Dynamic and static local distortions – relationships between local structure and macroscopic properties.

Frank Bridges UCSC

1. **Motivation for studying temperature dependence of local structure**
2. **Broadening parameter σ – relationship with other techniques; split peaks vs broadened peaks**
3. **Need for high signal-to-noise data: Collection and reduction of transmission EXAFS data – powder samples (manganite) with an unfocused Beamline.**
4. **Examples – manganites and cobaltites (Jahn-Teller distortions)**
5. **Examples – rattler systems skutterudites and clathrates**
6. **Examples – negative thermal expansion**

Lisa Downward
Yu Jiang
Jesse Guzman
Cooper Downs
Travis O'Brien
John Mitchell
John Neumeier
Nalini Sundaram
D. Belanger

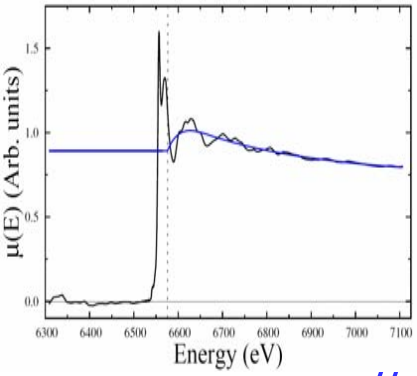
Support NSF

UCSC

Motivation

- Some systems have a Jahn-Teller distortion – e.g. the six O atoms around Mn^{+3} in $LaMnO_3$ are not equivalent; there is a distortion with two long bonds and 4 shorter bonds (the four are slightly split). In contrast for $CaMnO_3$, the 6 Mn^{+4}-O bonds are equal within 0.01Å. The competition between distorted and undistorted sites determines the magnetic and transport properties in substituted manganites ($La_{1-x}Ca_xMnO_3$) which are metallic and ferromagnetic at low T for some concentrations x, but non-metallic and insulating at high T.
- In large-unit-cell systems an atom may be weakly bonded to the rest of the crystal – can have large vibration amplitudes – called a "rattler". This disorder can strongly scatter thermal phonons and lead to a glass-like, low thermal conductivity.
- Parts of some systems may have very stiff bonds – in that case may need to consider some polyhedra (eg a tetrahedra) as a rigid unit. This unit acts like a "large atom". Other parts of the unit cell have weaker springs – can lead to interesting properties.
- **All these properties require knowledge about the vibrations of various bonds or atom-pairs in the system – usually described in terms of the width σ, of the atom-pair distribution function.**

UCSC



EXAFS Equation

$$\mu_{edge}(E) = \mu_0(E)(1+\chi(E))$$

$$k\chi(k) = \mathrm{Im}\sum_i A_i \int F_i(k,r)\, g(r_{0,i},r)\, e^{i(2kr+2\delta_c(k)+\delta_i(k))}/r^2\, dr$$

$$\approx \sum_i e^{-2k^2\sigma_i^2} A_i [F_i(k,r_{0,i})/r_{0,i}^2] \sin(2kr_{0,i}+2\delta_c(k)+\delta_i(k))$$

$F_i(k,r)$, δ_c, δ_i --calculated using FEFF

σ_i – width of pair distribution function, $g(r_{o,i},r)$

$A_i = N_i S_o^2$

$(\hbar k)^2/2m = E-E_o$

Simplify to first neighbor peak only (we will fit in r-space – Fourier transform space)

Use either:

FEFF to generate a theoretical standard (calculate $F_i(k,r)$, δ_c, δ_i)

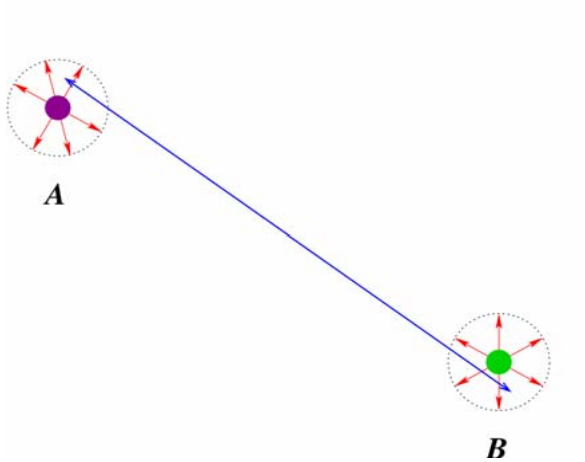
$$k\chi_{Mn-O}(k) = e^{-2k^2\sigma^2} A \left\{ [F(k,r_0)/r_0^2] \sin(2kr_0+2\delta_c(k)+\delta(k)) \right\}$$

or an experimental standard

$$k\chi_{Mn-O}(k) = e^{-2k^2(\sigma^2-\sigma_o^2)} A' \left\{ e^{-2k^2\sigma_o^2} NS_o^2 [F(k,r_0)/r_0^2] \sin(2kr_0+2\delta_c(k)+\delta(k)) \right\}$$

← **Experimental standard** →

Definition of σ

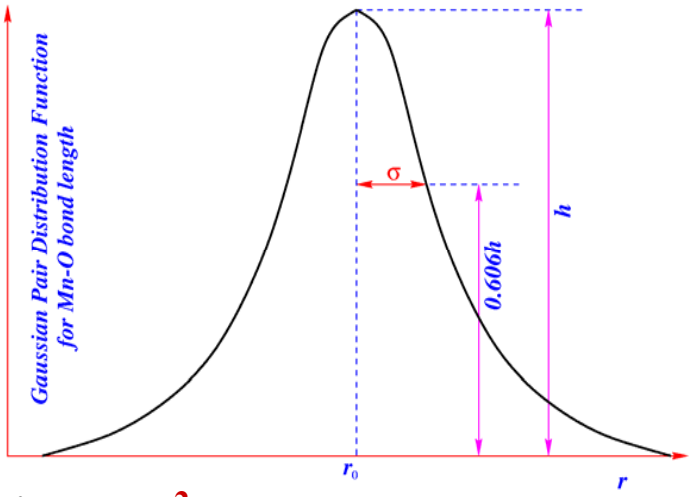


$$\sigma^2_{total} = \langle((\delta R_A - \delta R_B)\cdot r_{AB})^2\rangle$$

- Displacements δR_A and δR_B for atoms A and B , can be static or dynamic.
- σ^2 is the second moment of the pair -distribution function.
- Primarily sensitive to radial displacements

For uncorrelated mechanisms:

$$\sigma^2_{total} = \sigma^2_{static} + \sigma^2_{thermal} + \sigma^2_{polarons} +$$



Contributions to σ^2

- Thermal phonons – Einstein or Debye models.
- Polarons – a distortion associated with a partially localized charge.
- Static distortions – distribution of pair distances from strains, impurities, etc.
- Off-center displacements
- An (unresolved) split peak – effective σ is ~ Δr/2 where Δr is the peak splitting.
- $\Delta r \sim \pi/(2k_{max})$ to resolve

Simple example – isolated atom pair

Use reduced mass – M_R = 1/2m

x is the variation in the bond length, about r_0

κ is the spring constant

only one mode of vibration

$$E = \frac{1}{2} M_R v^2 + \frac{1}{2} \kappa x^2$$

$$< E > = < \frac{1}{2} M_R v^2 + \frac{1}{2} \kappa x^2 > = < \kappa x^2 > = \kappa < x^2 > = \kappa \sigma^2$$

$$< E > = < n + 1/2 > \hbar\omega$$

$$< E > \approx kT \qquad \text{at high T}$$

$$\sigma^2 = \frac{< E >}{\kappa} \approx \frac{k_B T}{\kappa} \quad at \quad high \quad T$$

$$\sigma^2 = \frac{\hbar \omega}{2\kappa} \quad at \quad low \quad T$$

zero-point motion

$\kappa = M_R\omega^2$

$\hbar\omega = k_B\Theta$

Split peaks and σ

When one has a split peak with small splittings it contributes to the broadening (See book by B. Teo), easiest seen at low T.

$$\sigma^2 = \sum_{j=1}^{N} \frac{(r_j - r_o)^2}{N}$$

Equal splitting of 6 bonds into two groups split by Δr

σ = Δr/2

Splitting into three peaks with equal splittings Δr.

Then σ = (2/3)Δr

Comparison between Einstein and Correlated Debye models – T Dependence I

(Simple systems)

Einstein model

(local modes, optical modes)

$$\sigma_E^2 = \frac{\hbar^2}{2M_R k_B \Theta_E}\coth\left(\frac{\Theta_E}{2T}\right)$$

$$= \frac{k_B\Theta_E}{2\kappa}\coth\left(\frac{\Theta_E}{2T}\right)$$

$$= < Energy > / \kappa$$

$$\approx k_B T / \kappa; \text{ at high T}$$

At T~0, $\sigma^2_E(0) = \hbar^2/(2M_R k_B \Theta_E) = k_B\Theta_E/(2\kappa)$

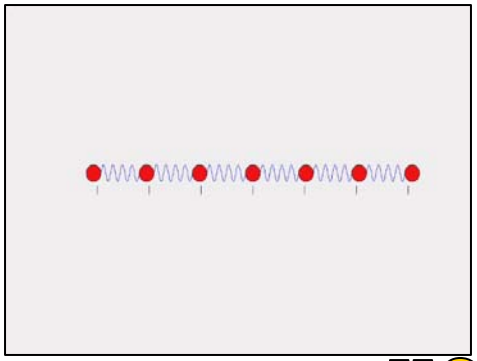
Correlated Debye Model

(All modes; sometimes restricted to Acoustic modes)

$$\sigma^2_{cD} = \frac{\hbar}{2M_R}\int_0^{\omega_{cD}} \frac{3\omega}{\omega^3_{cD}}\coth\left(\frac{\hbar\omega}{2k_B T}\right) C_{ij}(\omega)\, d\omega$$

$$C_{ij} = 1 - \frac{\sin((\omega/c)R_{ij})}{(\omega/c)R_{ij}}; \qquad R_{ij} \text{ is for atom pair ij}$$

