

# When local structure and average structure differ: Consequences and some examples

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<http://exafs.ucsc.edu/papers.html>

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## Outline

- Some general differences between local and average structure
- Brief introduction to EXAFS
- Examples
  - Cu-doped ZnS
  - Thermoelectric clathrates
  - Manganites
  - $\text{Ba}_3\text{CuSb}_2\text{O}_9$

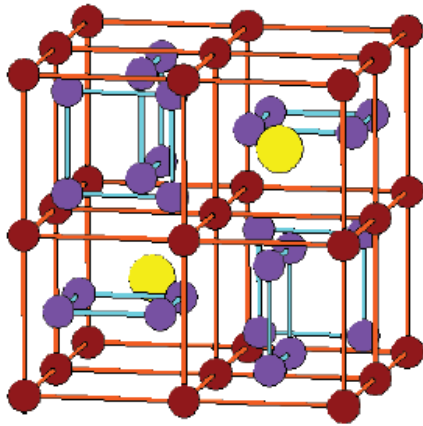
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## First: when do local and average structure agree?

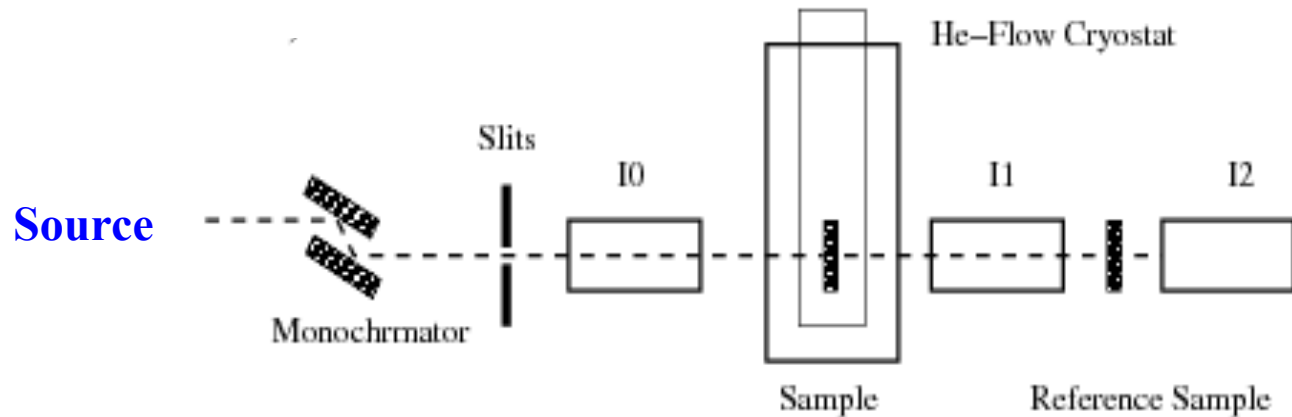
- **Average structure – a series of points forming a “unit cell” that has translational and rotational symmetry. Assign atoms to these points**
- Simple crystal structures: Cu metal, KCl, Si, CaMnO<sub>3</sub>, etc. with no dopants (exceptions: BaTiO<sub>3</sub> PE phase, PbTe?)
- When there are no shared sites as for Ba<sub>8</sub>Ga<sub>16</sub>Sn<sub>30</sub> or Ba<sub>3</sub>CuSb<sub>2</sub>O<sub>9</sub>; i.e. if a crystallographic site is occupied by two different atoms – say 50%-50% -- then average and local structures can differ.

# Simple example when local and average structures differ.

- Consider a mixture of two materials such as KBr and KI – can mix in any proportion. Average crystal is cubic and average bond length from diffraction increases linearly from KBr to KI.
- EXAFS shows two distinct bond lengths K-Br (short) and K-I (long); the average bond-length is the weighted average of these two bond lengths.
- Will talk about more complex systems, with dopants, and where two atoms share a given site

# Experimental set-up for X-ray spectroscopy

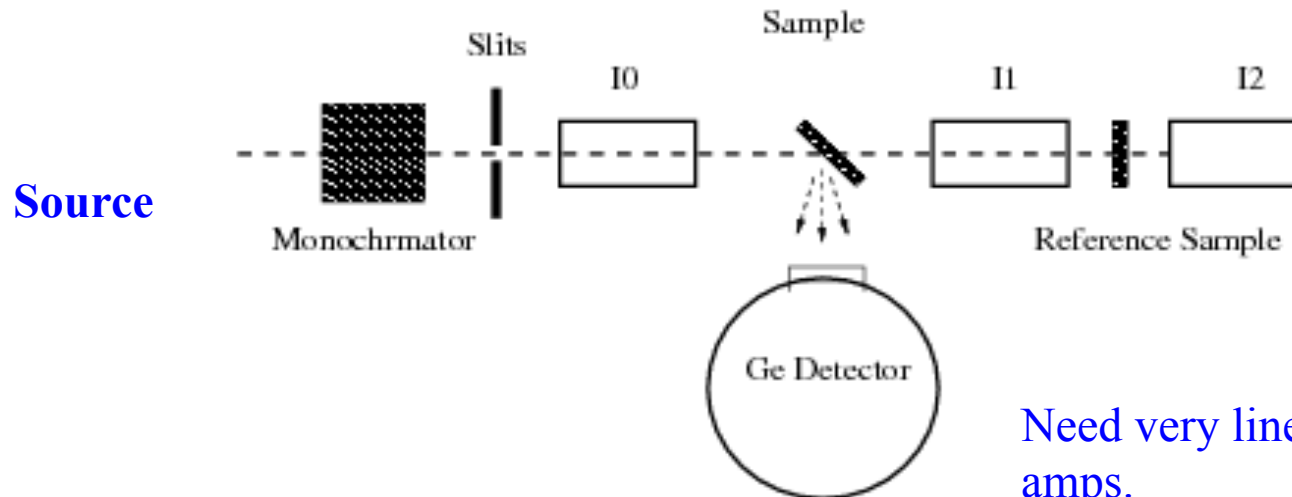
Side View



Typical set-up for transmission

$$\mu t = \ln I_0/I_1$$

Top View



Set-up for fluorescence detection.

For low concentrations

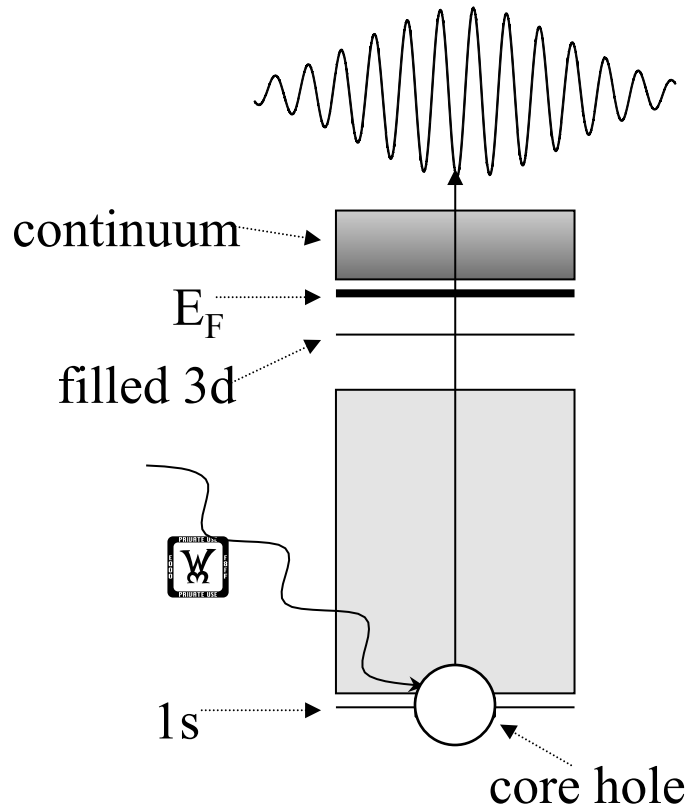
$$\mu \sim I_f$$

For concentrated samples & thick samples, need a correction.

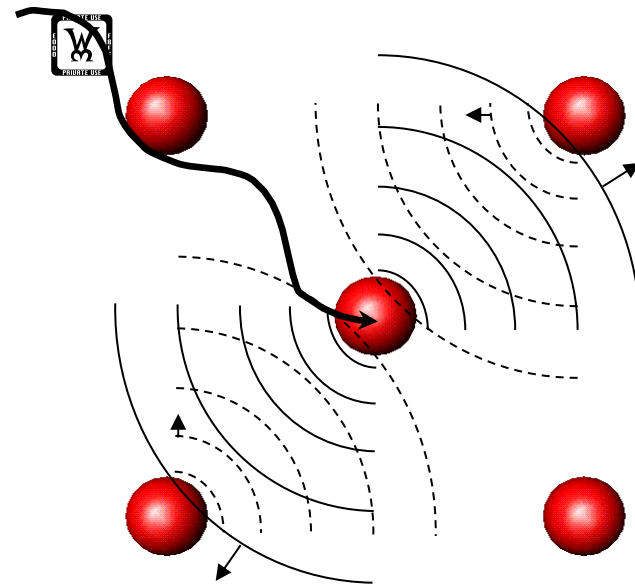
Need very linear detectors and amps.

# X-ray Absorption Spectroscopy

## Extended X-ray Absorption Fine structure (EXAFS)



Time scale –  $10^{-15}$  sec.

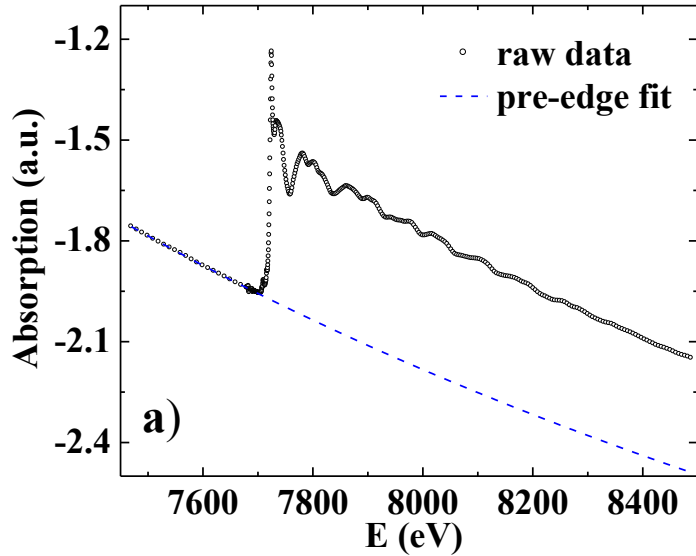


*“I was brought up to look at the atom as a nice hard fellow,  
red or grey in colour according to taste.”*

*- Lord Rutherford*

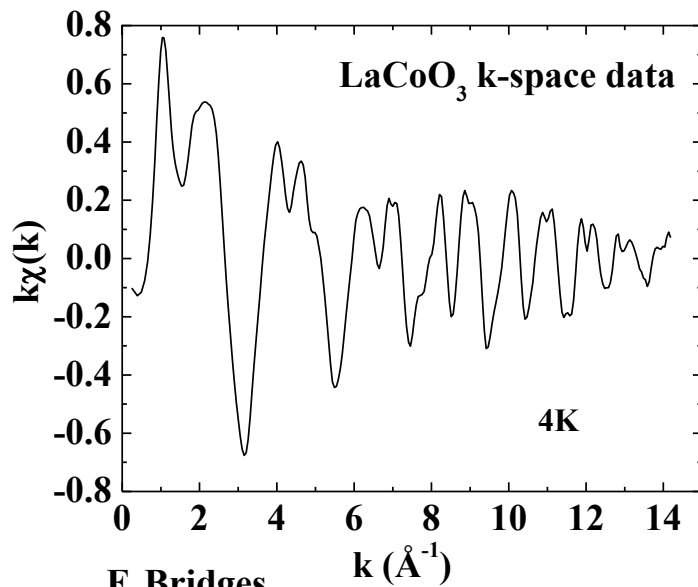
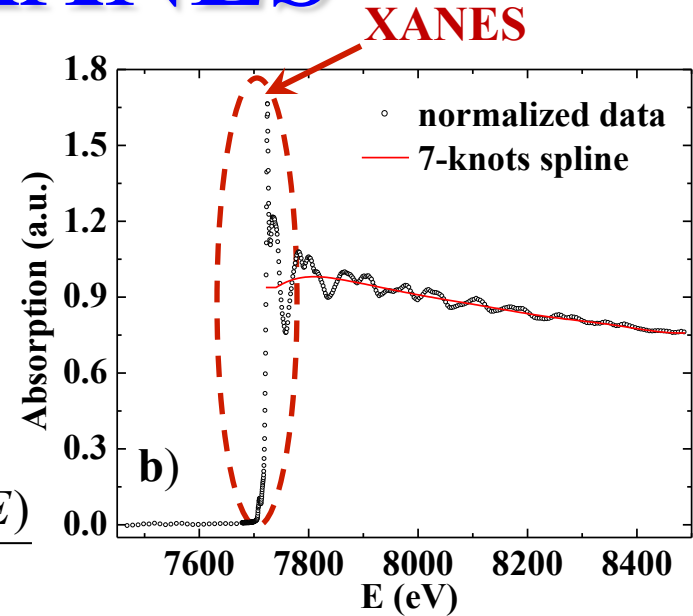
# EXAFS and XANES

$$\mu t = \ln I_0/I_1$$



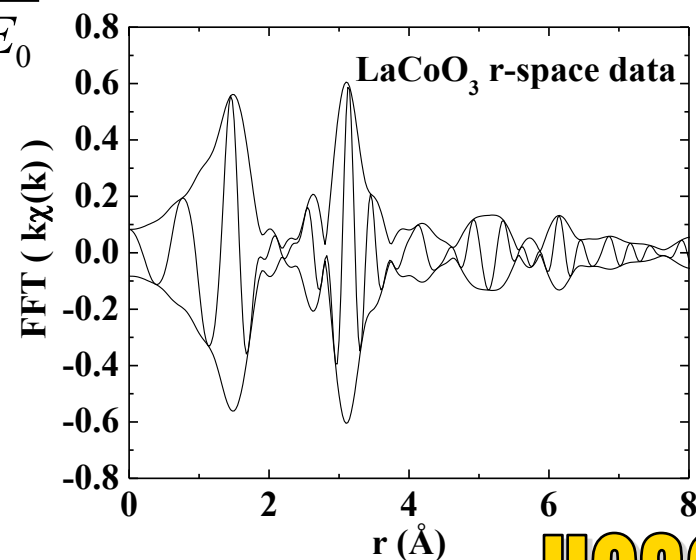
Dotted background constrained by Victoreen Equ. and the step height.

