FLORIDA STATE UNIVERSITY

Plasmonic Metal Oxide Nanocrystals

How a Semiconductor acts like a metal

Geoffrey F. Strouse

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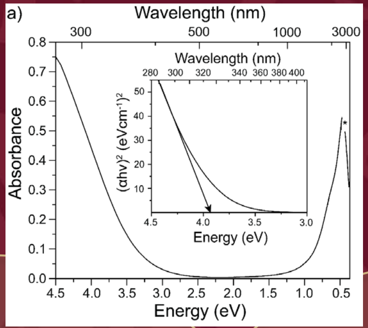
UV-VIS-NIR



Defect Engineering

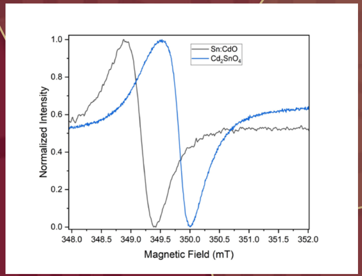
$V_{M/O}$,

M/O_i

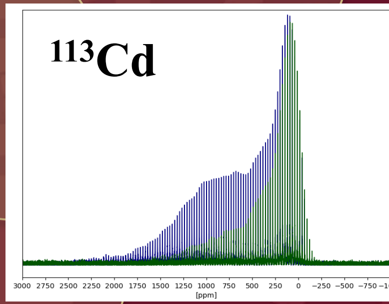
$M2_{M1}$ (antisite)

carrier density

$n \sim 10^{19} - 10^{21}$ carriers / cm^3



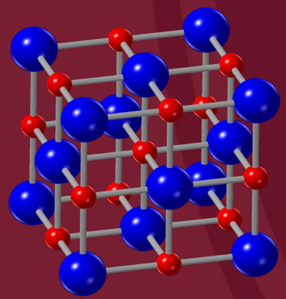
EPR

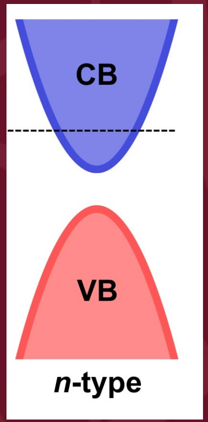


NMR

carrier type/ mass

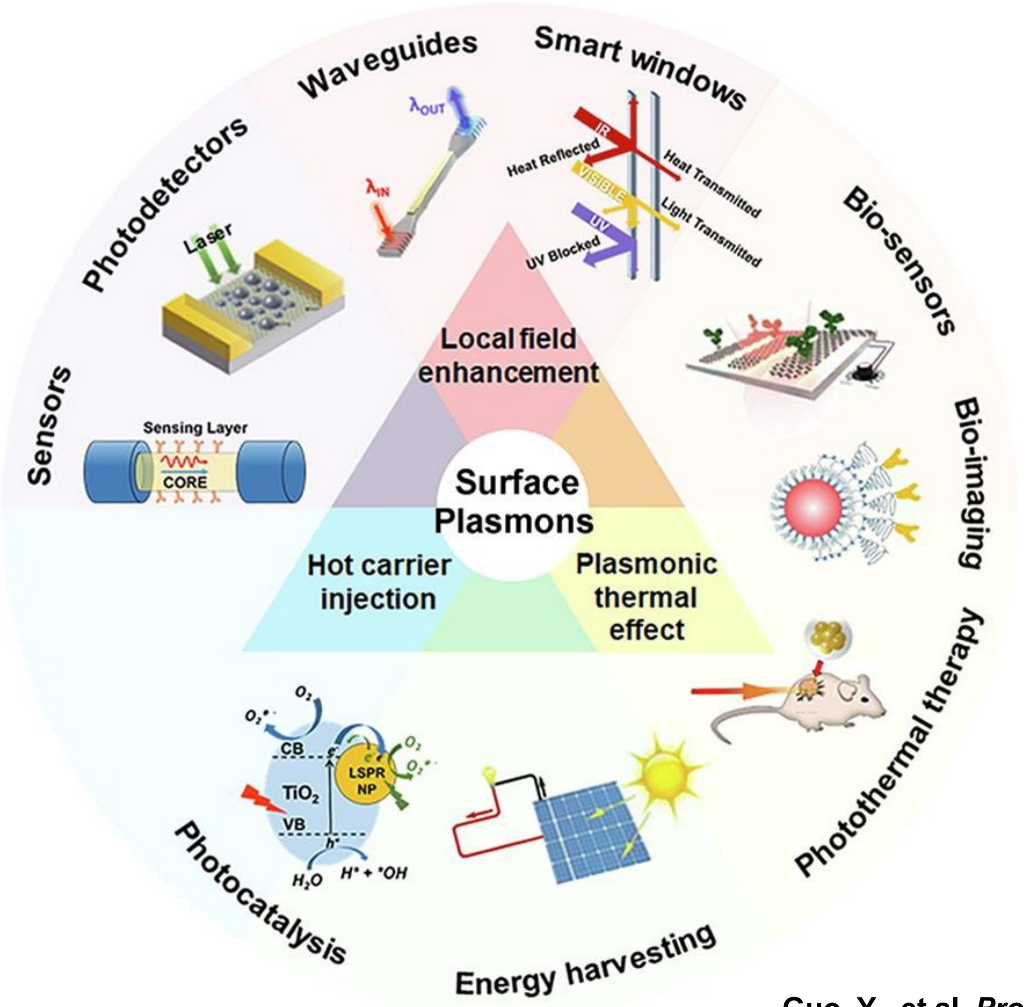
$m^* \sim 0.01 – 2.0\ m_e$

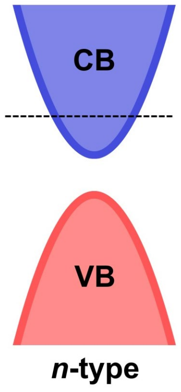


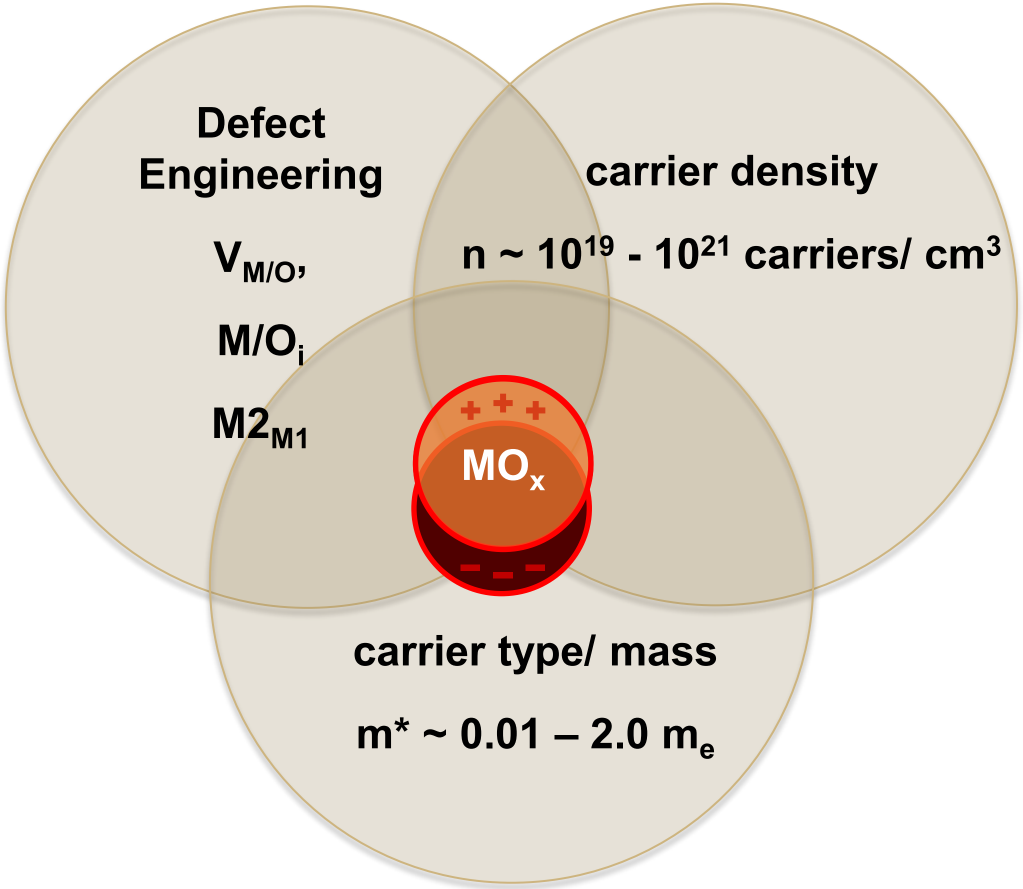


NSF-DMR #1905757

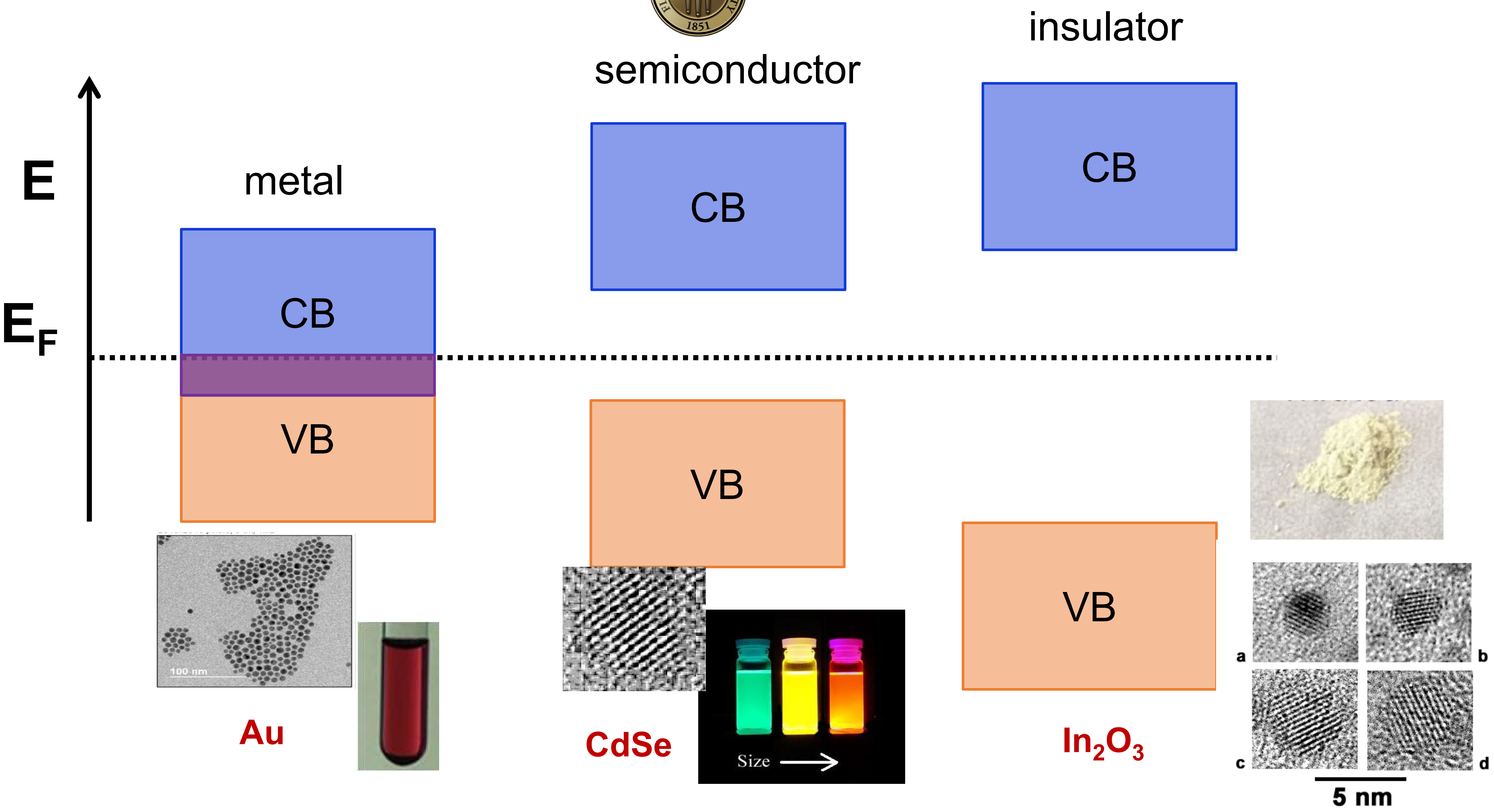
Plasmonic MO_x Semiconductor Nanocrystals

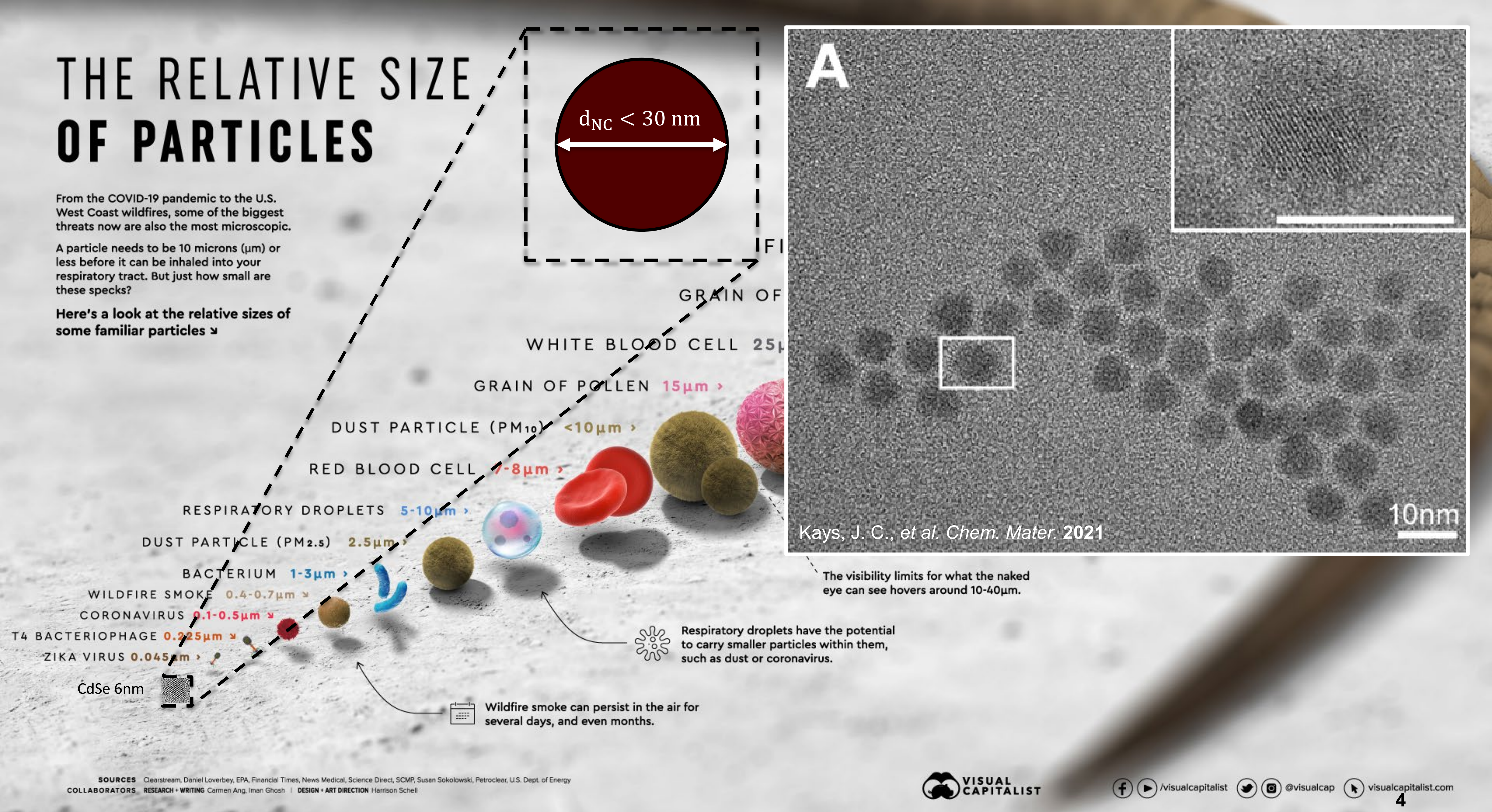






Guo, Y., et al, *Progress in Materials Science*, 2023


E
E_F
metal
CB
VB
100 nm
Au
semiconductor
CB
VB
Size
CdSe
insulator
CB
VB
In2O3
a
b
c
d
5 nm



THE RELATIVE SIZE
OF PARTICLES
From the COVID-19 pandemic to the U.S. West Coast wildfires, some of the biggest threats now are also the most microscopic.
A particle needs to be 10 microns (µm) or less before it can be inhaled into your respiratory tract. But just how small are these specks?
Here's a look at the relative sizes of some familiar particles
$d_{NC} < 30$ nm
GRAIN OF
WHITE BLOOD CELL 25
GRAIN OF POLLEN 15µm
DUST PARTICLE (PM_{10}) <10µm
RED BLOOD CELL 7-8µm
RESPIRATORY DROPLETS 5-10µm
DUST PARTICLE ($PM_{2.5}$) 2.5µm
BACTERIUM 1-3µm
WILDFIRE SMOKE 0.4-0.7µm
CORONAVIRUS 0.1-0.5µm
T4 BACTERIOPHAGE 0.225µm
ZIKA VIRUS 0.045µm
CdSe 6nm
A
10nm
Kays, J. C., *et al. Chem. Mater.* **2021**
The visibility limits for what the naked eye can see hovers around 10-40µm.
Respiratory droplets have the potential to carry smaller particles within them, such as dust or coronavirus.
Wildfire smoke can persist in the air for several days, and even months.
SOURCES Clearstream, Daniel Loverbey, EPA, Financial Times, News Medical, Science Direct, SCMP, Susan Sokolowski, Petroclear, U.S. Dept. of Energy
COLLABORATORS RESEARCH + WRITING Carmen Ang, Iman Ghosh | DESIGN + ART DIRECTION Harrison Schell
VISUAL CAPITALIST
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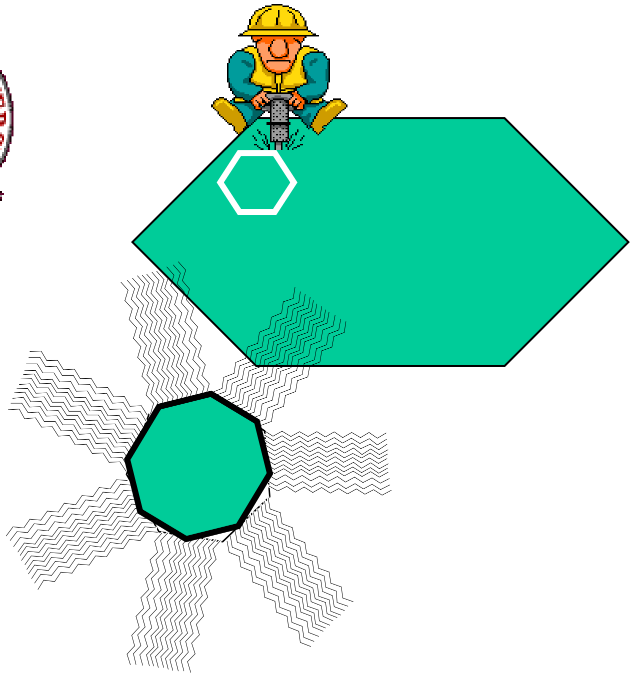

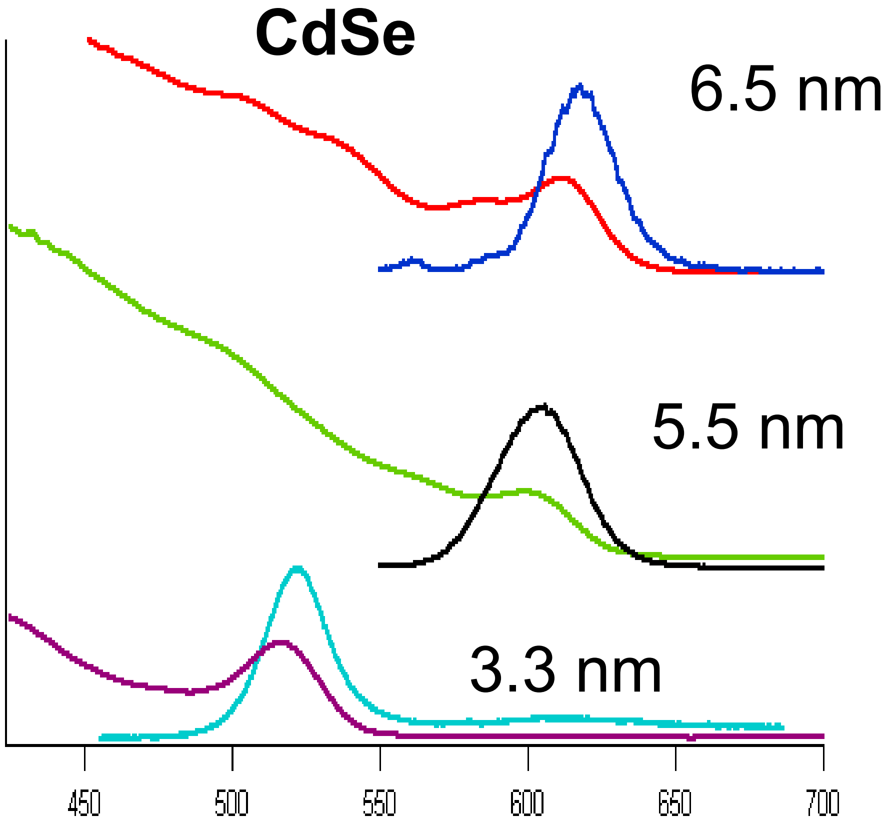

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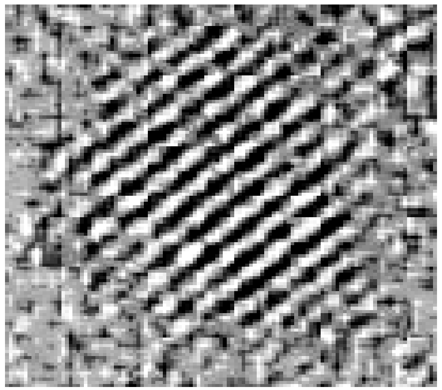

