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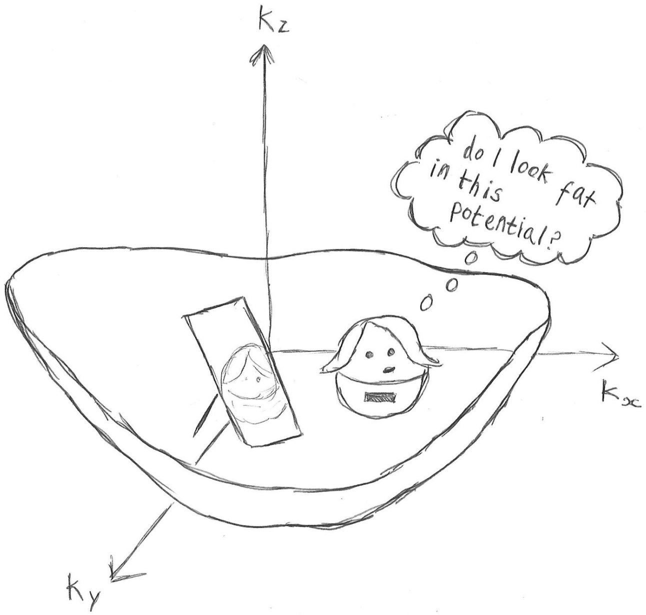
Nonparabolic electronic bandstructure in PV materials

Impact on optical and transport properties



Dr Lucy Whalley

Vice-Chancellor's Fellow

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From physics to materials

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University of Birmingham

Msci Theoretical Physics – w/ Prof. Andy Schofield

transverse magnetoresistance in a quasi-2D metal

Birmingham City University

PGCE in post-compulsory education and training

Imperial College London

PhD in Materials Science w/ Prof. Aron Walsh

defects and distortions in hybrid halide perovskites

Imperial College London

Research Associate in Solar Cells

Northumbria University

Vice-Chancellor’s Fellow

Newcastle, UK

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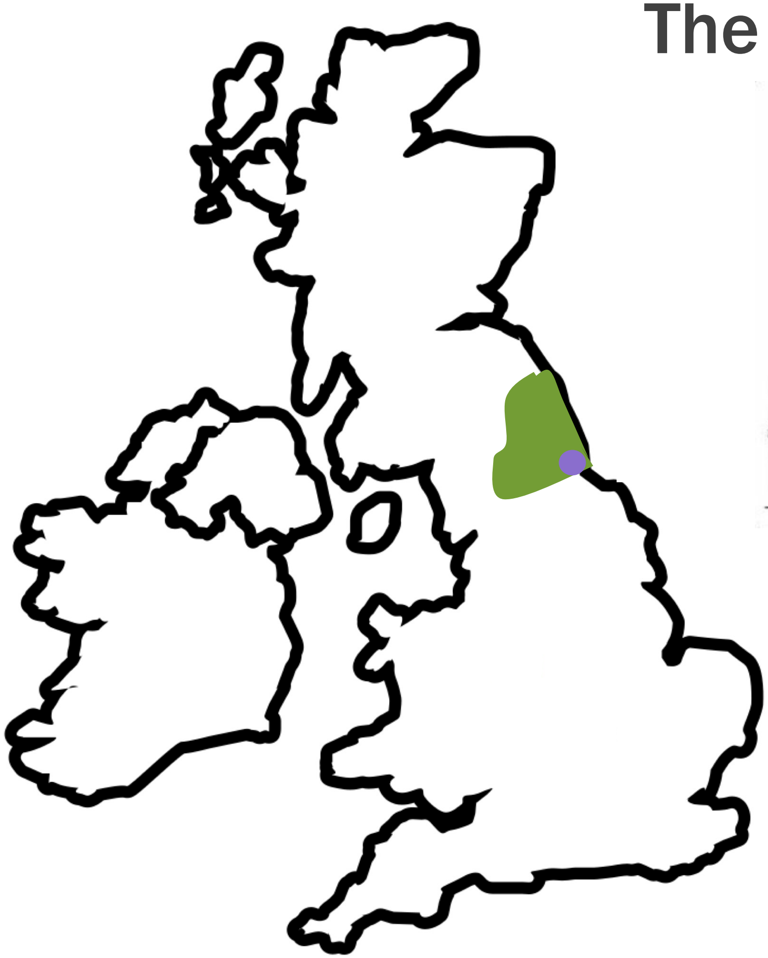
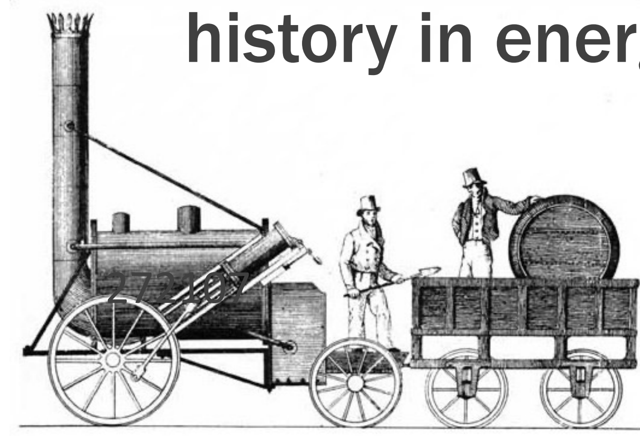
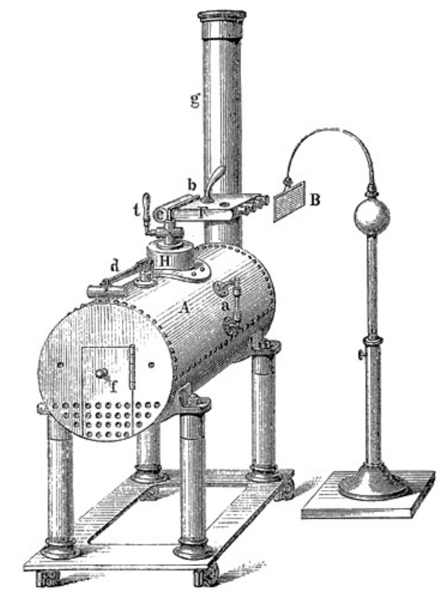