Positive correlations – finite wavelength, acoustic modes



M_R – reduced mass

κ – Spring constant

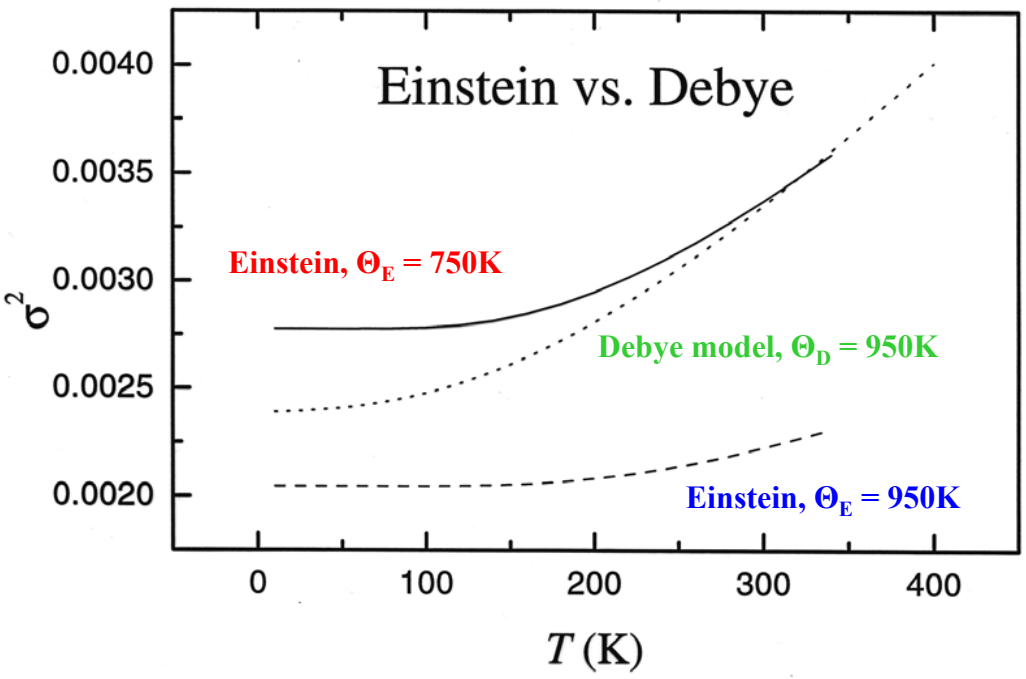
Θ_E – Einstein Temperature

Θ_{cD} – Correlated Debye Temperature; $\Theta_{cD} = \hbar\,\omega_{cD}/k_B$

c – effective speed of sound = ω_{cD}/k_D

UCSC

Temperature Dependence of σ^2 II



Some general properties:

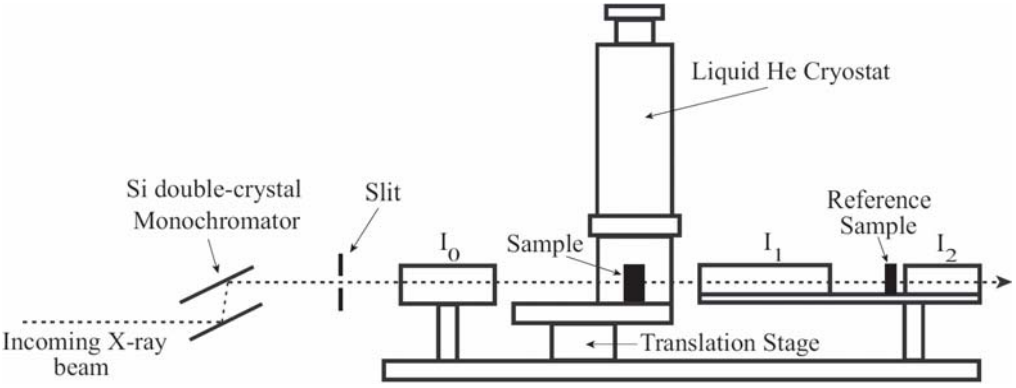
- For thermal vibrations $\sigma^2_{thermal}$ vs T has a positive slope; linear with T at high T. Einstein model has a sharper bend with T.
- Zero-point motion determines $\sigma^2_{thermal}$ at low T – for Einstein Model, should correlate with appropriate Raman mode .
- If static disorder present (σ^2_{static}), produces a rigid vertical shift [$\sigma^2 = \sigma^2_{static} + \sigma^2_{thermal}$].

General Beamline/data collection requirements for transmission EXAFS

- **1. Uniform X-ray beam over sample. A non-uniform X-ray beam profile ($I_o(x,y)$) couples with non-uniformities in the sample thickness. Good energy resolution, low harmonics.**

- **2. Linear detectors, amplifiers, and linear digitization over a wide dynamic range 10^4 -10^5 (10^6?) gas ionization detectors – keep recombination rate low in detectors I_o, I_1, and I_2. Can become non-linear when ionized region is too dense and not all electrons are extracted (focused beamlines, high synchrotron current --).**

- **3. Uniform sample–thickness: pinholes, cracks, taper in thickness; all vary the local thickness. Because the ln function is non-linear, variations in thickness do not completely average out. (similarly for an inhomogeneous composition for doped samples – but more complicated)**



$$I_1 = I_o e^{-\mu t}$$

$$\mu t = \ln(I_o / I_1)$$

$$(\mu t_i) = \ln(I_{o_i} / I_{1_i})$$

Coupling between Beam Intensity non-uniformity and sample non-uniformity

- **The signal obtained from a detector is an integral over the cross-sectional area of the beam.**

$$I_o = \int_{-a/2}^{a/2} \int_{-b/2}^{b/2} F(x,y,E)\,dxdy$$

$$I_1 = \int_{-a/2}^{a/2} \int_{-b/2}^{b/2} F(x,y,E)\,e^{-\mu(E)t(x,y)}\,dxdy$$

F(x,y,E) **is the X-ray flux (I/area)**

slit width a, slit height b

μ(E) absorption coefficient

t(x,y) sample thickness.

Simple case: One dimension and assume F(y,E) and t(y) vary linearly with y;
$t(y) = t_o(1 + \alpha y)$; $F(y,E) = F_o(E)(1 + \beta y)$

and $\mu(E)t_o\,\alpha y \ll 1$; $\exp(-\mu(E)t_o\alpha y) \sim (1 - \mu(E)t_o\alpha y)$

$$I_1 = F_o\,e^{-\mu(E)t_o} \int_{-b/2}^{b/2} (1+\beta y)(1-\mu(E)t_o\alpha y)\,dy$$

$$= F_o b\,e^{-\mu(E)t_o}\,(1-\mu(E)t_o\alpha\beta b^2/12)$$

$$= I_o\,e^{-\mu(E)t_o}\,(1-\mu(E)t_o\alpha\beta b^2/12)$$

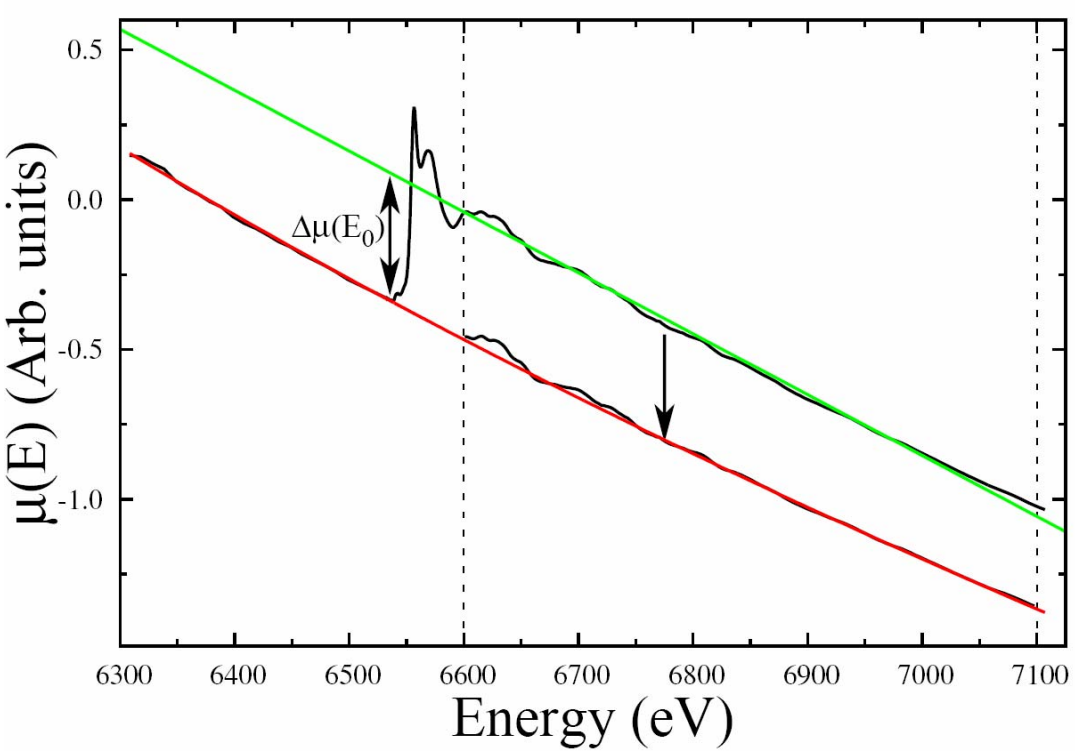
Non-uniformities couple when both Io and t vary spatially

For small α and β, correction 10^{-3} to 10^{-4}

Example – pre-edge removal

$La_{0.7}Ca_{0.3}MnO_3$: a CMR system with large Jahn-Teller distortion

Mn K-edge



Need to subtract the "background" absorption from other atoms in the X-ray path – air, windows, other atoms in sample, other absorption edges, etc.