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)}$$



$$k = 0.512\sqrt{E - E_0}$$

FT →



# Simple model for absorption

- Use Fermi's golden rule  $\mu \sim \langle f | (\boldsymbol{\varepsilon} \cdot \mathbf{r})^2 | i \rangle$
- Core hole is very small  $a_o/Z$ ;  $e^{i\mathbf{k} \cdot \mathbf{r}} \approx 1$
- Final state  $f$  is modified by backscattering + interference of outgoing and backscattered waves, i.e.  $f = f_o + \Delta f$
- Can write  $\mu = \mu_o(1+\chi)$ ; or

$$\chi = (\mu - \mu_o) / \mu_o$$

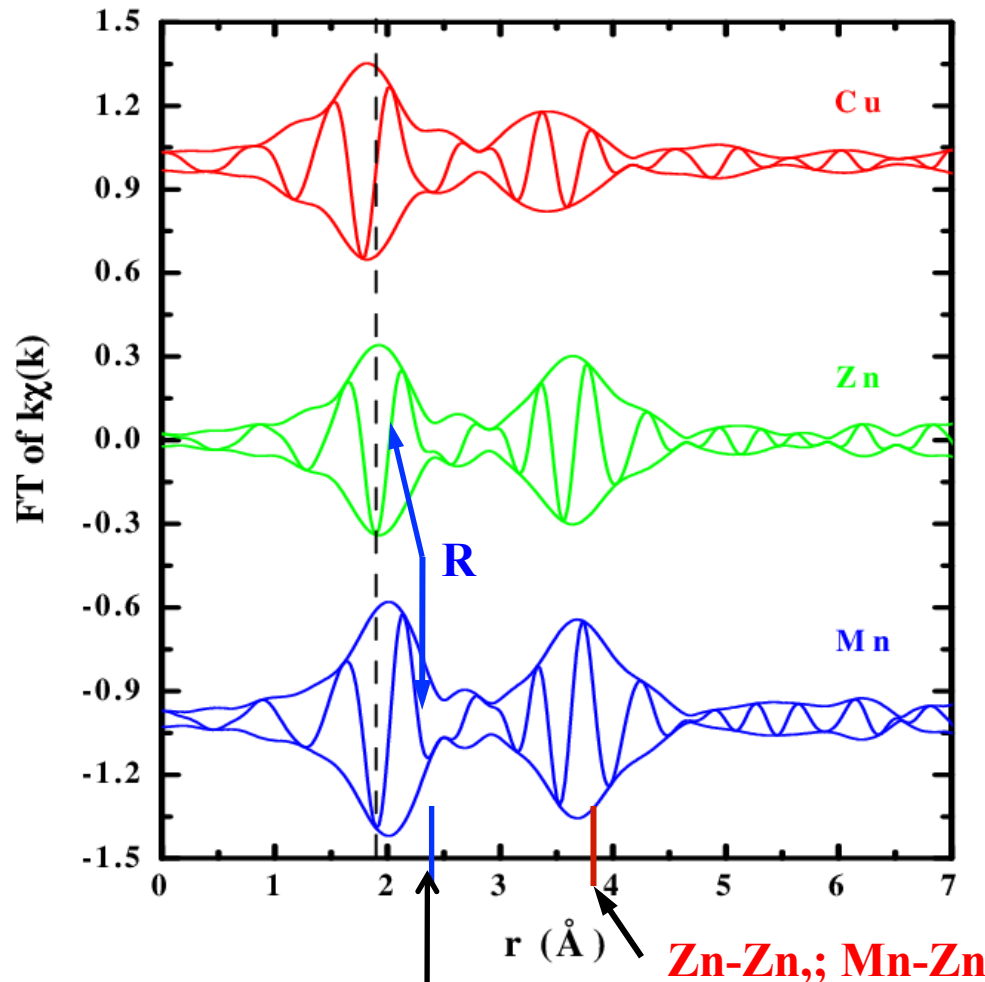
$\mu$ ,  $\mu_o$ , and  $\chi$  are all energy dependent

convert to  $k$ ;  $k = 0.512 (E - E_o)^{1/2}$

$$\chi(k) \approx S_o^2 \sum_i N_i (\hat{\boldsymbol{\varepsilon}} \cdot \hat{\mathbf{r}})^2 |f(\boldsymbol{\pi}, k)| e^{-2r/\lambda(k)} e^{-2k^2\sigma_i^2} \frac{\sin[2kr_i + 2\delta_c(k) + \delta_b(k)]}{kr_i^2}$$

$$k\chi_1(k) \approx A_1(k) e^{-2k^2\sigma_1^2} \sin(2kr + \phi)$$

# Describing EXAFS FT Spectra (cubic ZnS:Cu,Mn)



- Fast oscillation – real part ,  $R$ , of transform
- Imaginary part ,  $I$ , not shown.
- **NOTE:** shape of peaks determined mostly by **backscattering amplitude**  $|f(\pi, k)|$
- Envelope function  $\pm\sqrt{(R^2 + I^2)}$
- **Fit to  $R$  and  $I$**
- Peaks in EXAFS shifted in position by well known amount -  $\Delta r$ , from phase shifts  $\delta_c$  and  $\delta_b$  in term

$$\sin[2kr + 2\delta_c(k) + \delta_b(k)]$$

$$2\delta_c(k) + \delta_b(k) \approx -2\Delta r k + f(k)$$

Interference between peaks.

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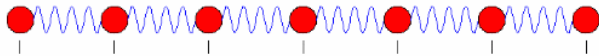
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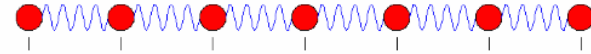


# Different Phonon Modes

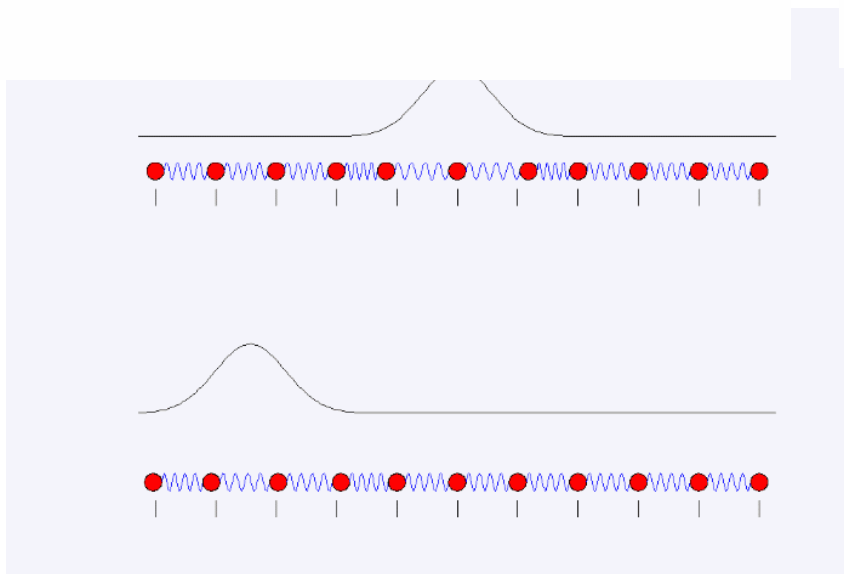
<http://physics.ucsc.edu/~bridges/simulations/index.html>



Long Wavelength Acoustic Phonon



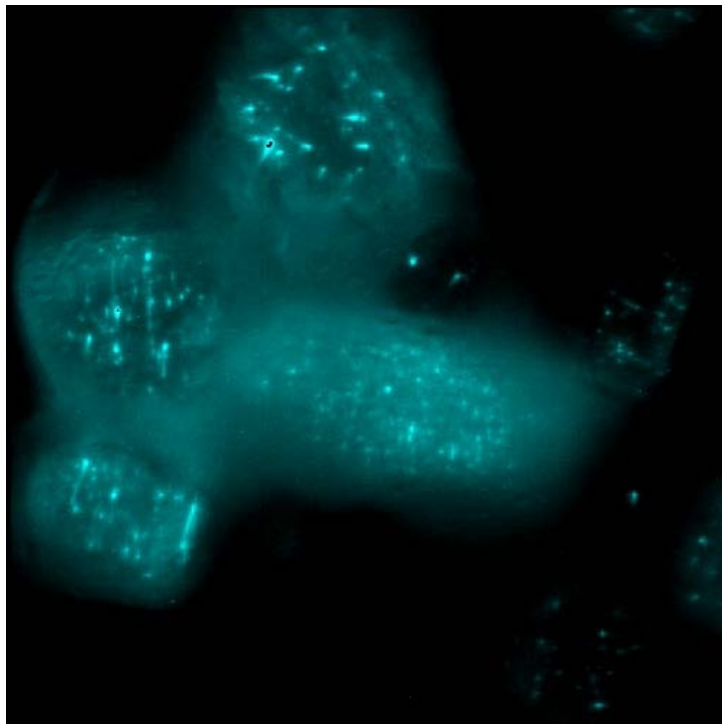
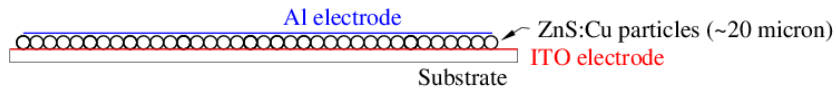
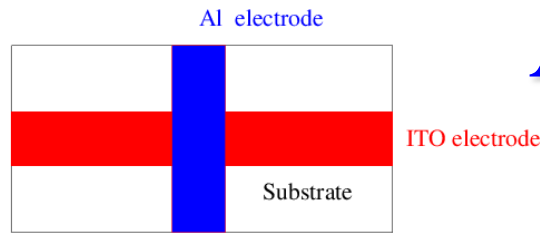
Short Wavelength Optical Phonon



Polaron transportation

**Motions of neighboring atoms are correlated**

# AC Electroluminescence and solid state lighting



Four ZnS:Cu,Cl particles (20-30  $\mu\text{m}$ )  
under AC excitation; 100 V square wave.

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- ZnS doped with Cu and Cl has the unusual property that it luminesces under AC voltage excitation (e.g. 100V across 50  $\mu\text{m}$ ) but does not luminesce using DC voltages.
- Further the luminescence is not uniform but emanates from many tiny points < 1  $\mu\text{m}$ .
- Cu is not soluble in ZnS and nanoprecipitates of  $\text{Cu}_x\text{S}$  form; for Cu concentrations of 0.15% Cu (75% precipitate, 25% Cu dopants).
- $\text{Cu}_x\text{S}$  nanoparticles are thought to be **needle-like** in nature and **enhance the local E-field** when the voltage is switched.

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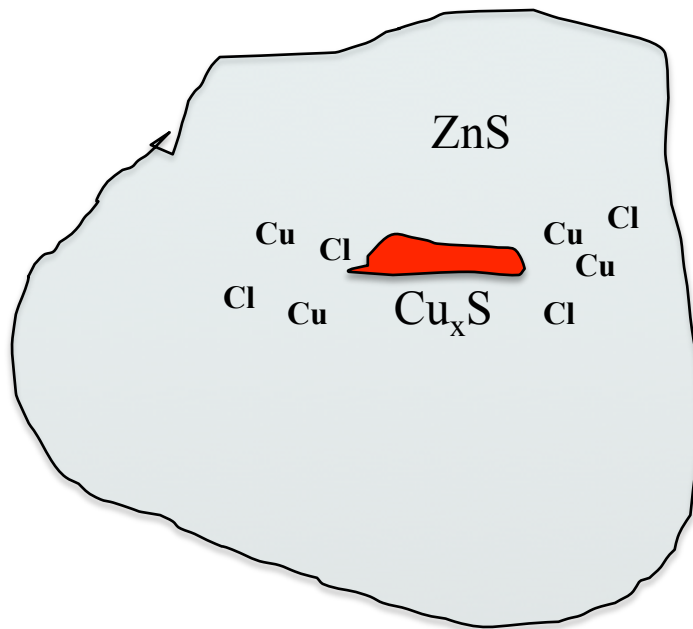
J. Phys.: Condens. Matter , 22,  
055301 (2010); Phys. Rev. B , 75,  
075301 (2007); J. Lumin. 134, 251  
(2013)

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# Current model for AC EL ZnS:Cu,Cl

CuS has a different crystal structure – layered.

Fischer 1960's



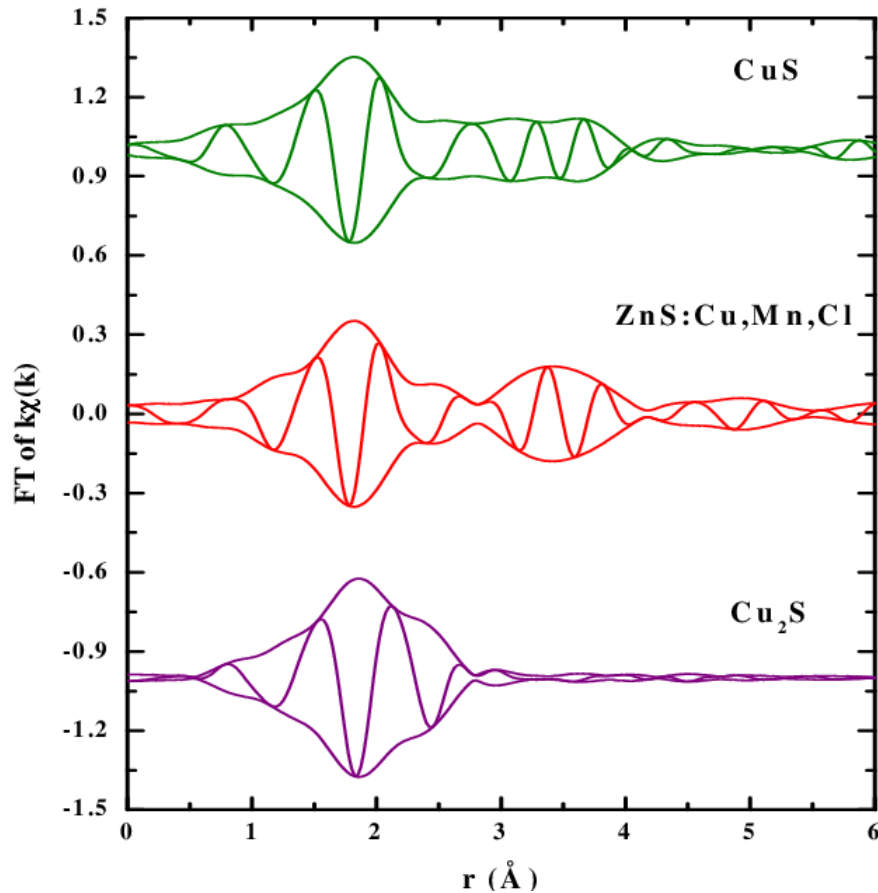
- $\text{Cu}_x\text{S}$  precipitate (NP); conductor in an insulating host. Small – nm scale.
- Isolated Cu – hole traps
- Cl atoms -- shallow electron traps.
- During field switching, large fields at sharp tips – injects holes and electrons on opposite ends of NP.
- Injected electrons/ holes trapped; next time field is switched, then electron-hole recombination occurs emitting light.