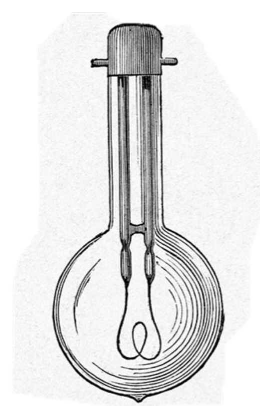
The North-East of England has a long history in energy technology



Steam locomotive
1829



Hydroelectric generator
1842



Lightbulb
1879

Newcastle, UK

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The North-East of England has a lot of activity in energy technology

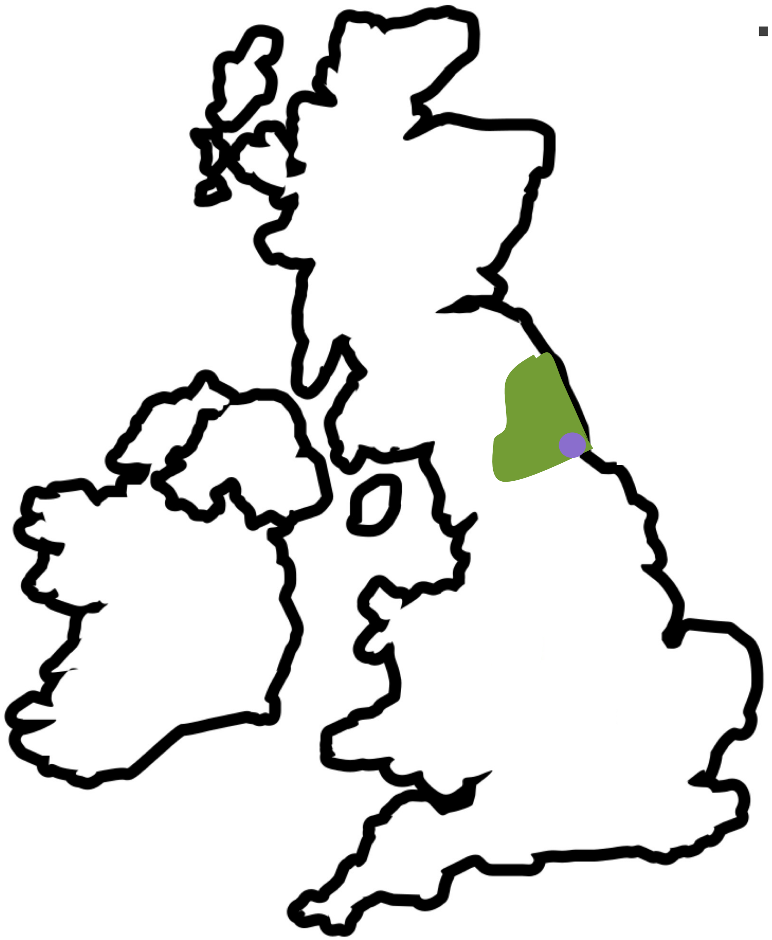
ReNU Renewable Energy Northeast Universities

DOGGER BANK WIND FARM

necem

Newcastle, UK

Northumbria University NEWCASTLE



...but the North-East of England is better known for..

Football

Beer

Dielect – “Geordie”

Newcastle, UK

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“shy bairns get nowt”

=

shy children get nothing

..so speak up and don’t be shy

Talk outline

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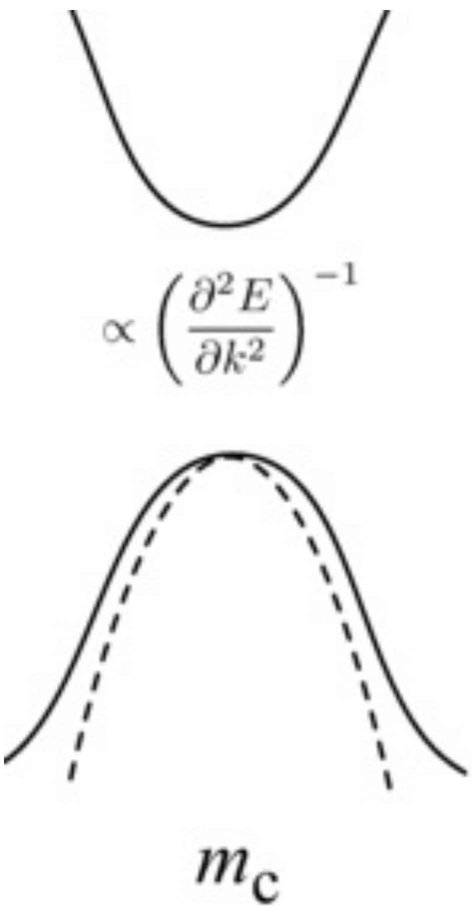
A. Effective mass is not as simple as it might seem

B. Band non-parabolicity is very sensitive to the electronic structure method used

C. Non-parabolicity can impact on various material properties (case study: hybrid halide perovskite)

Paper: L. Whalley et al. *Phys. Rev. B* 99, 085297 (2019)

Effective mass refresh



"Using DFT, we calculated the effective mass to be $0.34m_e$"