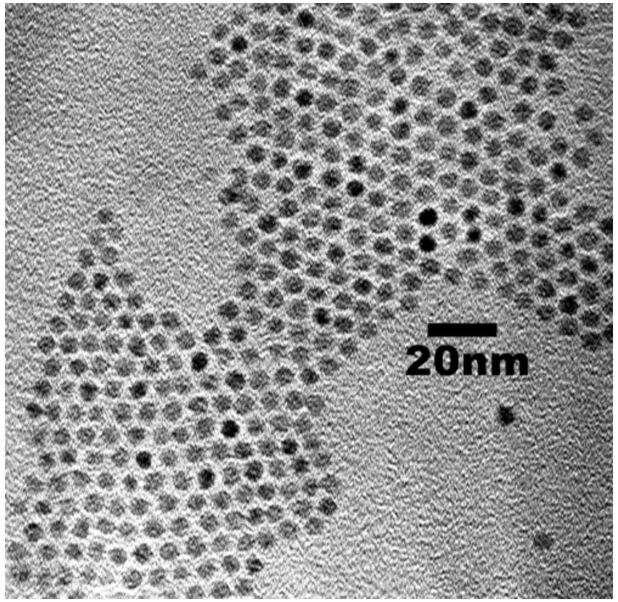

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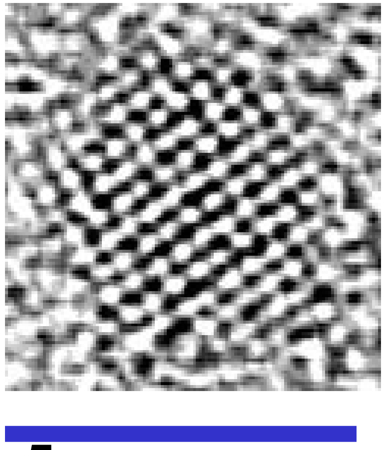
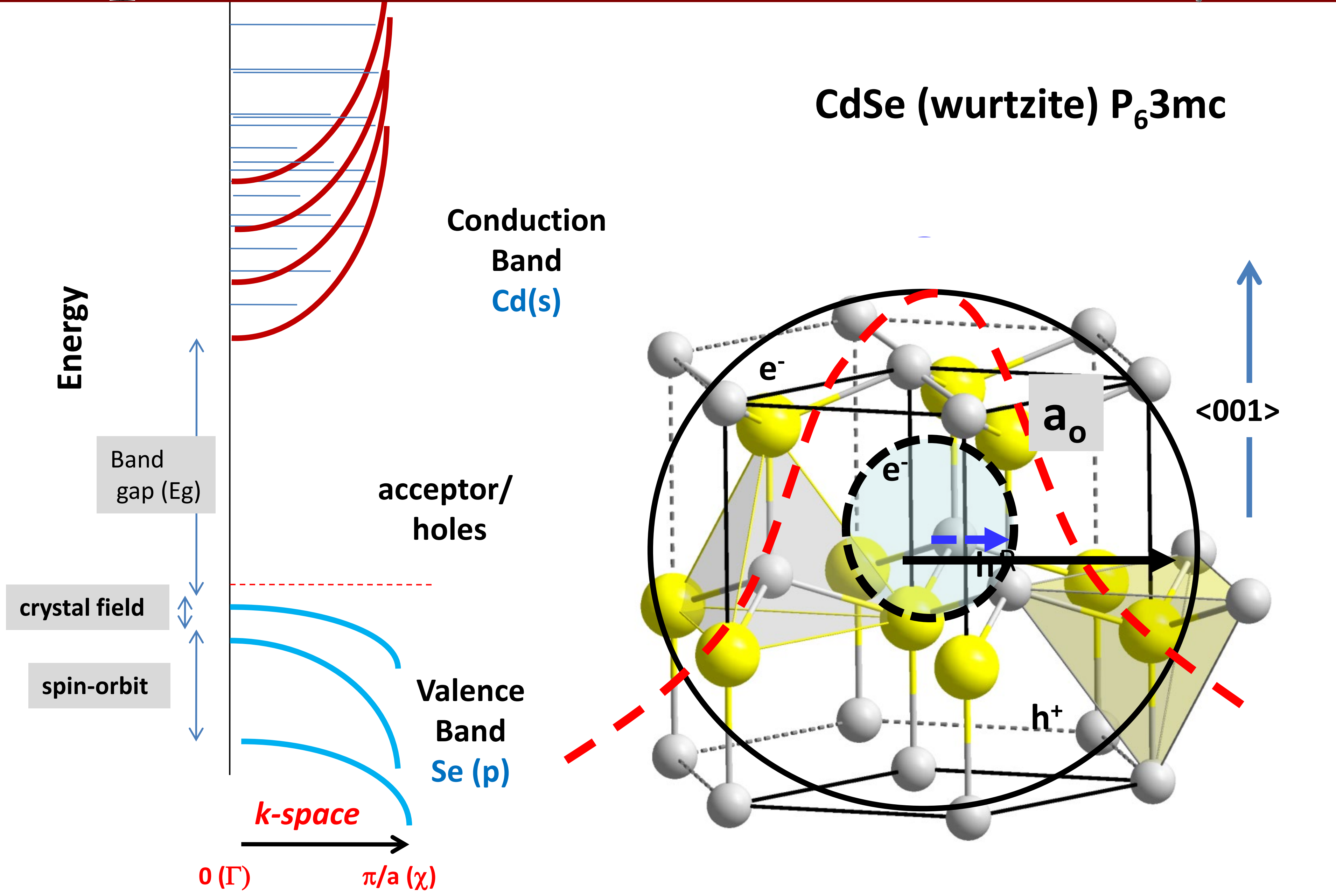


5 nm



CdSe (wurtzite) P_63mc
Energy
Conduction
Band
Cd(s)
Band
gap (Eg)
acceptor/
holes
crystal field
spin-orbit
Valence
Band
Se (p)
k-space
0 (Γ)
π/a (χ)
e⁻
e⁻
a_o
<001>
h⁺

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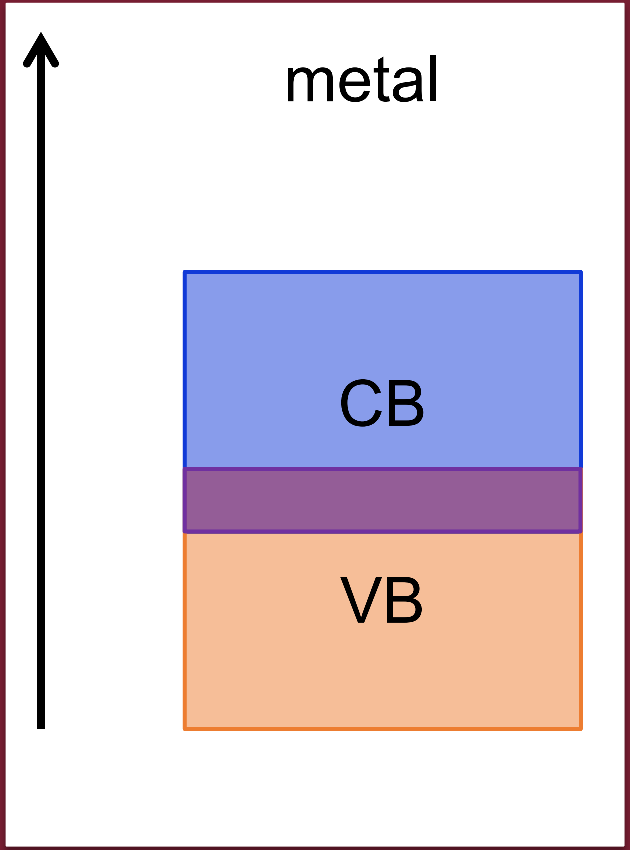
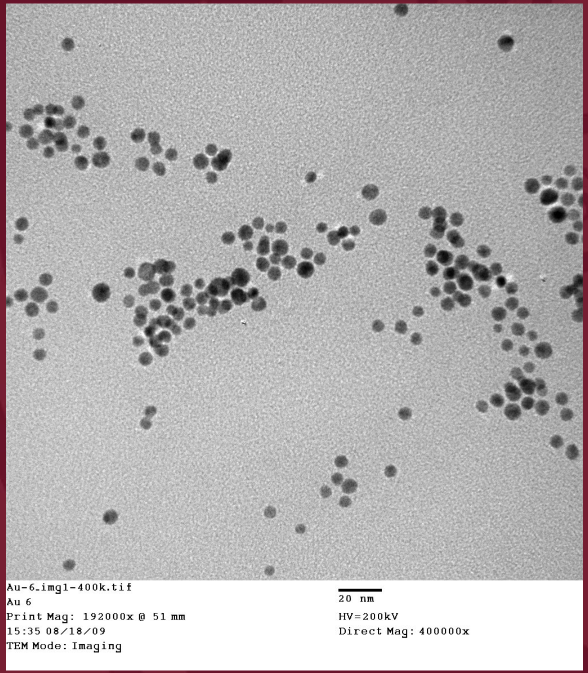
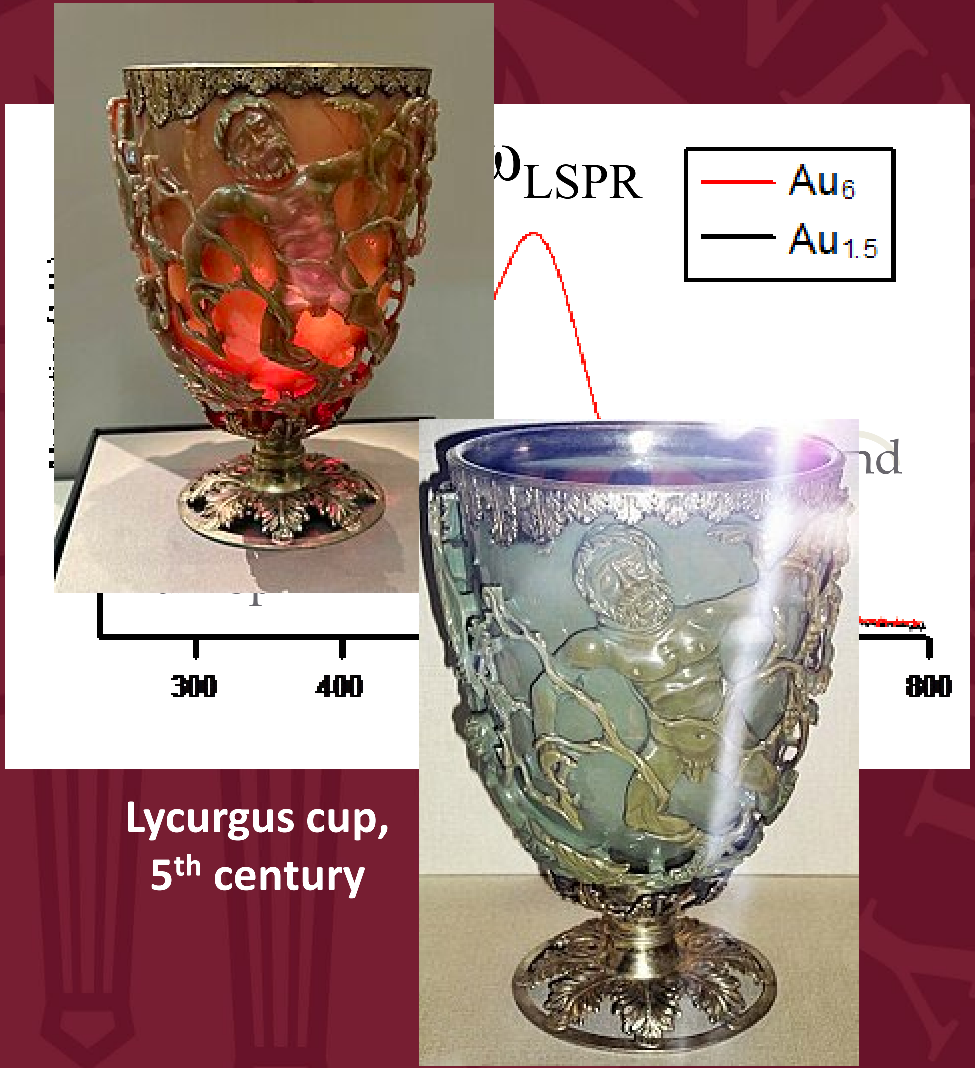
LSPR Extinction Spectra for Au







Lycurgus cup, 5th century

Plasmons, Photons, and Permittivity, Oh my

The Dielectric Function

(relative permittivity)

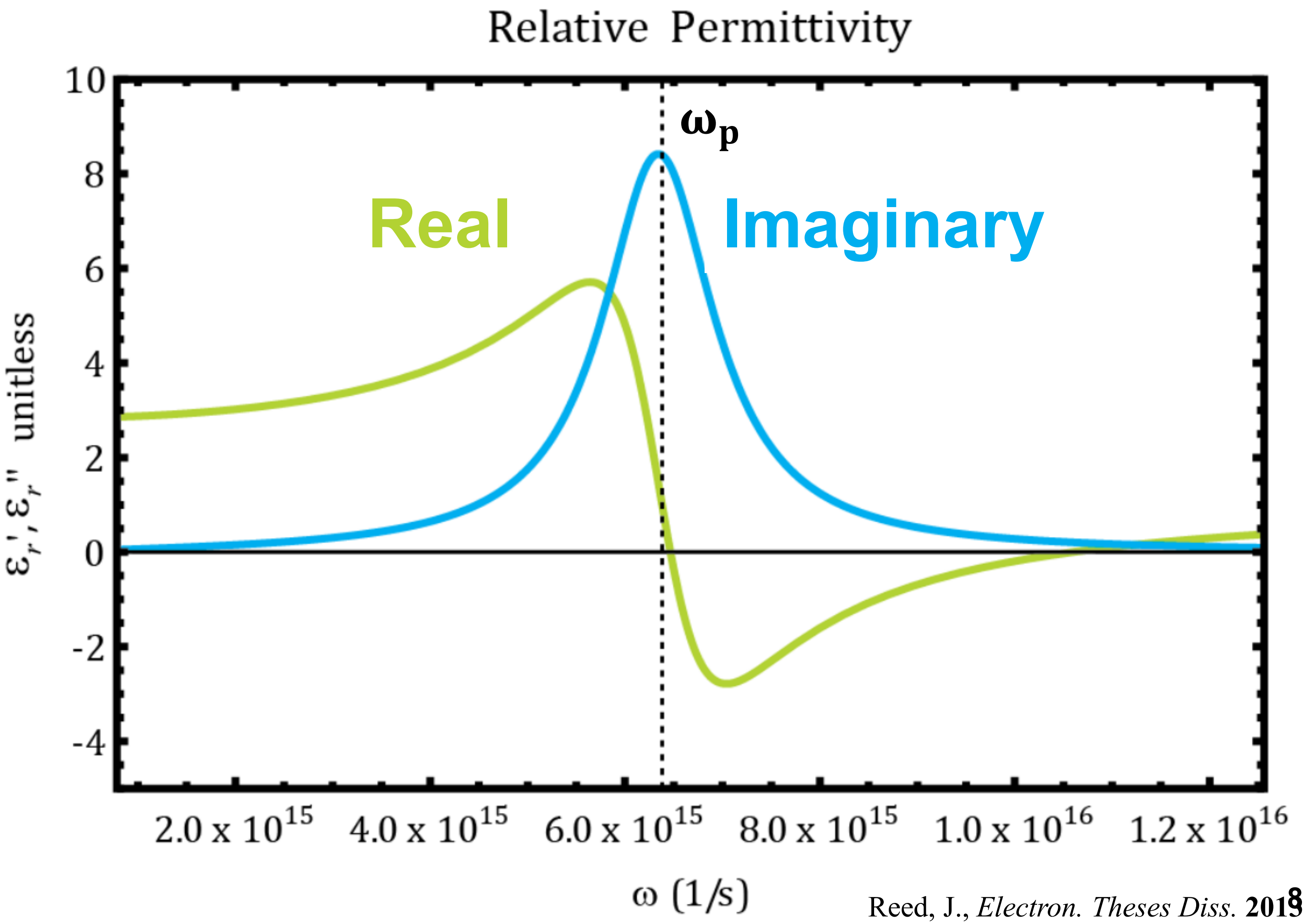
$$\boldsymbol{\varepsilon_r(\omega)} = \varepsilon_r'(\omega) + i\varepsilon_r''(\omega)$$

$\varepsilon_r(\omega)$ describes the interactions of materials with applied electric fields.

$$\varepsilon_r(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} \qquad \boldsymbol{\omega_p^2} = \frac{\boldsymbol{ne^2}}{\boldsymbol{\varepsilon_0 m^*}}$$

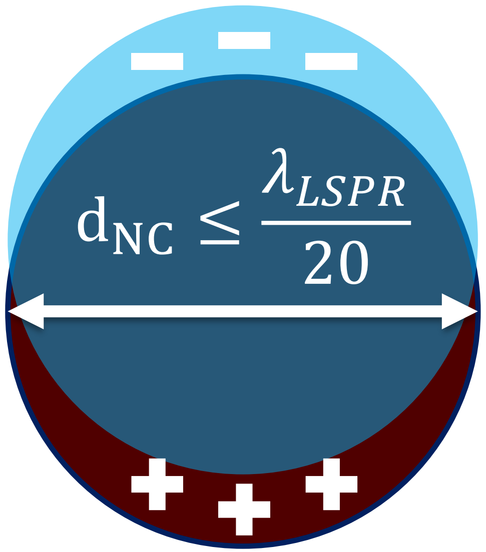
size dependent damping

Maximum extinction arises at maximum ε_r''. Here, a resonance condition is met



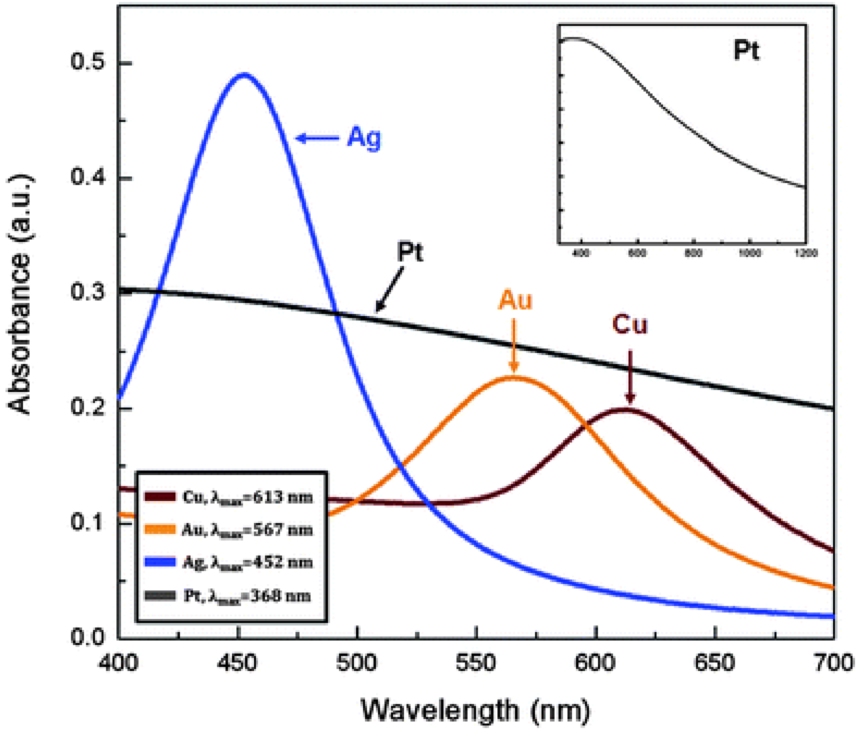
Reed, J., *Electron. Theses Diss.* 2018

Metals:
Localized Surface Plasmon Resonance (LSPR)

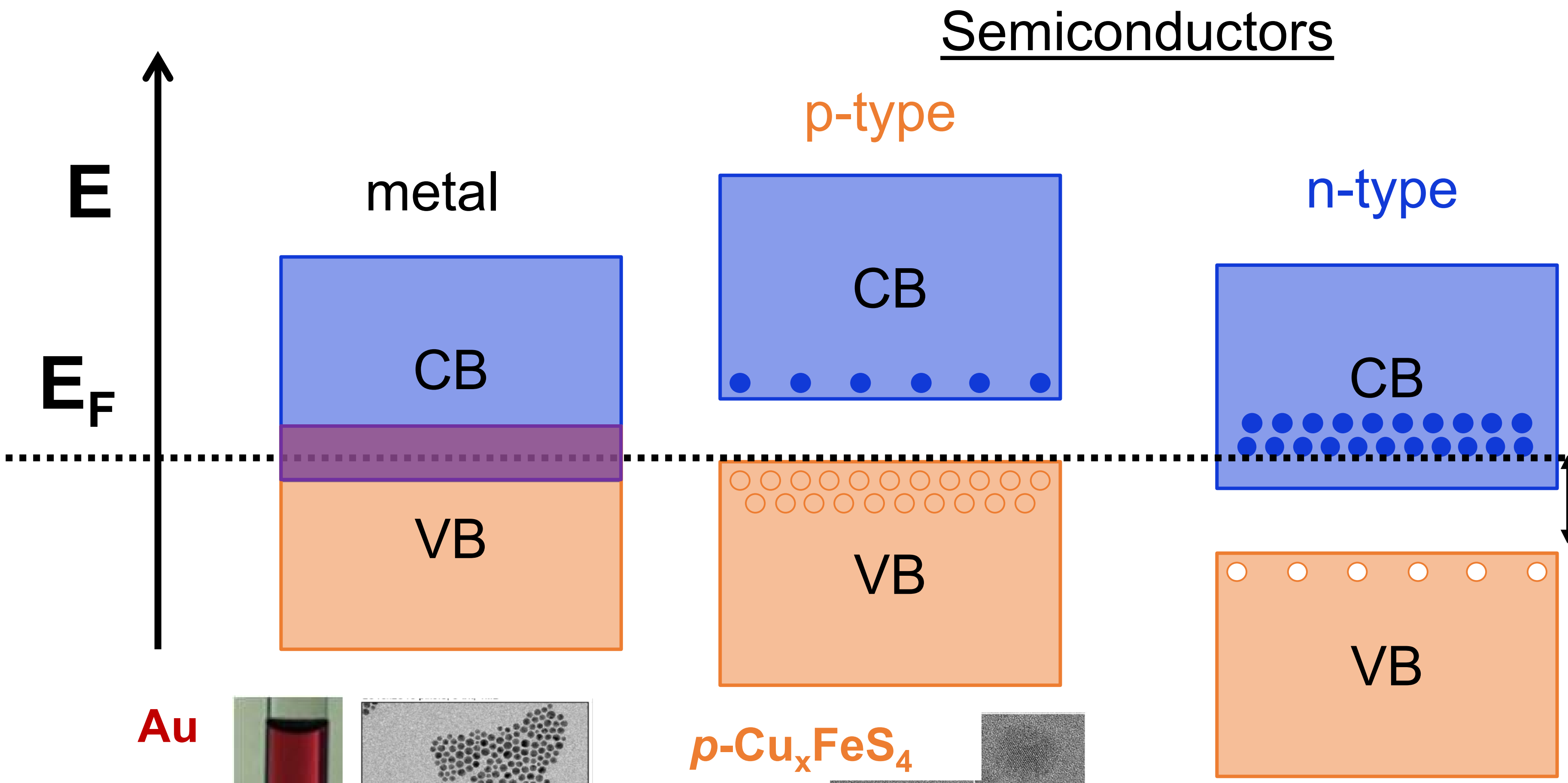


Nobel Metals (metallic)

Shin, D. O., *et al.*, *J. Mater. Chem.*, **2010**

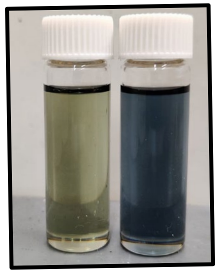


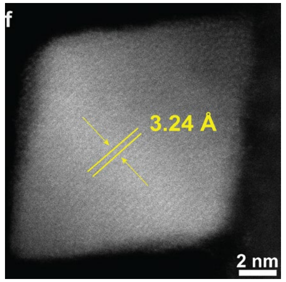
Plasmons require carriers (or electrons) above the Fermi Energy Level