Cu plays *two* roles, part of  $\text{Cu}_x\text{S}$  and isolated Cu is hole trap

# Some Unanswered Questions

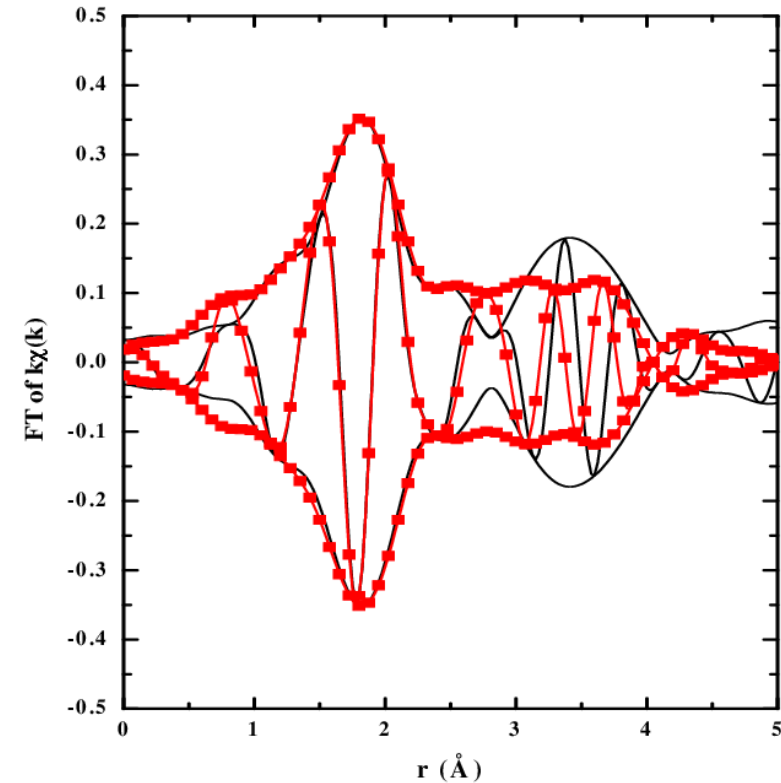
- **Local structure problems for bulk material:**
  - What is the  $\text{Cu}_x\text{S}$  structure  $\text{CuS}$  or  $\text{Cu}_2\text{S}$ ?
  - Can we determine the environment about isolated Cu atoms?

# $\text{Cu}_x\text{S}$ is CuS-like to $2.6\text{\AA}$



Structure beyond  $4\text{\AA}$  for ZnS:Cu suggests CuS epitaxially bonded to ZnS

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Substitutional Cu in ZnS has a very small shoulder in  $2\text{-}2.5\text{\AA}$  region,  $\text{Cu}_2\text{S}$  has a large shoulder; CuS has a moderate shoulder.

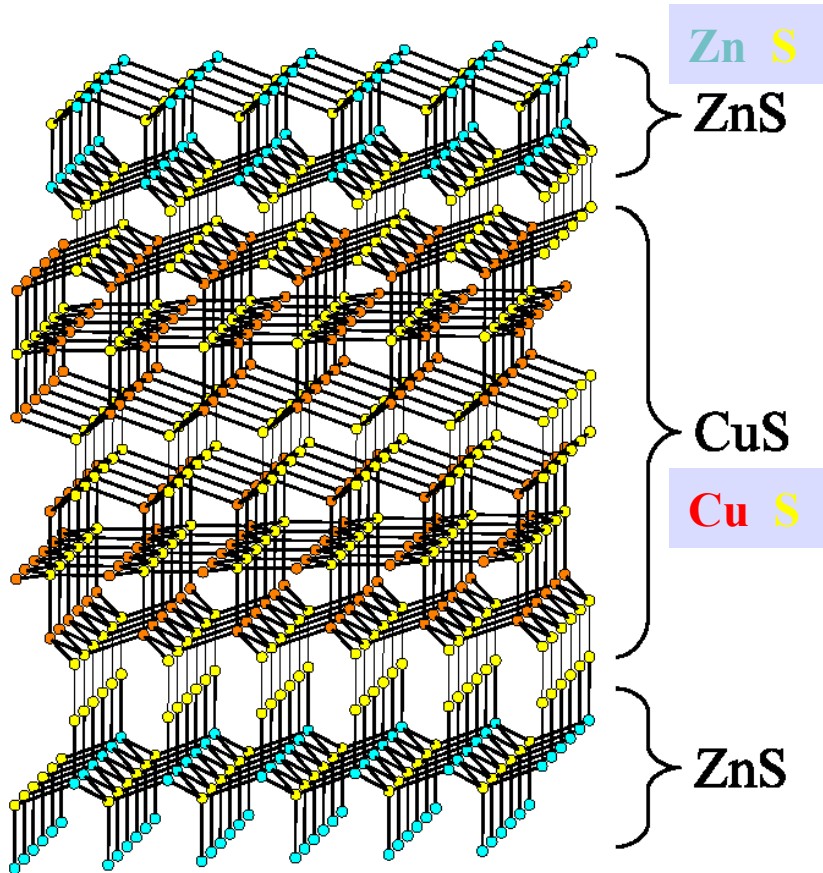
Fits to the CuS data with only tiny change in broadening and  $r$ .

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J. Phys.: Condens. Matter, 22,  
055301 (2010); Phys. Rev. B, 75,  
075301 (2007)

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# CuS layer in the 111 plane of ZnS



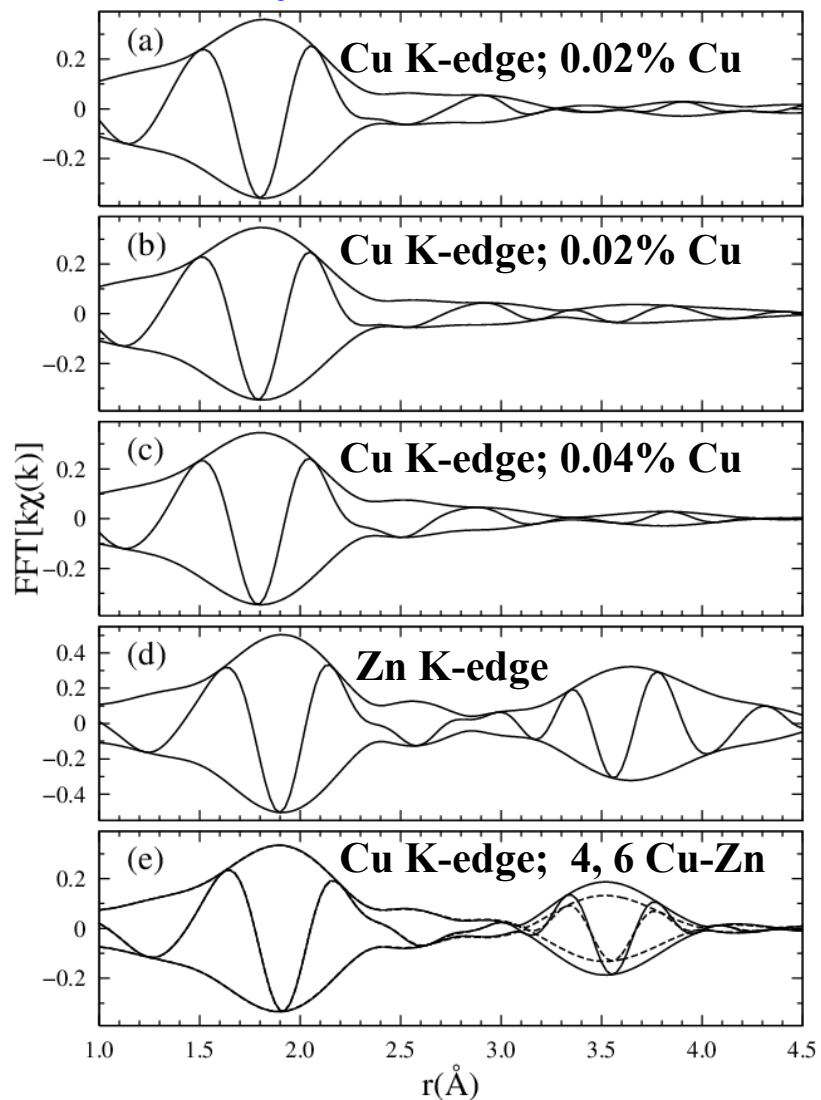
One c-axis unit cell plus one S-S double bond =  $18.4\text{\AA}$   
Two 111 cube diagonals =  $18.7\text{\AA}$ ; 1.6% mismatch  
Along interface, S-S distance in CuS is  $3.80\text{\AA}$   
while in ZnS (111 plane) S-S distance =  $3.825\text{\AA}$ ,  
only a 0.66% strain.

*Phys D.: Appl. Phys.*, **44**, 205402 (2011)

# Isolated Cu defect in ZnS

- **Problem: Cu nearly insoluble in ZnS – solubility limit near 0.04%.**
- **Forms CuS precipitates: at 0.15% Cu, 75% of Cu in precipitates; only ~ 25% Cu are isolated defects.**
- **Need very low concentrations to have only single defects.**
- **Collaborators make Cu doped ZnS nanoparticles. Optical fluorescence changes with added Cu.**
- **Used low concentrations 0.02 and 0.04%; for these concentrations and NP ~ 4 nm, < 1 Cu atom per nanoparticle on average – avoids clustering.**
- **Observe same EXAFS signal for many samples including up to ~ 0.4%**

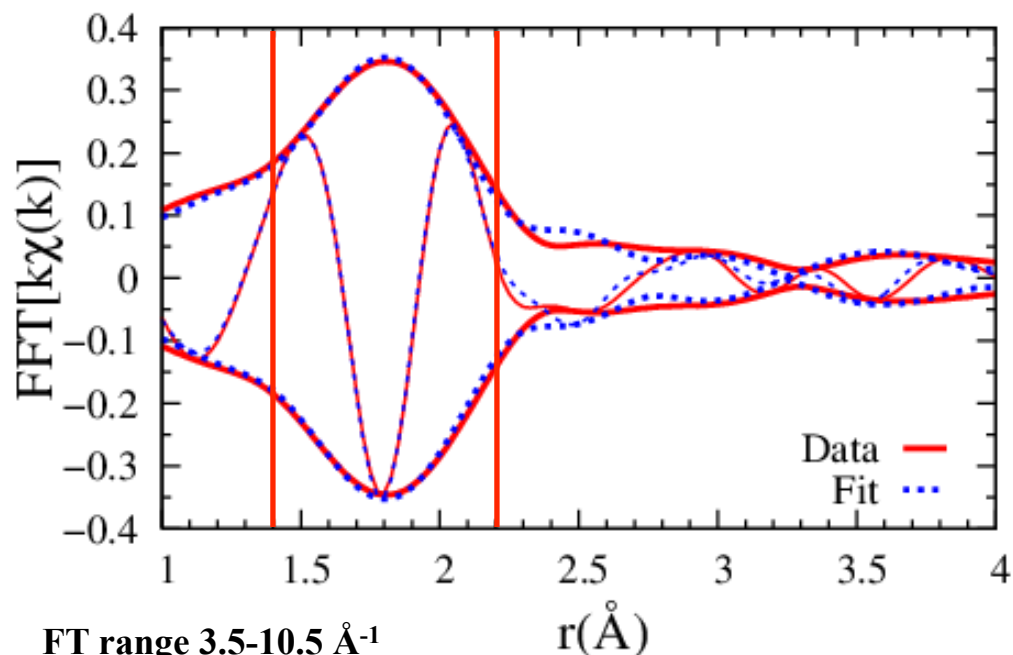
10K



Observe same Cu signal for many samples including up to ~ 0.4% Cu; Cu-Zn peak (12 nbrs) suppressed, Cu-S bond short

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## Fit of Cu data



FT range 3.5-10.5 Å<sup>-1</sup>

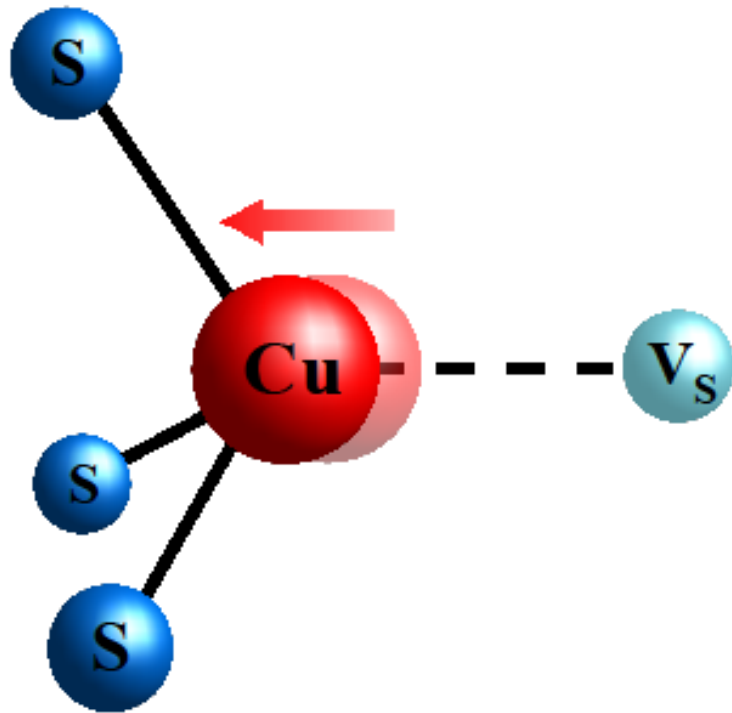
- Used experimental Cu-S standard function for first fits; R-space fit 1.4-2.2 Å.
- Number of S neighbors ~ 3.2 and Cu-S distance short by 0.07-0.08 Å.

