites

$$Mu_{BC} \rightleftharpoons Mu_T$$

Spin flip of the muonium electron

$$|\uparrow_\mu \uparrow_e\rangle \rightleftharpoons |\uparrow_\mu \downarrow_e\rangle$$



Structure of Si showing tetrahedral (T) and bond centered (BC) muon sites.

Blundell, S. J., Contemporary Physics 1999, 40 (3), 175–192.

What Would Spin Exchange Look Like?

$v =$ Spin flip rate

$$\omega_0 = \frac{A}{\hbar}$$

$$x = \frac{B(\gamma_{el} + \gamma_{\mu})}{A}$$

$\gamma_{el/\mu} =$ Gyromagnetic ratios

$A =$ Hyperfine coupling strength

$B =$ Applied magnetic field

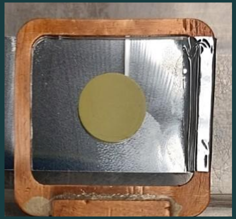
Fast Spin Flip

$$\frac{1}{T_1} = \frac{\omega_0^2}{4v}$$

Slow Spin Flip

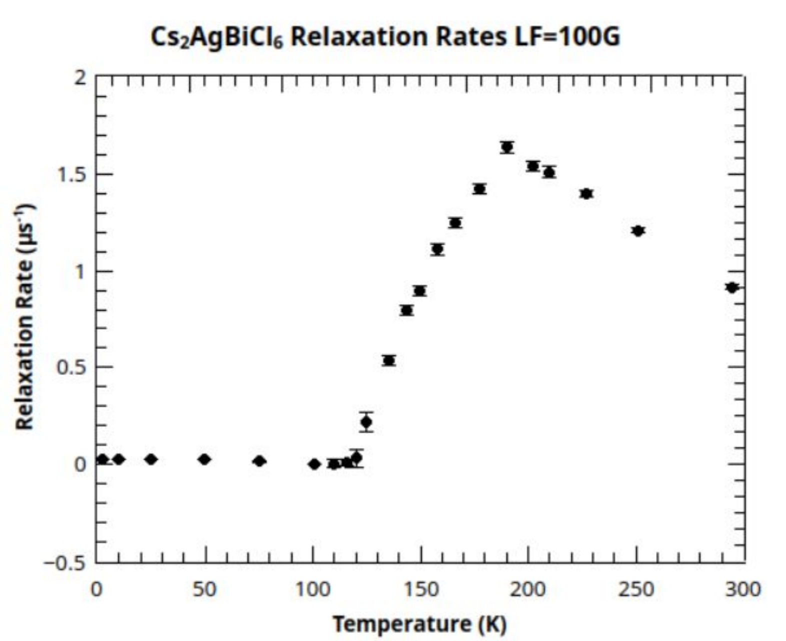
$$\frac{1}{T_1} = \frac{v}{1 + x^2}$$

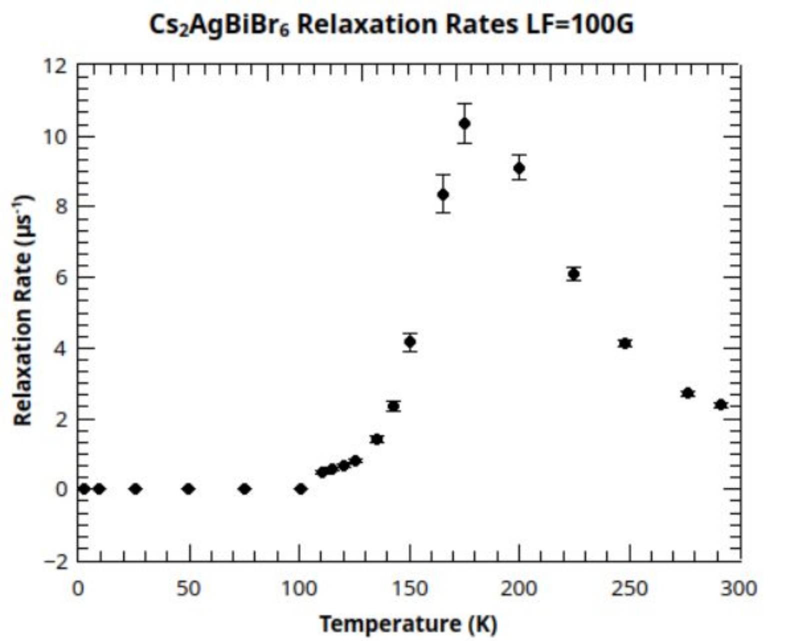
Formulas from: Nosov & Yakovleva, Soviet Physics JETP 1963, 16 (5)