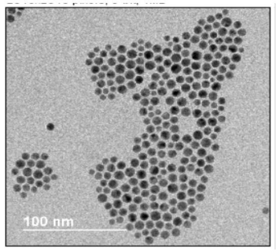
E_g (< 5 eV)

n-CTO

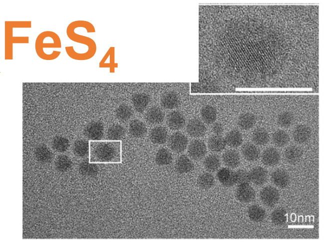




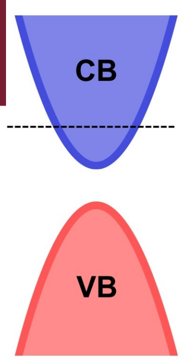
Au



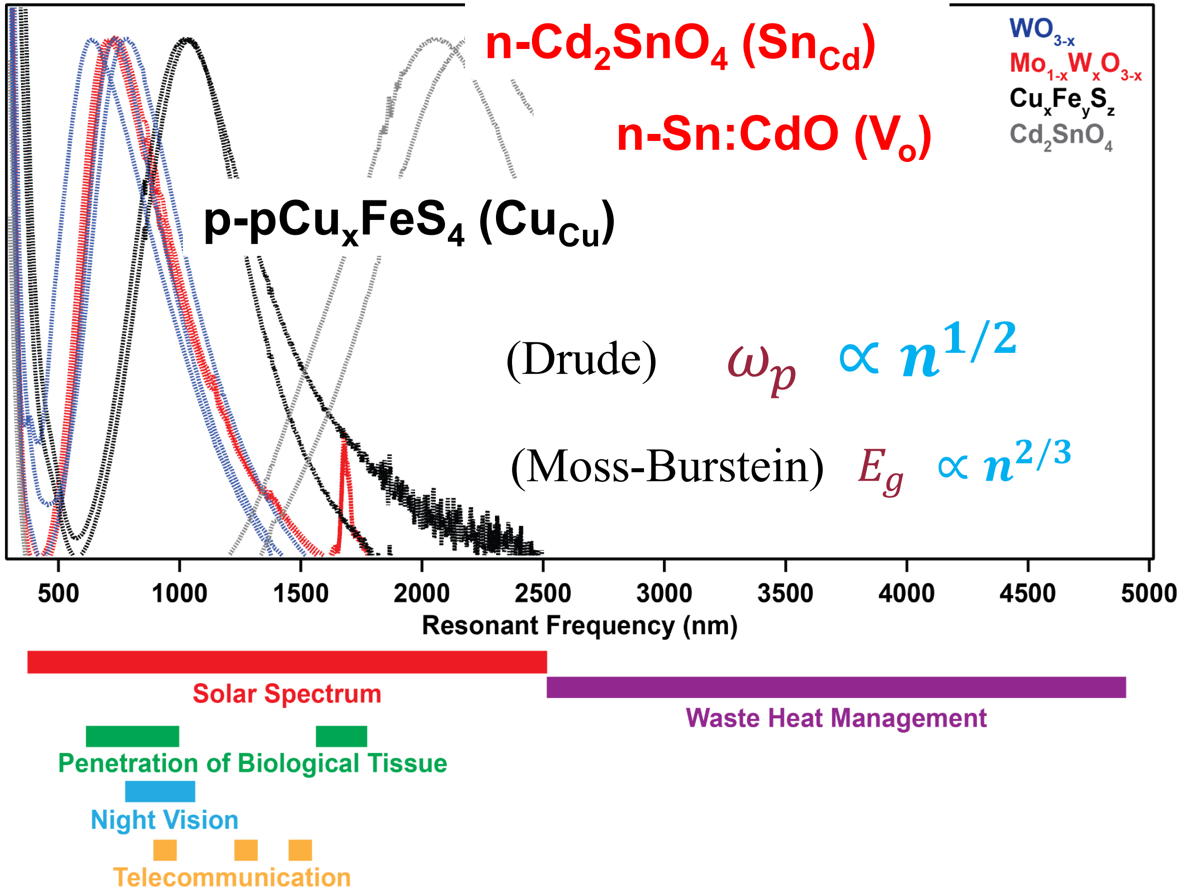
p-Cu_xFeS_4

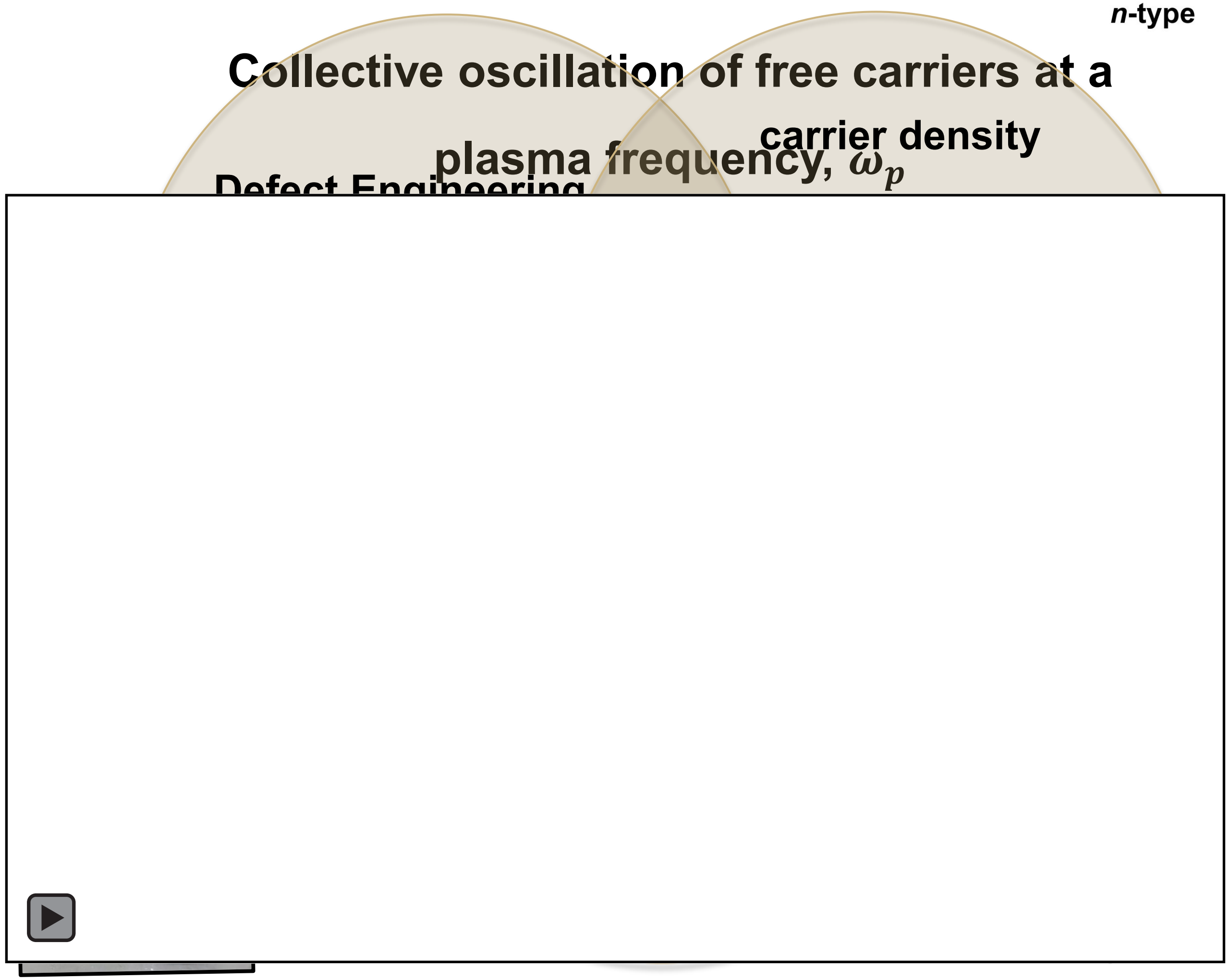


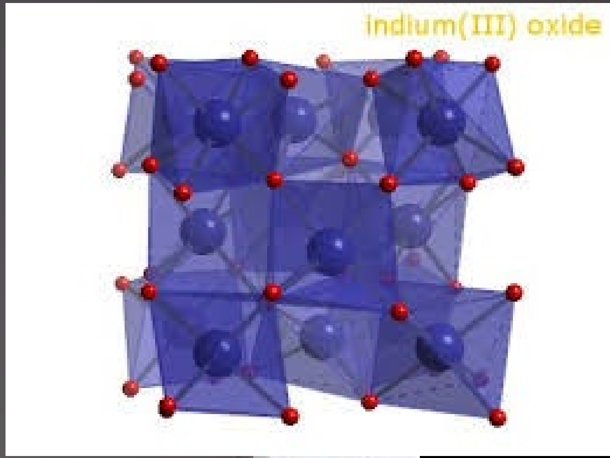
Plasmonic Semiconductor Nanocrystals (PSNC)



n-WO_{3-x} (V_O)







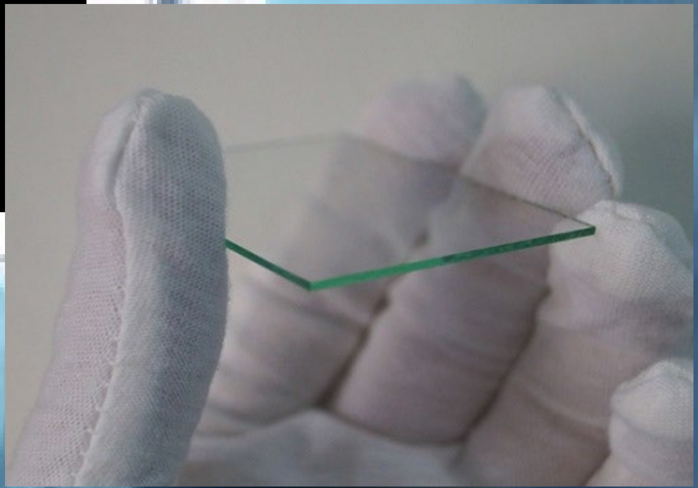
Conducting glass: an industrial standard

Indium-Tin Oxide

n-In_2O_3

ITO

V_o and Sn_{In} lead to n-doping



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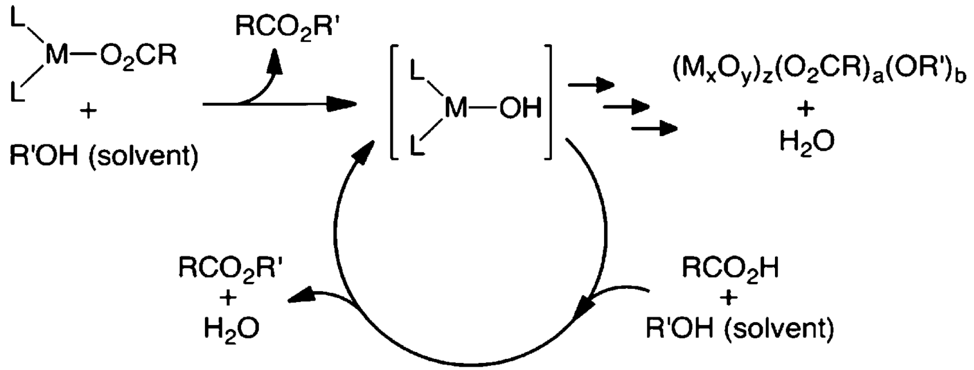
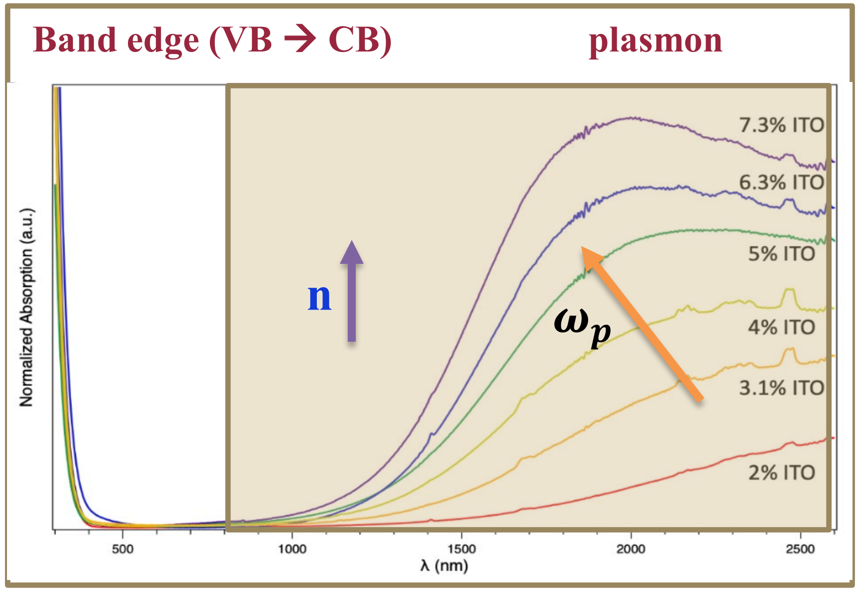
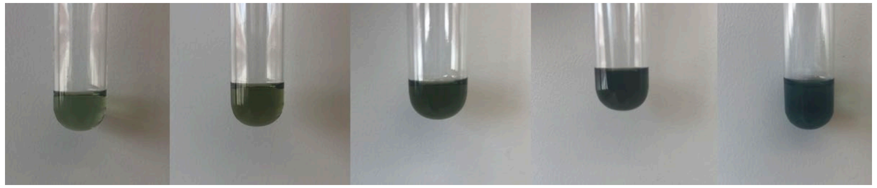
Carl R. Conti III, Giovanni Quiroz-Delfi, Joanna S. Schwarck, Banghao Chen, and Geoffrey F. Strouse*

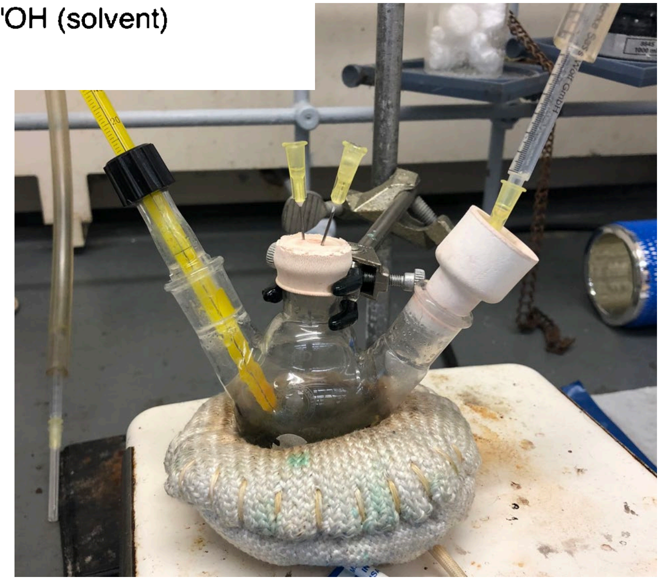
Cite This: J. Phys. Chem. C 2020, 124, 28220–28229 Read Online





Increasing Sn_{In}





Materials Chemistry at the Boundary of Technology Discovery

FLORIDA STATE UNIVERSITY

THE JOURNAL OF PHYSICAL CHEMISTRY C

pubs.acs.org/JPCC Article

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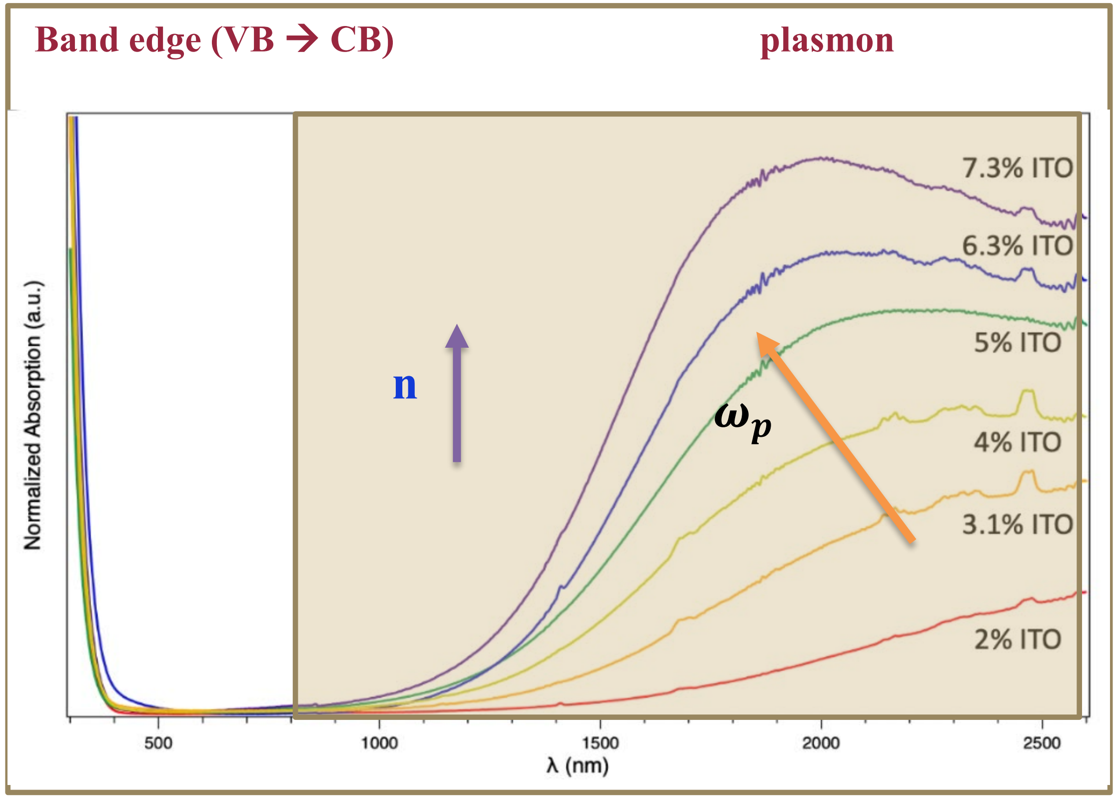
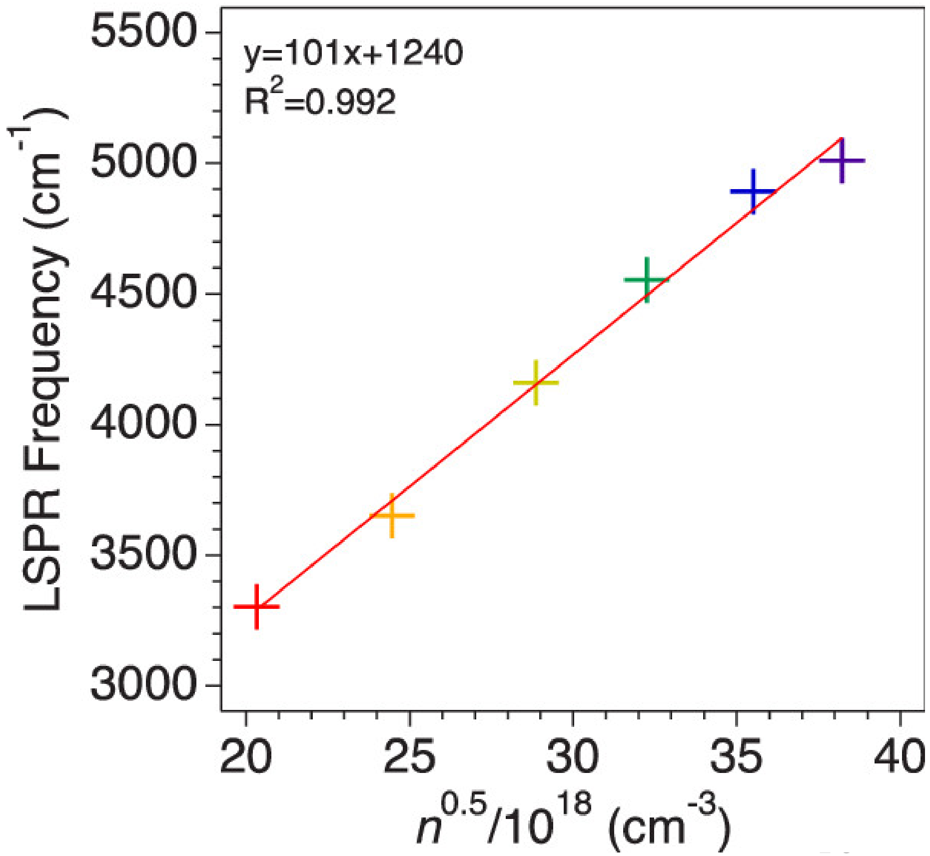
(simplified)

The Drude Model

$$\omega_p^2 = \frac{n\, e^2}{m^*\, \varepsilon_0}$$



b.



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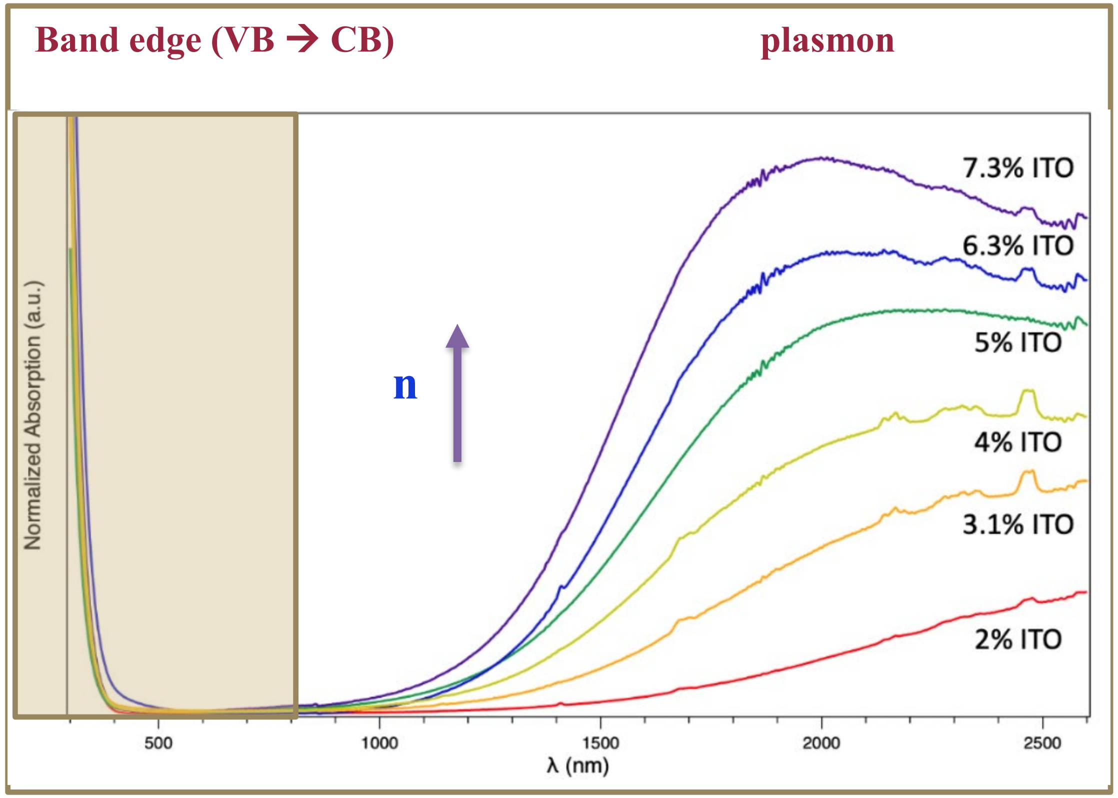
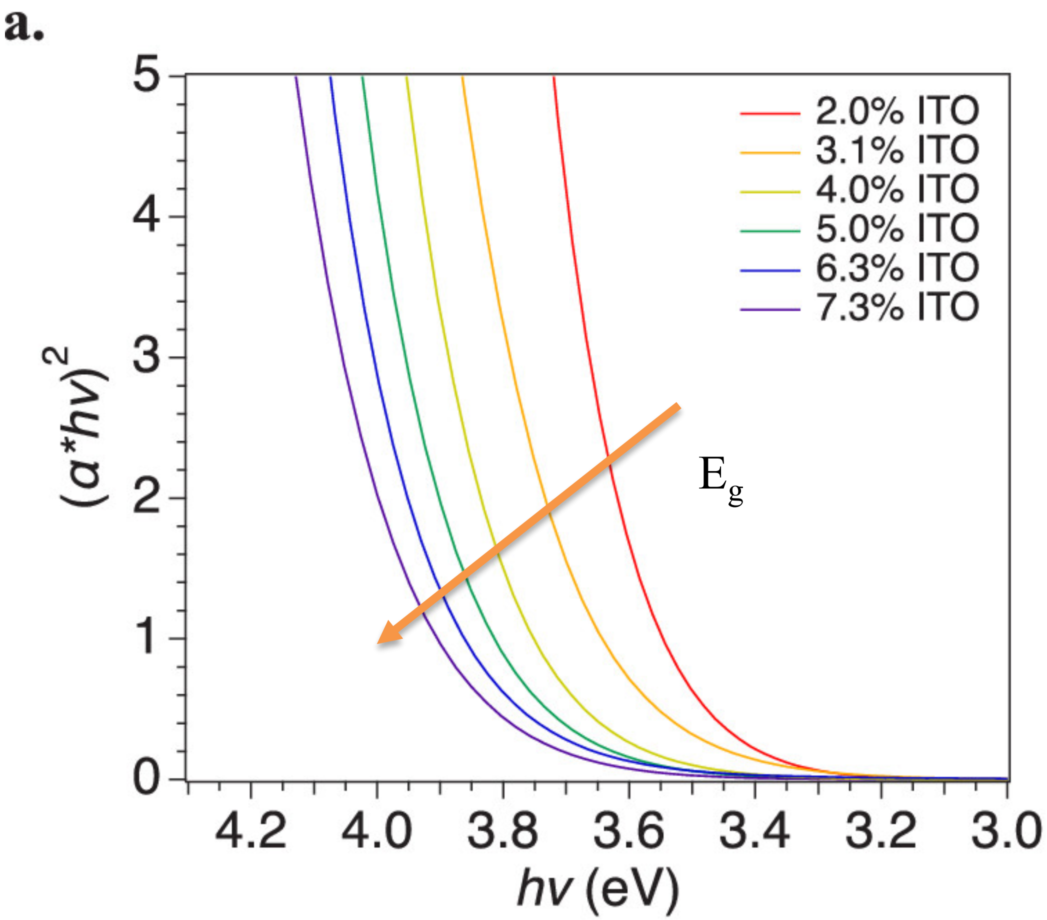
Moss-Burstein (E_g)

$$\Delta E_{abs} = E_g^{Sn} - E_g^{0} = \left(\frac{\hbar^2}{2m^*}\right)(3\pi^2 n)^{2/3}$$