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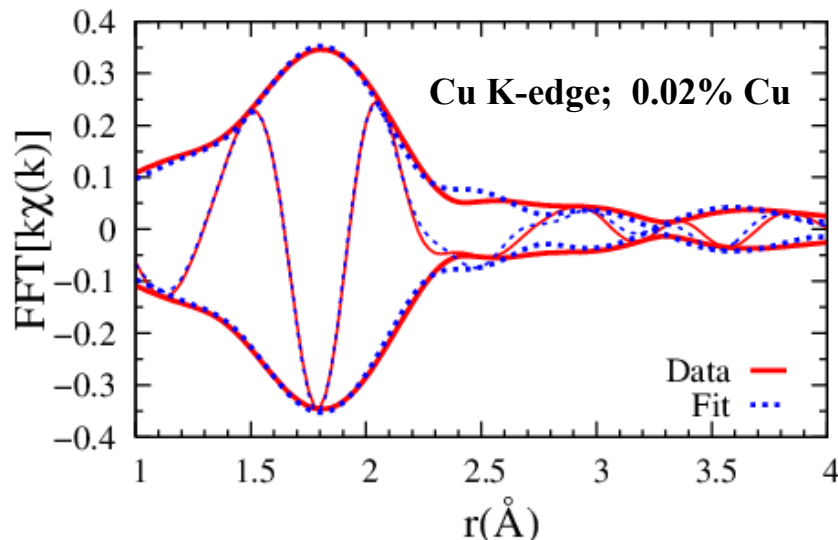
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# New off-center Cu defect in ZnS:Cu



- Only  $\sim 3.2$  S neighbors – must be a S vacancy for many Cu atoms
- Cu is  $\text{Cu}^+$  in ZnS;  $V_S$  can compensate two  $\text{Cu}^+$  defects.
- If Cu moves toward 3 S, moves away from vacancy; net displacement  $\sim 0.24\text{\AA}$  from  $V_S$ .
- Off-center displacement splits Cu-Zn into three widely split peaks.
- Constrained the Cu-Zn distances to the shortened Cu-S peak for a long r-space fit 1.2-3.8 $\text{\AA}$ .



Nanoscale DOI: 10.1039/c1nr10556f

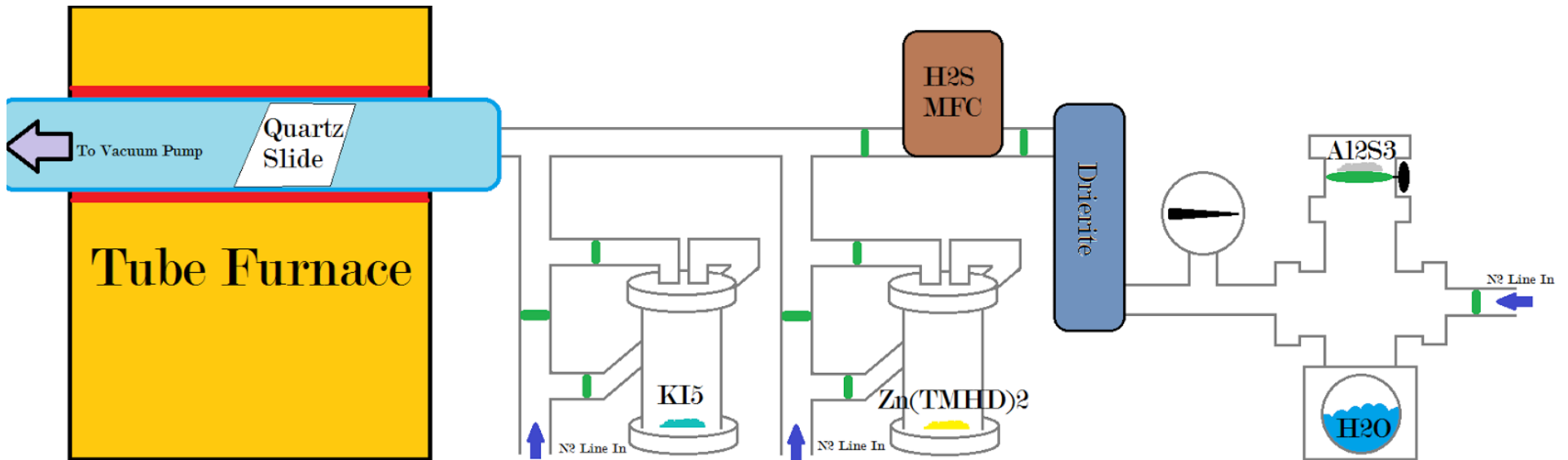
# Solar Cell Applications

- Current technologies involve expensive processing and expensive/rare materials (eg Cd, In )
- Need materials made of common materials – one such material is  $\text{Cu}_2\text{ZnSnS}_4$  – but difficult to control stoichiometry (ratio of components).
- One proposed method to combine Cu Zn Sn and S is via atomic layer deposition – ALD.
- First need to characterize films of ZnS  $\text{Cu}_x\text{S}$  etc including multilayers – use EXAFS.

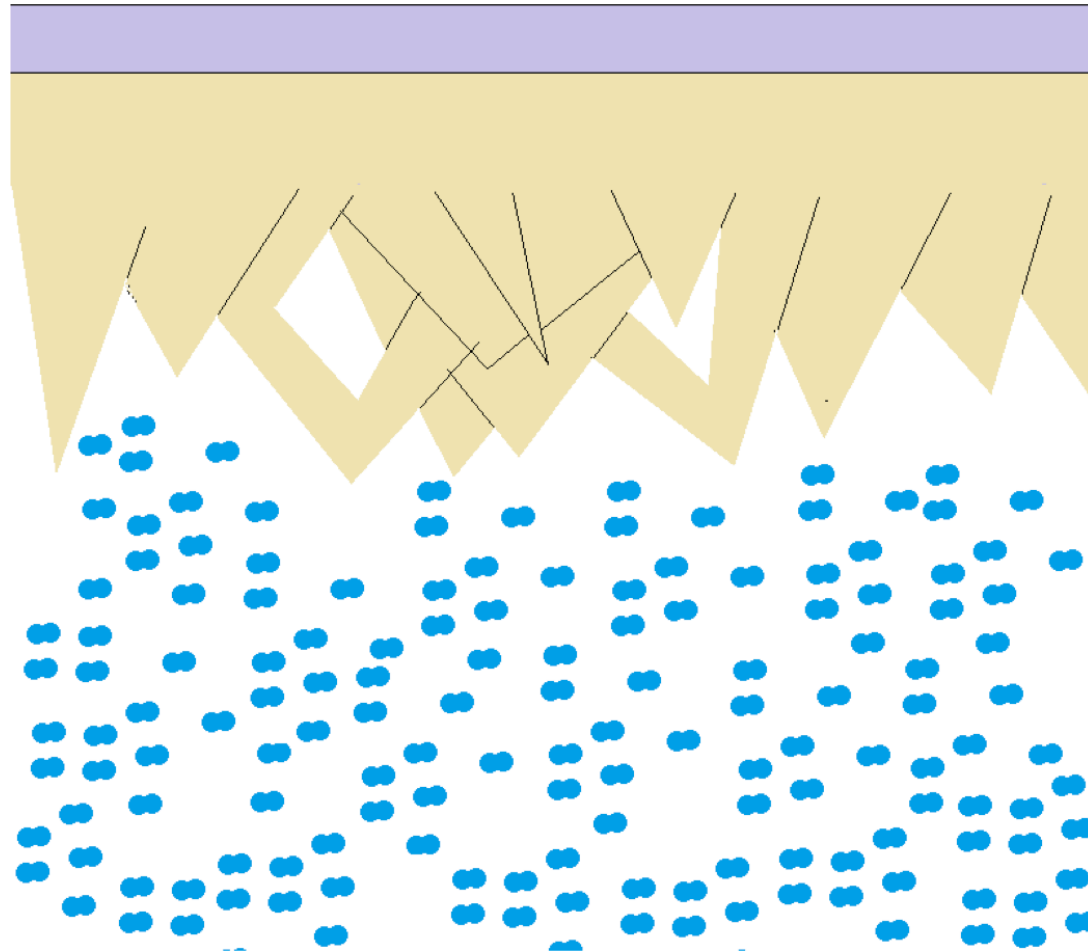
# Atomic Layer Deposition

- **Vacuum-based deposition process**
- **Similar to CVD, but breaks reaction into two half-reactions on the substrate itself**
- **Surface is sequentially exposed to gas-phase precursors containing components of final product**
- **Good deposition penetration=fills holes in nanostructured interface, highly conformal**
- **Thickness of resulting film is controlled by number of cycles**

# Apparatus Diagram

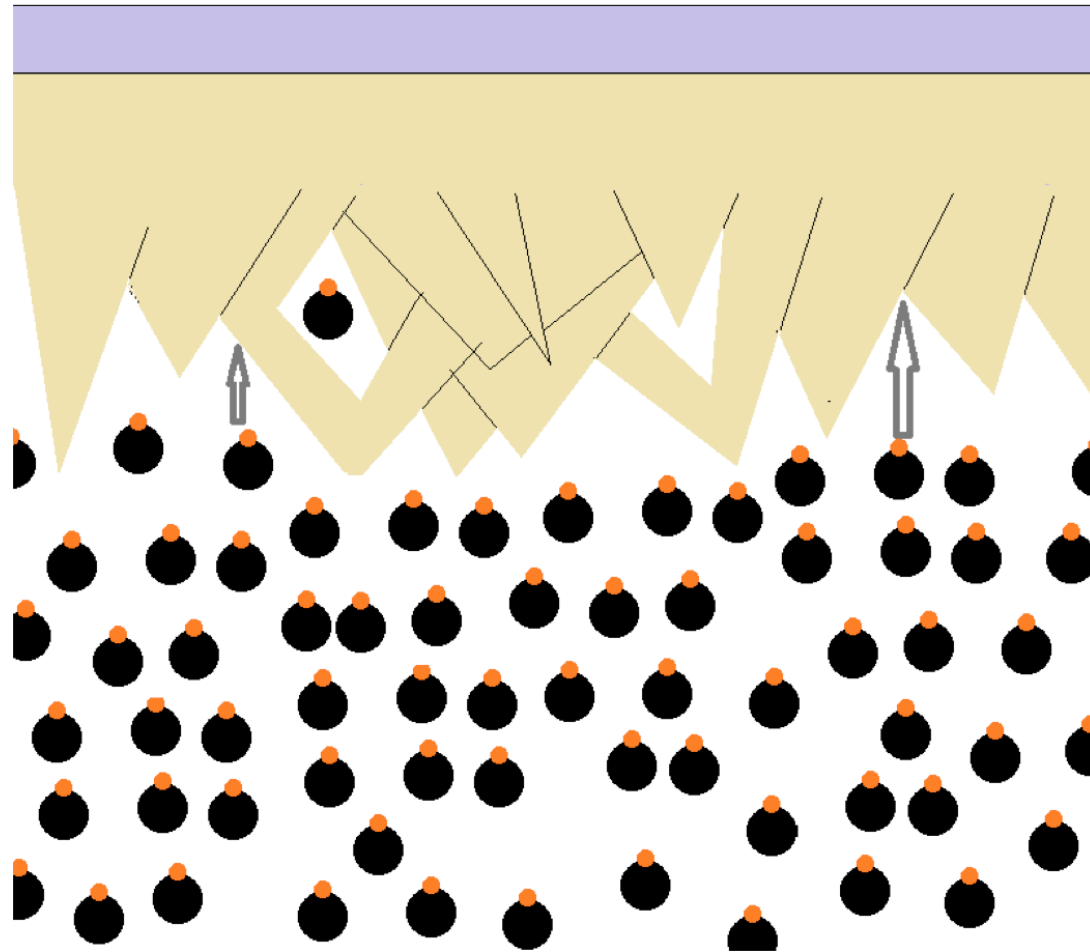


# Visualizing ALD: Purge



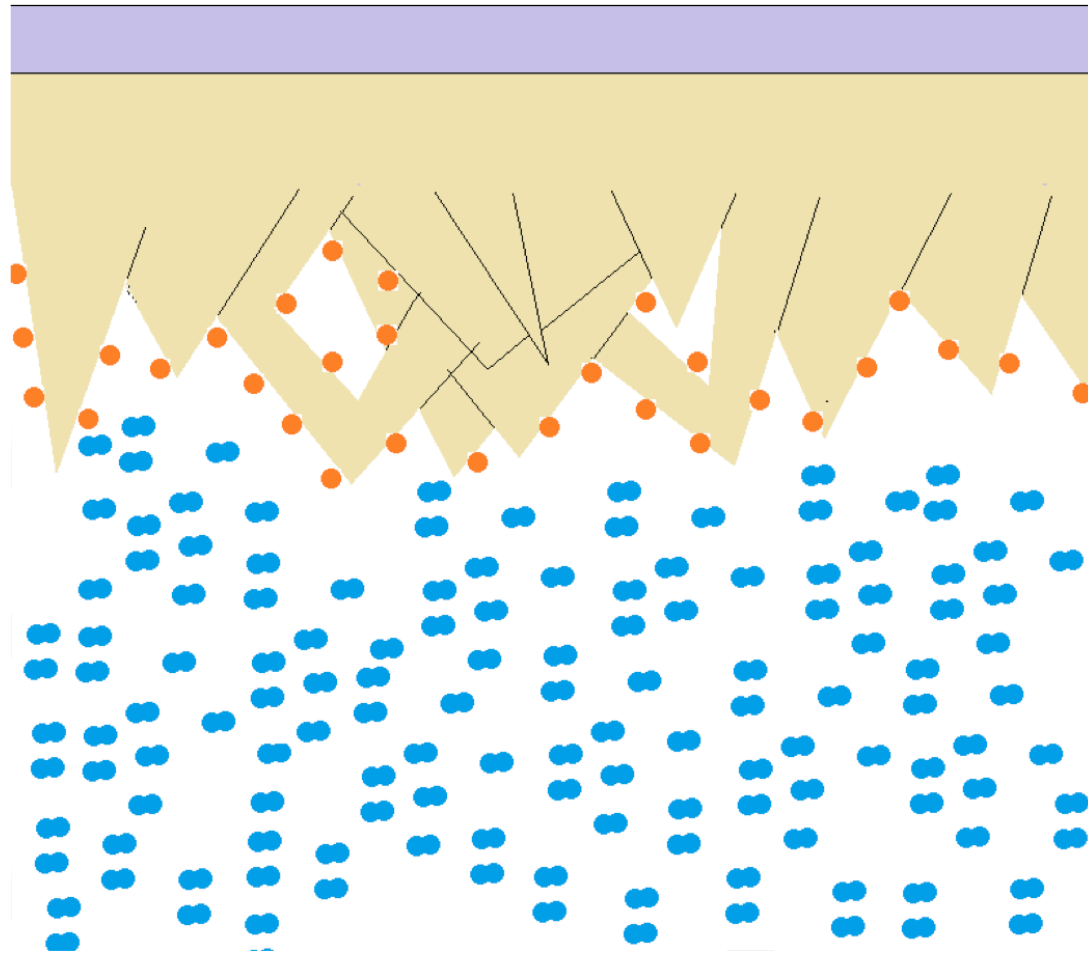
(Images by A. Short)