Effective mass refresh

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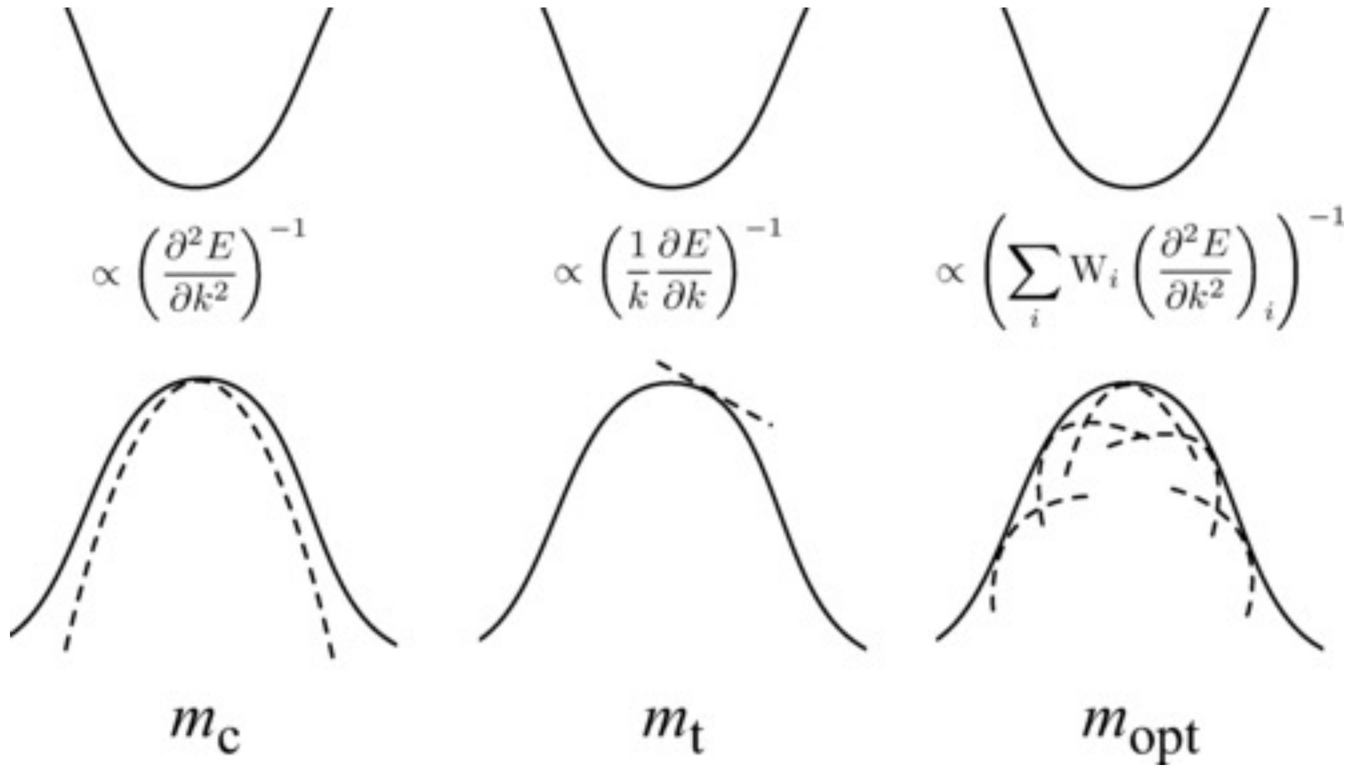
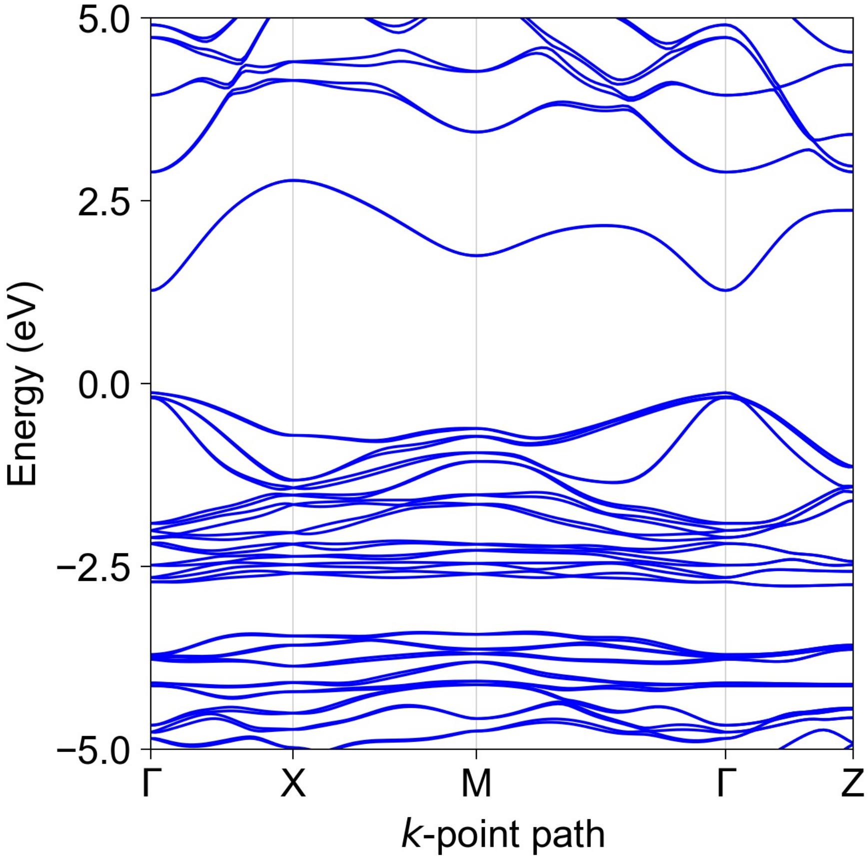
There are several definitions for effective mass