Assumptions:

1. The background absorption is a smooth function of energy over EXAFS region.

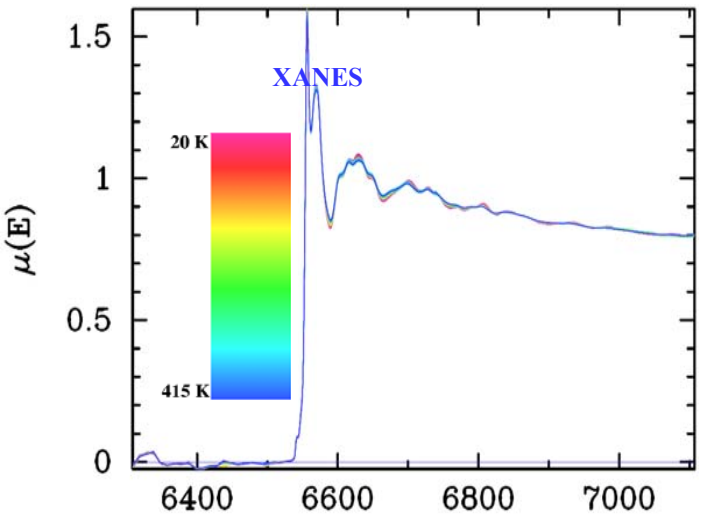
2. We can use the Victoreen formulas and the edge step height to obtain the correct slope of data above the edge.

$$\mu_T(E) = \mu_{background}(E) + \mu_{edge}(E)$$

$$\mu_{edge}(E) = \mu_T(E) - \mu_{background}(E) = \mu_o(E)(1+\chi(E))$$

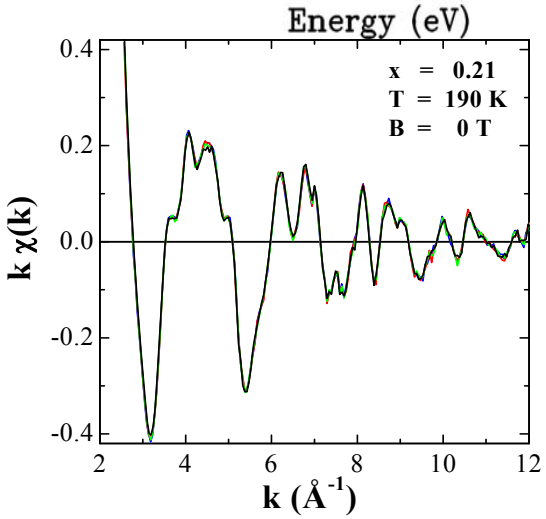
Pre-edge subtracted data and k-space data

overlay of 65 files



Note - all files overlap extremely well– otherwise it will cause small differences in the value of σ extracted.

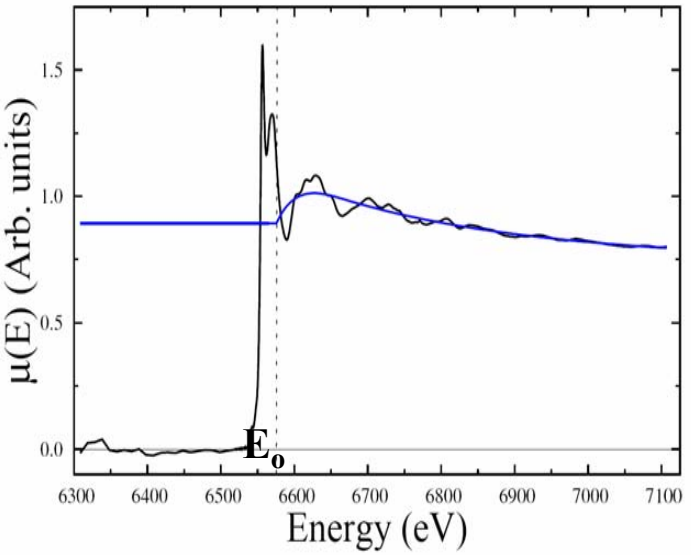
Slope correction:
$\mu_o(E) \sim \mu_1(E)(1-\alpha(E-E_o))$
$= \mu_1(E)((1-2\beta^2k^2)$



Next, Fourier Transform k-space data to r-space.

Assumption: need to set low end of transform window.
– for Mn, $k_{min} = 3.5$Å^{-1}.

Post-edge background



Above E_o, fit post-edge background to series of splines (or a polynomial) – adjust start of this fit (E_{min}) to minimize any low frequency oscillations. Assumptions/input

$$\mu_{edge}(E) = \mu_o(E)(1+\chi(E))$$

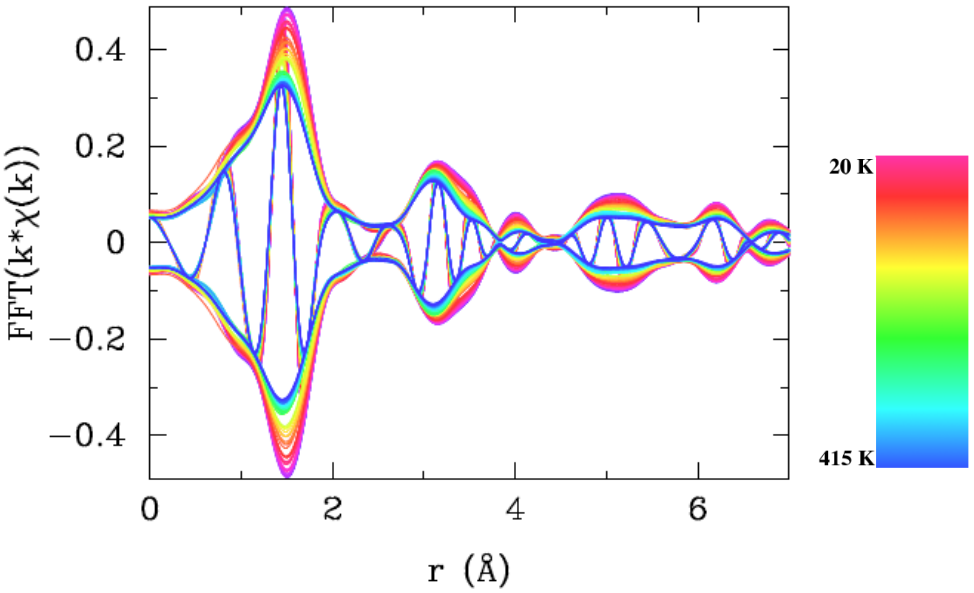
$$\chi(E) = \frac{\mu_{edge}(E) - \mu_o(E)}{\mu_o(E)}$$

$$k = 0.512\sqrt{E-E_o}; \qquad E - E_o = \gamma k^2$$

r-space data - reproducibility

Fourier Transform into r-space

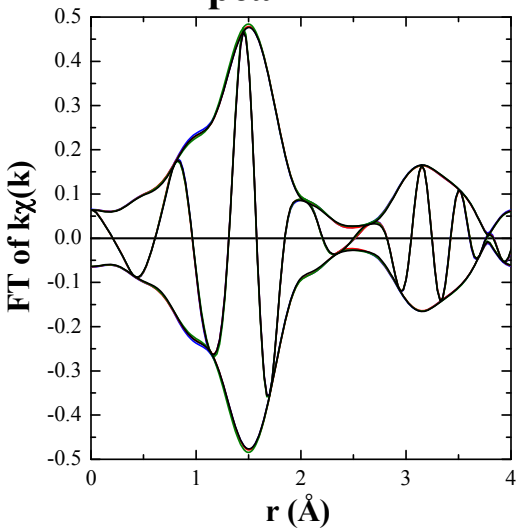
$La_{1-x}Ca_xMnO_3$; x= 0.3



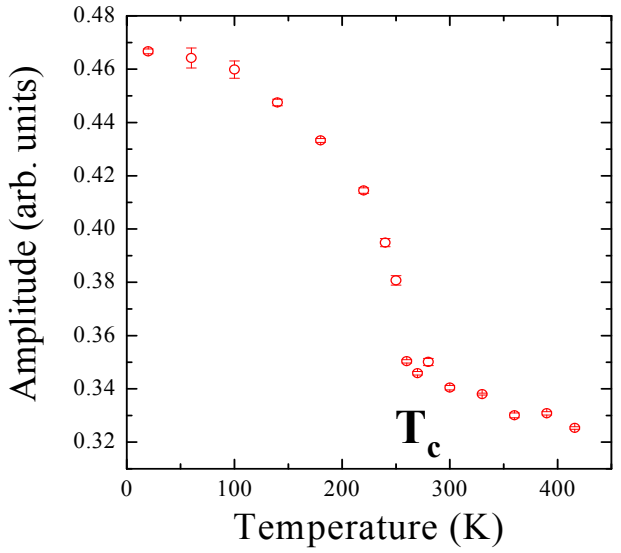
Mn-O peak

4 traces overlaid

50K

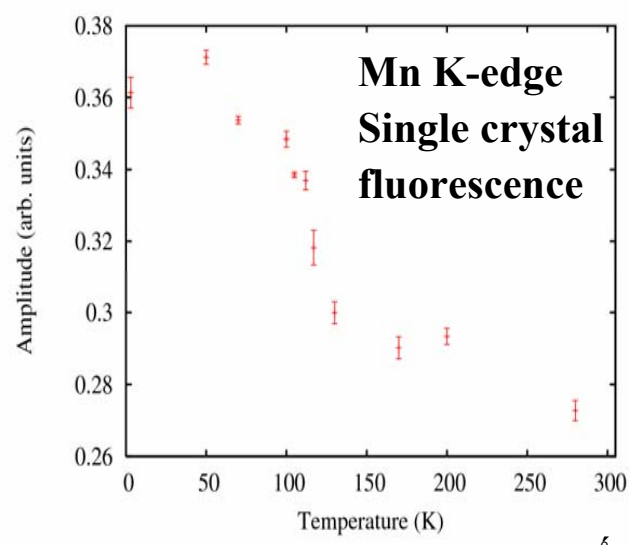


- **collect 4 traces at each temperature**
- **measure Mn-O amplitude for each trace – calculate average and rms variation.**



Reproducibility of Data and Fits

$La_{1.2}Sr_{1.8}Mn_2O_7$



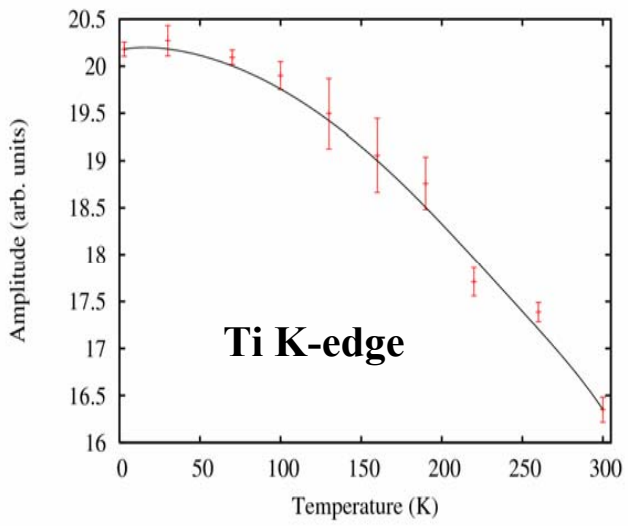
3 or 4 trace average of peak amplitudes in r-space

error bars are the rms variation in amplitude.