# Visualizing ALD: Metal Precursor



(Images by A. Short)

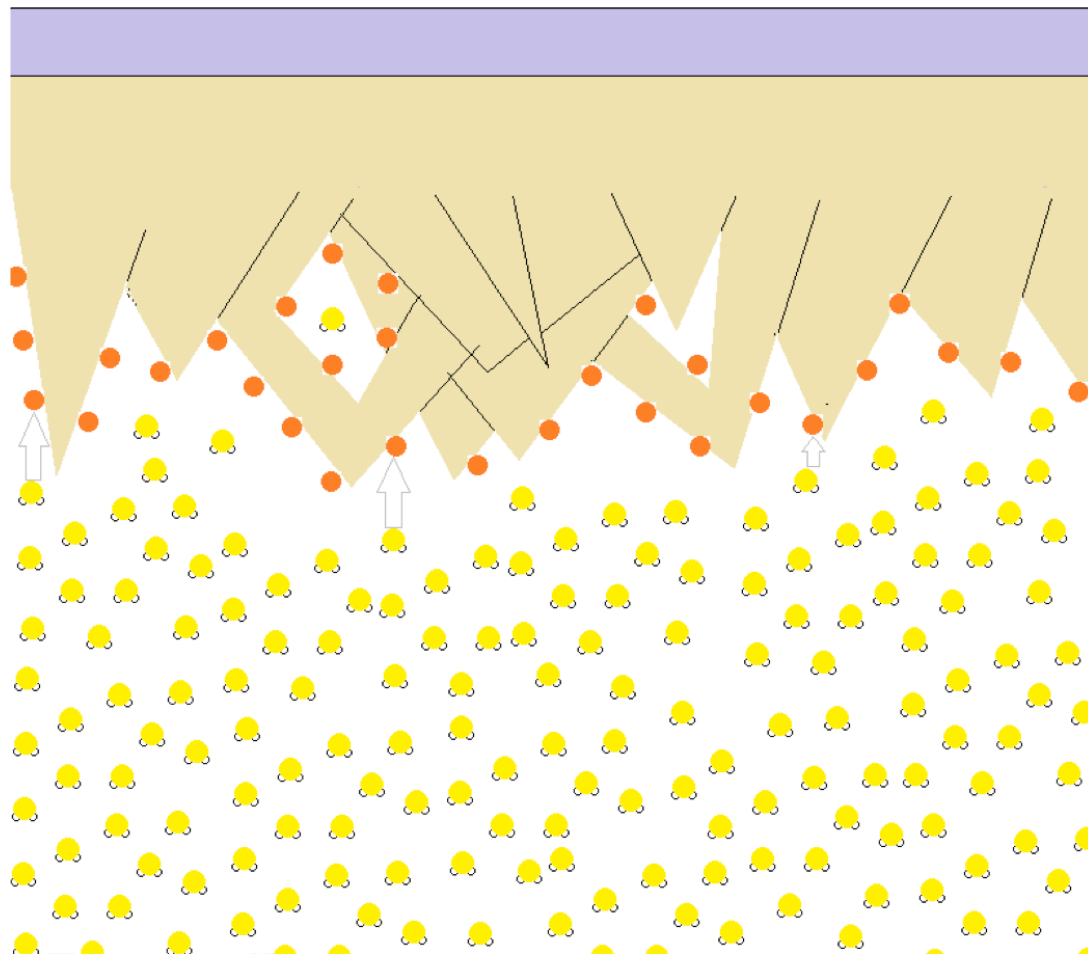
# Visualizing ALD: Purge



(Images by A. Short)

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# Visualizing ALD: H<sub>2</sub>S



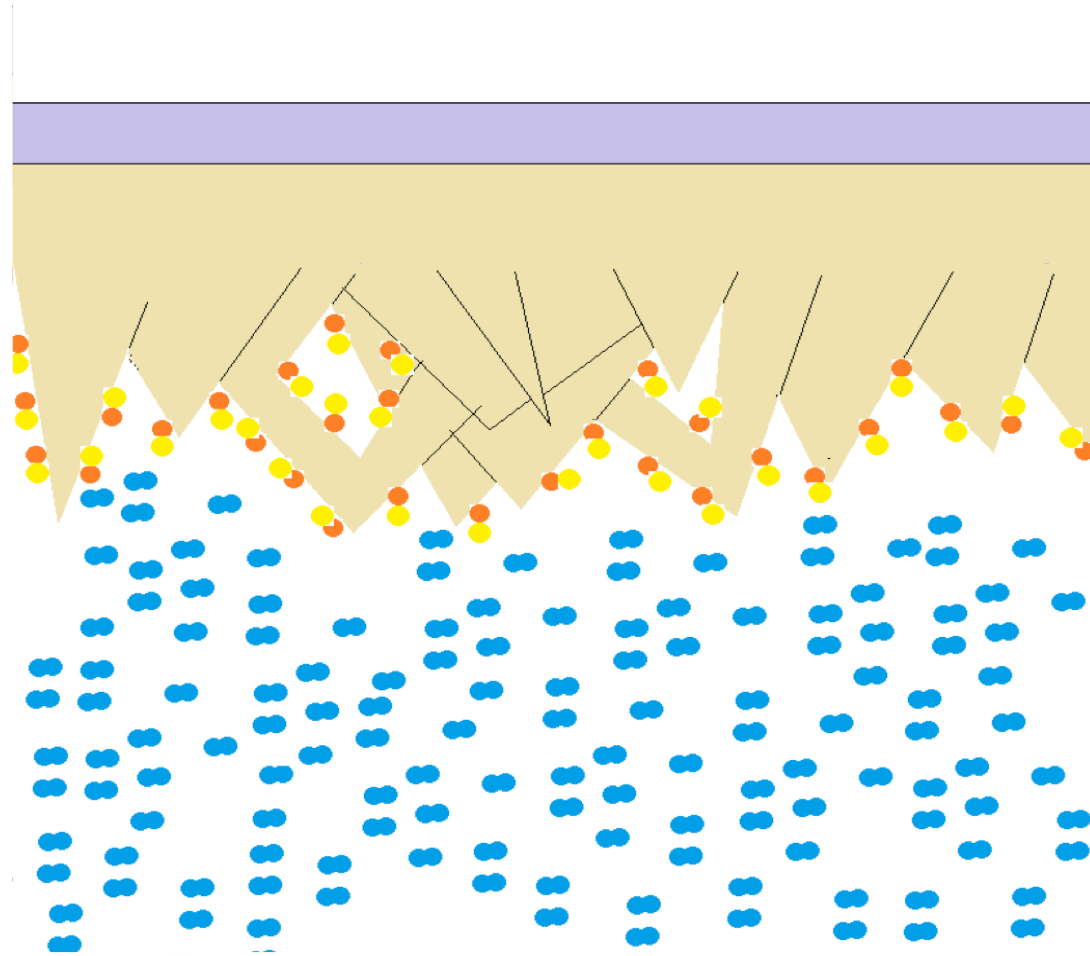
(Images by A. Short)

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# Visualizing ALD: Purge

1 cycle = 1 partial monolayer

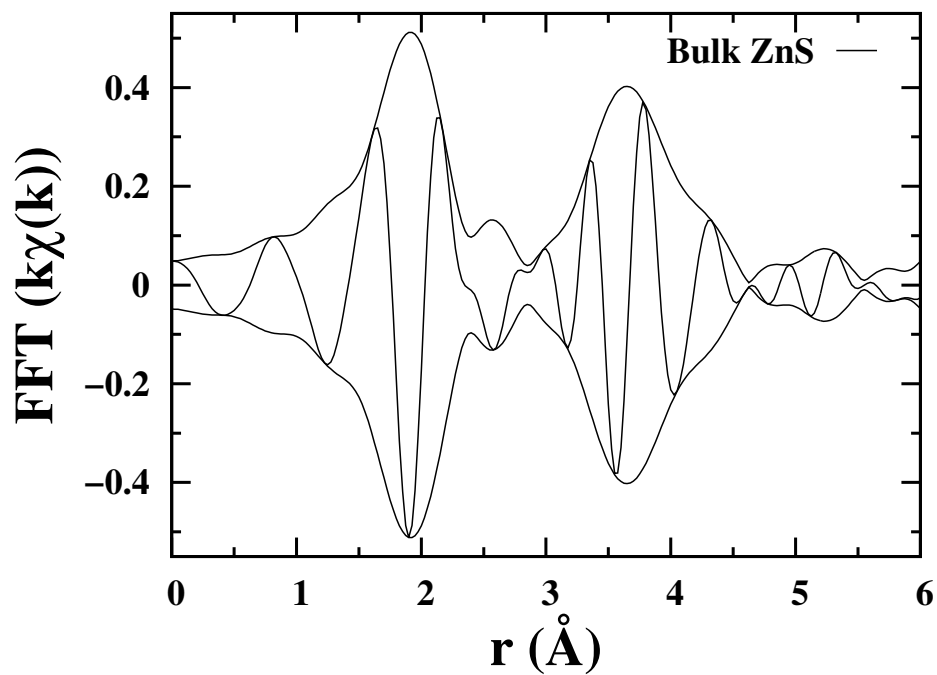


(Images by A. Short)

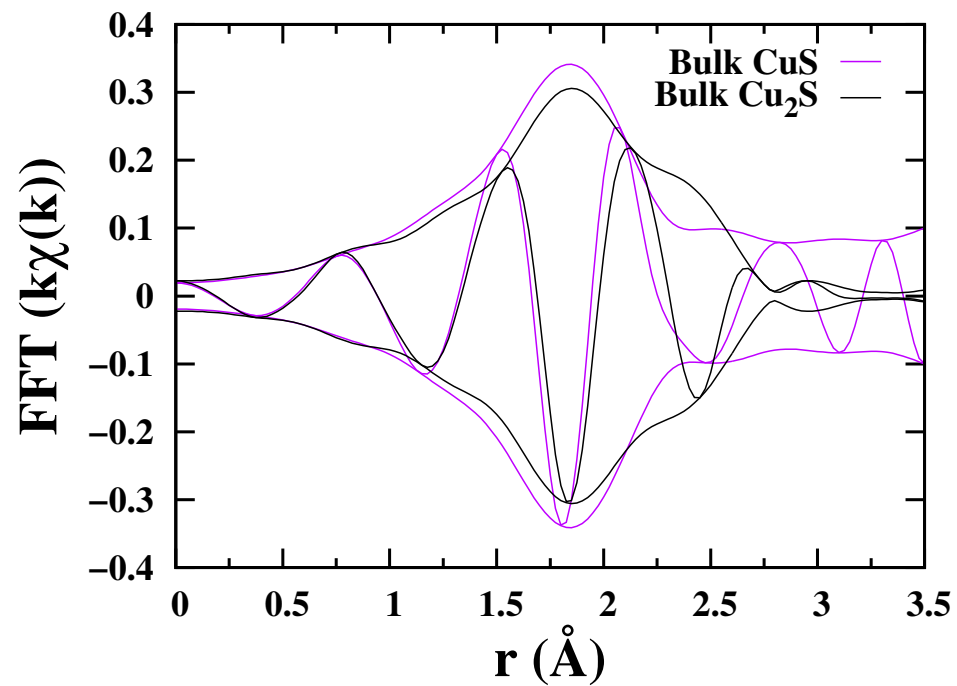
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# EXAFS Results for Bulk

## Bulk ZnS



## Bulk CuS & Cu<sub>2</sub>S



# Sample Details

Precursors	
Zn	Zn (TMHD)2
Cu	Cu (TMHD)2
S	H <sub>2</sub> S

Process	Time (s)
Purge (N <sub>2</sub> )	25
H <sub>2</sub> S	5
Purge (N <sub>2</sub> )	25
Zn, Cu precursor	2
<b>TOTAL</b>	<b>57</b>

Sample		# of Cycles	Time/cycle (s)	Fluorescence Peak Height
330-1		10:10	2:2	2 : 1
517-4		10:20	2:2	1 : 3
517-2		10:10	2:4	1 : 2
822-4	Extra thick layers (ZnS first)	50:50	2:2	1 : 1.3
822-3	Cu <sub>x</sub> S base, then multilayers	100 Cu <sub>x</sub> S, 10:10	2:2	1 : 3.3

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(All ratios are

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# ZnS/Cu<sub>x</sub>S Multilayer Films

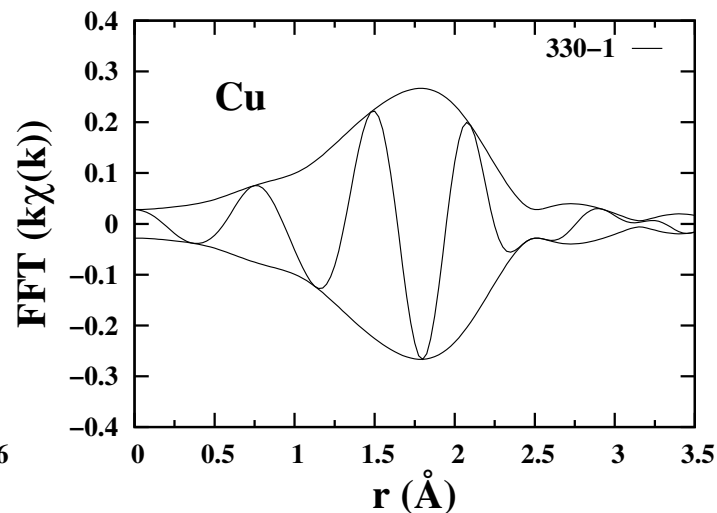
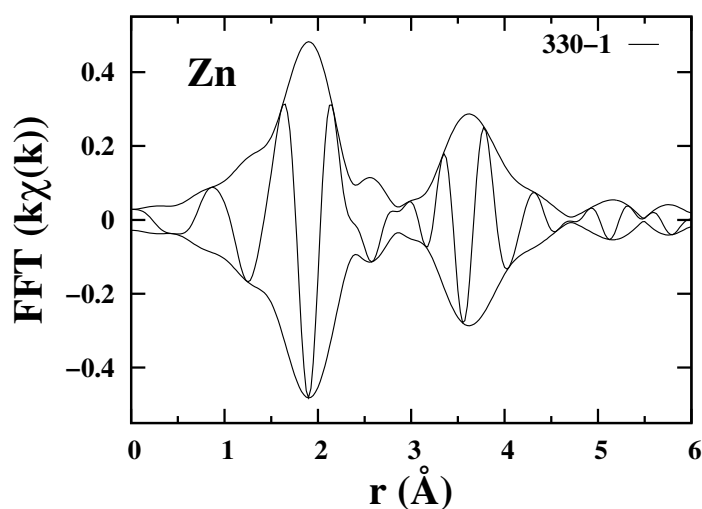
330-1