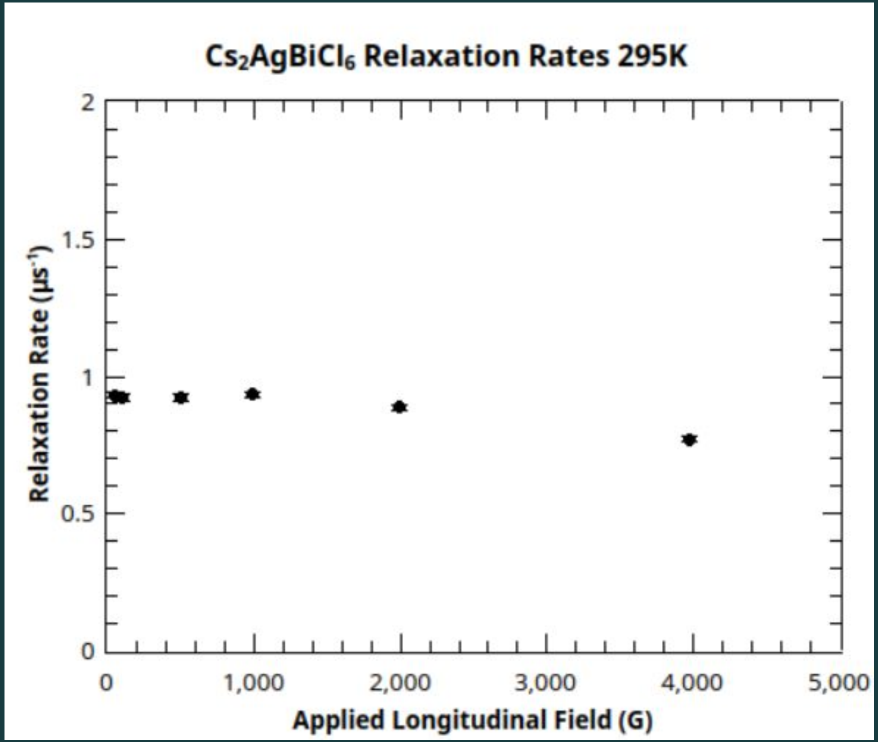
Pressed powder sample of $Cs_2AgBiCl_6$

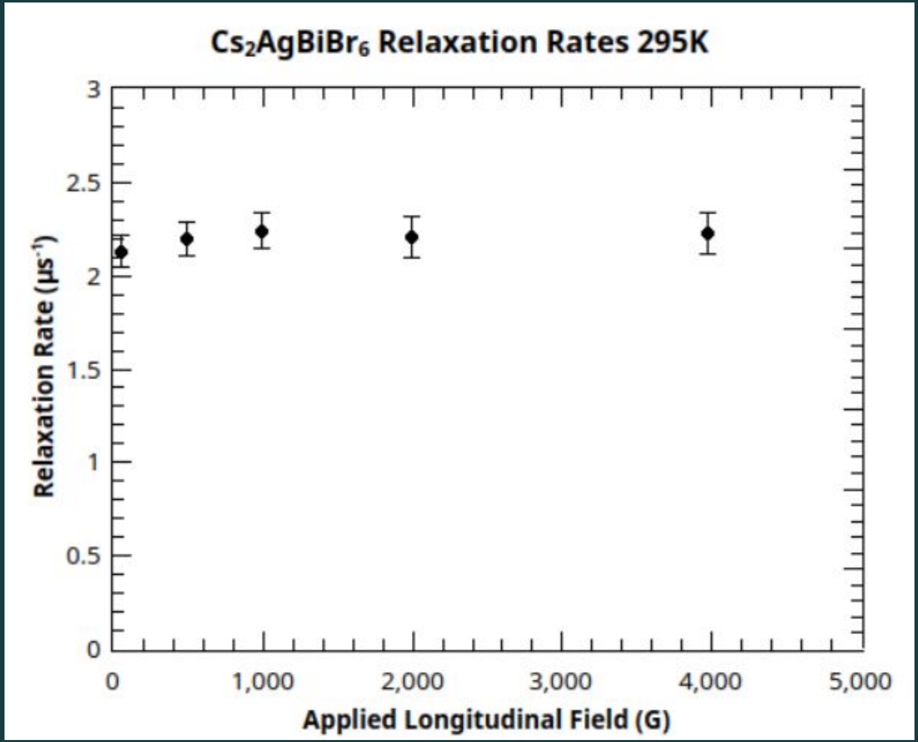
Temperature Scans



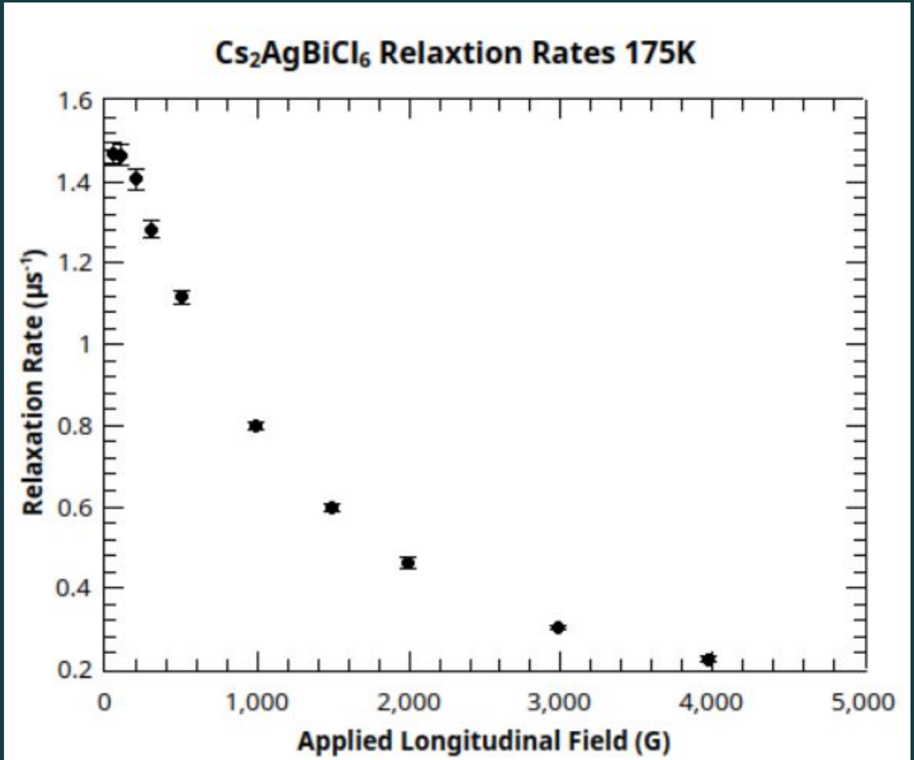


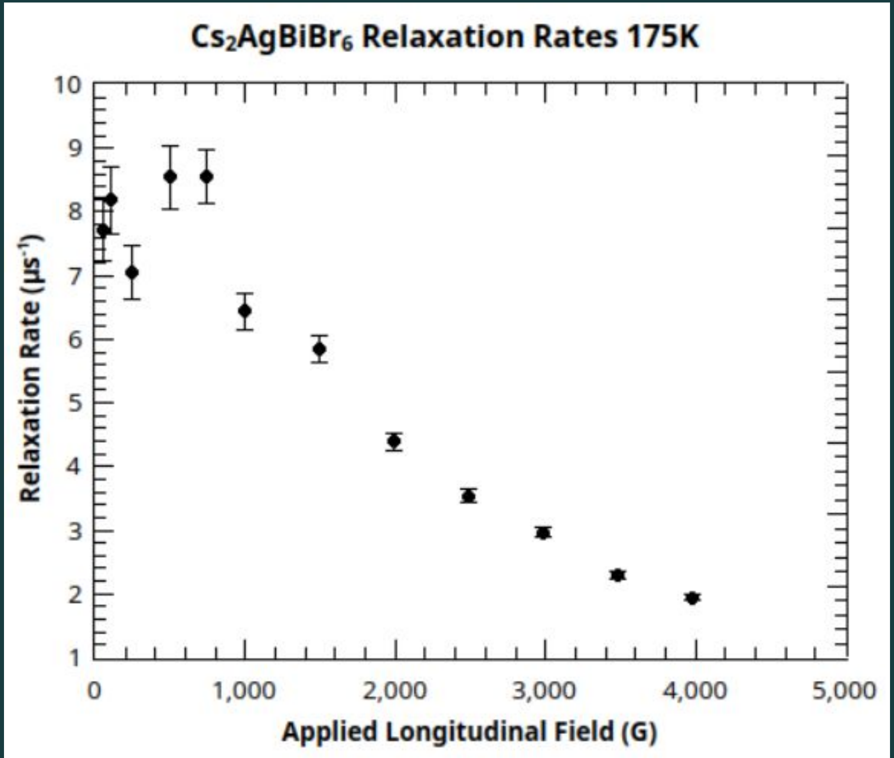
Field Scans – Fast Spin Flip





Field Scans – Slow Spin Flip





Summary

- Studied double perovskite samples with μSR
- Interested in the structures for photovoltaic applications
- We see a loss of asymmetry that repolarizes with applied longitudinal field - evidence for muonium formation
- The muon polarization relaxes, implying some dynamics occur