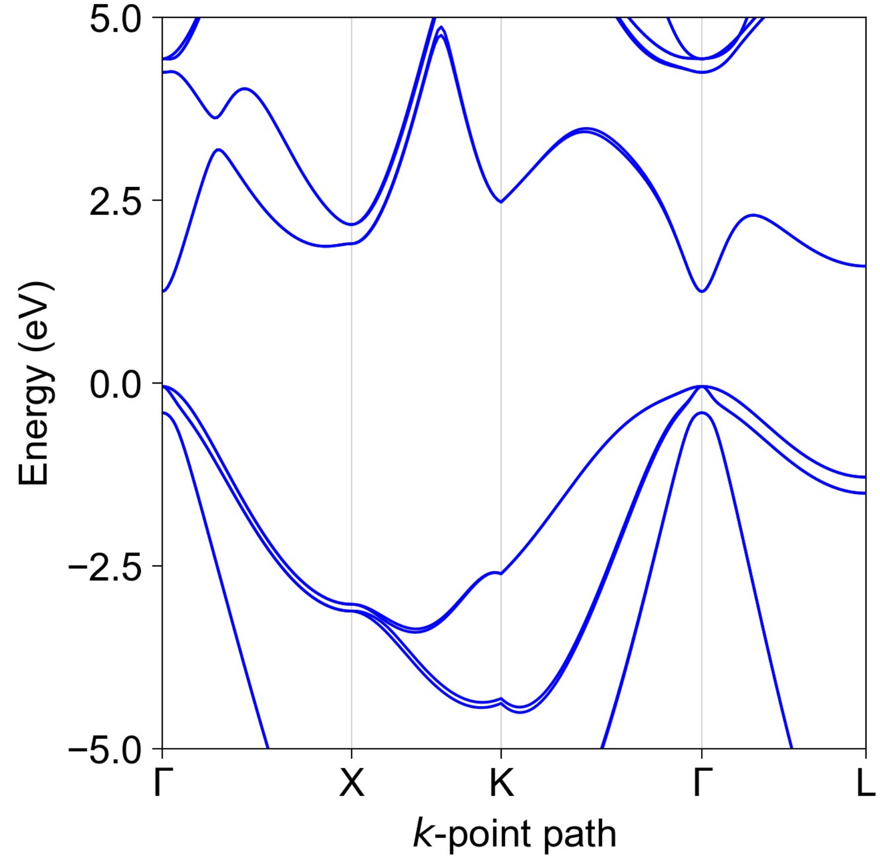


Describes:	acceln of electron in applied electric field	velocity of electron wavepacket	average inertial effective mass

Real materials are not so simple



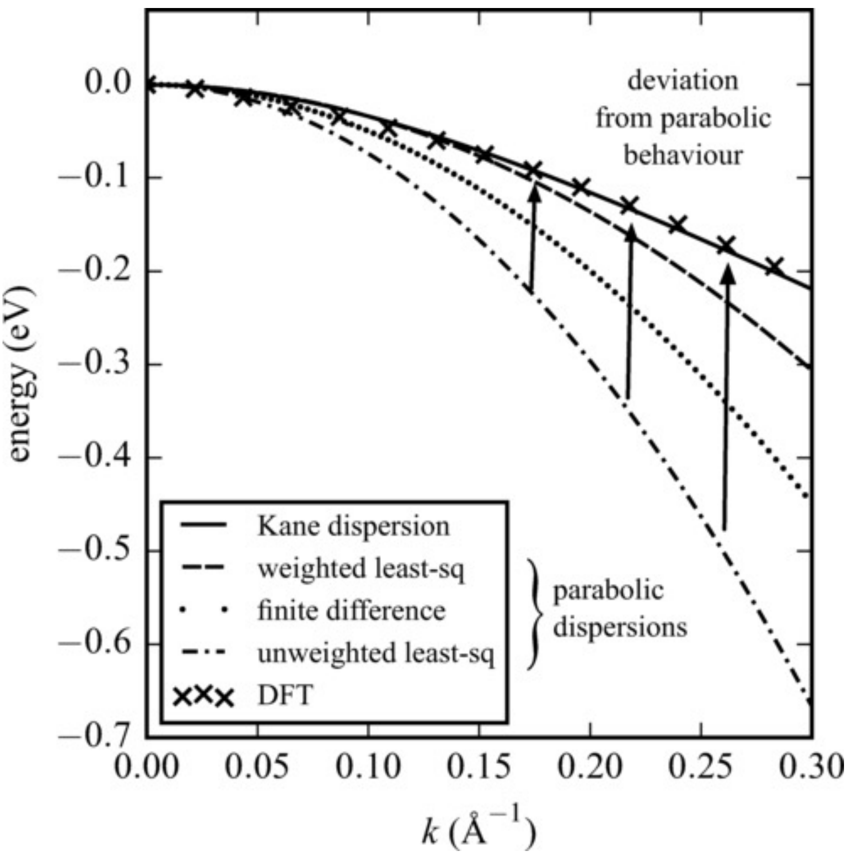
CZTS – HSE06 - SoC



GaAs – HSE06 - SoC

Real materials are not so simple

Non-parabolicity can be described using the Kane quasilinear dispersion



$$\frac{\hbar^2 k^2}{2m_{t,0}} = E(1+\alpha E)$$

$$m_t(E) = m_{t,0}(1+2\alpha E)$$

CZTS valence band [110]
HSE06+SoC

Real materials are not so simple

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Effective mass depends on the sampling range in reciprocal space and numerical method used

sampling density

fitting method

	0.005A^{-1} (m_e)	0.025A^{-1} (m_e)
Finite-difference (3-points)	0.06	0.12
Unweighted LSQ (3-points)	0.05	0.08
Fermi-Dirac weighted LSQ (many points)	0.07	0.07

See the effmass package for an implementation of these methods: github.com/lucydot

JOSS
The Journal of Open Source Software

CZTS valence band [100], PBESol+SoC

Real materials are not so simple

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"Using DFT, we calculated the effective mass to be $0.34m_e$"

- *Which effective mass?*
- *Over what range?*

Talk outline

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A. Effective mass is not as simple as it might seem

B. Band non-parabolicity is sensitive to the electronic structure method used

C. Non-parabolicity can impact on various material properties (case study: hybrid halide perovskite)

Paper: L. Whalley et al. *Phys. Rev. B* 99, 085297 (2019)