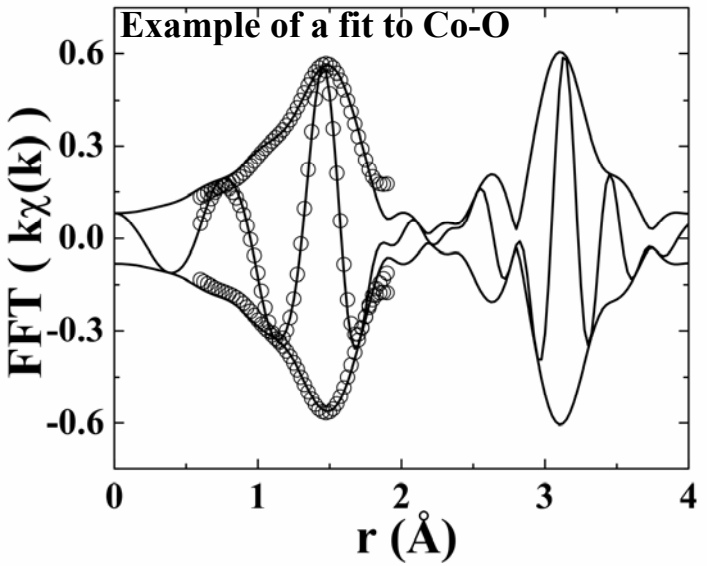
Relative errors ±1-3%

Error bars comparable to scatter.

$CaCu_3Ti_4O_{12}$



$LaCoO_3$ at 3K; fit from 1.1-1.8 Å; k 3.3-12Å^{-1}



Fit to real and imaginary part of FT, vary σ and r; fix coordination number.

Use same FT window for data and standard – fit and σ^2 are then almost independent on FT range.

Determine S_o^2 at low T and keep S_o^2 constant for higher T data. To first order: errors in S_o^2 produce vertical shift of $\sigma^2(T)$.

EXAFS -manganites

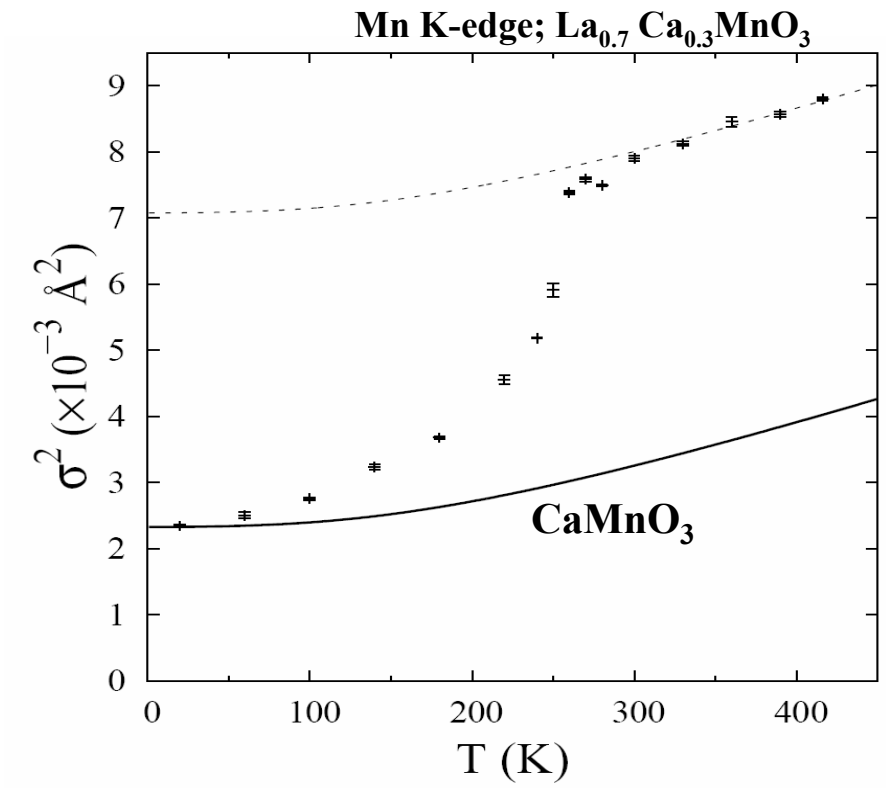
PRL 95 106401 2005

σ^2(T=0) gives zero-point motion value.

For a simple split peak, $\sigma_{static} = \Delta R/2$

Step in σ^2(T) corresponds to $\Delta R < 0.13$Å

$$\sigma^2_{total}(T) = \sigma^2_{static} + \sigma^2_{phonons}(T)$$



Relationship to macroscopic properties

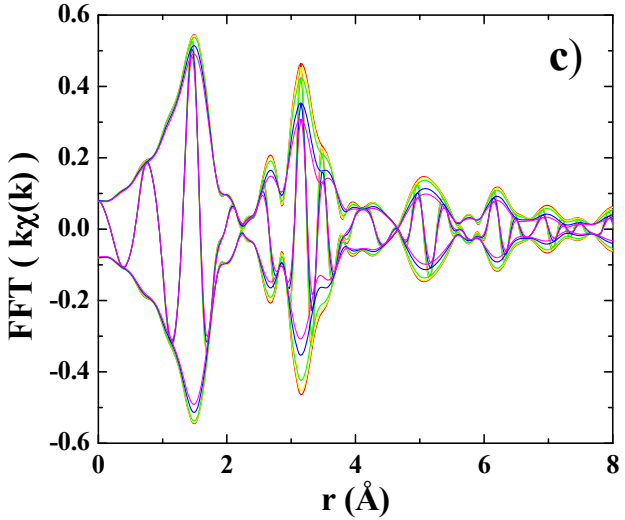
At high T large J-T distortion – the long bonds inhibit electron hopping and decrease the conductivity significantly.

At low T the electrons hopping faster than phonons – lattice does not have time to react. Fast electron hopping means good conductivity.

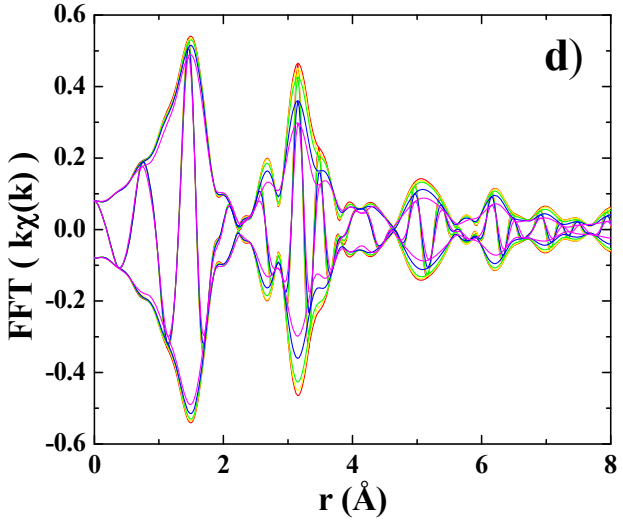
When electrons hop rapidly they couple magnetic moments on the Mn sites – leads to ferromagnetism - T_c about 260K for this system.

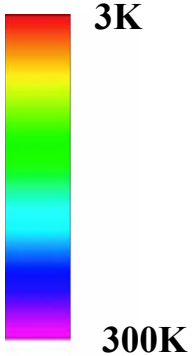
$La_{0.8}Sr_{0.2}CoO_3$ – Co K-edge (is there a Jahn-Teller distortion?)

20% Bulk - Mitchell

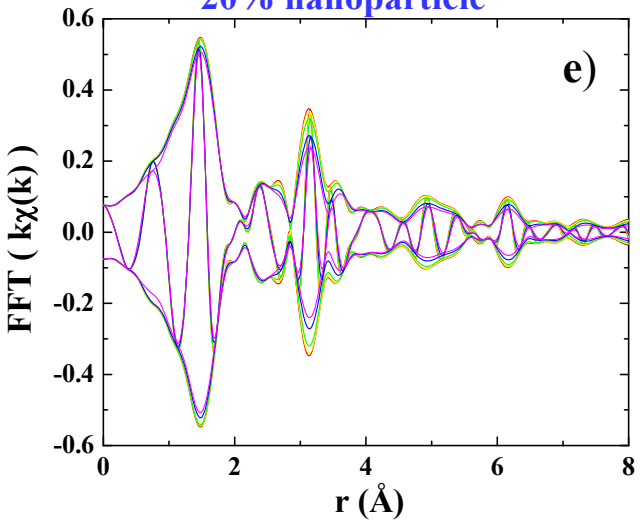


20% Bulk - Sundaram





20% nanoparticle

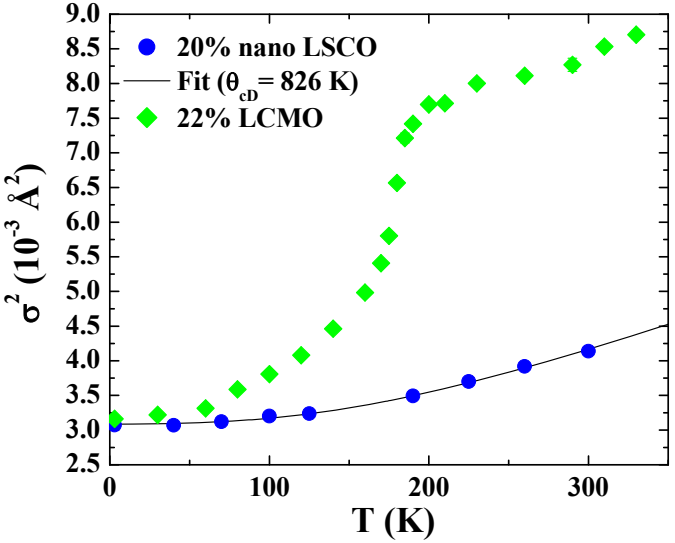


Bulk samples made by different sample-makers – have same EXAFS – same amplitudes and same T dependence for different neighbor peaks. Highly reproducible.

Nanoparticle sample (20-50 nm) clearly show more disorder for further neighbor peaks but essentially the same behavior as bulk for first neighbors Co-O.