- Similar temperature and field dependencies between two samples
- Temperature and field scans suggest spin exchange is occurring, with the spin flip rate matching hyperfine coupling strength just under 200K

Hamiltonian

$$H = -\gamma_\mu S_\mu \cdot B - \gamma_e S_e \cdot B + \frac{2\pi}{\hbar} A \cdot S_\mu \cdot S_e$$

- First term Zeeman interaction of muon
- Second term Zeeman interaction of electron
- Third term hyperfine coupling of muon and electron spins

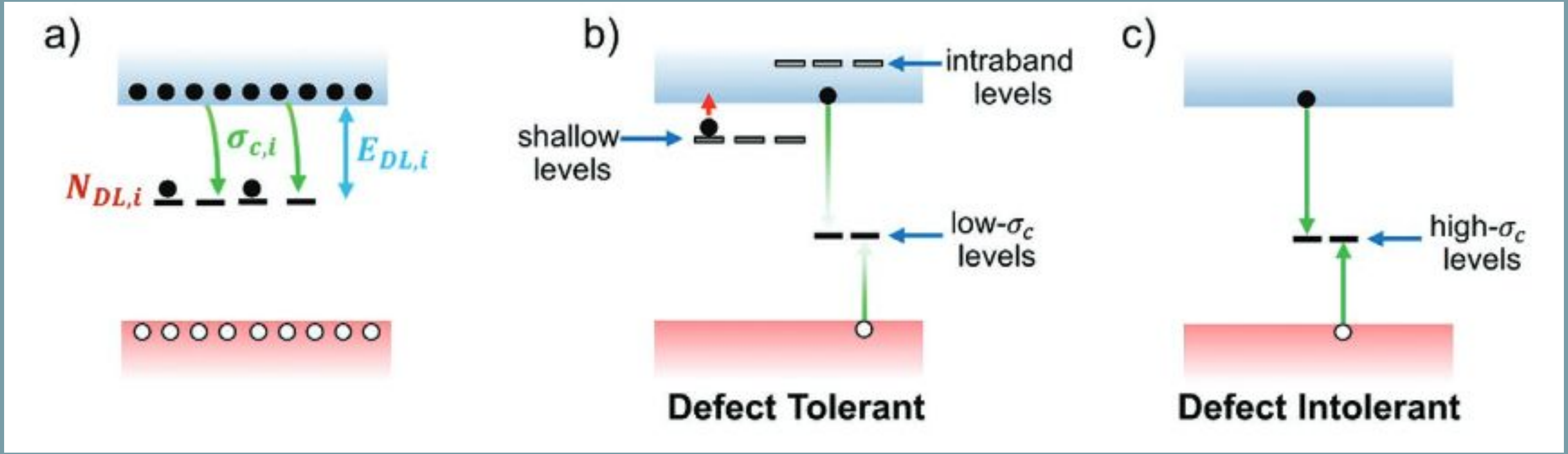
Hyperfine Couplings

Vacuum Mu A = 4463 MHz
Si tetrahedral site = 2006.4 MHz
Si bond-centered site = 16.82 MHz & 92.59 MHz

Gyromagnetic Ratios

Muon = 135.54 MHz/T
Electron = 27992.48 MHz/T

Defect Tolerance



$\sigma_{c,i}$: capture cross section; $N_{DL,i}$: concentration; $E_{DL,i}$: energy depth

Pecunia et al., Assessing the Impact of Defects on Lead-Free Perovskite-Inspired Photovoltaics via Photoinduced Current Transient Spectroscopy. Advanced Energy Materials 2021, 11 (22), 2003968. https://doi.org/10.1002/aenm.202003968.

References

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