Alpha parameter

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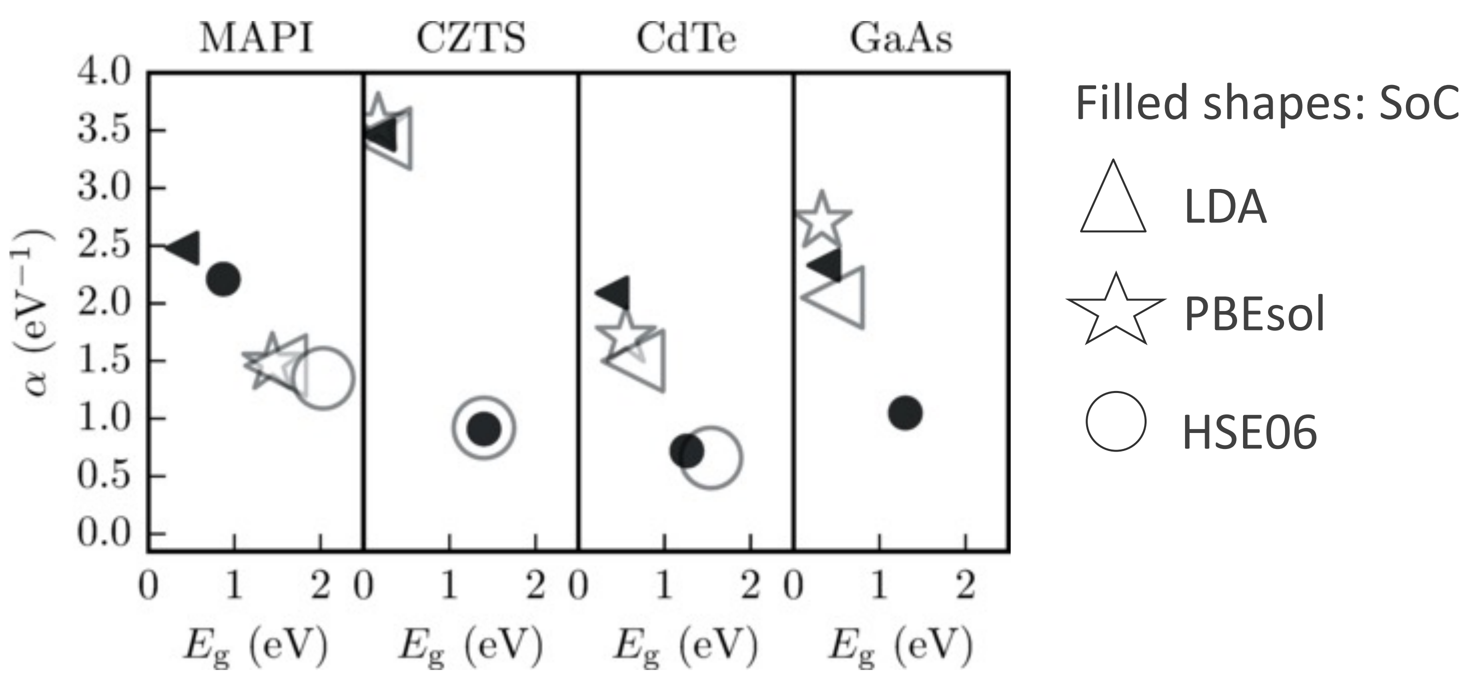
Local and semilocal approximations underestimate the band gap and overestimate non-parabolicity



Conduction band [100]

Alpha parameter

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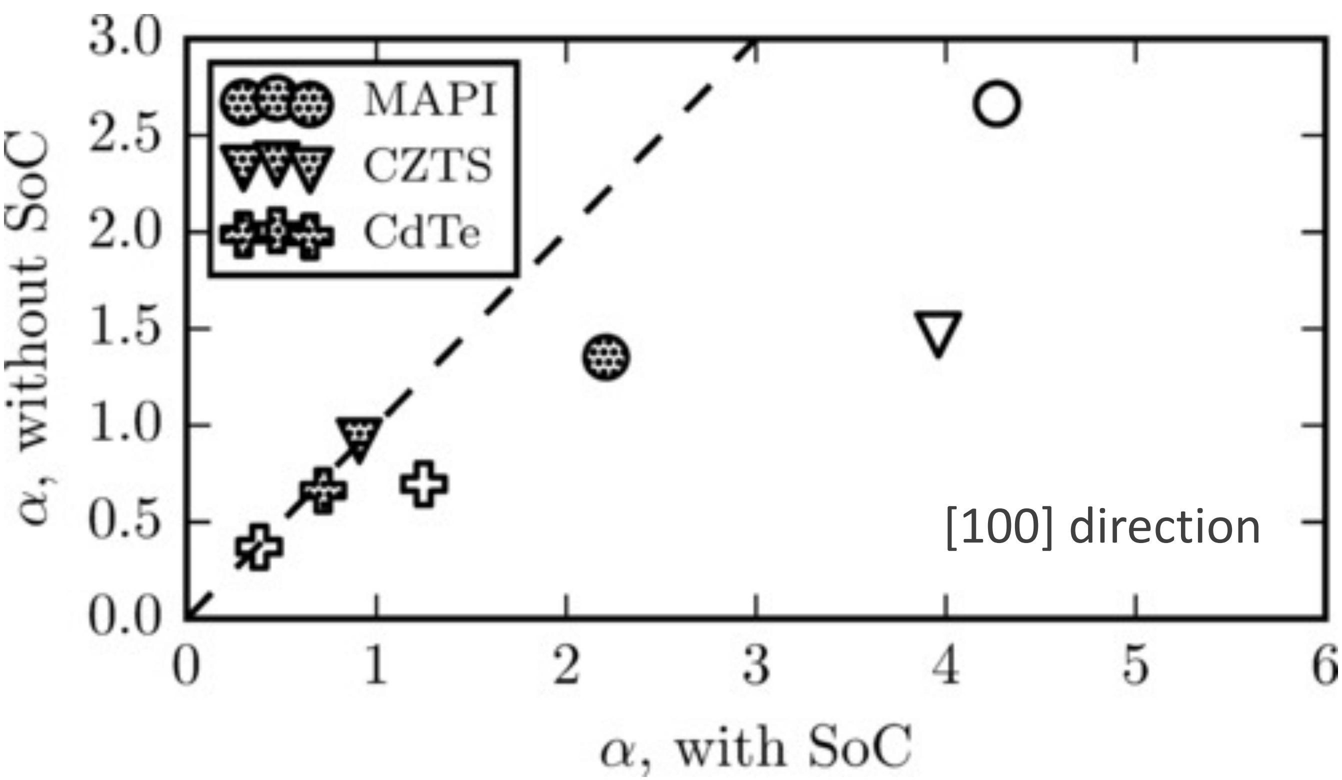
Spin-orbit effects lead to increased non-parabolicity in the valence band