# of cycles

10:10

Time/cyc

2:2



R = 2:1

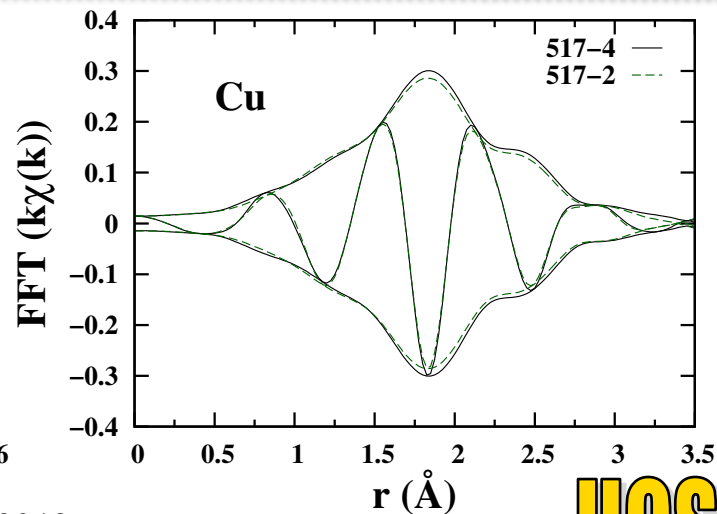
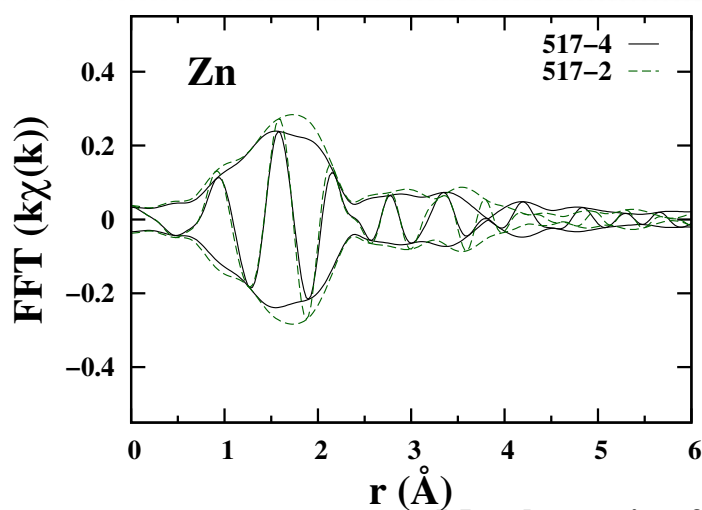
517-2, 517-4

# of cycles

10:20 / 10:10

Time/cyc

2:2 / 2:4



R = 1:3

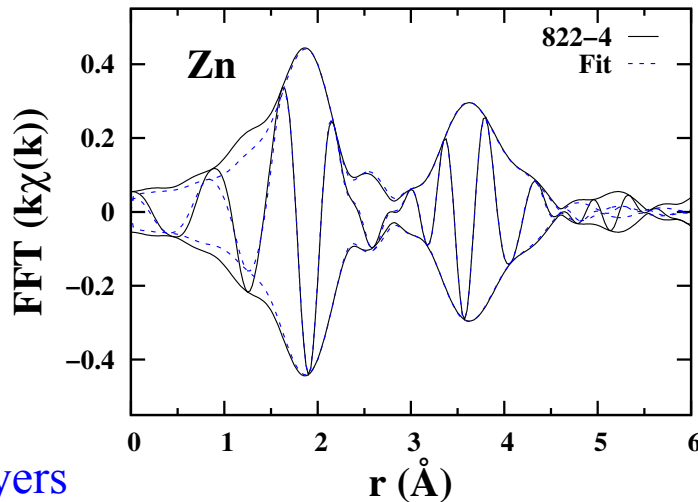
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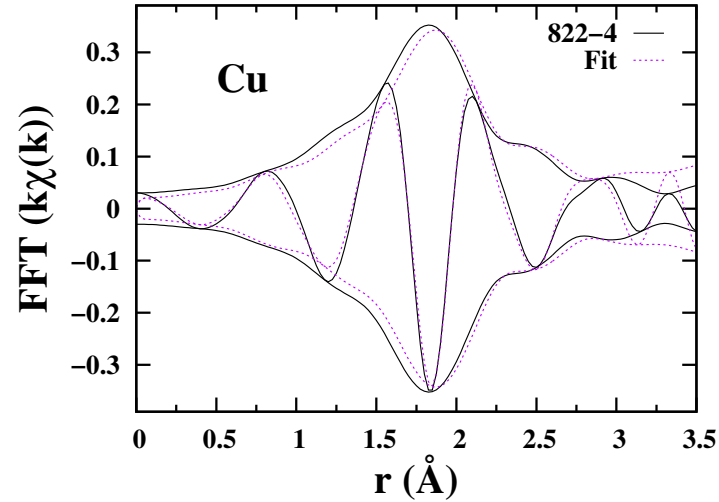
# ZnS/Cu<sub>x</sub>S Multilayer Films

822-4

ZnS first,  
~10nm layers

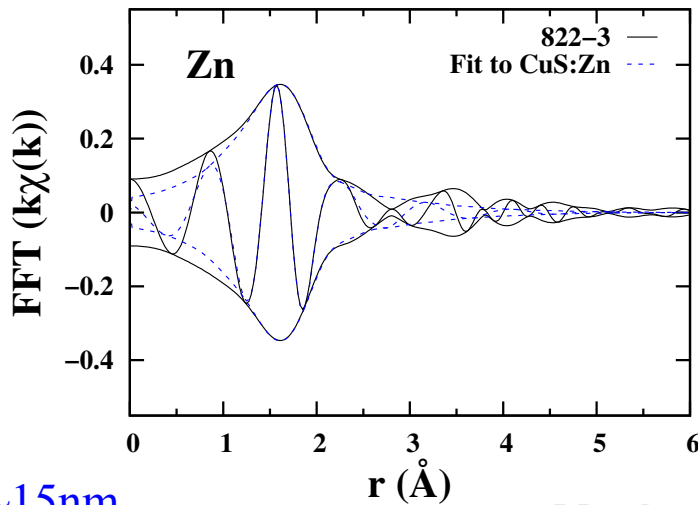


R = 1:1.3

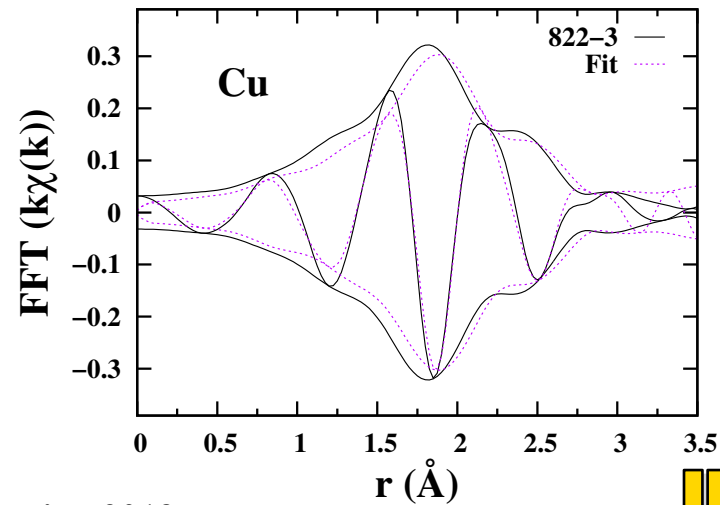


822-3

Cu<sub>x</sub>S base ~15nm,  
~2-3nm layers



R = 1:3.3

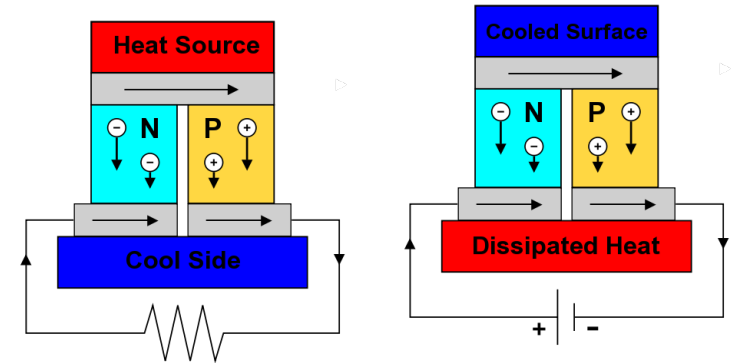


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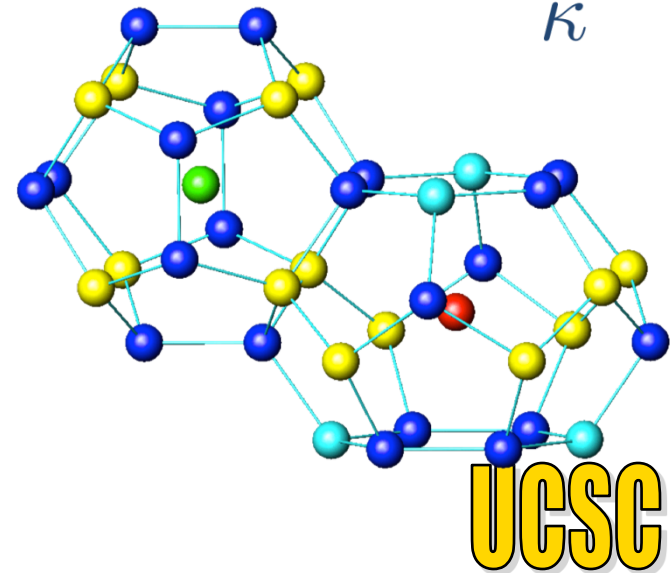
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# Background: Thermoelectric Materials

- Can be used for heating or cooling.
- Can generate electricity from waste heat (improving efficiency).
- Good thermoelectric materials have high electrical conductivity and low thermal conductivity.
- Clathrates are good because they have cage structures with rattler atoms that decrease thermal conductivity.
- PbTe:Tl surprisingly good.



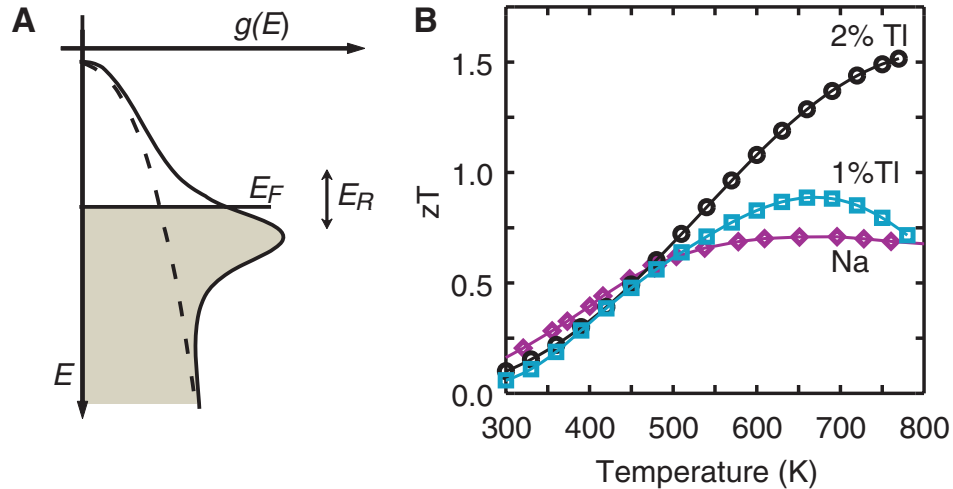
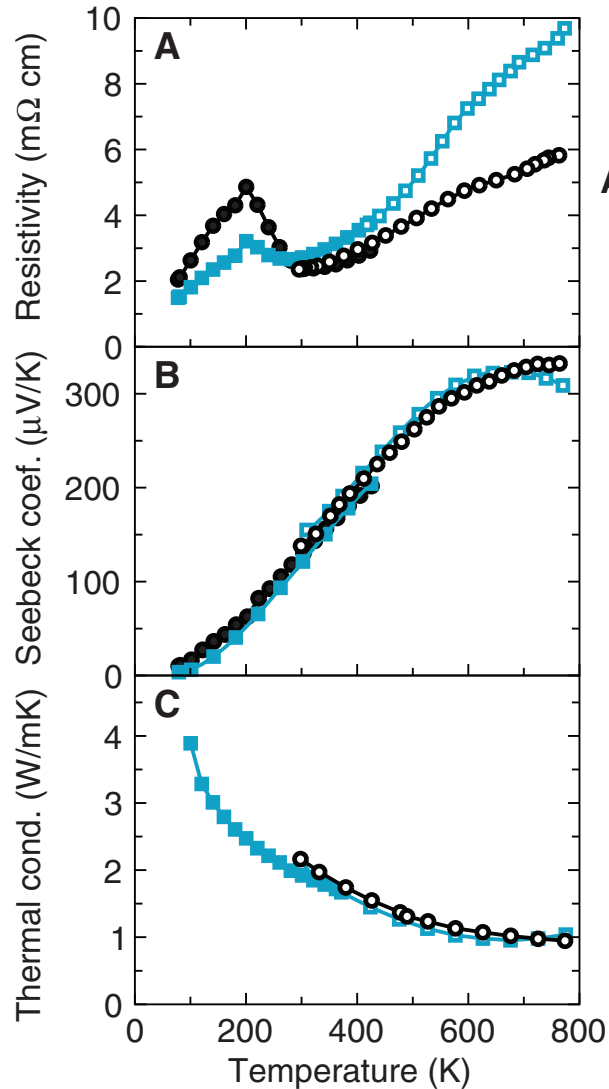
$$ZT = S^2 T \frac{\sigma}{\kappa}$$