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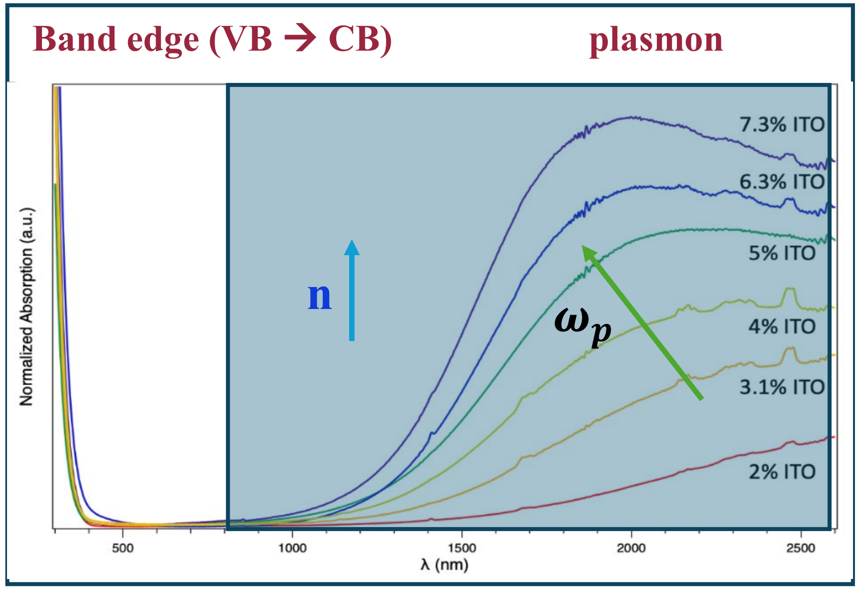
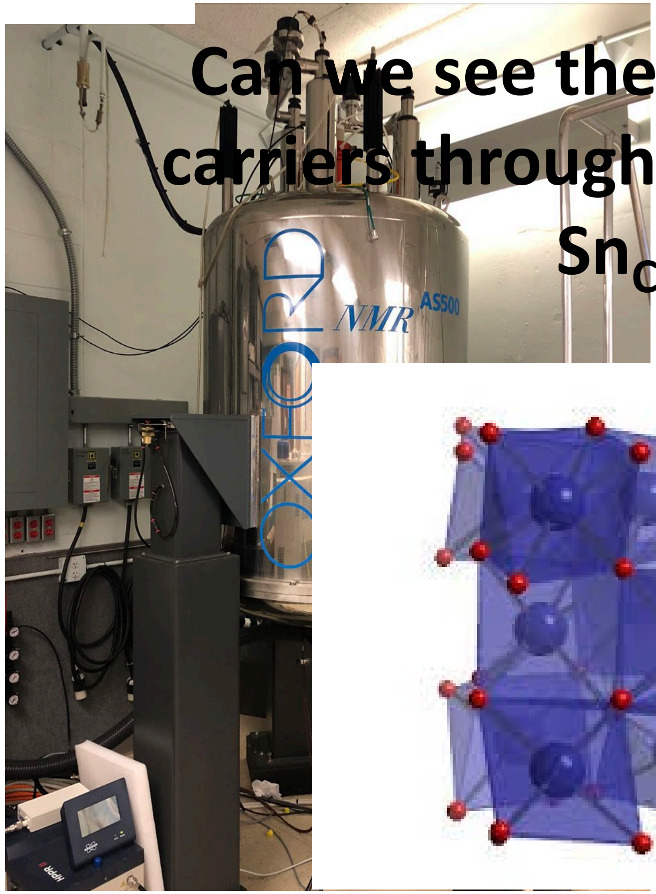
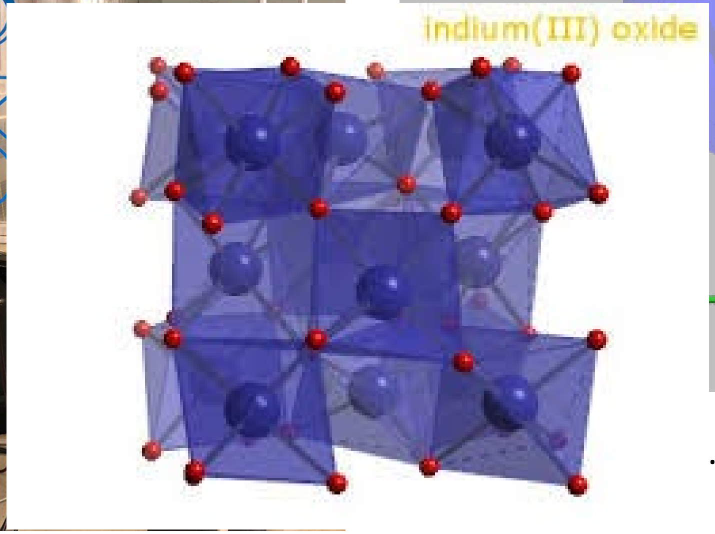
^{119}Sn MAS Solid-State NMR

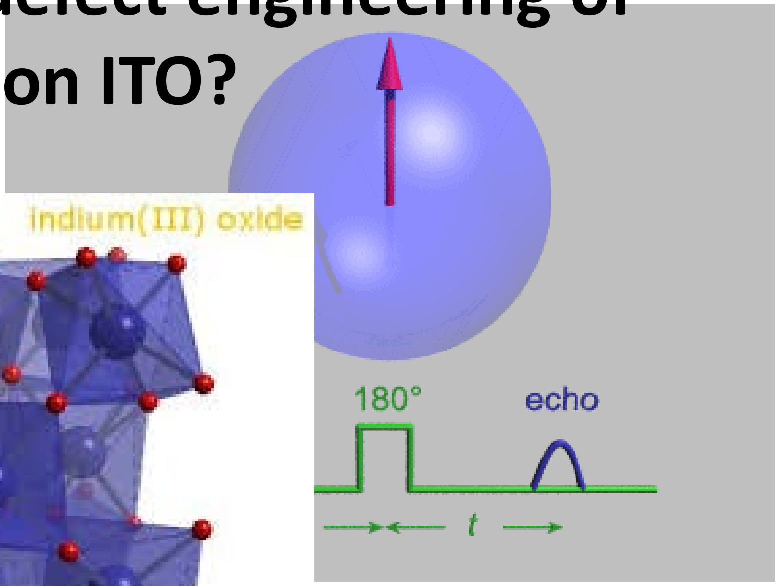
Can we see the effect of introducing carriers through defect engineering of Sn_{Cd} on ITO?

Spin-Echo Experiment









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Bruker AVIII HD 500 MHz WB NMR

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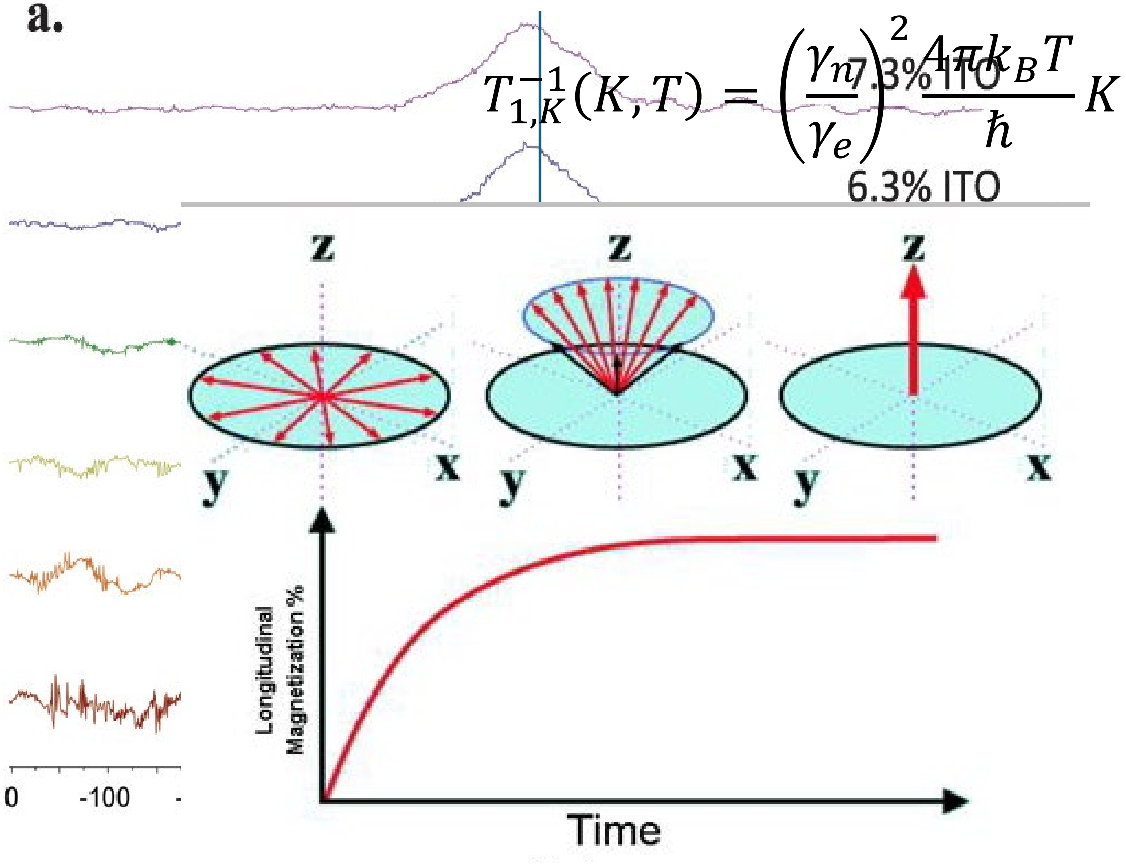
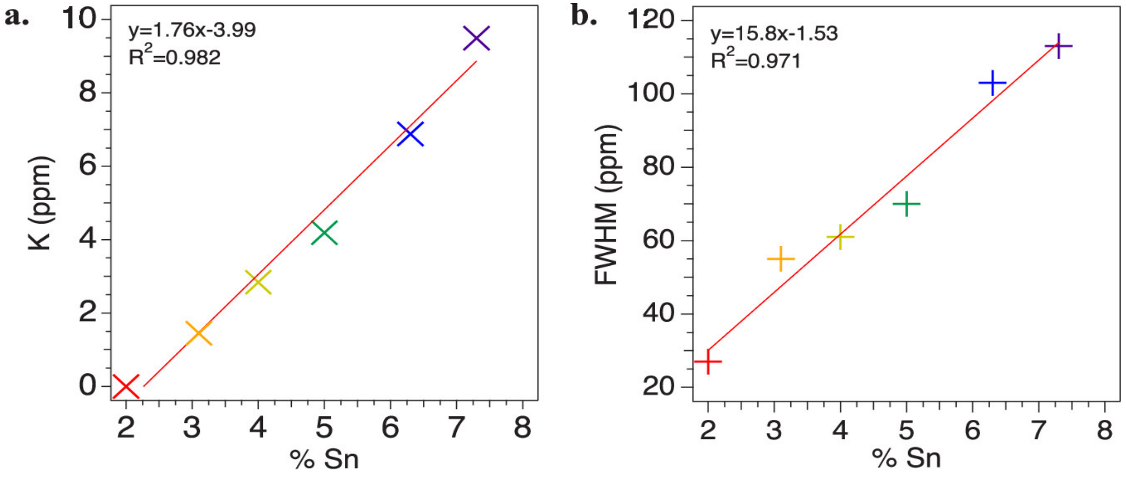
^{119}Sn MAS ssNMR spin-echo

Knight-Korringa

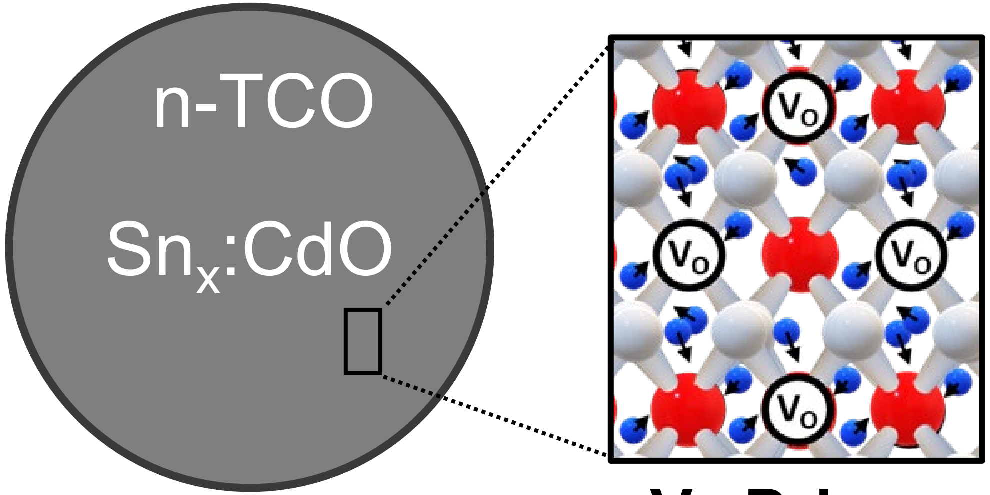
$$T_{1,K}^{-1}(K,T) = \left(\frac{\gamma_n}{\gamma_e}\right)^2 \frac{4\pi k_B T}{\hbar} K^2$$



Knight shift (Δδ) FWHM (Δν)



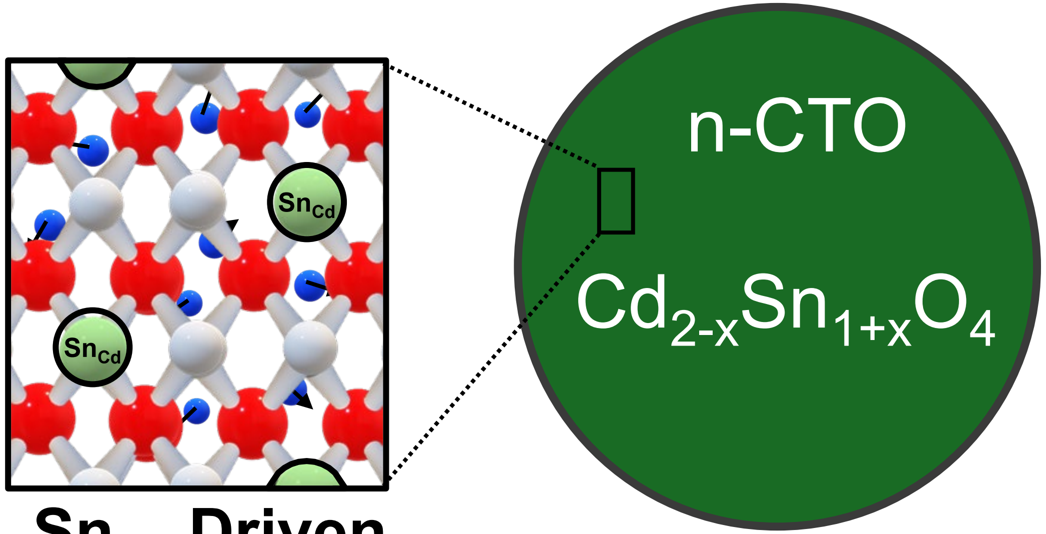
The ternary Cd – Sn – O PSNCs and the impact of structure on plasmonic properties



V_O Driven

$O_o^x \Leftrightarrow V_o^{\cdot\cdot} + 2\,e^-$

- **Rock salt**
- **Sn(IV)**
- **V_o**
- **Carriers increase with *x***
- **CdO = $0.26m_e$**



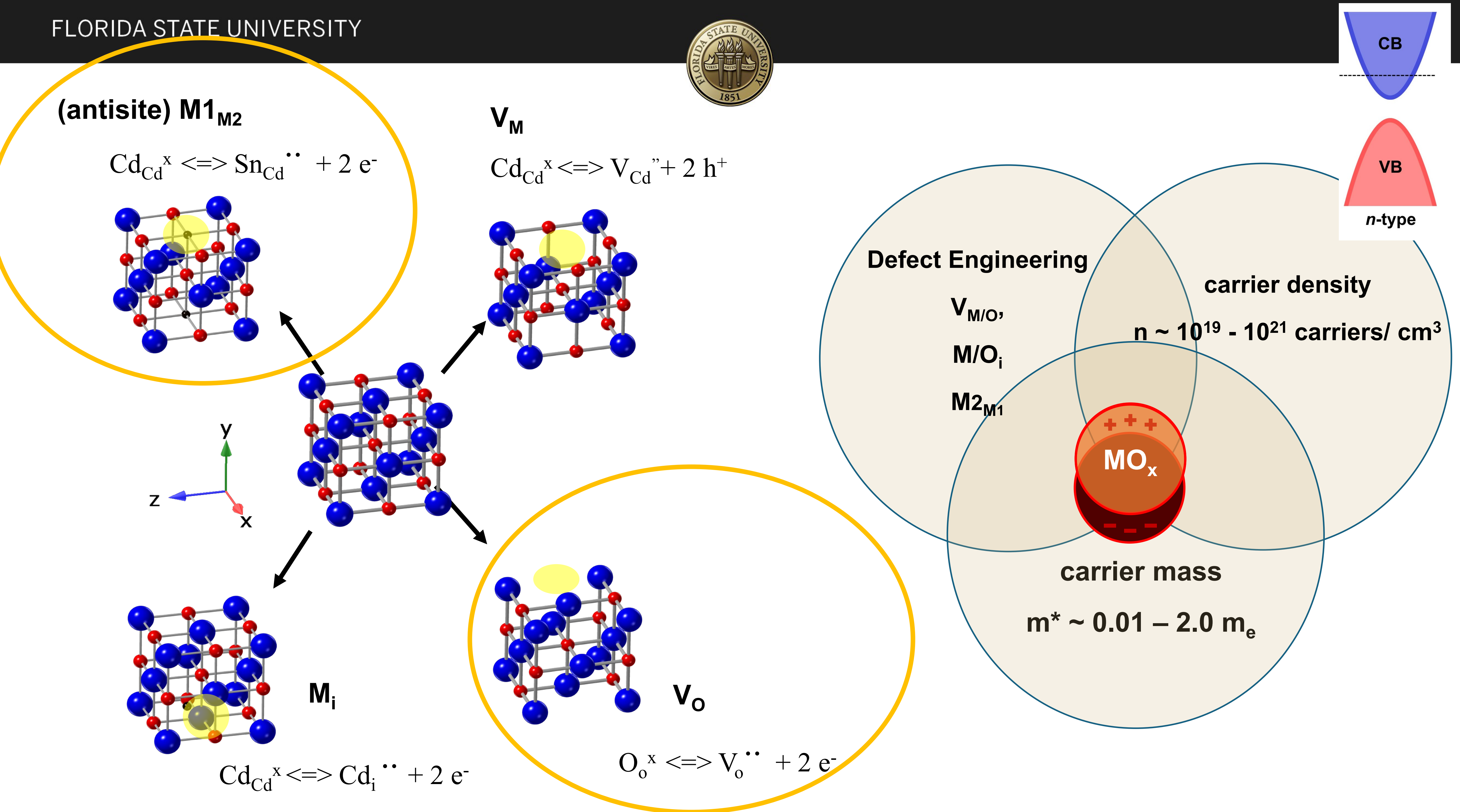
Sn_{Cd} Driven

$Cd_{Cd}^x \Leftrightarrow Sn_{Cd}^{\cdot\cdot} + 2\,e^-$

- **Inverted spinel**
- **Sn(IV)**
- **Sn_{Cd}**
- **Carriers increase with *x***
- **$Cd_{1.86}Sn_{1.14}O_4$ = $0.022m_e$**

CB Murray *J. Am. Chem. Soc.* 2014, 136, 13, 5106−5115

Xingchen Ye *Chem. Mater.*, **2021**


(antisite) $M1_{M2}$
$Cd_{Cd}^{x} <=> Sn_{Cd}^{\cdot\cdot} + 2\,e^{-}$
V_M
$Cd_{Cd}^{x} <=> V_{Cd}^{''} + 2\,h^{+}$
y
z
x
M_i
$Cd_{Cd}^{x} <=> Cd_{i}^{\cdot\cdot} + 2\,e^{-}$
V_O
$O_{o}^{x} <=> V_{o}^{\cdot\cdot} + 2\,e^{-}$
CB
VB
n-type
Defect Engineering
$V_{M/O}$,
M/O_i
$M2_{M1}$
carrier density
n ~ 10^{19} - 10^{21} carriers/ cm^3
MO_x
carrier mass
m* ~ 0.01 – 2.0 m_e

$Cd(acac)_2$ + n SnF_2 → (oleic acid, octadecene; 316 ^{o}C, 70 mins) →

- Sn:CdO NCs (< 33% Sn)
- Cd_2SnO_4 NCs (> 33% Sn)

Sn:CdO

(V_o carriers)

Rock salt

vs.

Cd_2SnO_4

(antisite carriers)

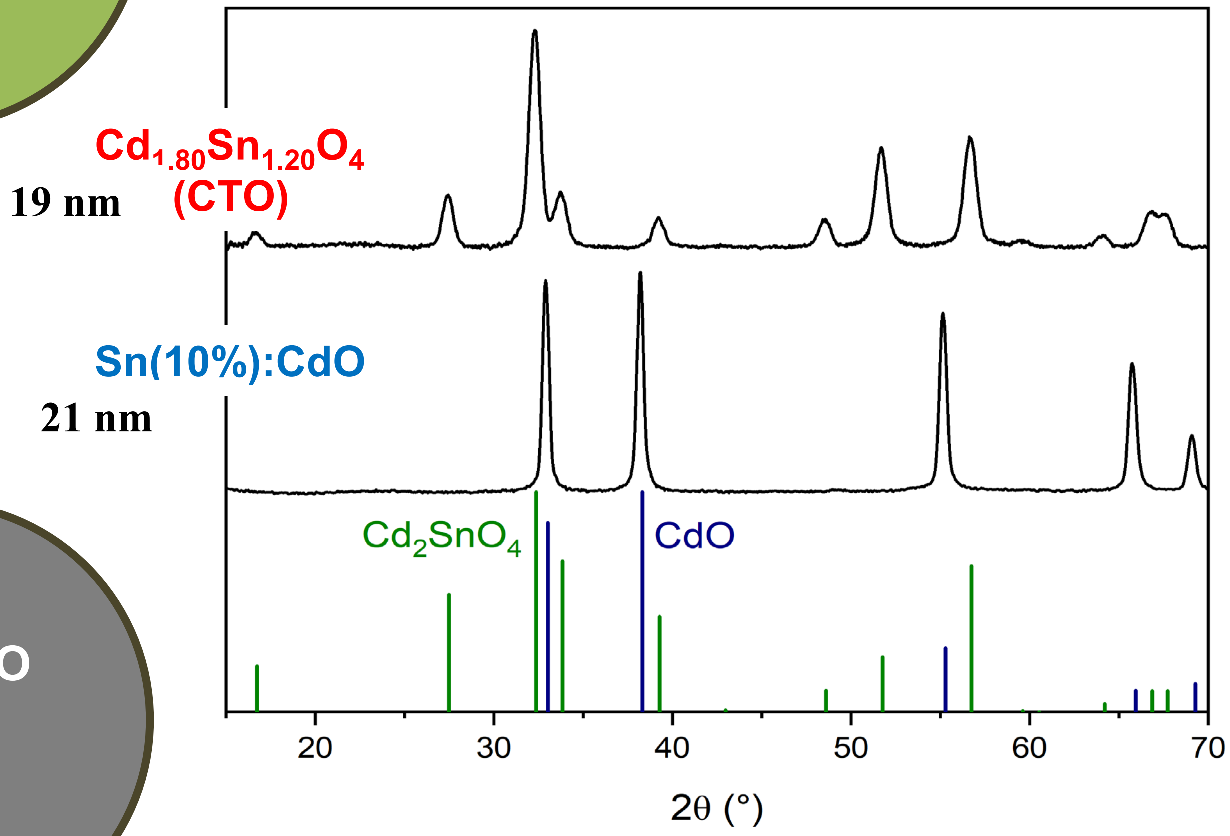
inverted spinel

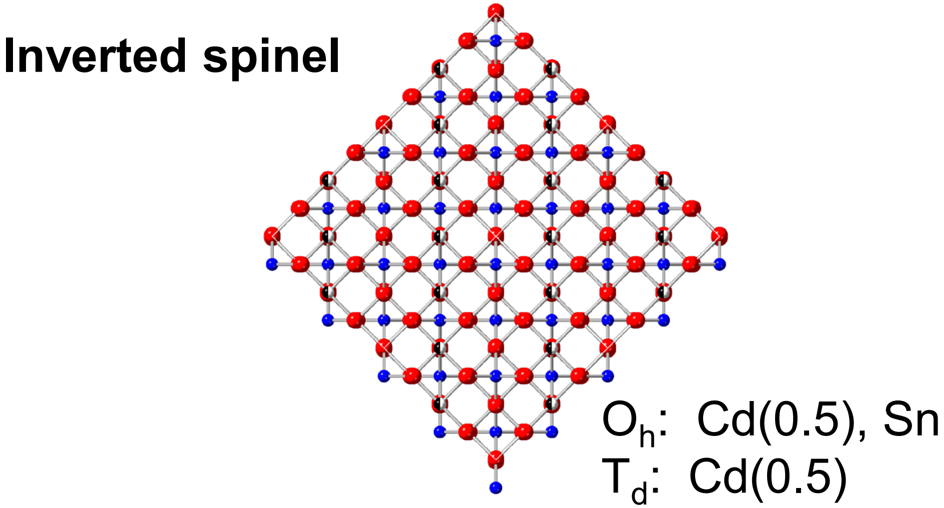
CB Murray *J. Am. Chem. Soc.* 2014, 136, 13, 5106−5115