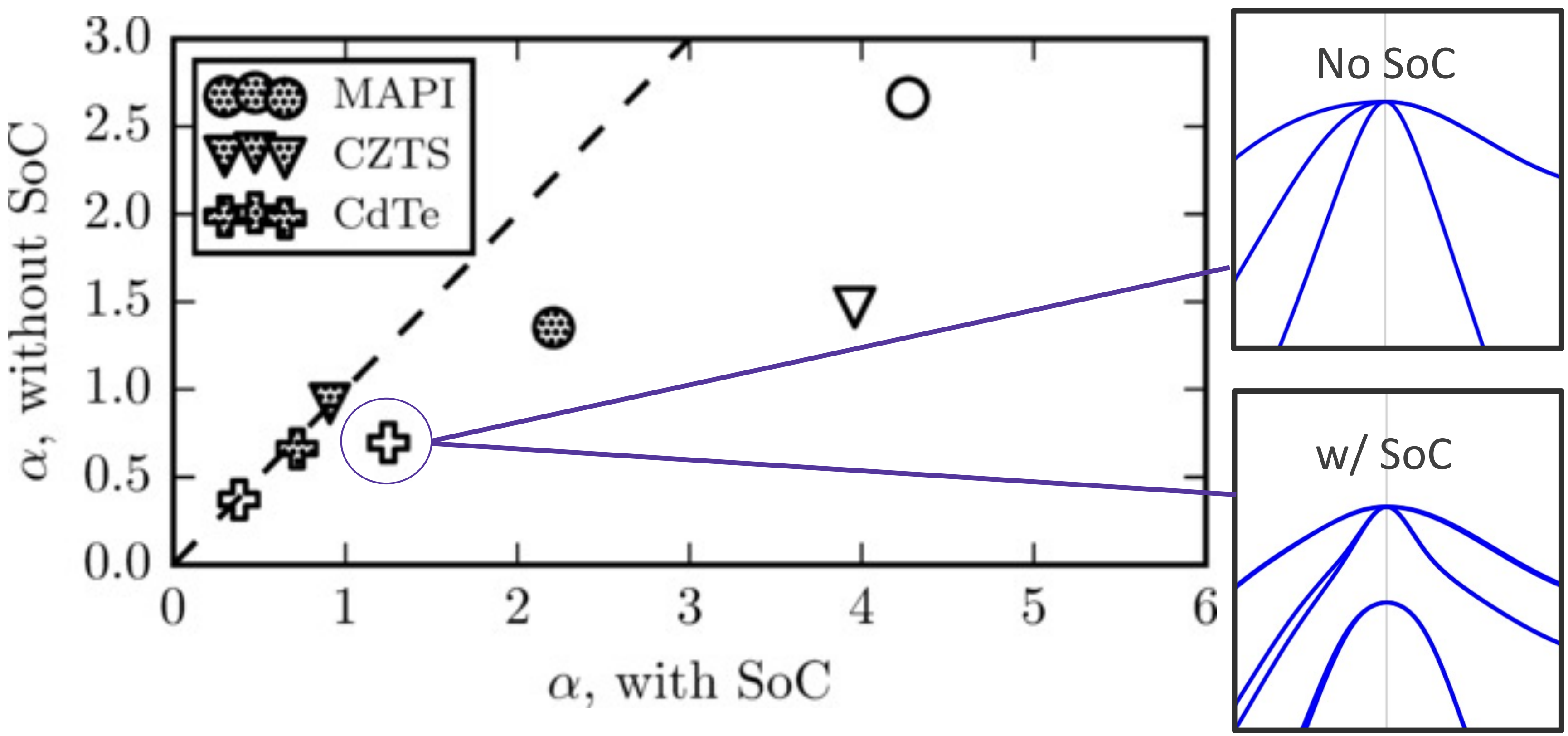


Filled shapes: Electron

Empty shapes: Hole

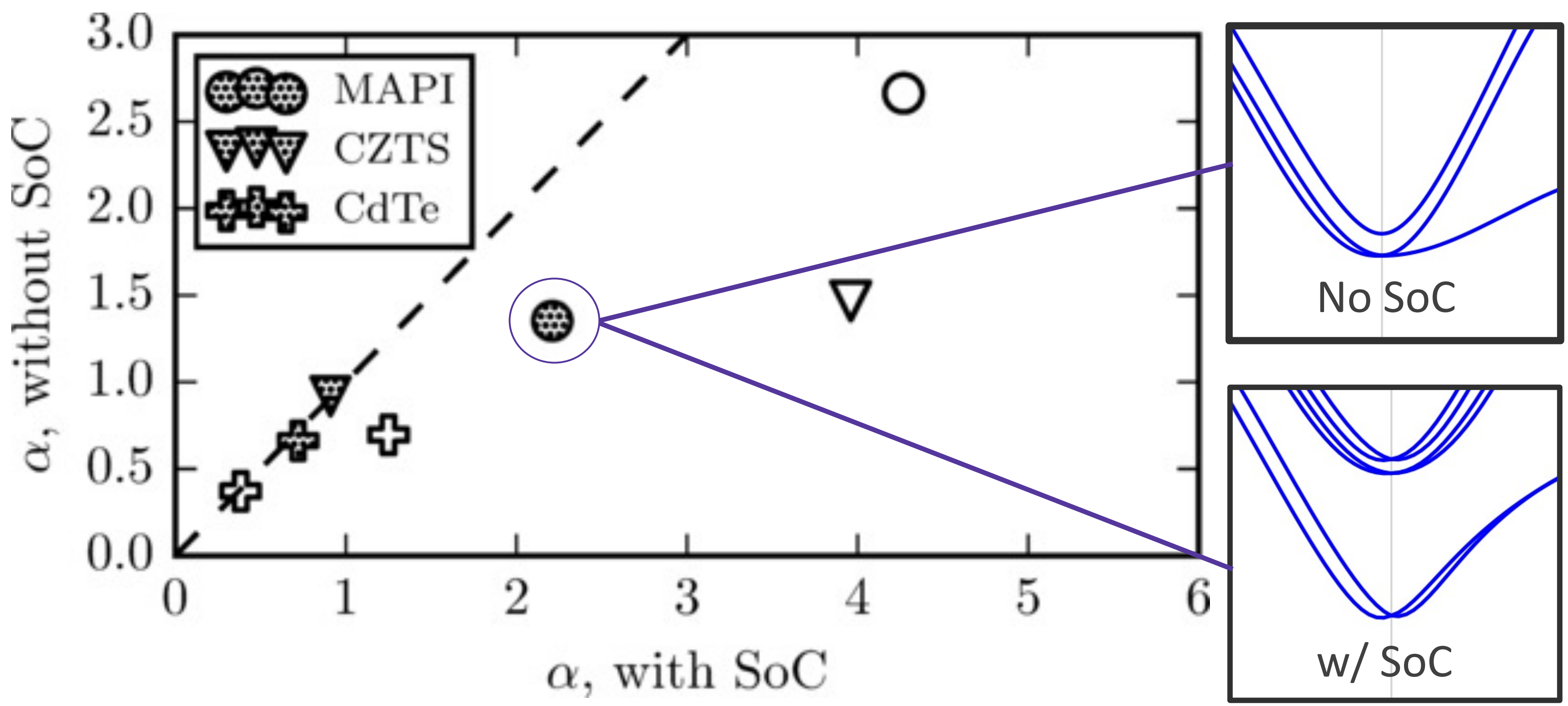
Alpha parameter

Spin-orbit effects lead to increased non-parabolicity in the valence band



Alpha parameter

For MAPI, spin-orbit effects lead to increased non-parabolicity in the valence and conduction bands