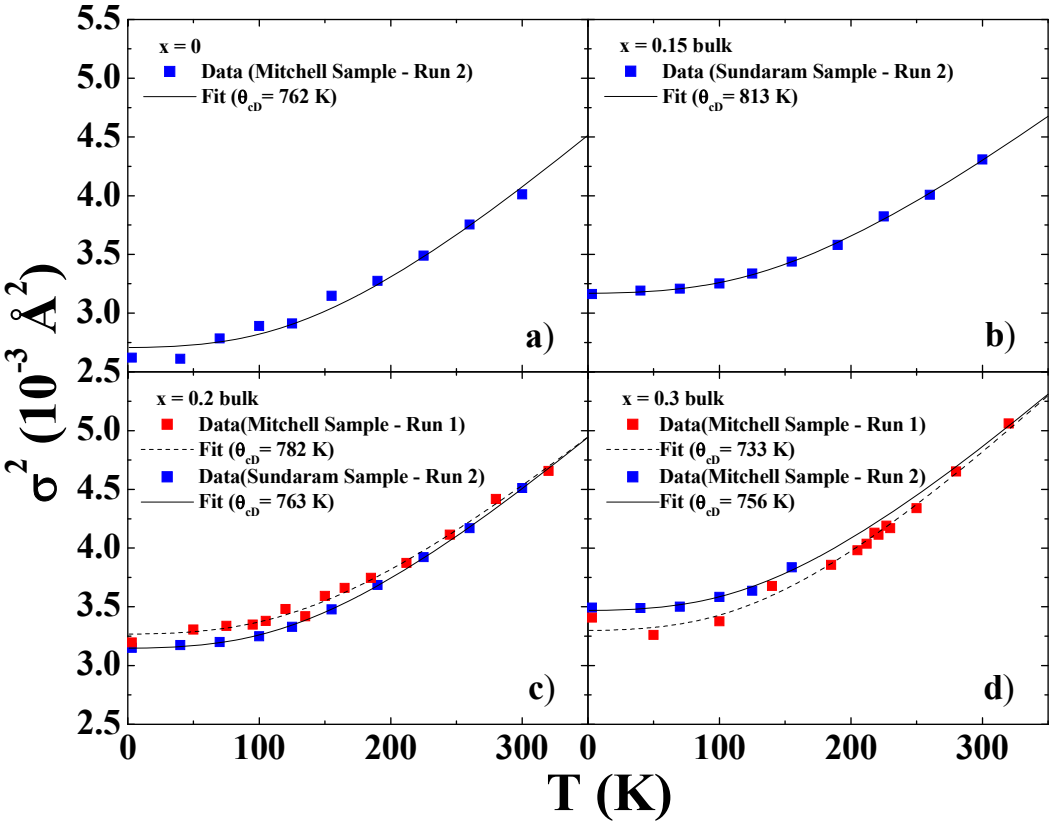
UCSC

σ^2 vs T plots for $La_{1-x}Sr_xCoO_3$



Mn (LCMO) results from PRB 76, 224428 (2007).

Above: Comparison between a manganite (22% Ca) which shows a large J-T distortion and cobaltite (20% Sr) which has no indication of a J-T distortion. σ^2 at low T is close to zero-point motion value.



Correlated Debye fits to data for a variety of samples

Similar σ^2 near T=0, Similar Θ_D.

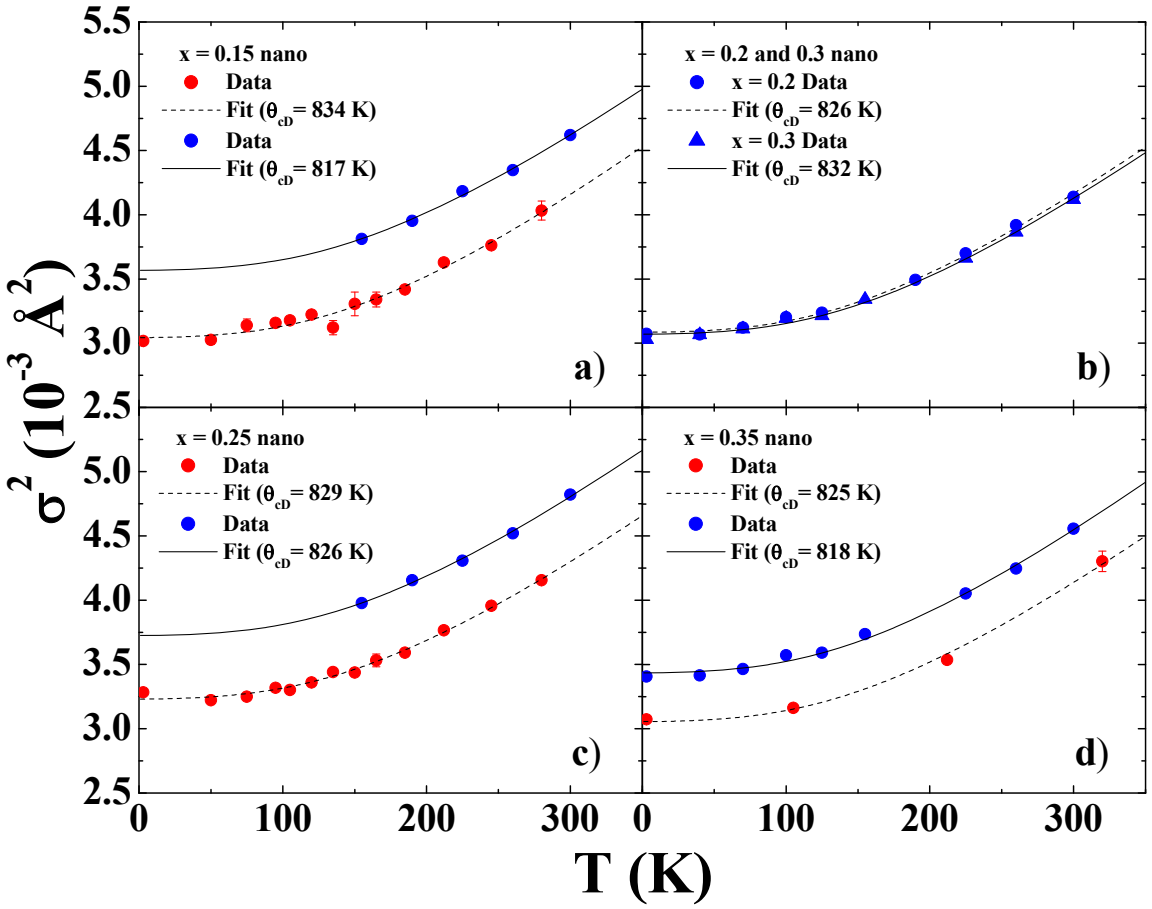
Debate about magnetism – Co can have a low spin state S=0, a high spin state S=0, and perhaps an intermediate state S=1; the S=1 spin state should be J-T active – but no evidence for a distortion. Suggests M is a mixture of S=0 and S=2.

UCSC

Can see static changes

Nanoparticle samples (20-50 nm) stored on tape (in glue) for a year show increased disorder compared to as-made samples or samples stored as a powder and fresh EXAFS samples prepared.

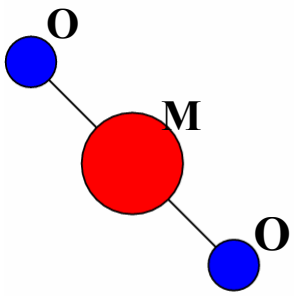
Possibly an oxidation from contact with glue.



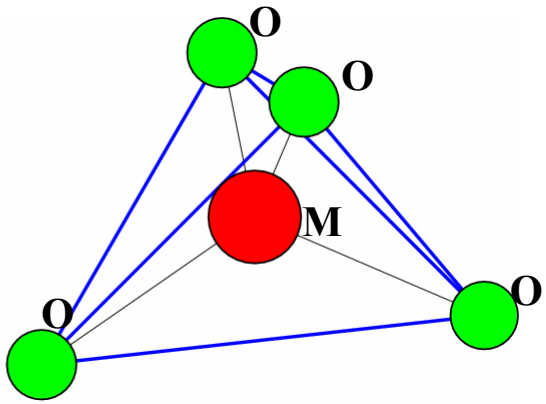
More complex crystals

Some unit cells are composed of two or more molecular units – such as "dumbells", tetrahedra, or octahedra, with very strong bonds within the molecular unit but much weaker "springs" between them .

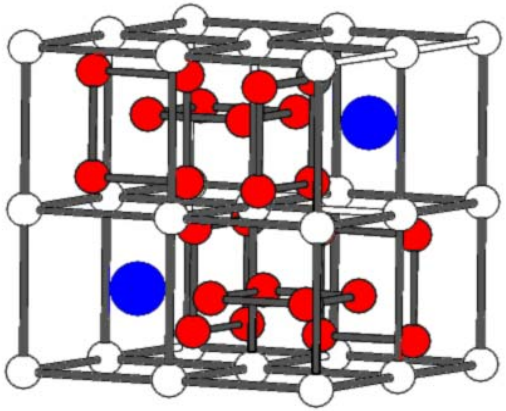
Other structures form cages that can contain other atoms, weakly bound.



Dumbell, MO_2, with two very strong M-O bonds.



Tetrahedron, MO_4, with four very strong M-O bonds



Cage structure: skutterudite

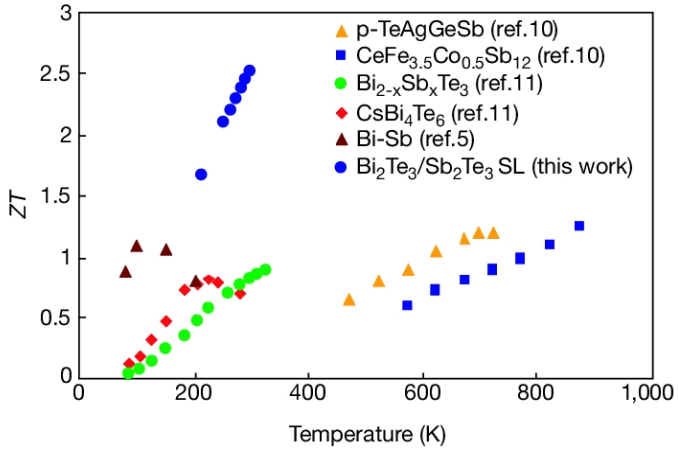
Blue atom is weakly bonded to cage; small spring constant.

All described by Einstein models for nearest neighbor bond.

Thermoelectrics – filled skutterudites LnT_4X_{12}

Ln rare-earth, T =Fe,Os,Ru; X=P,As,Sb

Venkatasubrmanian *etal* Nature **413** 597 2001



Sales *etal* PRB **56** 15081 1997.