Zhong, Y. et al. *Chem. Mater.*, **2021**

$Cd_{2-x}Sn_{1+x}O_4$

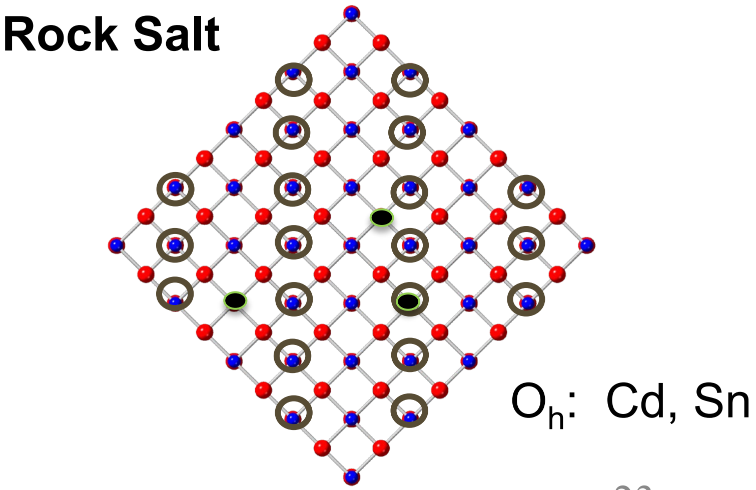
Sn_{Cd}

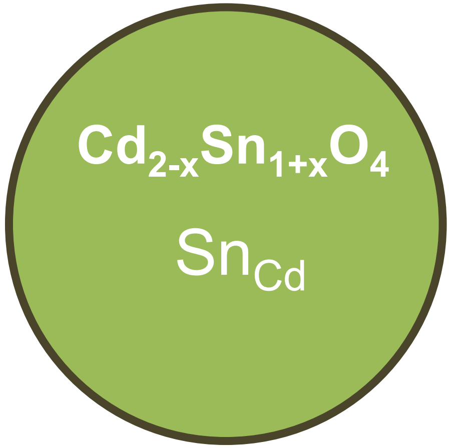




Sn_x:CdO

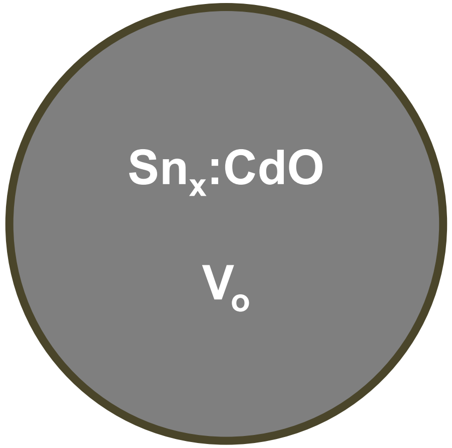
V_o

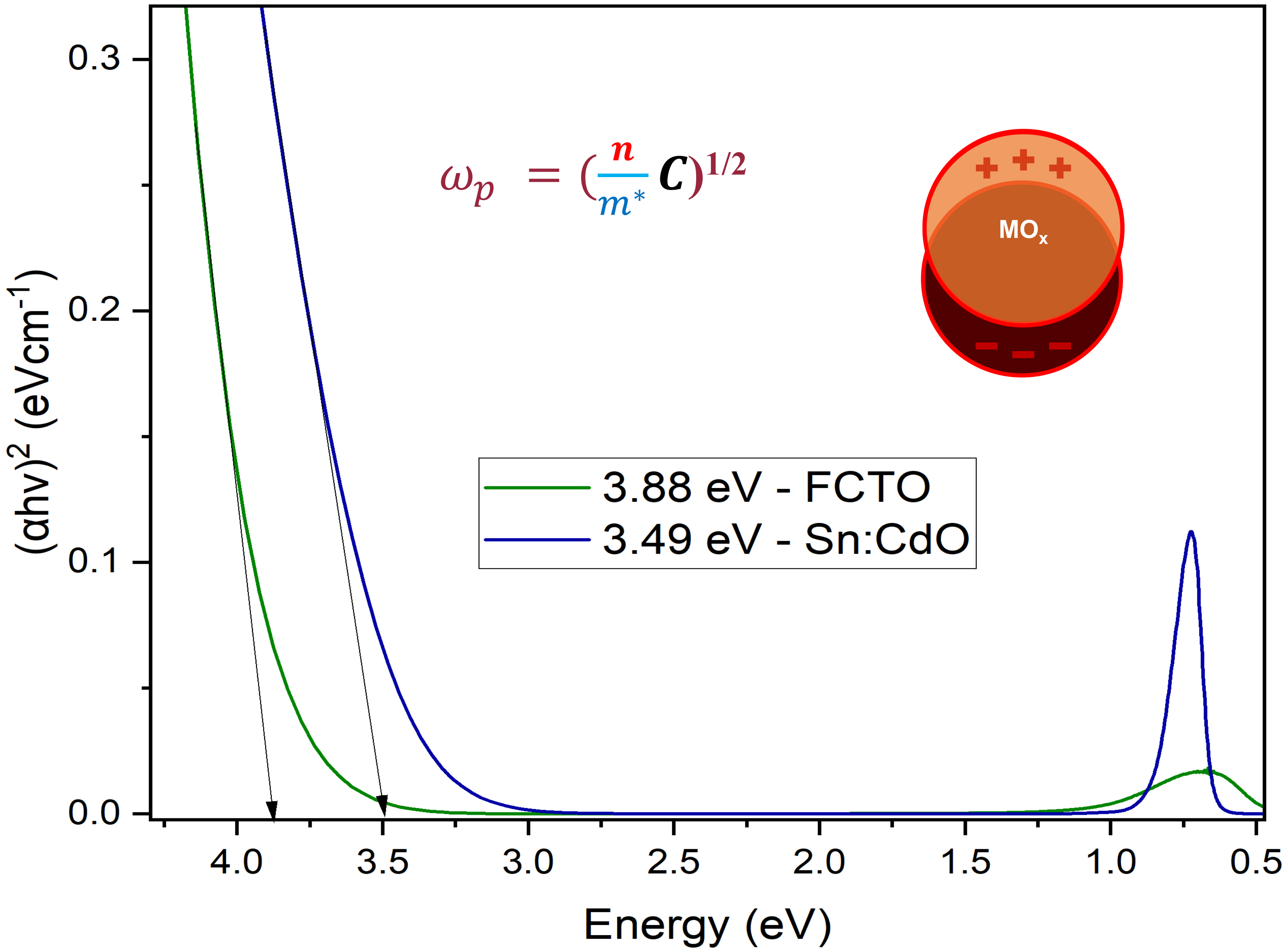


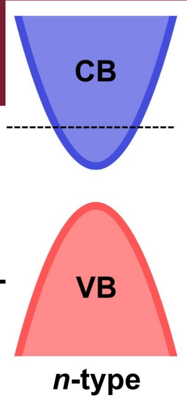

$Cd_{2-x}Sn_{1+x}O_4$
Sn_{Cd}

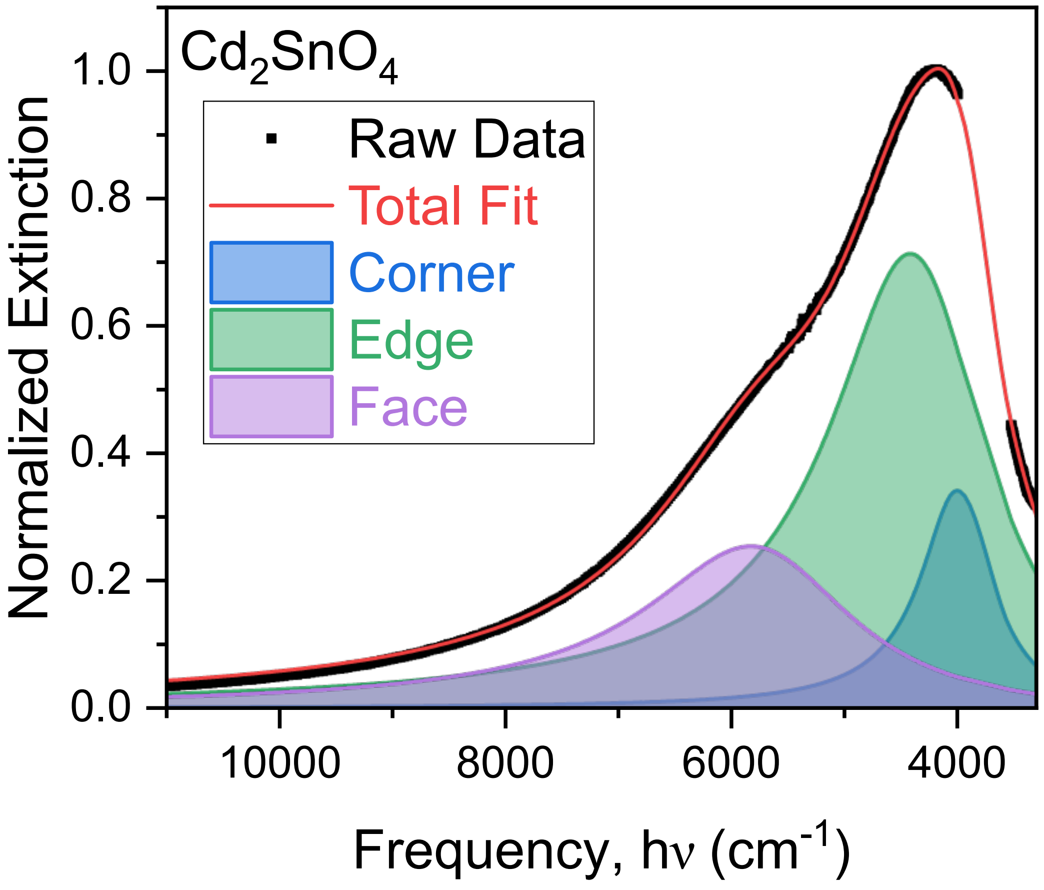
16 nm

21 nm


Sn_x:CdO
V_o

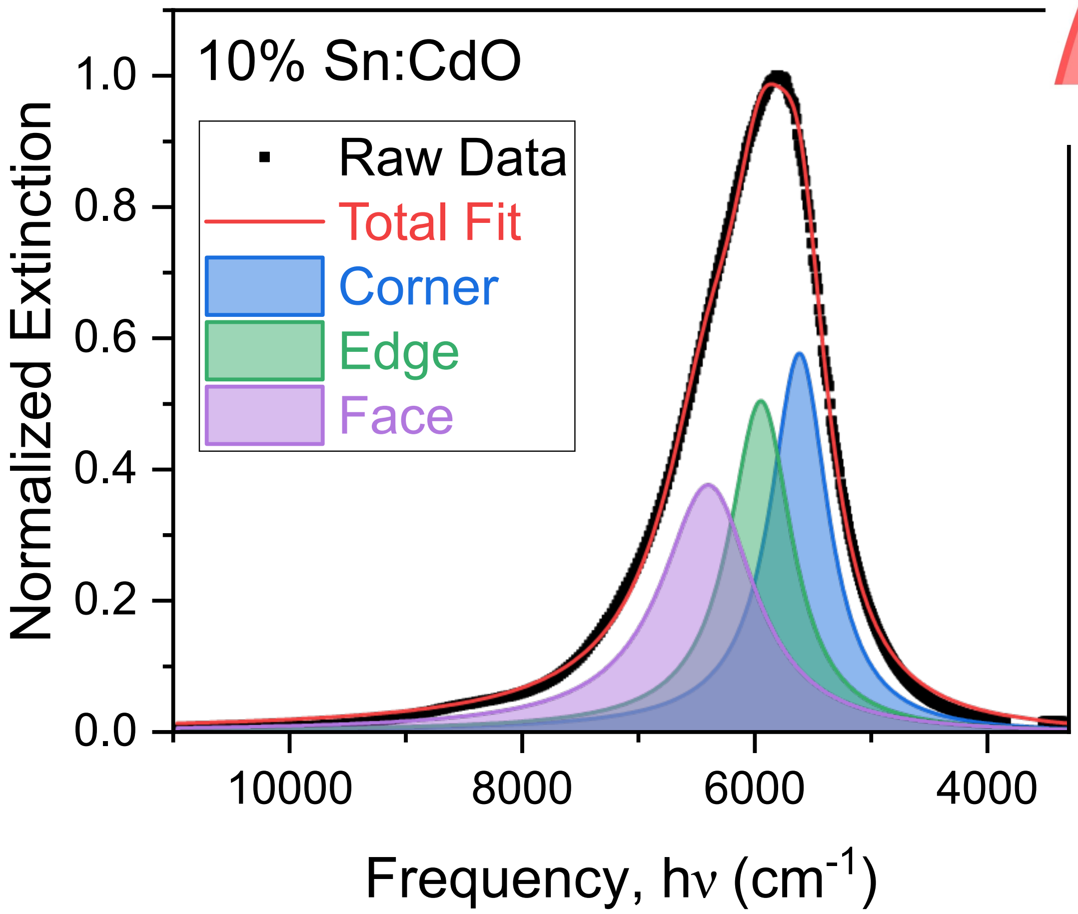

$\omega_p = (\frac{n}{m^*} C)^{1/2}$
MO_x
+ + +
3.88 eV - FCTO
3.49 eV - Sn:CdO
$(\alpha h\nu)^2$ $(eVcm^{-1})$
0.0
0.1
0.2
0.3
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Energy (eV)





$n = 5 \times 10^{19}$ carriers/cm^3

m*(Lit) = 0.022m$_e$

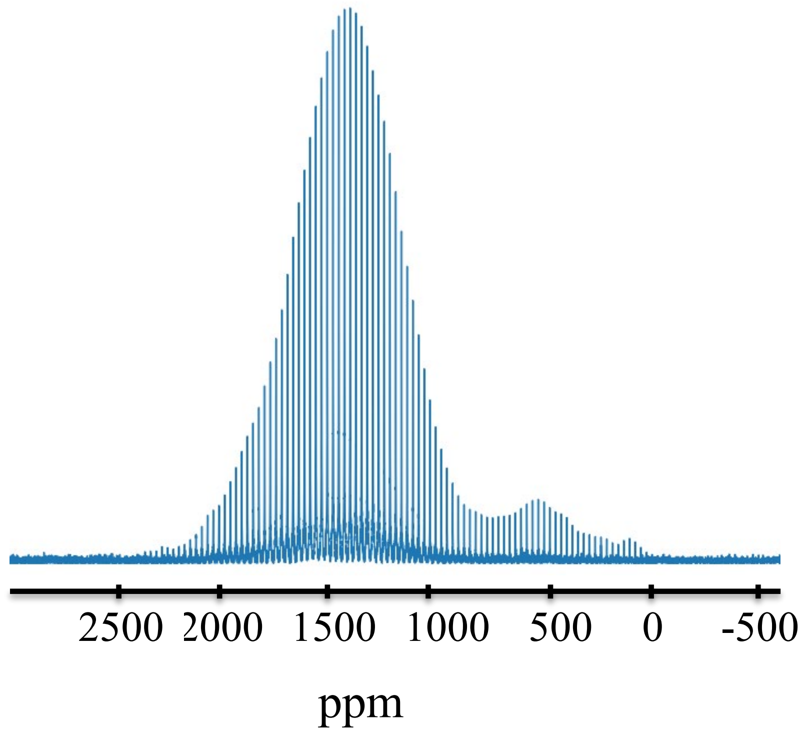


$n = 1.5 \times 10^{21}$ carriers/cm^3

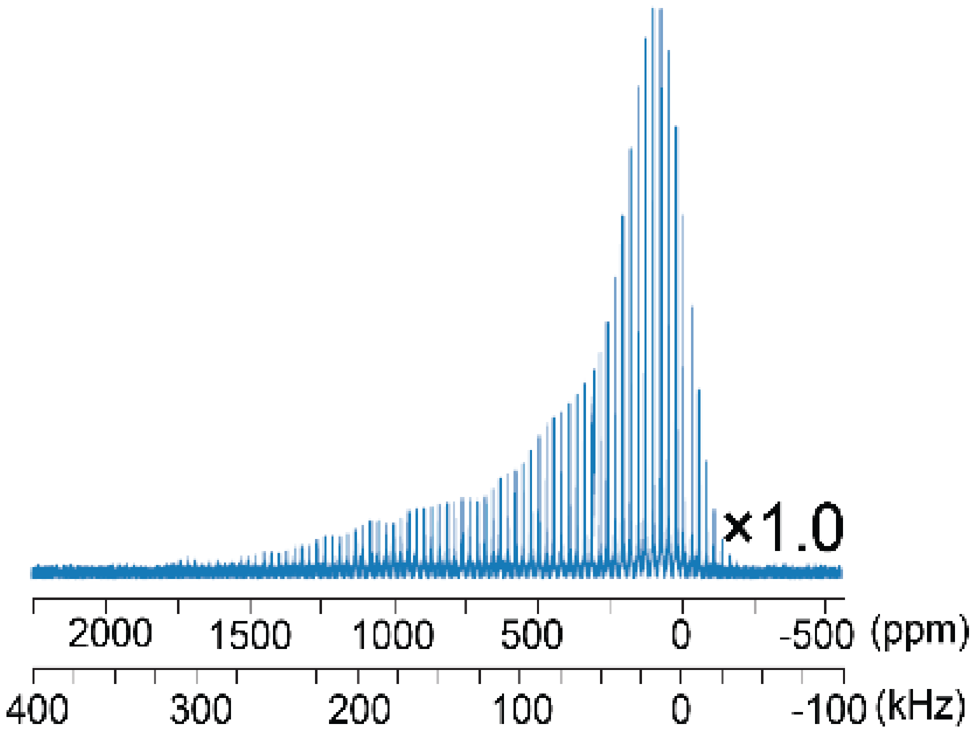
m* (Lit) = 0.26m$_e$

^{113}Cd solid state NMR to probe site dependent effect in Sn:CdO vs. CTO

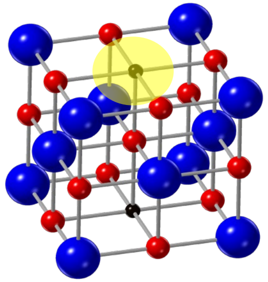
^{113}Cd of 10% Sn:CdO PSNCs collected using a WURST-CPMG pulse sequence



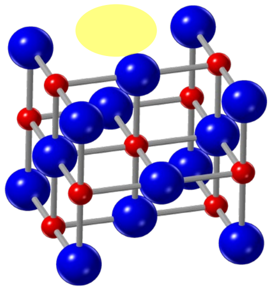
^{113}Cd of CTO PSNCs collected using a WURST-CPMG pulse sequence



(antisite) Sn_{Cd}

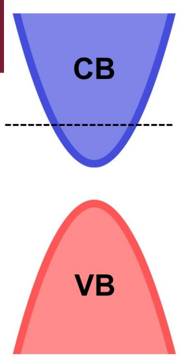


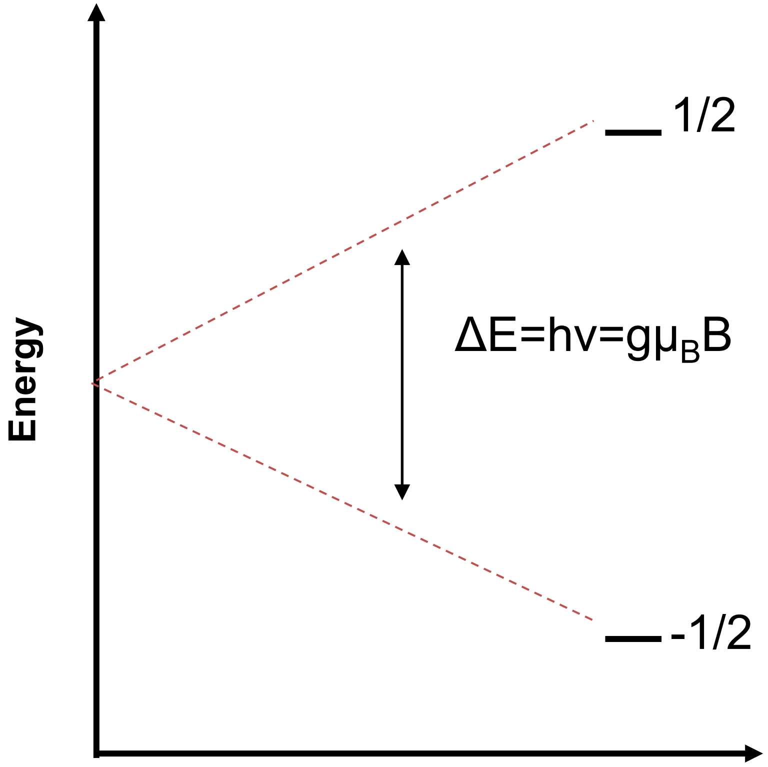
V_O

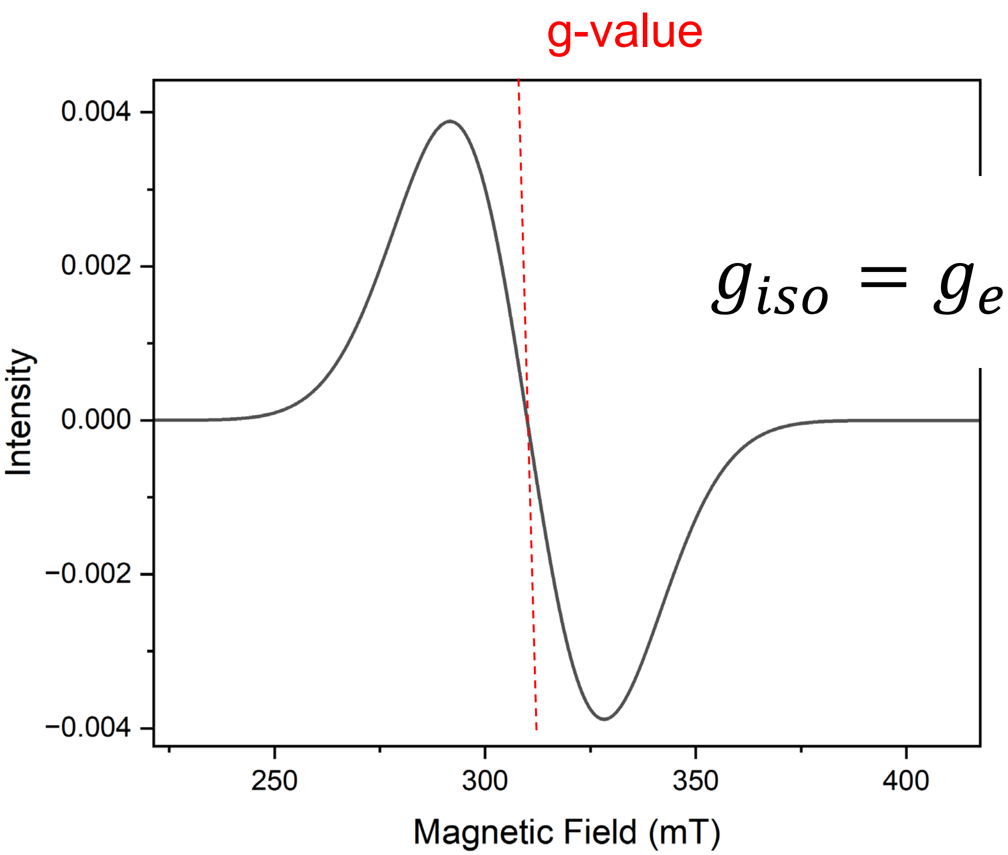


Are the carrier parentage really different?