PbTe:Tl – 1% Tl; 2% Tl

# Background II

Heremans et al., Science 321, 554 (2008)



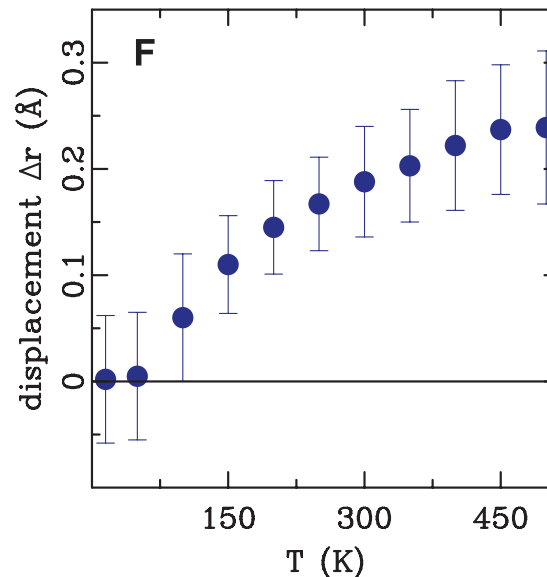
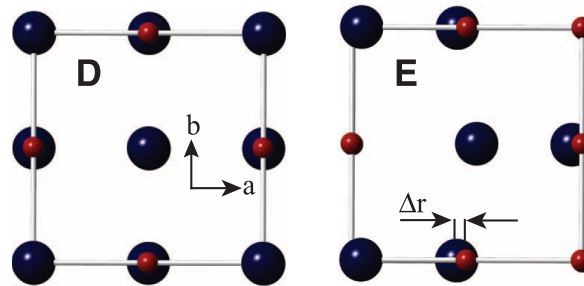
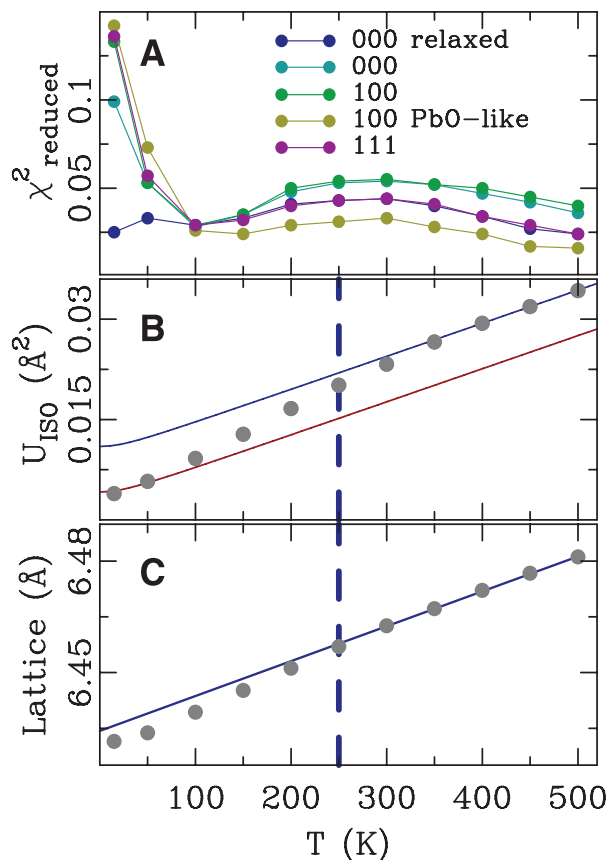
- Pure PbTe is already a good thermoelectric.
- However when it is doped with Tl  $ZT$  is greatly enhanced.
- Tl is unusual in that its valence is either +1 or +3, but it replaces Pb(+2).
- The electronic structure and local environment about Tl is not yet known.

$$ZT = S^2 T \frac{\sigma}{\kappa}$$

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# Unusual off-center displacement of Pb at high temperatures

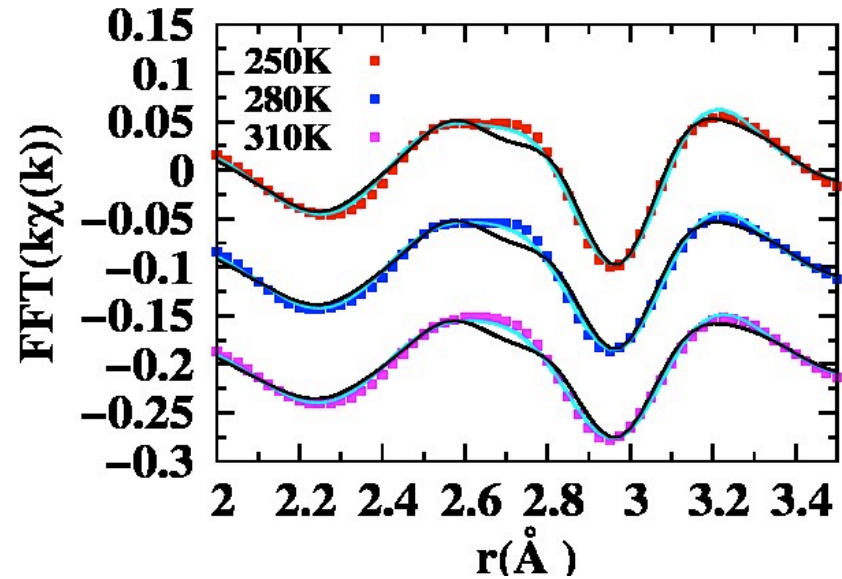
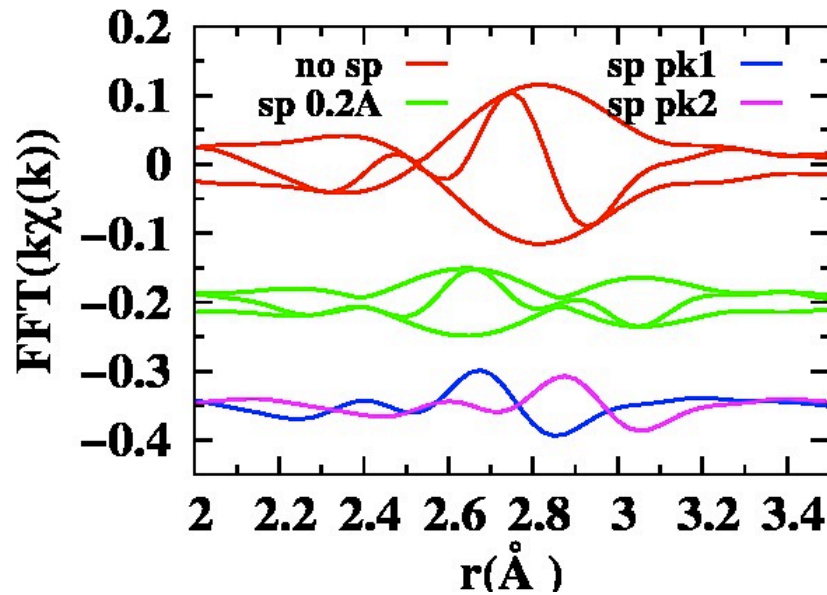
Bozin et al. Science 330, 1660 (2010)



- Based on the temperature dependence of diffraction thermal parameter for Pb and also the T dependence of the lattice constant, Bozin et al propose that Pb moves off-center along the 100 direction.
- The off-center displacement is close to zero up to 100K, is about 0.18 Å at 300K and reaches ~ 0.23 Å at 400K. Also correlations.
- This very surprising for the simple NaCl structure – and with the off-center displacement only occurring at high T.
- Other phonon anomalies also recently reported - Delaire et al. Nature Mater. (2011). DOI: 10.1038 .



# Phase information in EXAFS



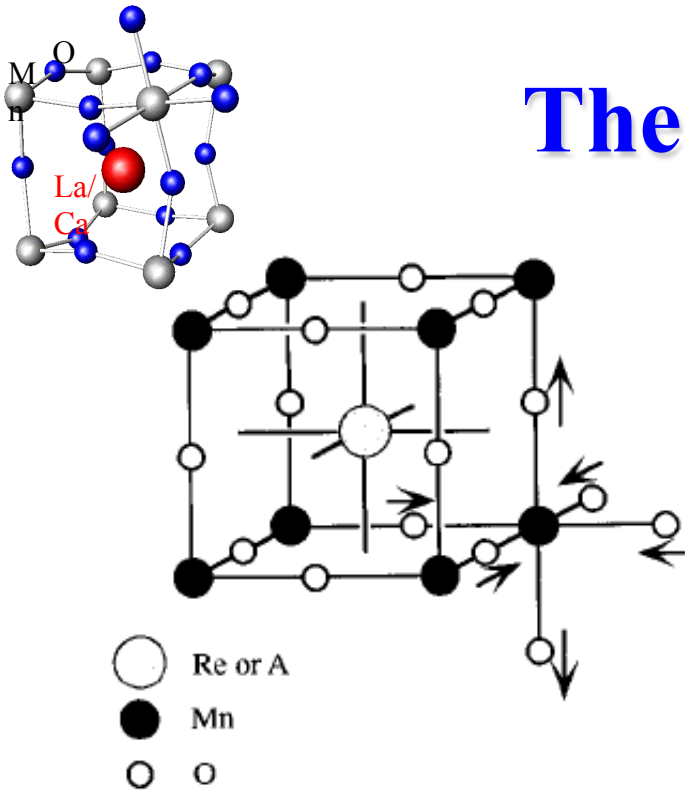
- Effects of interference
- When peak splits the real part of transform can interfere destructively leading to a shape change and a low amplitude.
- Pb  $L_{III}$  edge data -- real part of transform; squares- data; Black line - using split peak of Bozin et al. Blue line no splitting, just broadened.

# Ba<sub>3</sub>CuSb<sub>2</sub>O<sub>9</sub> an unusual magnetic system

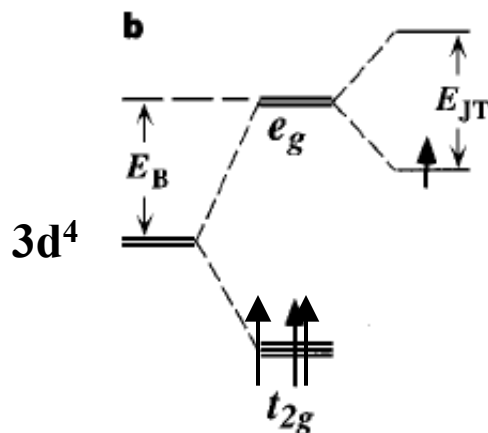
- Cu should be Cu<sup>+2</sup> in this material and therefore **Jahn-Teller (JT) active (d<sup>9</sup>)**.
- Cu<sup>+2</sup> is a spin ½ atom; if there is a crystal field splitting from a significant JT interaction, then spin interactions should be anisotropic – i.e. **g-factor in ESR should be anisotropic**.
- However in most samples g-factor appears isotropic and sample retains C<sub>3v</sub> symmetry about the hexagonal axis. Appears inconsistent with a JT active atom or indicates that the JT distortion is small! – or?
- One of samples does show an orthorhombic distortion in neutron scattering – and an anisotropic g-factor at low T - more as expected, but why only one of many samples?
- Problem for diffraction in orthorhombic space group : **Cu and one Sb share a crystallographic site and form Cu-Sb pairs**. In diffraction the Cu and Sb occupations are random – but in EXAFS strongly correlated; always Cu-Sb, and never Cu-Cu or Sb-Sb.

*Science*, **336**, 1212154 (2012).

# The Jahn-Teller (JT) Distortion



- JT distortions lead to a distribution of long and short Mn-O bond lengths.
- $\text{Mn}^{3+}$  ( $\text{LaMnO}_3$ ) has  $3d^4$  configuration – one  $e_g$  elect.
- The oxygen displacements about  $\text{Mn}^{3+}$  for a Jahn-Teller distortion are indicated by arrows
- Assumes one **quasi-localized  $e_g$**  electron is present on Mn; localized for times long compared to optical phonon period ( $<10^{-13}$  sec.).
- $\text{Mn}^{4+}$ ,  $3d^3$  config., ( $\text{CaMnO}_3$ ) - no  $e_g$  electrons, no JT.
- What happens for  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ??
- Not just a mixture of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ .



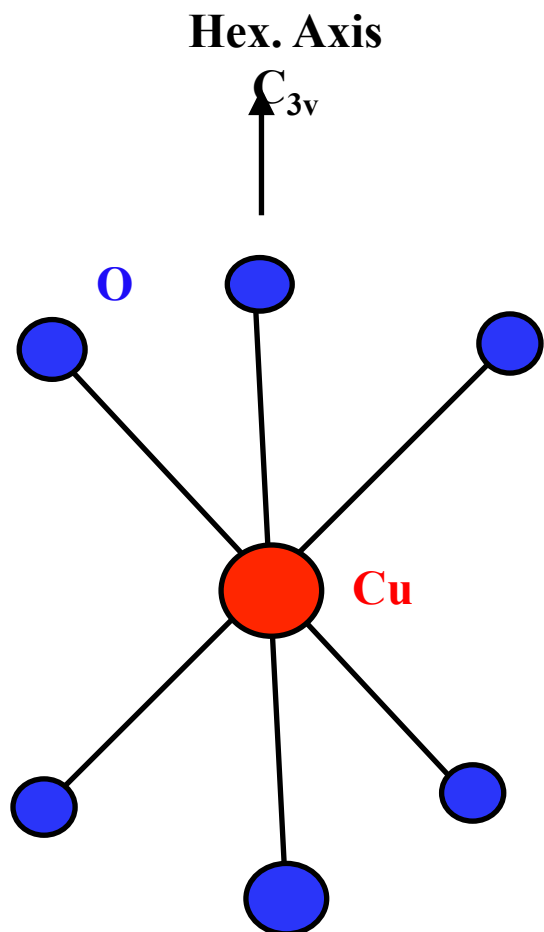
- Simplified energy level diagram;  $e_g$  and  $t_{2g}$  split by crystal field.
- Large exchange energy (Hubbard  $U$ ), so each level can only be singly occupied.
- For only one  $e_g$  electron, a JT distortion of the surrounding  $\text{O}_6$  octahedron can occur spontaneously; this splits the  $e_g$  doublet by an energy  $E_{JT}$ , and lowers total energy by  $\Delta E = -E_{JT}/2 + E_{\text{strain}}$
- If  $\Delta E < 0$ , Jahn-Teller distortions form.