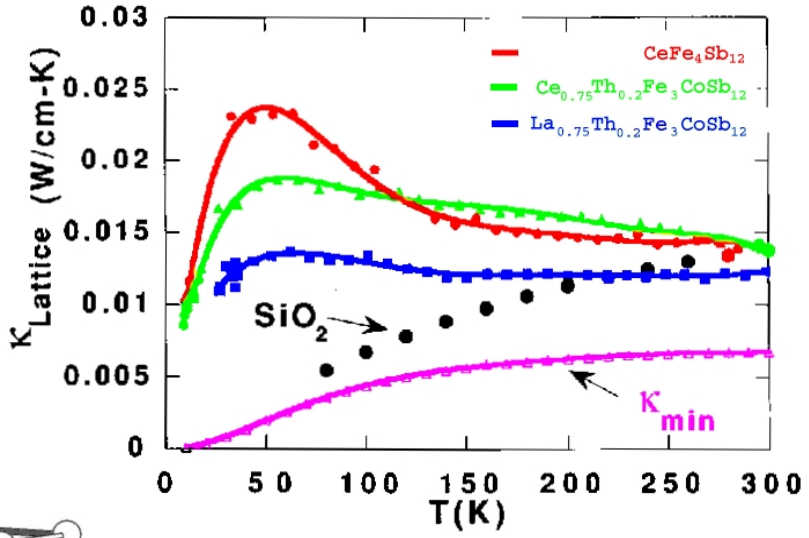
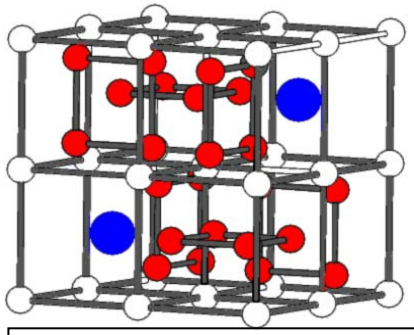


Figure of merit for thermoelectric cooling: $ZT = TS^2\sigma_e/\kappa$

- **S Seebeck coefficient**
- **σ_e Electrical conductivity**
- **κ Thermal conductivity (phonons)**
- **κ and σ_e determined by different scattering mechanisms!**



- **Filled skutterudites (eg $CeFe_4Sb_{12}$) -- low lattice thermal conductivity κ attributed to "rattling" motion of rare earth "filler" atom (Ce, Eu, Pr etc)**
- **Low κ Comparable to SiO_2 glass**

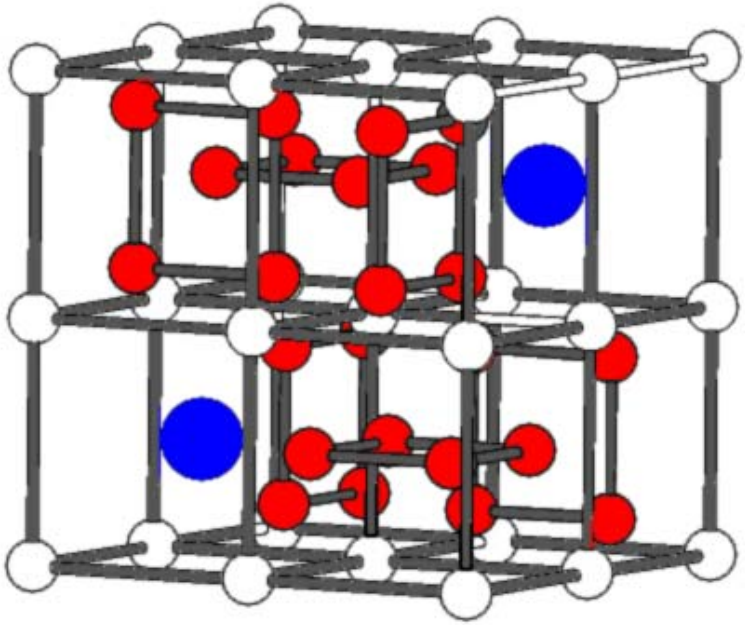
Unusual macroscopic properties

High quality crystals, metallic electrical conductivity but glass-like thermal conductivity – why?

UCSC

Skutterudites LnT_4X_{12}

Ln rare-earth, T =Fe,Os,Ru; X=P,As,Sb



Blue: filler atom (Ce); white: T (Fe); red: X (Sb)

Ce has 12 Sb nearest neighbors and 8 Fe 2nd neighbors

Contrast ($CeFe_4Sb_{12}$)

Fe-Sb lattice quite stiff – from both the Fe or Sb perspective – stiff springs.

Ce-Sb and Ce-Fe "bonds" are very soft – weak springs.

Two characteristic energies

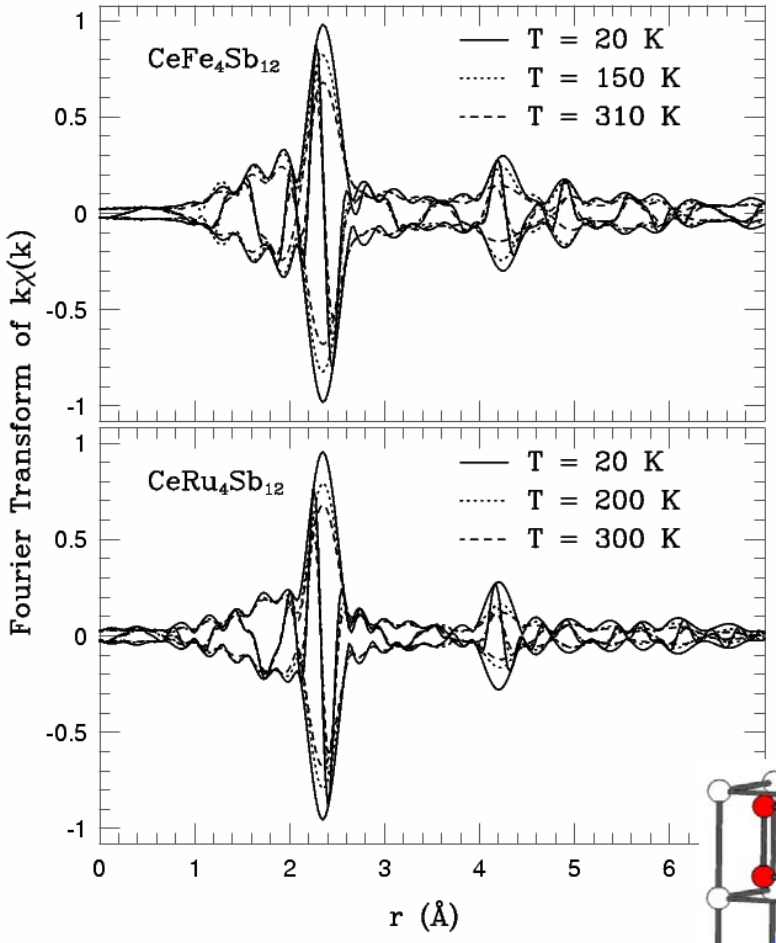
Properties relevant for thermoelectric applications:

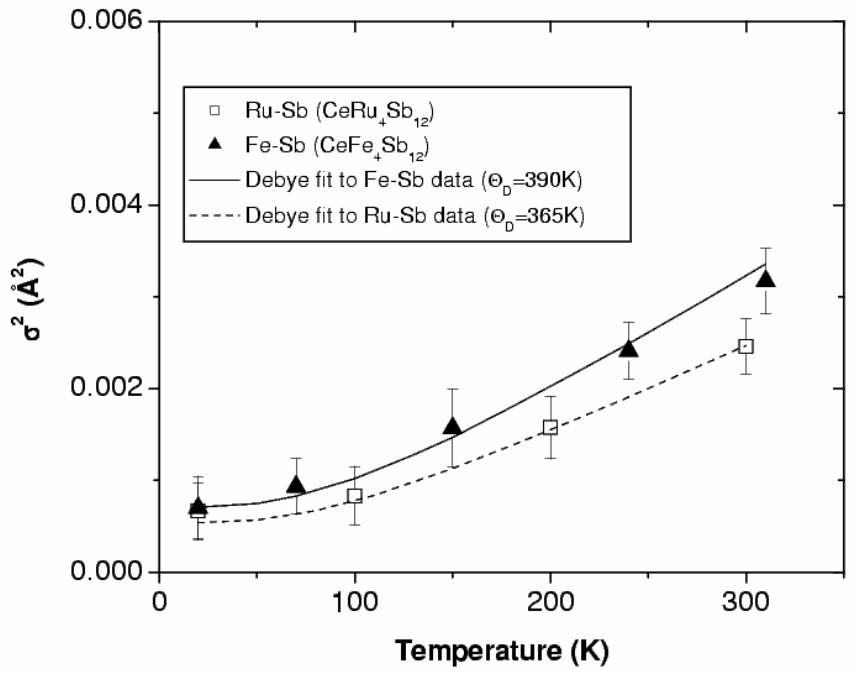
- **Good electrical conductivity. Fairly good figure of merit.**
- **Glass-like thermal conductivity -- why?**
- **What are the vibration properties of the filler atom?**
- **Is the filler atom off-center?**
- **How does the rattling behavior depend on type of rattler, or antimonide vs phosphide?**

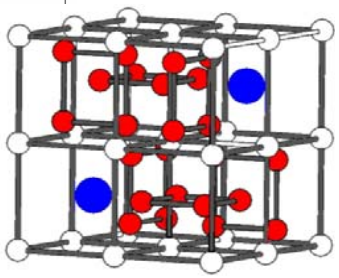
UCSC

Fe and Ru k-edges – antimonides

are the cages rigid?