Electron Paramagnetic Resonance (EPR)





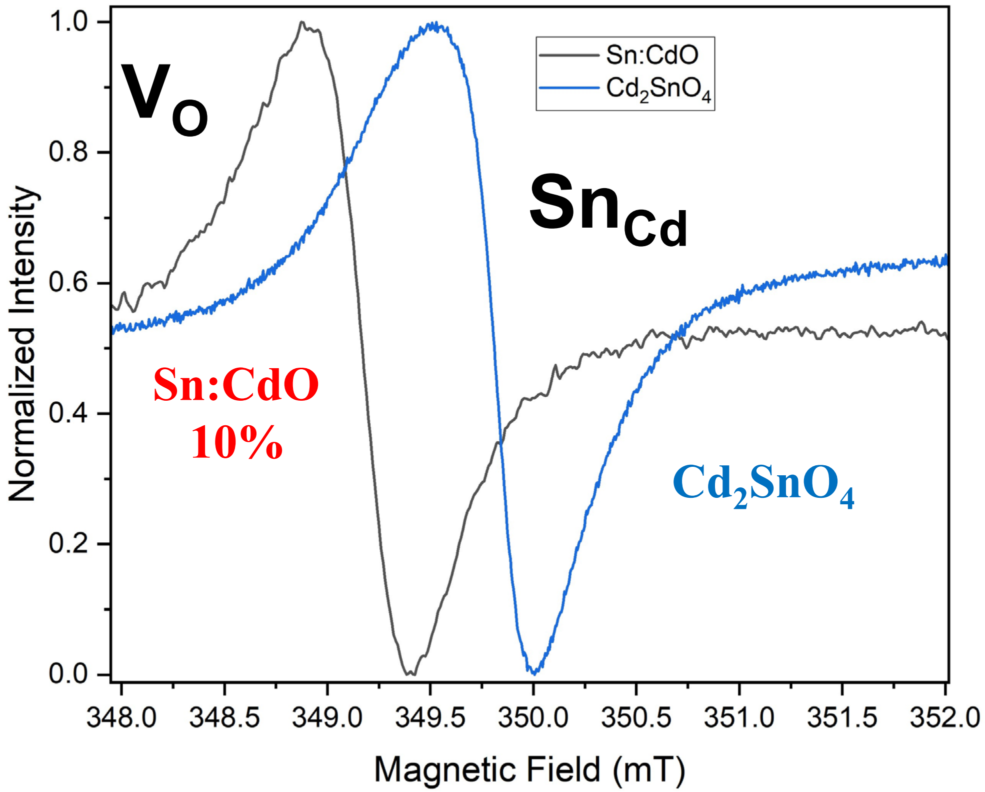


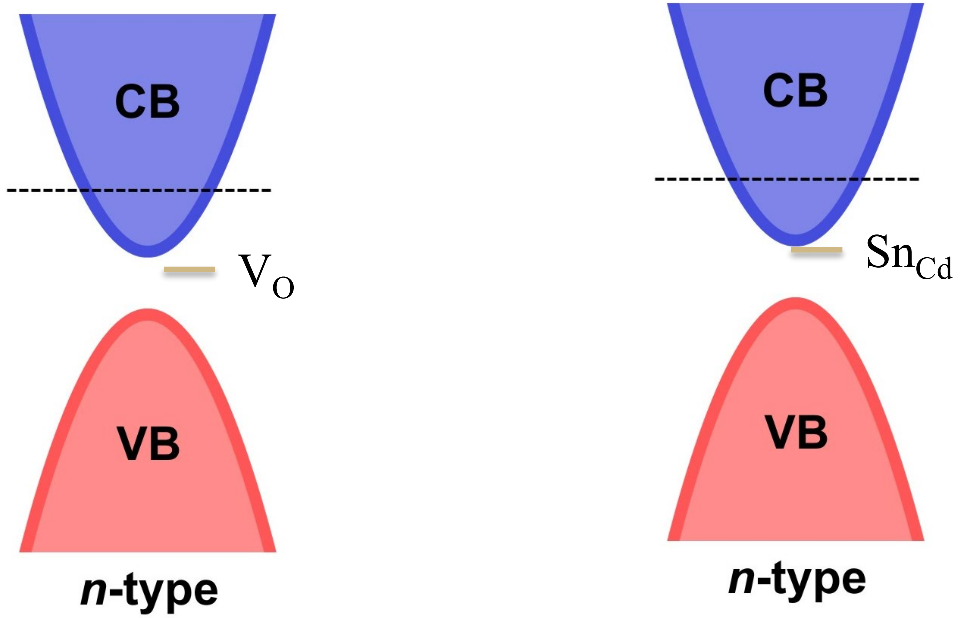
$$g_{iso} = g_e - \frac{2\,|\lambda|}{\sqrt{\lambda^2 + \Delta^2}}$$

λ = spin-orbit coupling
Δ = crystal field

Identifying the defct type by EPR

(X-band, RT)



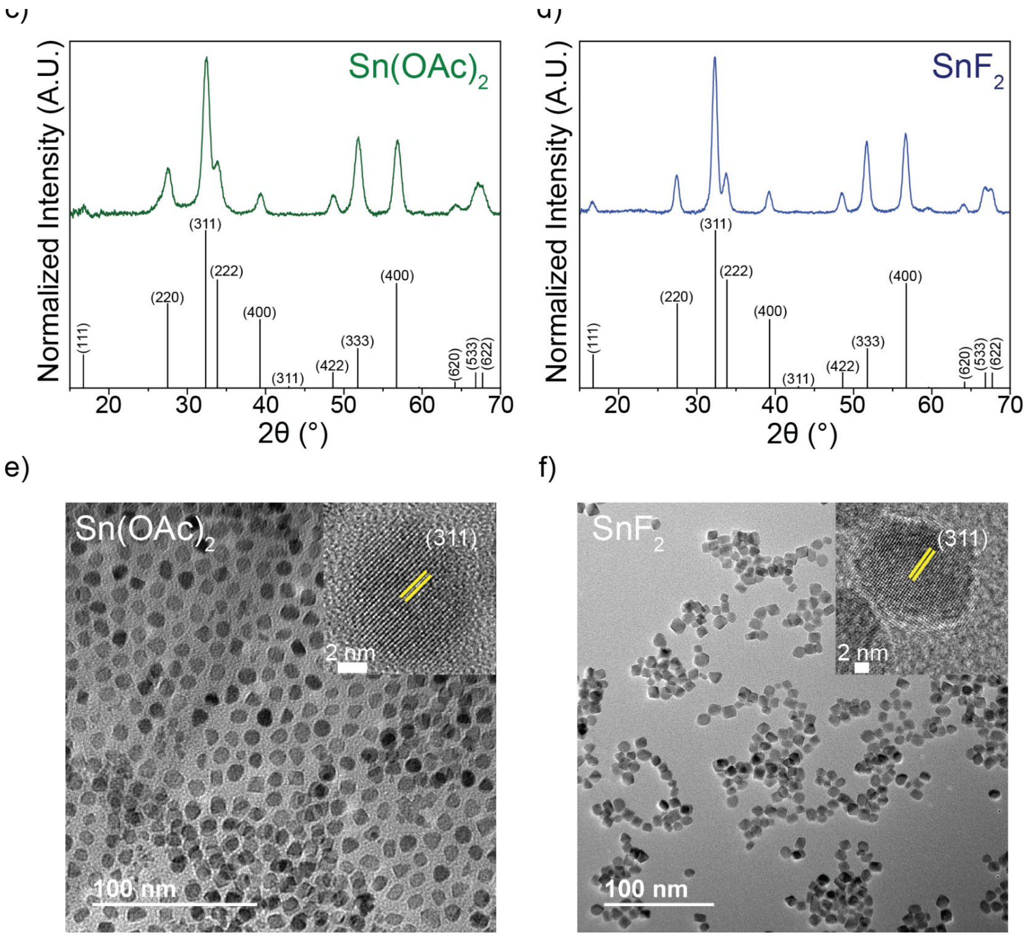


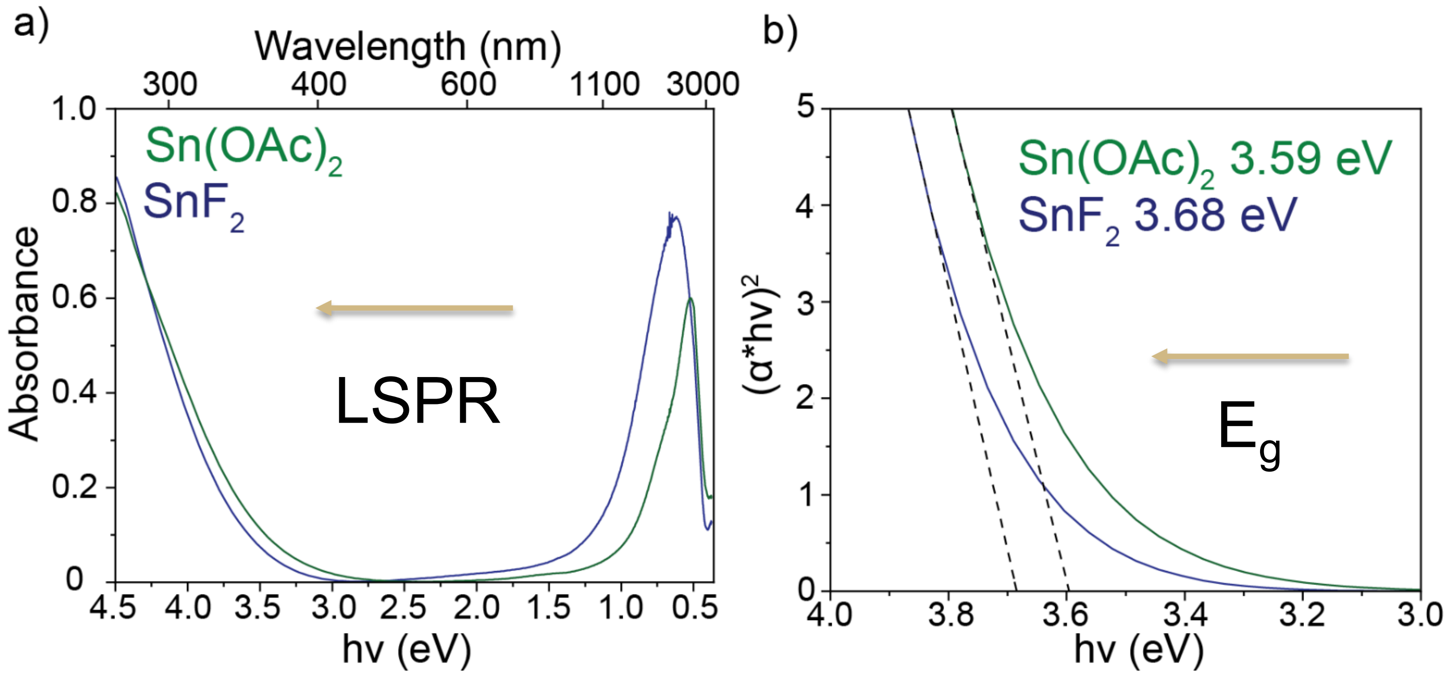
Sn(10%):CdO	Cd_2SnO_4
$V_O^{\cdot}$	Sn_{Cd}
$g(O_h)$ ~2.005	g ~2.001

CdO Liu, Z. et al., ACS Nano., 2020

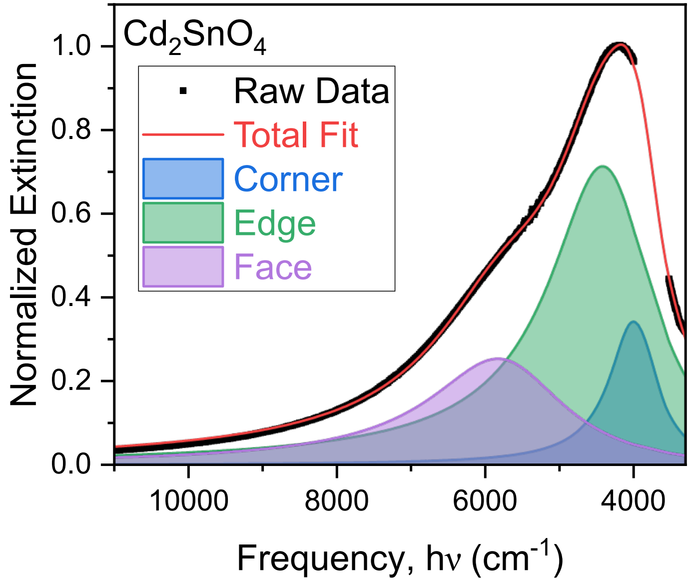
ZnO Ayoub, I. et al., *Nanotechnol. Rev.*, 2022

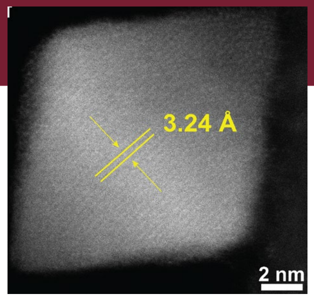
Can we increase carrier densities by removal of V_o (Oxygen vacancy) by active etching using SnF_2 as reactant instead of $Sn(acac)_2$?





a-CTO ($Cd_{1.86}Sn_{1.14}O_4$)





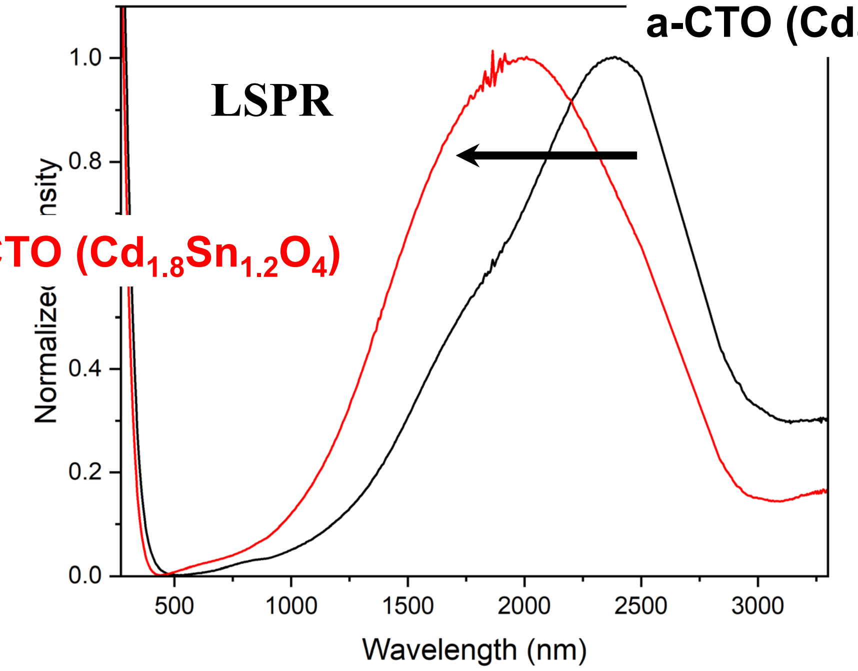
19 x 14 nm

Aspect ratio: 1.36

n = 5 x 10^{19} carriers/cm^3

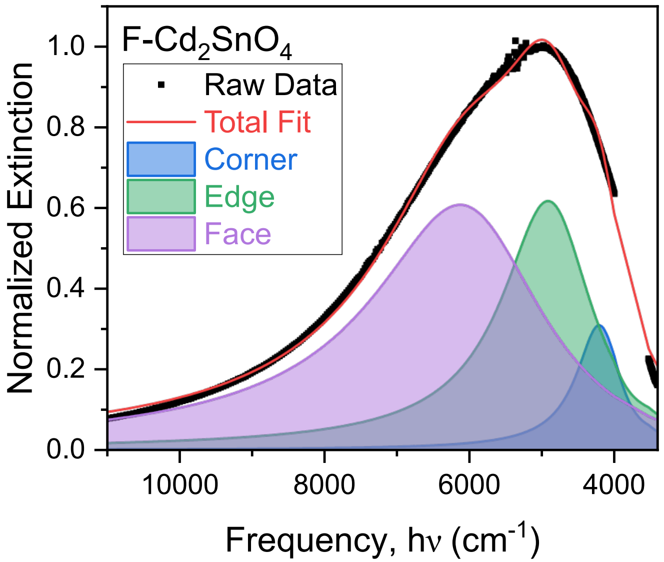
$$\omega_p^2 = \frac{ne^2}{m^* \varepsilon_0} = \frac{n}{m^*} C$$

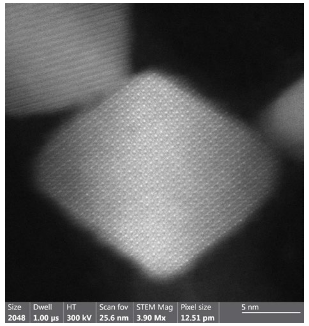
a-CTO ($Cd_{1.86}Sn_{1.14}O_4$)



F-CTO ($Cd_{1.8}Sn_{1.2}O_4$)

F-CTO ($Cd_{1.8}Sn_{1.2}O_4$)



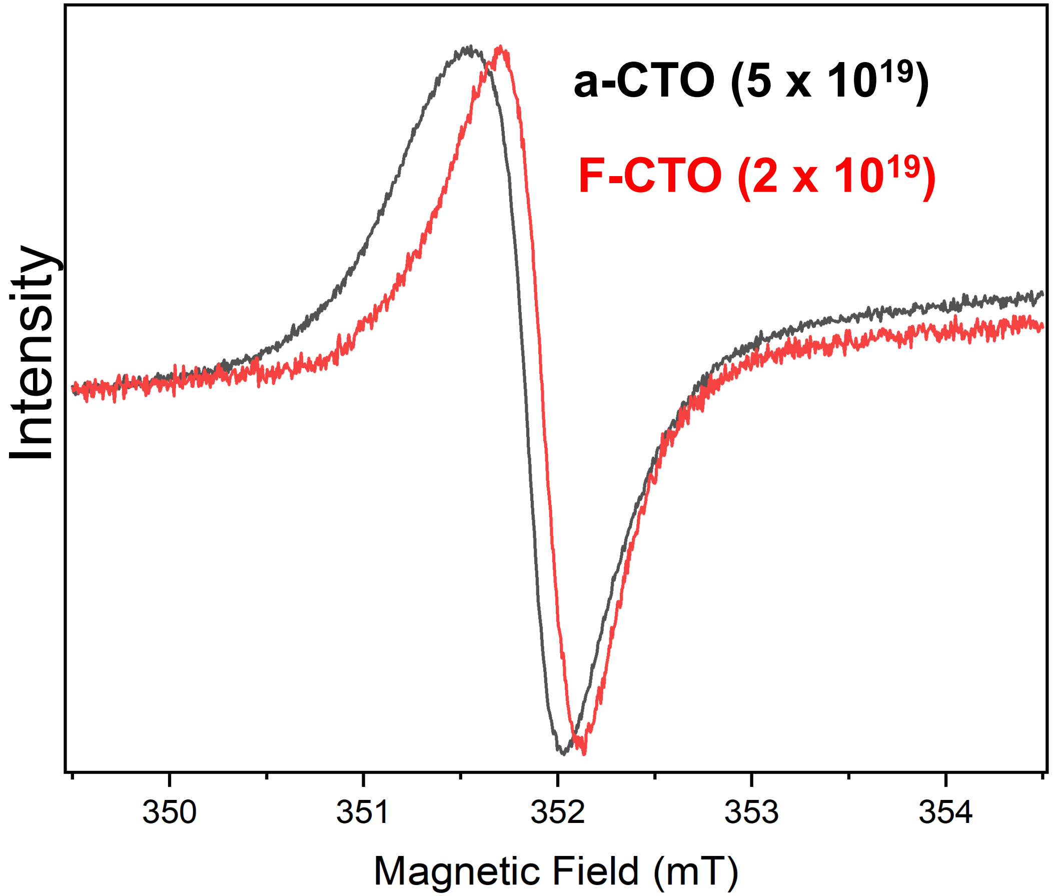


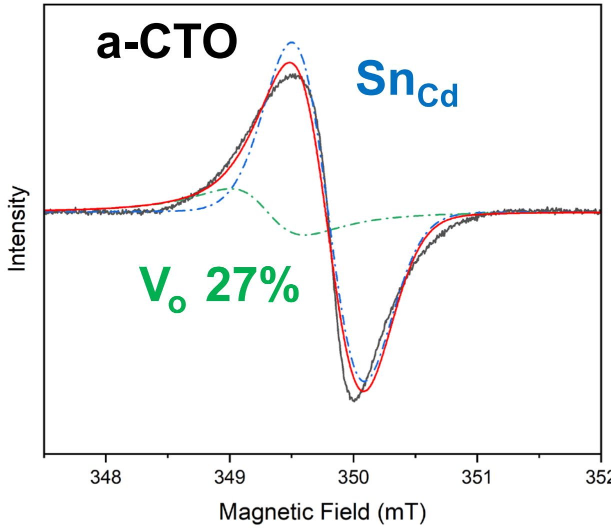
22 x 18 nm

Aspect ratio: 1.22

n = 2 x 10^{19} carriers/cm^3

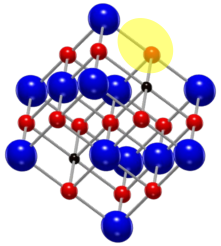
Does EPR help us understand?

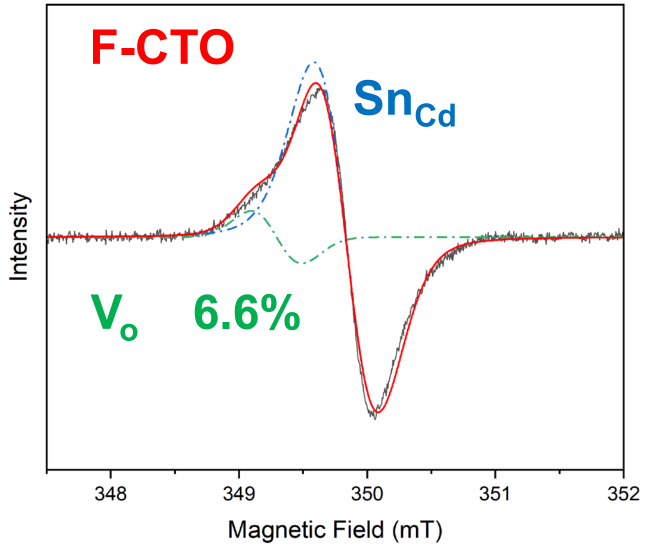




Sn_{Cd}

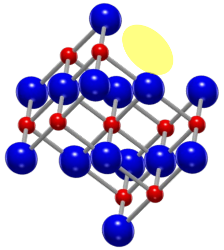
g ~2.001



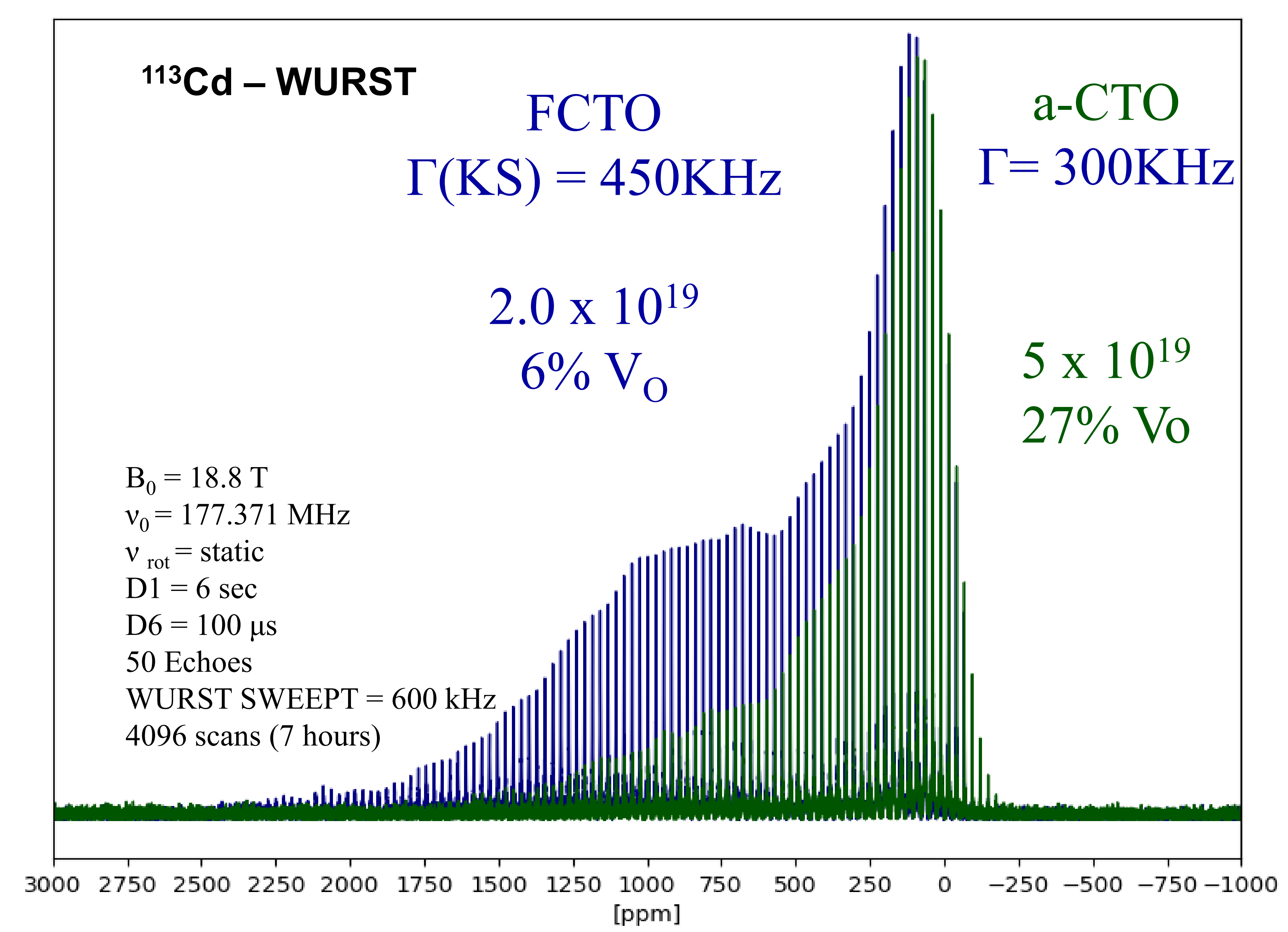


$V_O^{\cdot}$

$g(O_h)$ ~2.005



EPR confirms lower V_o for F-CTO, but why no increase in *n*?