A.J. Millis, Nature 392, 147 (1998)

F. Bridges

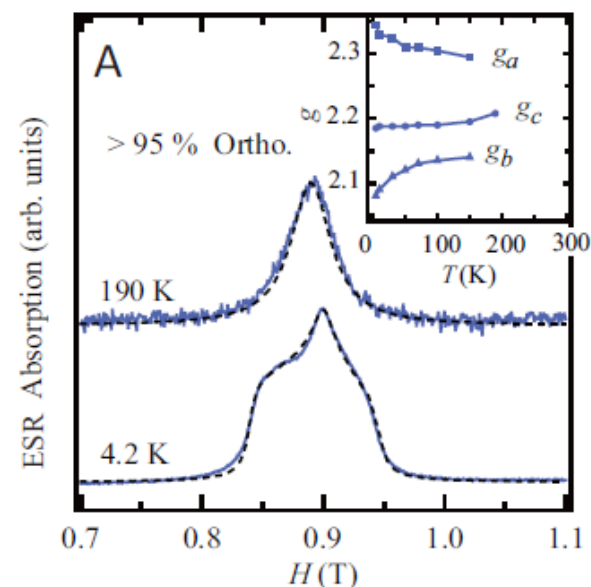
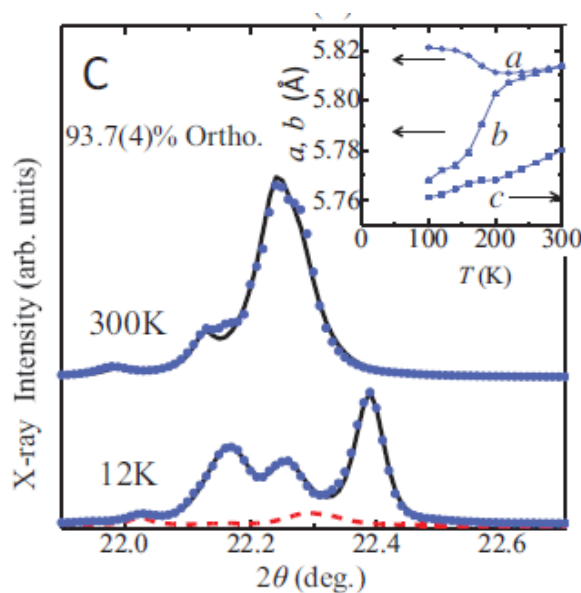
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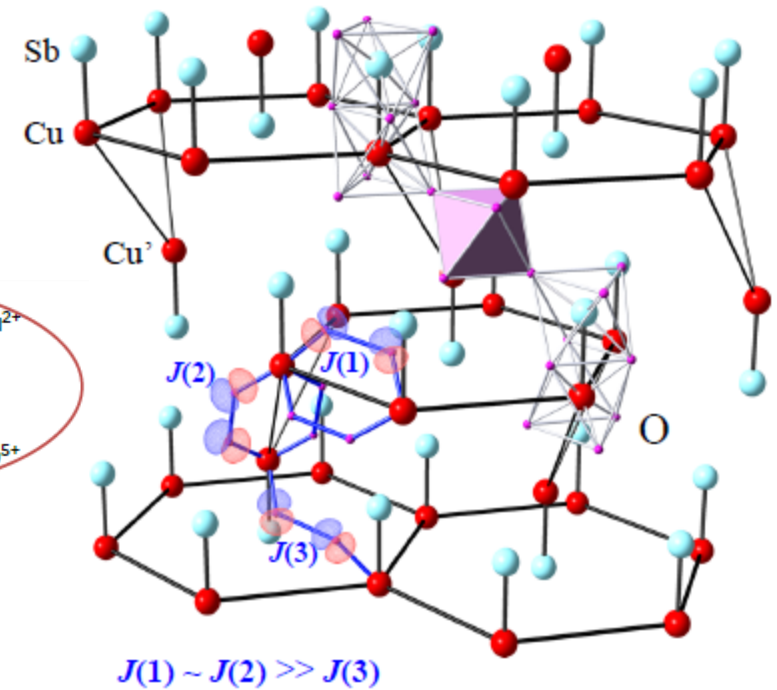
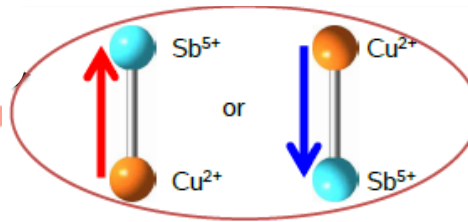
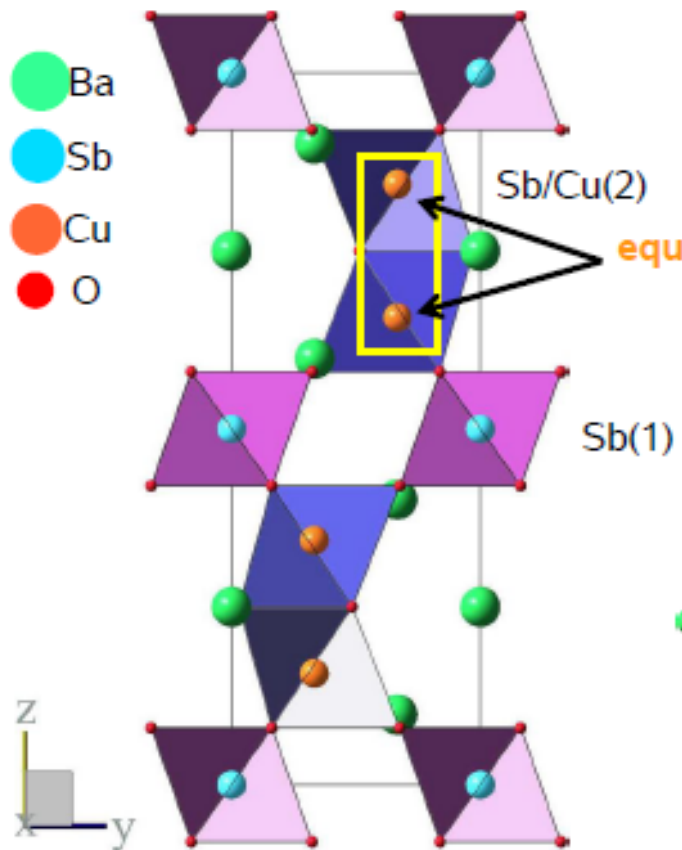
# CuO<sub>6</sub> Octahedra

- If  $C_{3v}$  symmetry retained, all axes equal.
- No static Jahn-Teller distortion (i.e. would require one of axes to lengthen).
- For JT distortion, the Cu-O distribution would split into two long and four short Cu-O bond.
- JT theorem does not require static distortion – may be dynamic. Then time scale becomes important.
- On ESR time scale ( $10^{-10}$  s)  $C_{3v}$  symmetry retained on average.
- For diffraction,  $C_{3v}$  average symmetry retained at 300K in Ortho sample.



# Possible structures from neutron diffraction

Average Hexagonal structure  
 $P6_3/mmc$

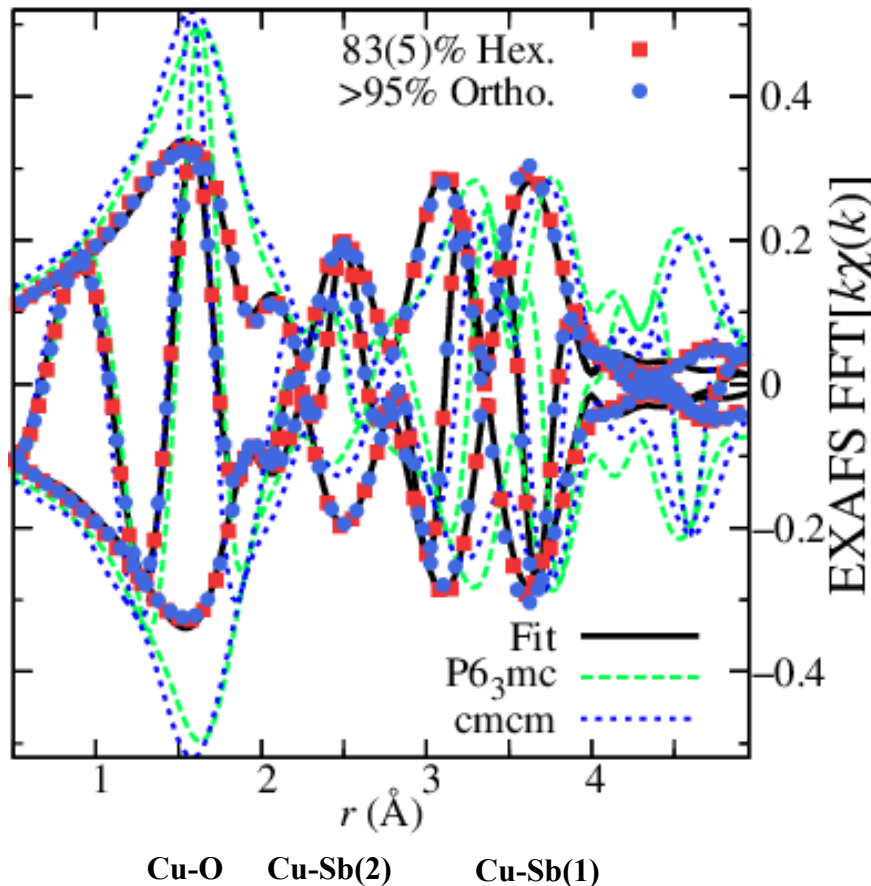


Are Cu/Sb(2) randomly occupied or correlated ?

Is the octahedron about Cu symmetric or JT distorted?

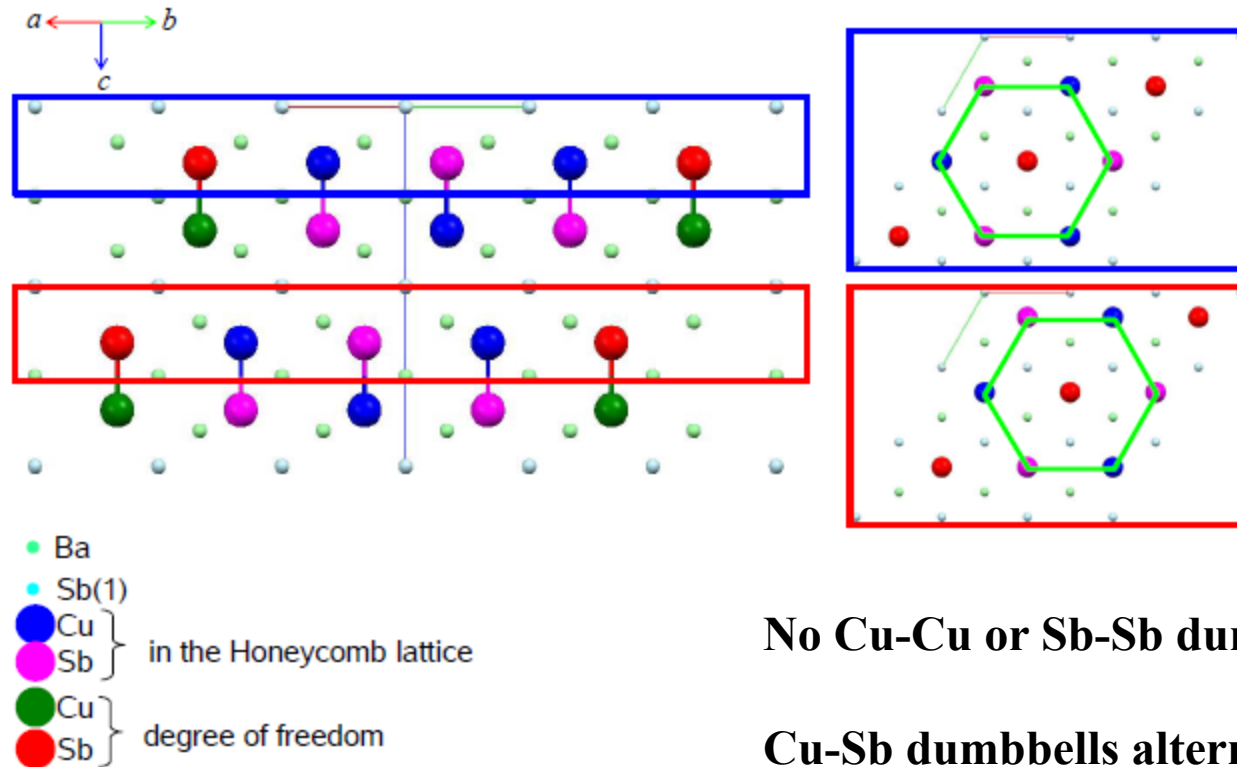
# Ba<sub>3</sub>CuSb<sub>2</sub>O<sub>9</sub> local structure different from average structure

Cu K-edge data, 10K



- EXAFS data on the **Orthorhombic** and **Hexagonal** samples are identical (blue dots, red squares)
- Large differences between EXAFS peak positions experimentally and those calculated from structure determined in diffraction - **P6<sub>3</sub>mc**, P6<sub>3</sub>/mmc, or **cmcm**.
- Cu-O peak strongly suppressed in EXAFS data – consistent with significant Jahn-Teller distortion for both samples.
- Surprisingly, the small Cu-Sb peak (one neighbor) is large in EXAFS but smaller and at a shorter distance in the calculated structure (for any structure -

# Combining EXAFS and Diffraction



**No Cu-Cu or Sb-Sb dumbbells.**

**Cu-Sb dumbbells alternate in some way.**

# Ba<sub>3</sub>CuSb<sub>2</sub>O<sub>9</sub> - fit results

Cu-O peak is split - large JT splitting - and identical in both samples in EXAFS, and almost unchanged from 10 to 300K.

Cu-Sb peak is very well ordered (small  $\sigma^2$  at low T) and significantly longer (0.07Å) compared to diffraction.

**How can the ESR data show no JT splitting in most samples and the neutron scattering data only shows a large JT distortion at low T?**

**Answer: must consider time scales:** ESR  $10^{-9}$  -  $10^{-10}$  sec; neutron scattering  $10^{-12}$  sec; phonons  $10^{-13}$  sec; EXAFS  $10^{-15}$  sec. The JT distortions are fluctuating rapidly, generally much faster than ESR time scales and comparable or faster than neutron scattering time scales. Fluctuations are slow on EXAFS time scales and the full JT distortion is observed.

**For magnetism the spin interaction with the structure is motionally averaged!  
Thus can consider the spin  $\frac{1}{2}$  interactions without structural interaction.**



# A view of Monterey bay from above UCSC



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