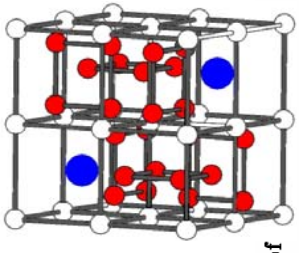


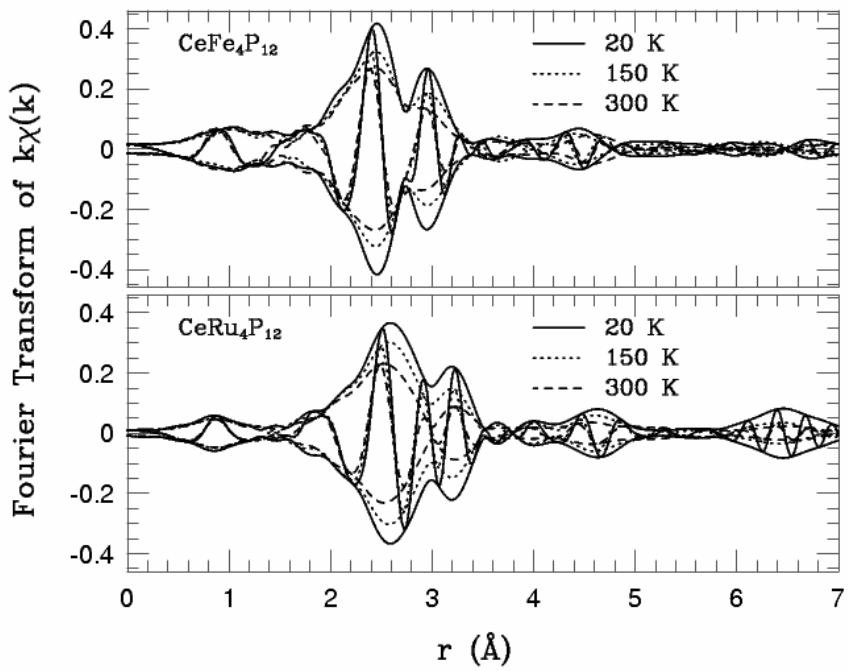


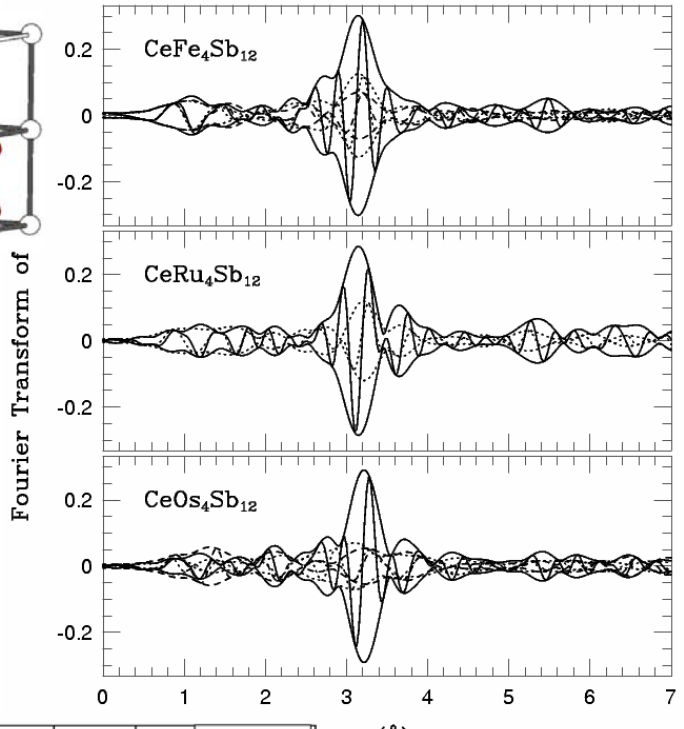
Cages are rigid

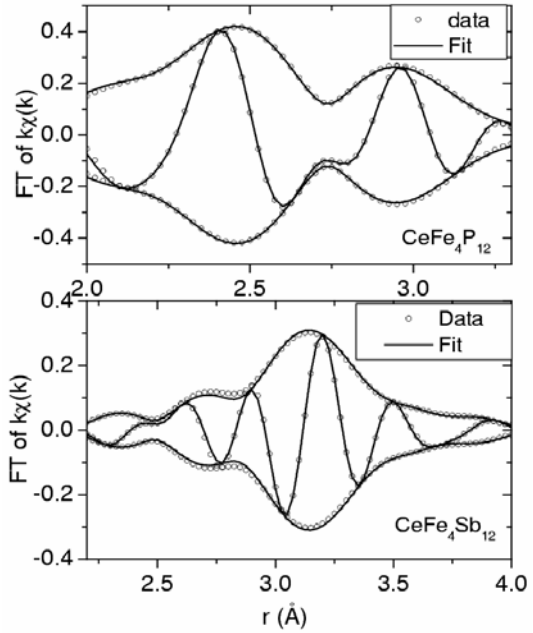
- θ_D is quite high 365-395K
- Similar for other antimonide skutterudites

Ce L_{III}-edge data





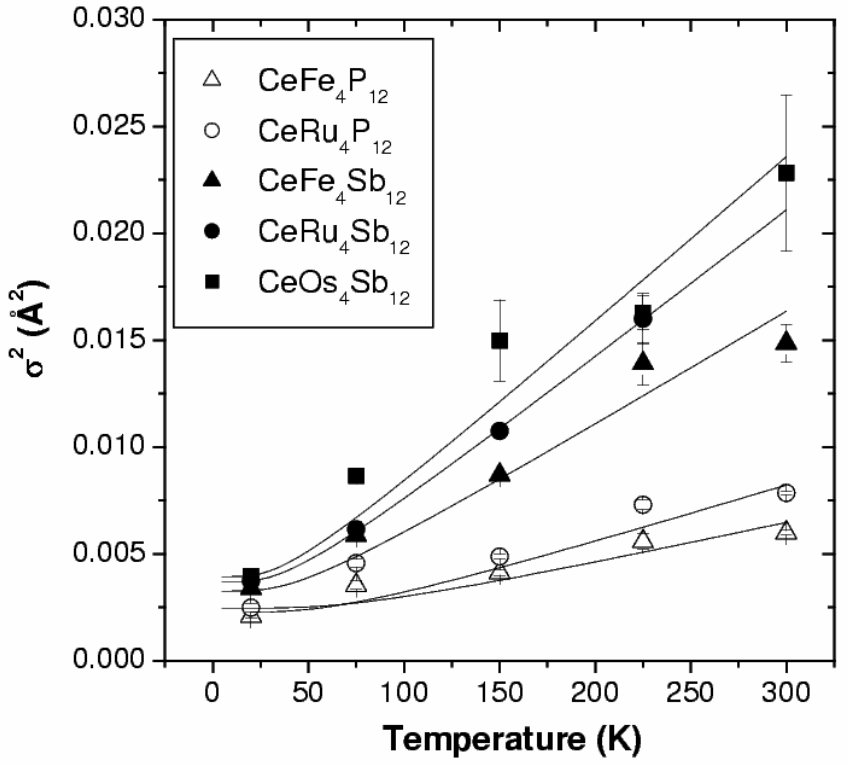




- **Ce-P bond length much shorter than Ce-Sb**
- **Ce-Sb peak has a much stronger T dependence than Ce-P**
- **Similar results for many similar systems**

Fits using standards from FEFF

Einstein model for Ce rattler



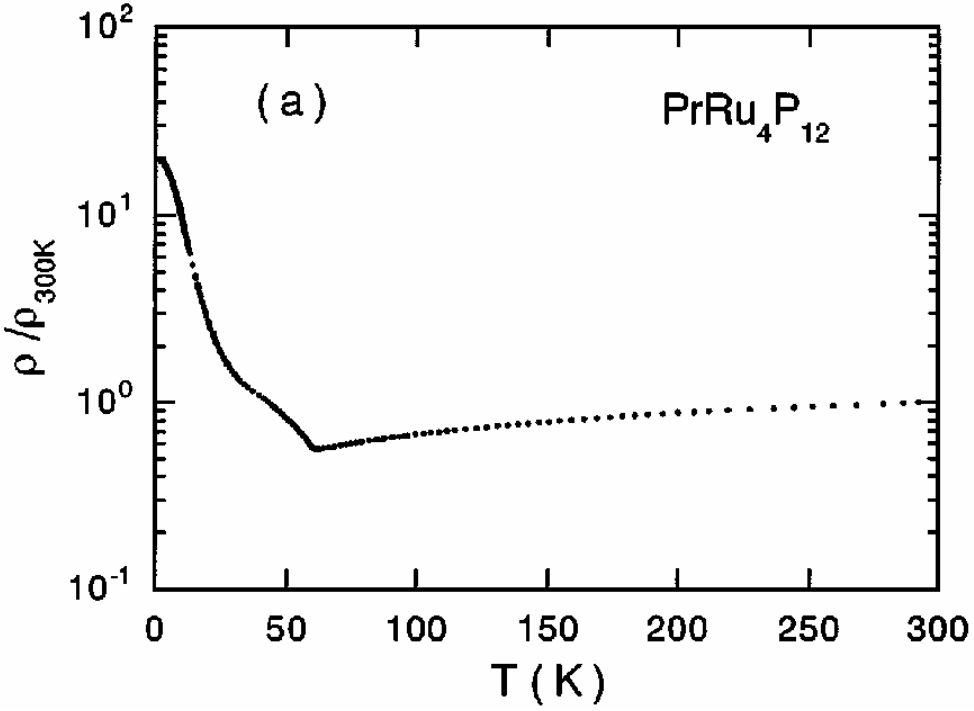
Sample	lattice constant (Å)	Θ_E (K)	σ^2_{static}(Å^2)
$CeFe_4P_{12}$	7.792	148	0.0015
$CeRu_4P_{12}$	8.038	125	0.0012
$CeFe_4Sb_{12}$	9.135	86	0.0018
$CeRu_4Sb_{12}$	9.266	73	0.0010
$CeOs_4Sb_{12}$	9.299	71	0.0020

$\sigma^2_E = C/(M_R\Theta_E)\coth(\Theta_E/2kT) + \sigma^2_{static}$

Three parameters M_R, Θ_E, and σ^2_{static}

- **Treat cage as rigid – use Ce mass as the oscillator mass**
- **No significant static contribution to σ^2 – Ce is not off-center.**
- **Einstein temperature decreases as the cage size increases.**
- **Similar Einstein temperatures for Eu, Yb, and Pr filler atoms.**