Observe a large increase in Knight Shift (KS)

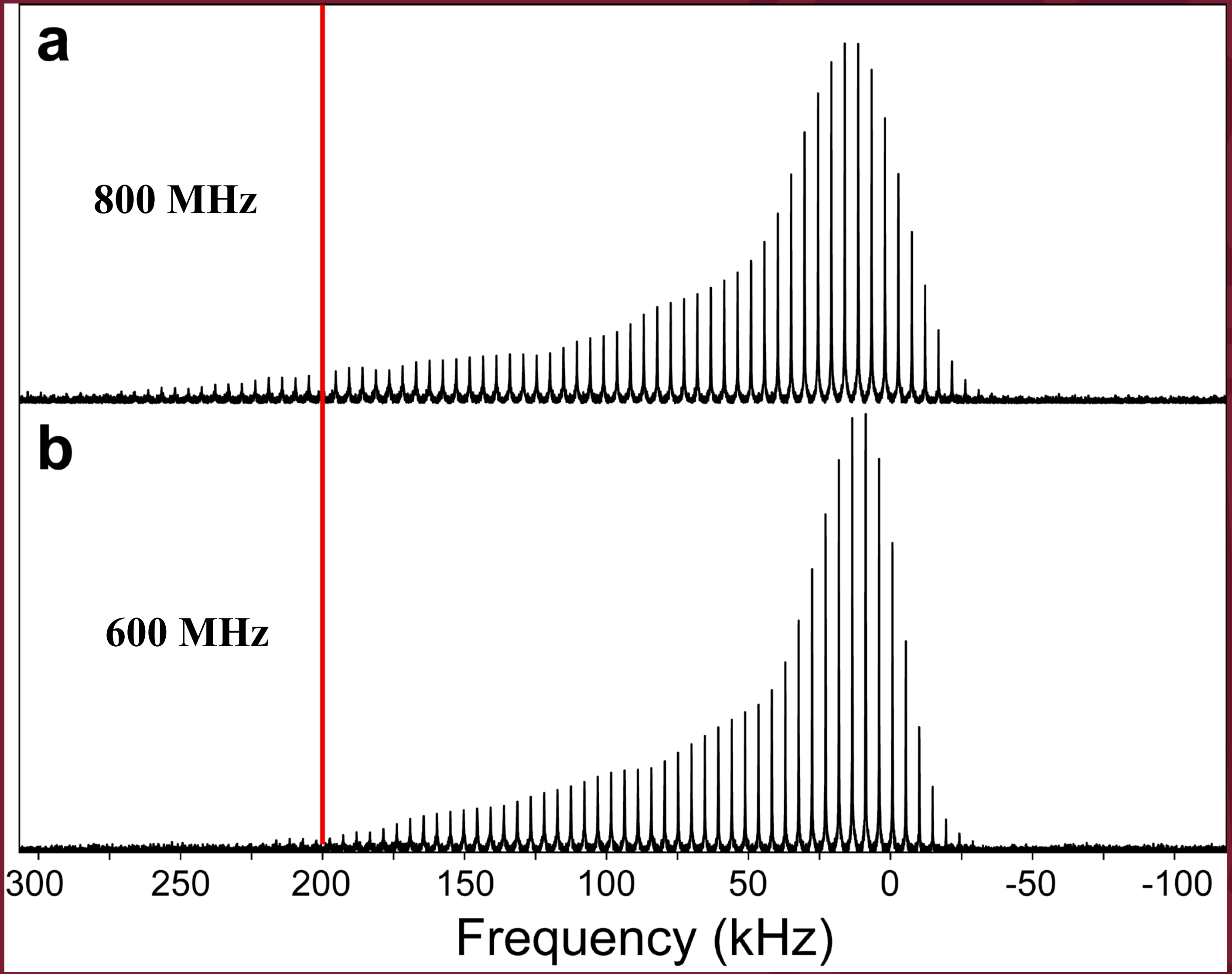
$KS \propto n^{1/3}$

FCTO has lower carrier density but also lower V_o

Slower relaxation, T_1
Knight-Korringa

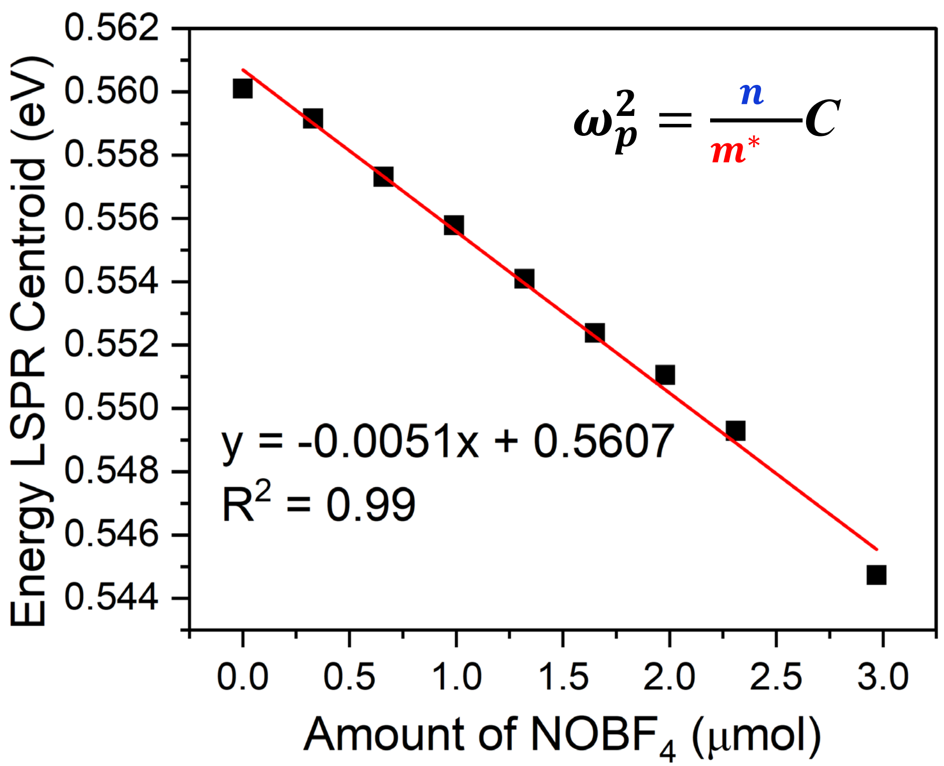
FLORIDA STATE UNIVERSITY

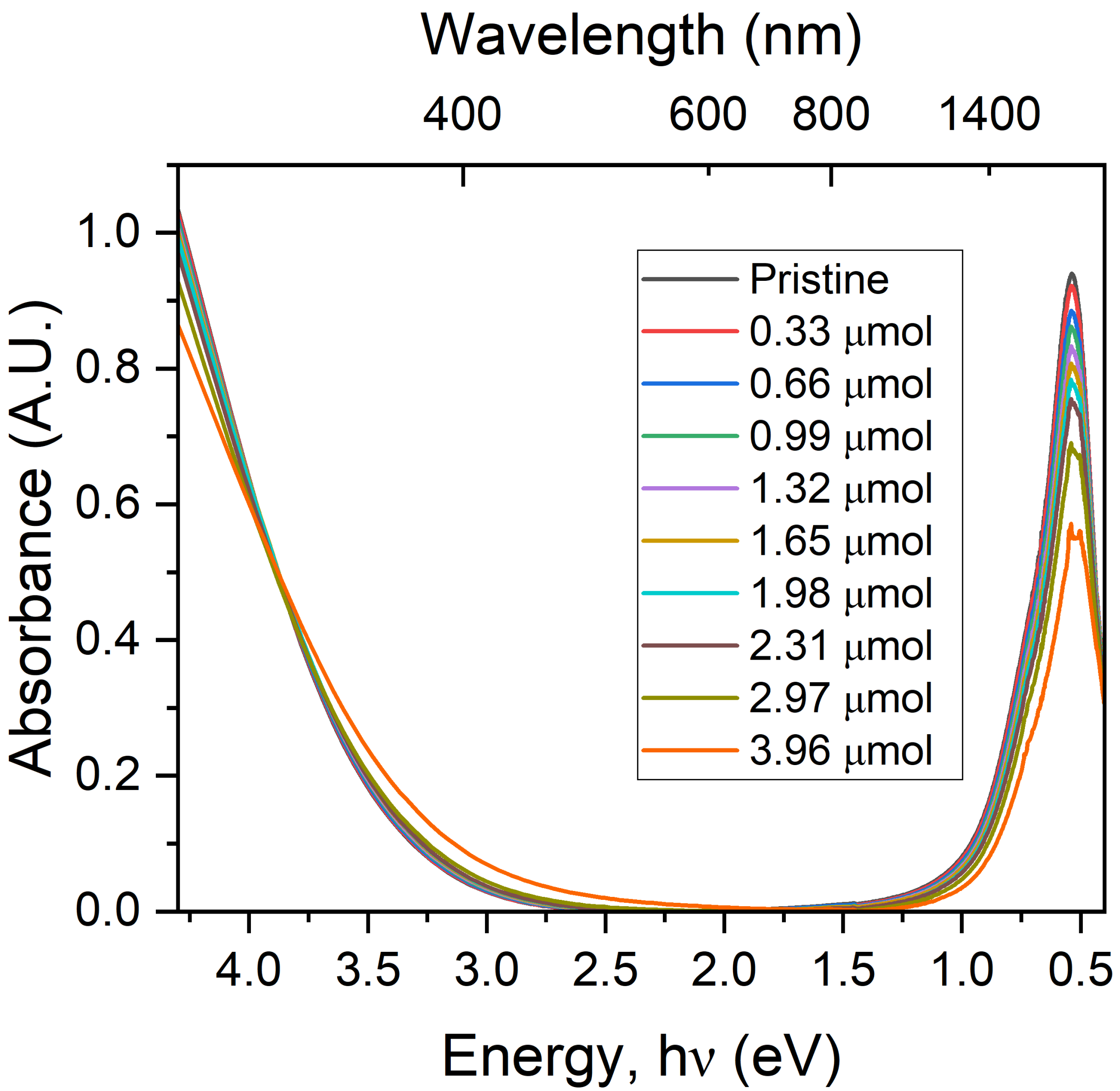
But are we sure its KS and not CS?



KS frequency shift will be dependent on applied field

Can we prove it by chemically removing carriers in **CTO** using the 1-electron oxidant **$NOBF_4$**?

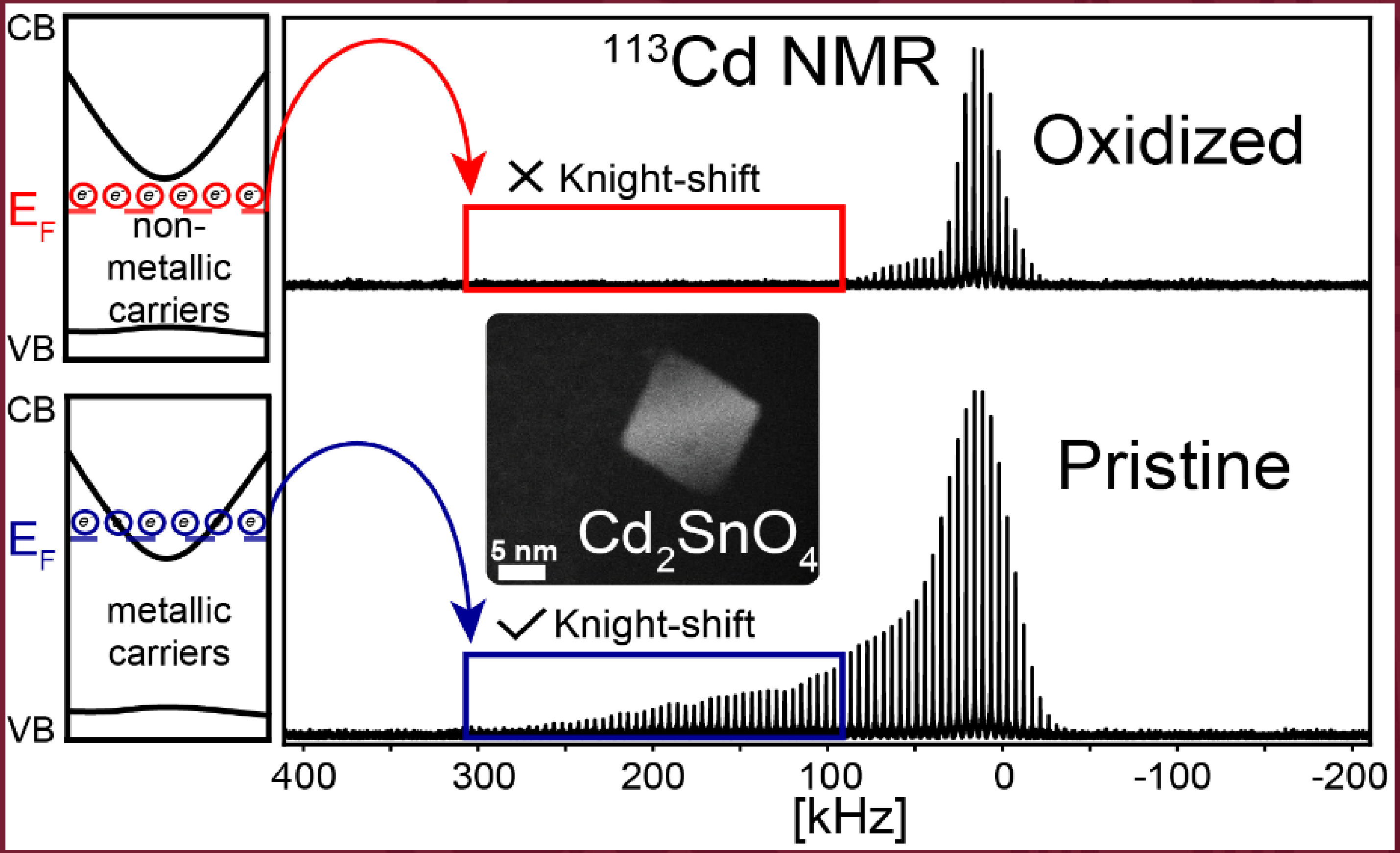




Can we be sure it is KS and not CS?

FLORIDA STATE UNIVERSITY

F-CTO Titrated with $NOBF_4$

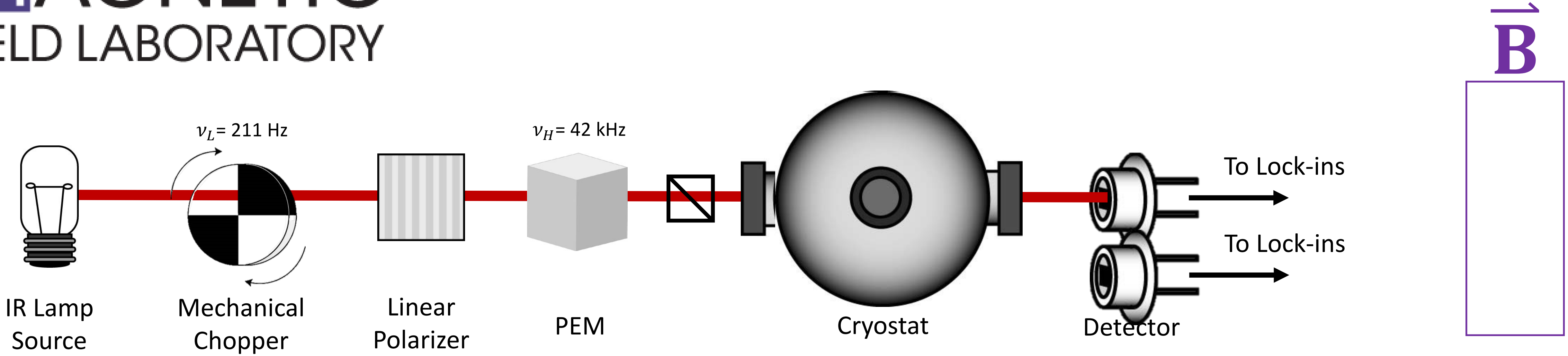


Spectral change suggests shift arises from metallic like carriers (Knight shift) since CS is site dependent

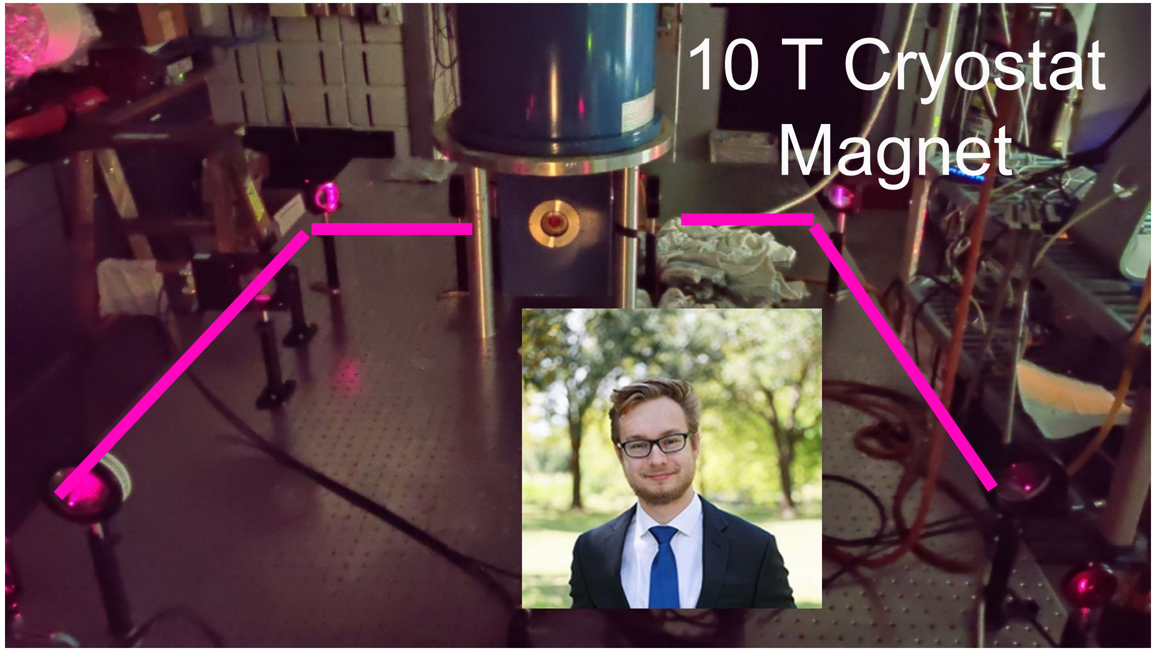
$$KS \propto n^{1/3}$$

NATIONAL HIGH MAGNETIC FIELD LABORATORY

VT, VH-MCD Experiment



Detector

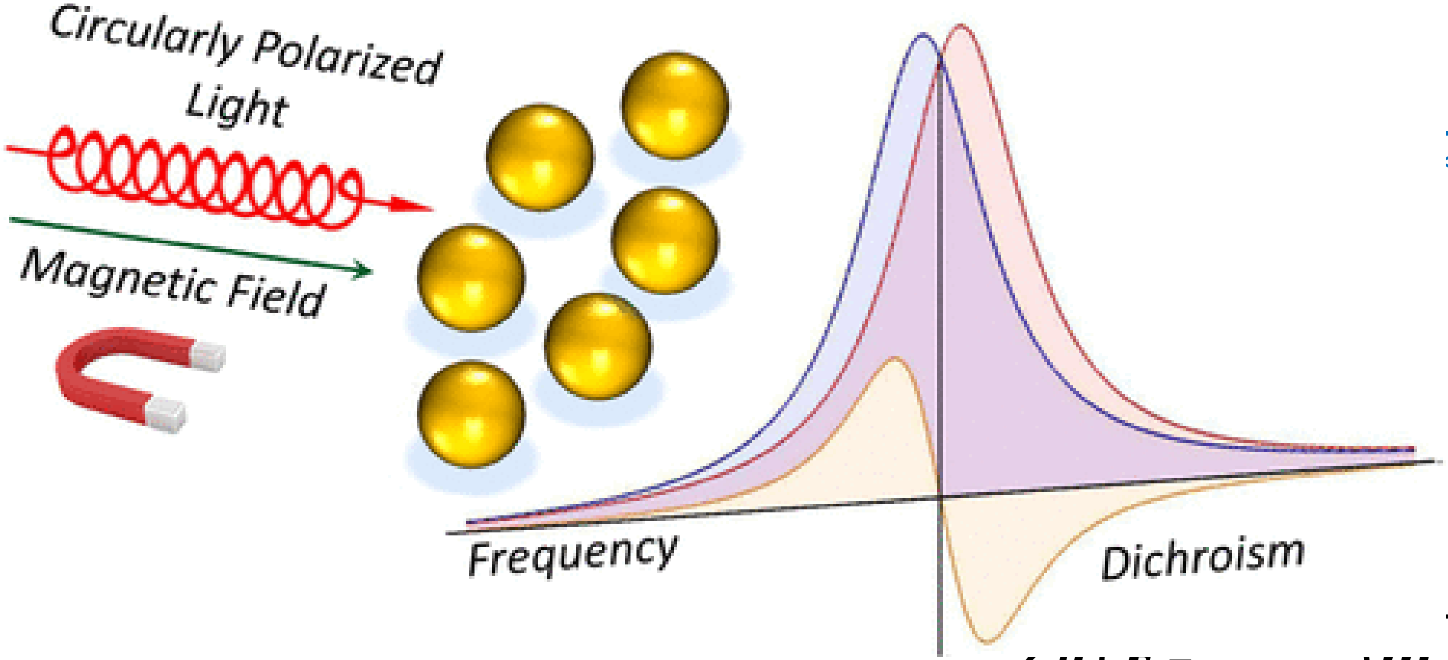


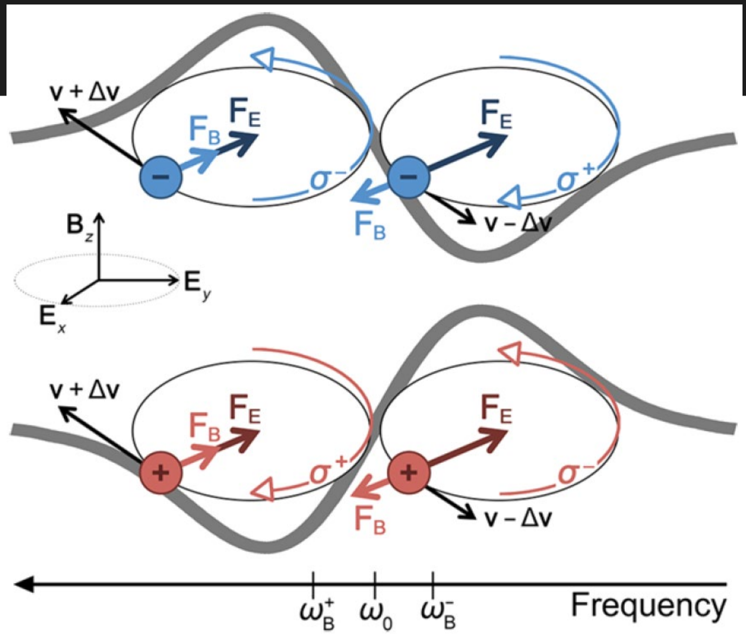
Magnetic Circular Dichroism (MCD)