Talk outline

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Paper: L. Whalley et al. *Phys. Rev. B* 99, 085297 (2019)

Hybrid perovskites: A computational challenge

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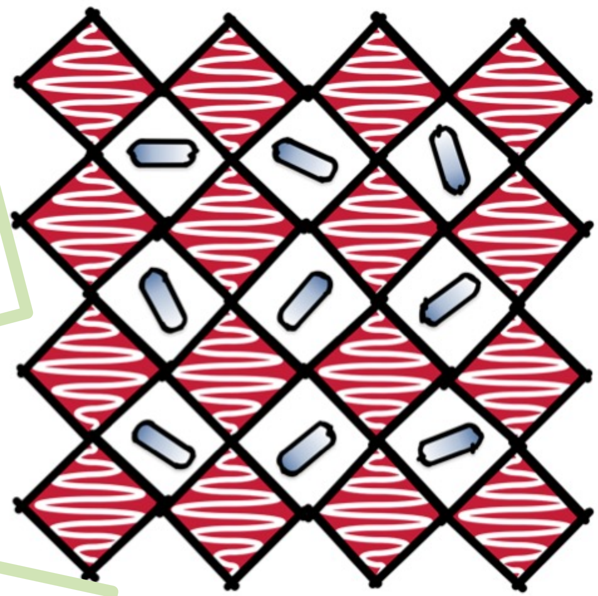
My daughter Robin

Soft

Messy

Surprisingly heavy



Hybrid-halide perovskite

Hybrid perovskites:
A computational challenge

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NEWCASTLE

Soft

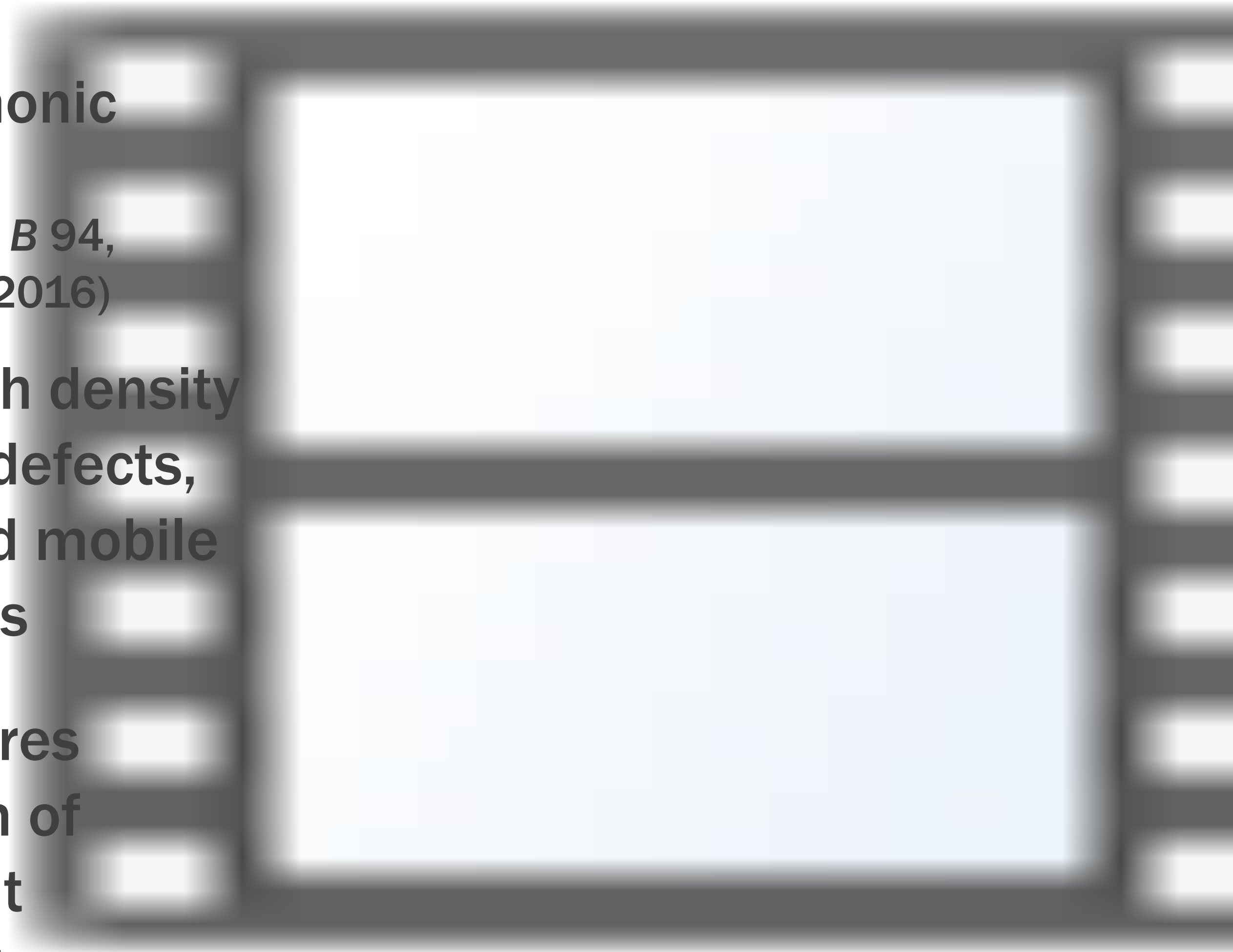
large, anharmonic lattice
Phys. Rev. B 94, 220301 (2016)

Messy

high density of defects, and mobile ions

heavy

Pb requires inclusion of spin-orbit coupling



m* from Transient Absorption Spectroscopy

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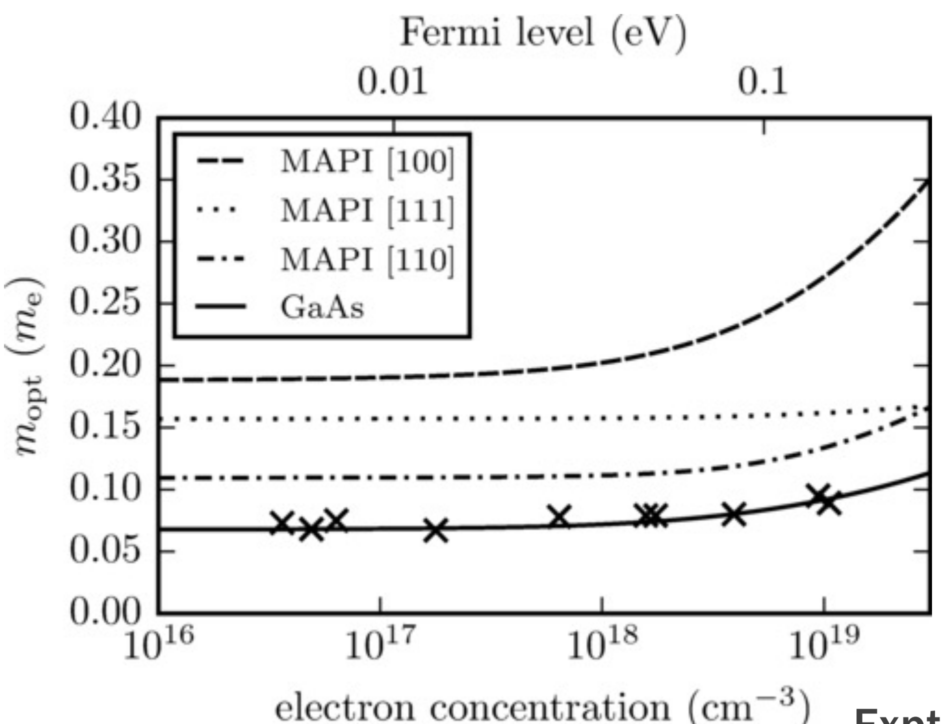
The kane quasi-linear approximation can explain variations in TAS data



m* estimations from TAS vary :

0.14 - for concentrations up to $6x10^{18}$

0.30 - for concentrations up to $1.5x10^{19}$

Our calculated effective mass varies from 0.19 to 0.35

Expt: The Fermi level is shifted into the conduction band at a carrier concentration $\sim 10^{18} cm^{-3}$

Polaron mobility in MAPI

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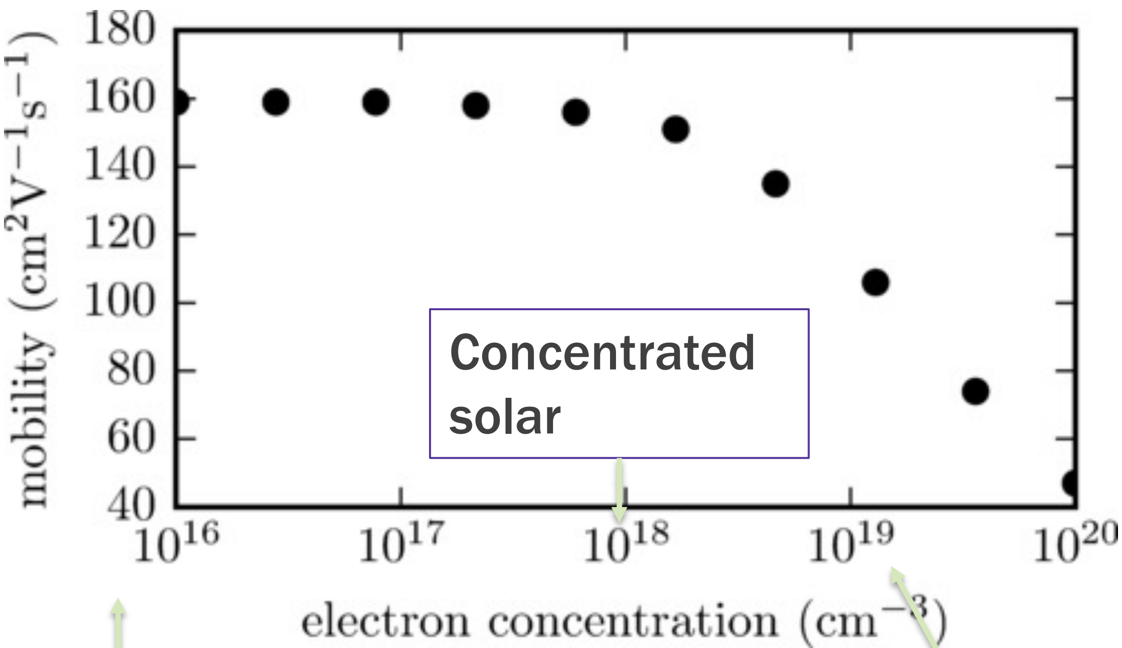
Polaron mobility decreases above a carrier concentration of ~10^{18}cm^{-3}



Concentrated solar

AM1.5

PL studies

Scattering from polar optical modes limits charge carrier mobility at RT

Prediction: 158cm^{2}V^{-1}s^{-1}

Experiment: 73±58cm^{2}V^{-1}s^{-1}

Summary

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A. Effective mass is not as simple as it might seem
   The definition, range in k-space and numerical implementation matter
B. Band non-parabolicity is very sensitive to the electronic structure method used
   Best results for accurate E_g and inclusion of SoC
C. Non-parabolicity can impact on various material properties (case study: hybrid halide perovskite)
   Impacts at concentrations > 10^{18} (concentrated solar, PL studies)

Thank you

GitHub matplotlib Vim python NumPy phonopy

  

L.D. Whalley, J.M. Frost, B.J, Morgan and A.Walsh

Phys. Rev. B 99, 085297 (2019)