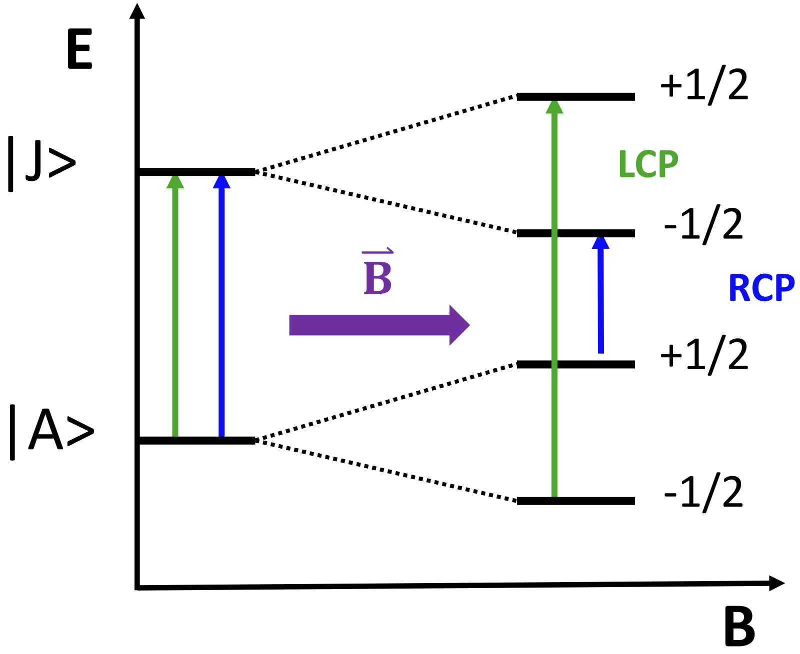
Extraction of m*

Cyclotron resonance

$$\omega_c = \frac{q\mathbf{B}}{\boldsymbol{m}^{*} m_e}$$



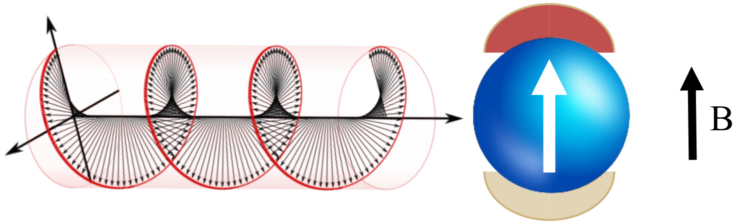


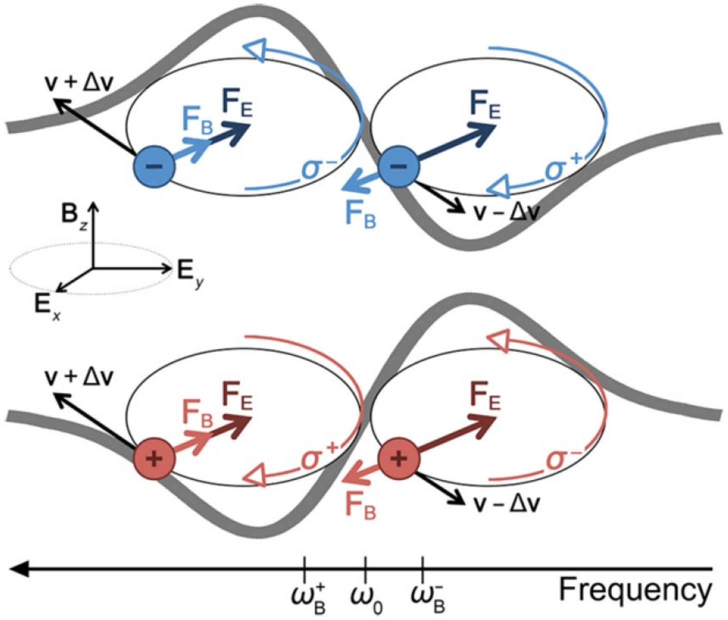


1. Pineider, F. et al, *Nano Lett.* **2013**
2. Hartstein, K. H. et al., *J. Phys. Chem. Lett.* **2017**
3. Kimura, T. and Hiroshi, Y., *J. Phys. Chem. C.* **2022**

Is this a question of trapping at donor levels due to V_O?

Then it should be reported as a change in **m*** measured by MCD

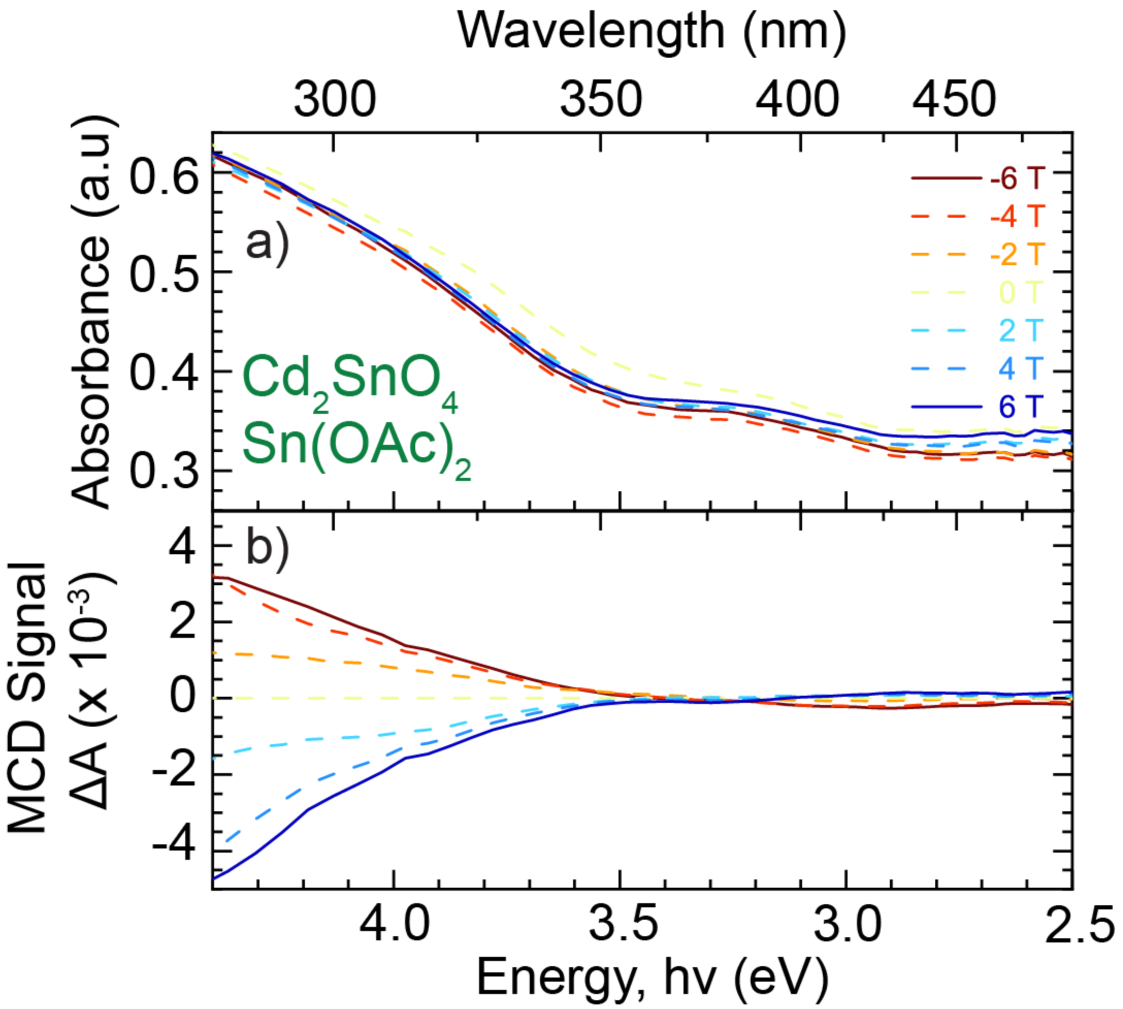


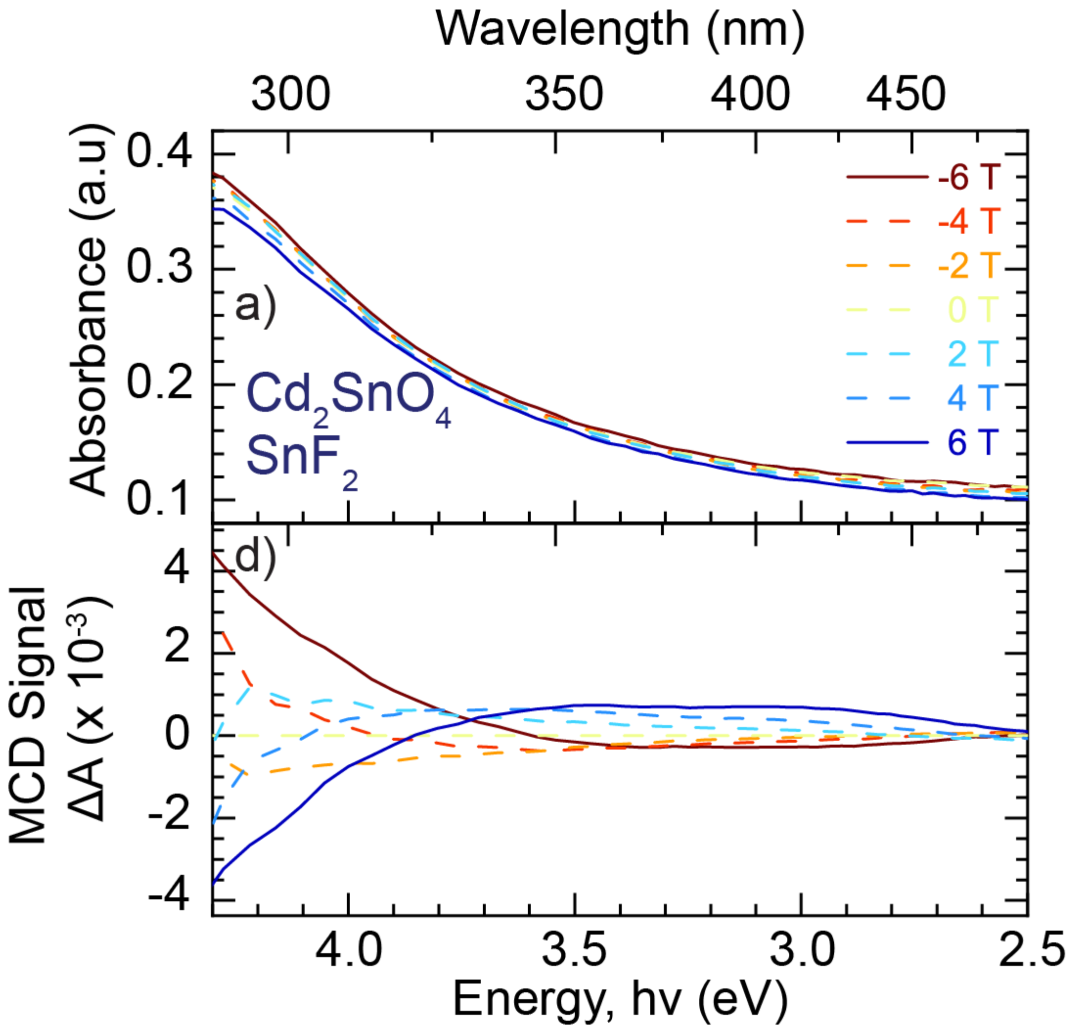


$$\omega_B^{LCP/RCP} = \omega_0 \pm \frac{qB}{2m^*}$$

$$m^* = \frac{qBc}{2\pi(E_{Zeeman})m_e}$$

Pineider, F. et al, *Nano Lett.* **2013**
Hartstein, K. H. et al., *J. Phys. Chem. Lett.* **2017**
Kimura, T. and Hiroshi, Y., *J. Phys. Chem. C.* **2022**
Kuszynski, J., et al *J. Phys. Chem. C* **2022**

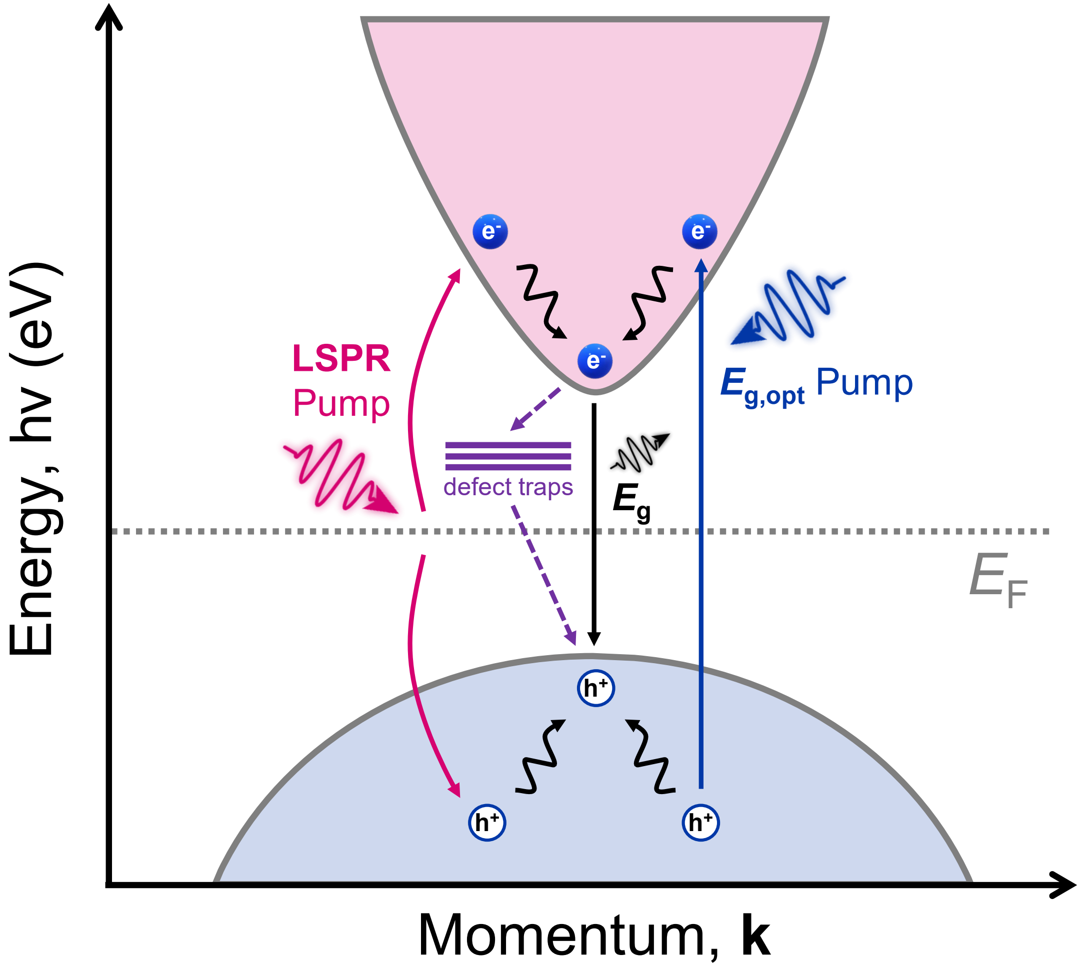




0.022 m* for a-CTO

0.006 m* for F-CTO

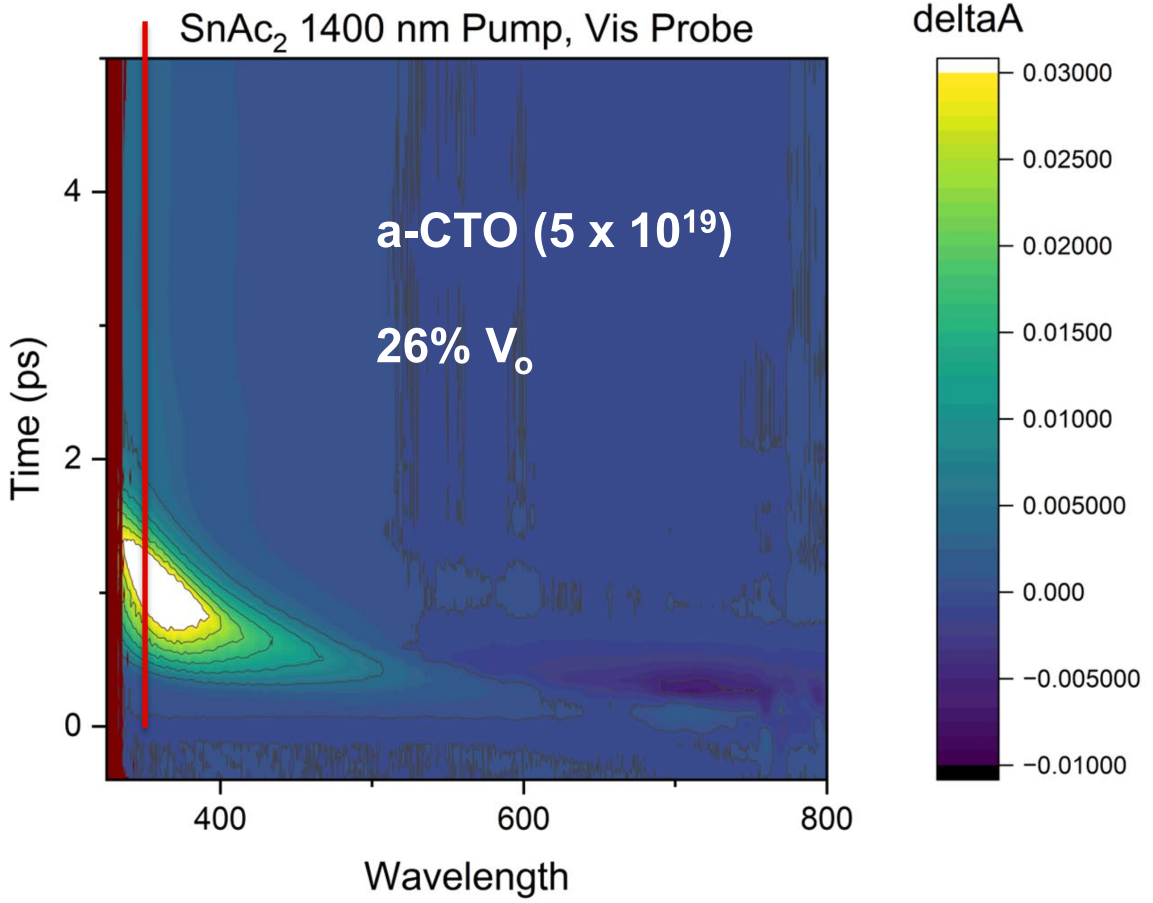
It will also show up in the LSPR Relaxation Processes

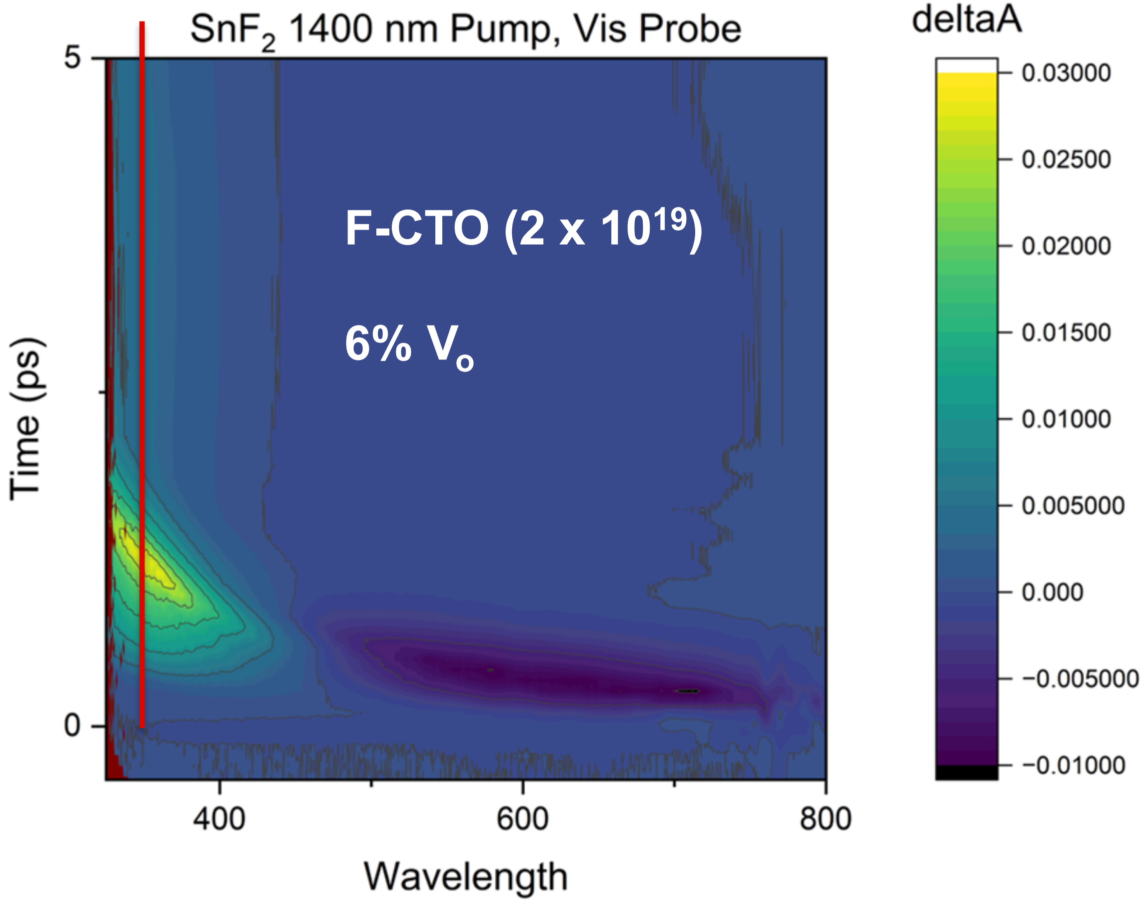


Cd_2SnO_4 fs-TA Data

350 nm Probe (0.99+ R^2 Fits)

LSPR Pump	Decay (fs)	Decay (ps)
$SnAc_2$	184.0 ± 5.8	27.19 ± 3.95
SnF_2	192.2 ± 6.4	99.51 ± 53.51



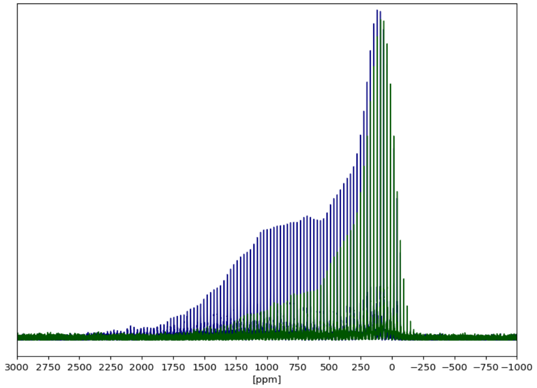


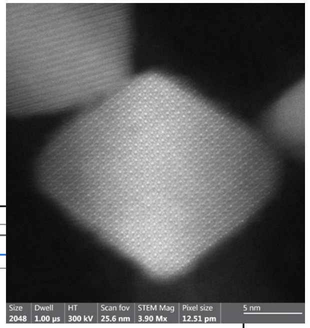
NSF-DMR #1905757

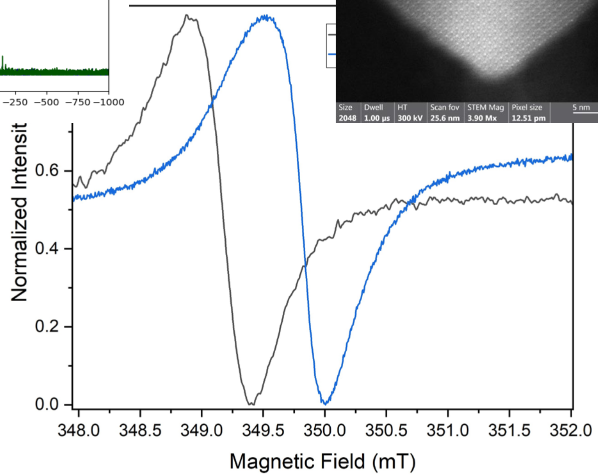
SMART
SCIENCE, MATHEMATICS, AND RESEARCH FOR TRANSFORMATION
PART OF THE NATIONAL DEFENSE EDUCATION PROGRAM

Does carrier parentage matter?

- Sn_{cd} or V_O results in change in carrier mobility
  - (XPS, XSTM, TA, NMR and EPR T_1 and T_2)
- Site and lattice matter (lattice energies) – DFT
- Impacts w_d – surface interface damping
- Impacts LSPR damping/ hot carrier formation







- **Way more to do to fully understand carrier parentage in a PSNC**
  shape, concentration, chemical interface damping, T-dependence,