Metal-Insulator transition in $PrRu_4P_{12}$

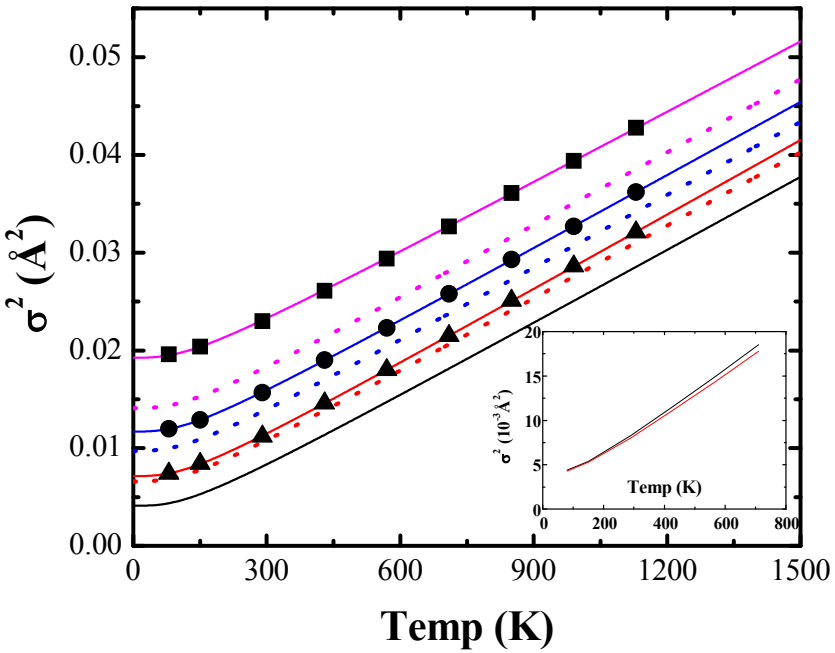


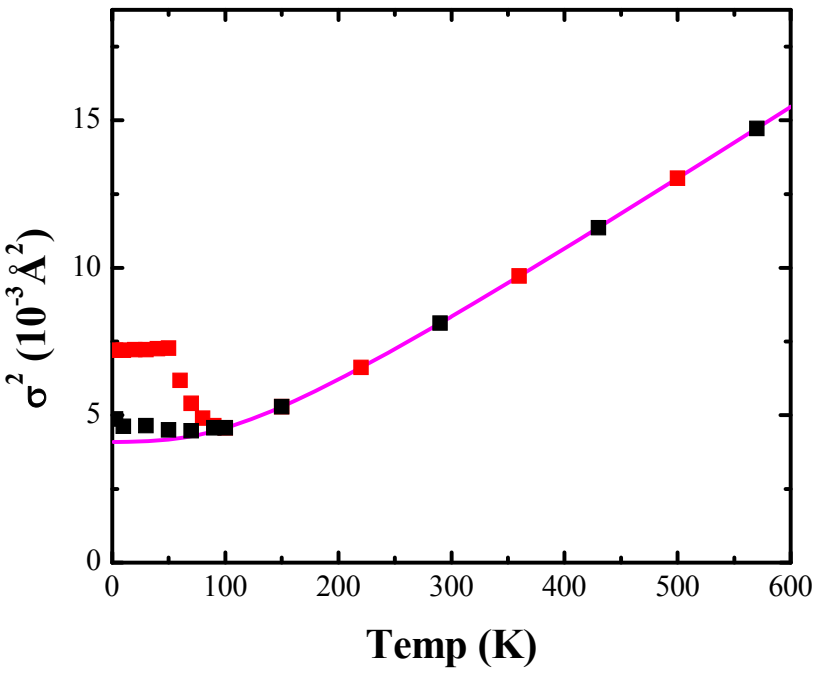
Macroscopic behavior

- **Metallic above 60K**
- **Insulating below 60K – Why?**
- **Sekine *etal* did not find evidence for a structural transition**

Sekine *etal* PRL **79** 3219 1997

Simulations for split peaks





Data: – sum of two split peaks, splittings 0.1, 0.15, and 0.2Å; r_{av} = 1.93Å; broadened with corr. Debye model (θ_{cD} = 500K)

Fits: fit to one FEFF peak, r-range, 0.8-1.8Å, k-ranges 3-9, 3-11, 3-16 Å; N and E_0 constant. σ^2 independent of k-range. Red - .1Å, Blue – 0.15Å, Purple – 0.2Å

Dotted lines – assuming $\sigma^2_{static} = \Delta r/2$ (Teo '86)

Extracted θ_{cD} very close to initial value (1%) in all cases.

Static value of $\sigma^2_{static} > \Delta r/2$; an upper limit on any splitting

Data: above 100K, single peak; below 100K splitting develops, Black: Δr = .05Å, Red: 0.1Å. Peaks broadened using corr. Debye model (θ_{cD} = 500K)

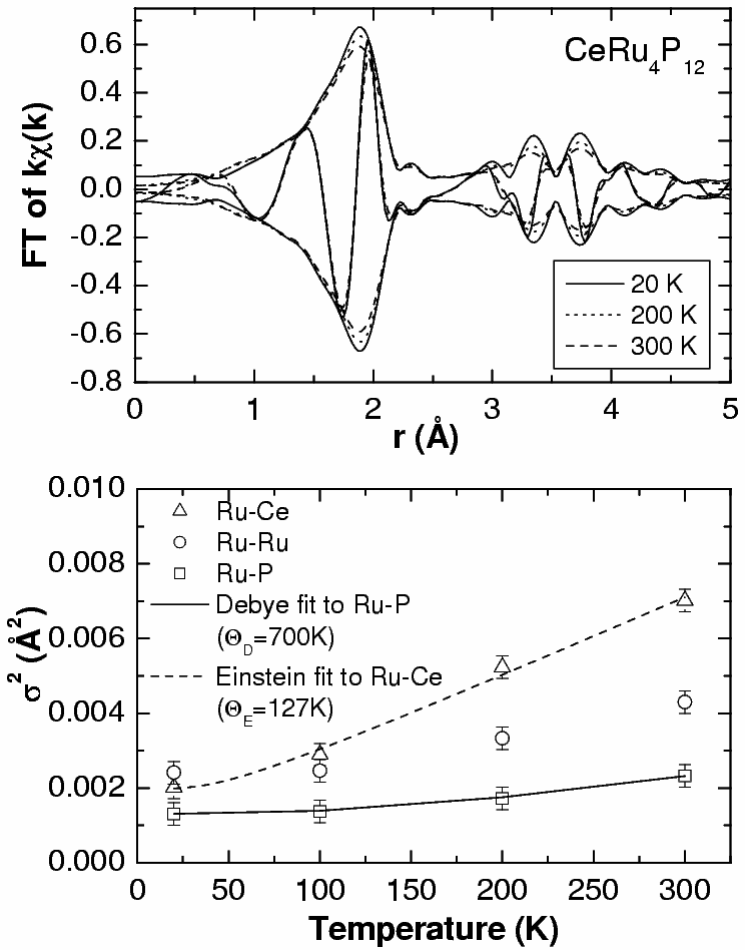
Purple line shows fit to corr. Debye model.

Black and Red squares show increased σ^2 below 100K.

Relative deviation depends on θ_{cD} and reduced mass.

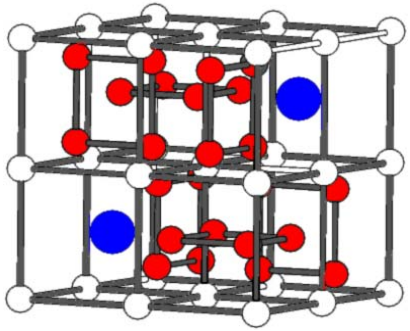
UCSC

Ru k-edge -- Phosphide

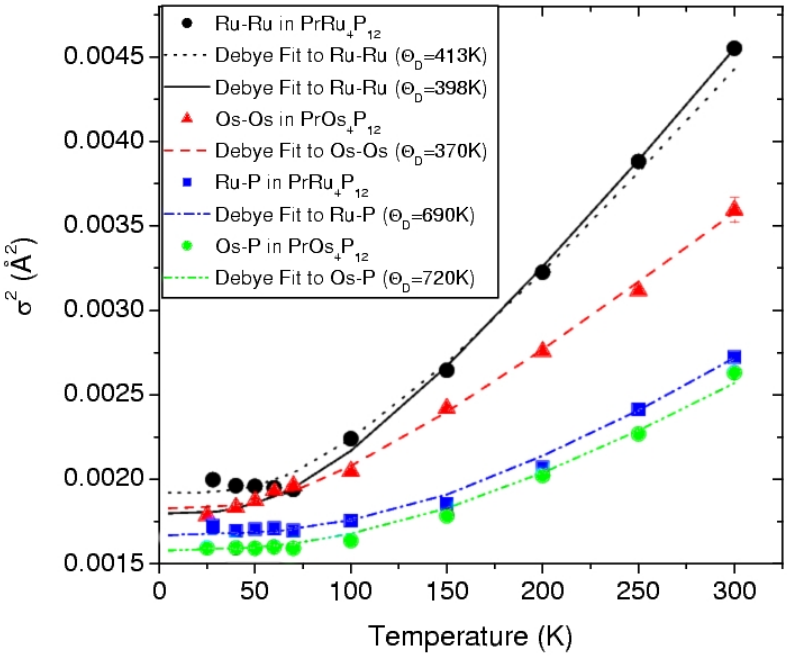


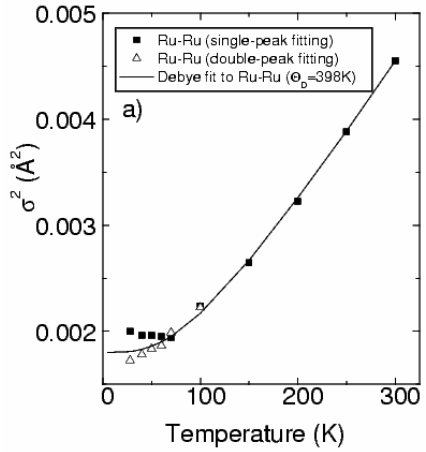
Very high Debye temperature (700K) for phosphides – stiff cage.

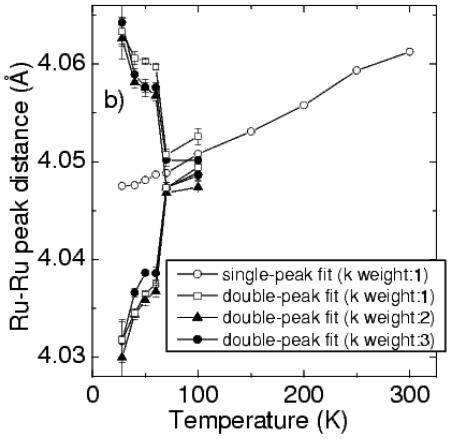
Quite low Einstein temperature (127K)

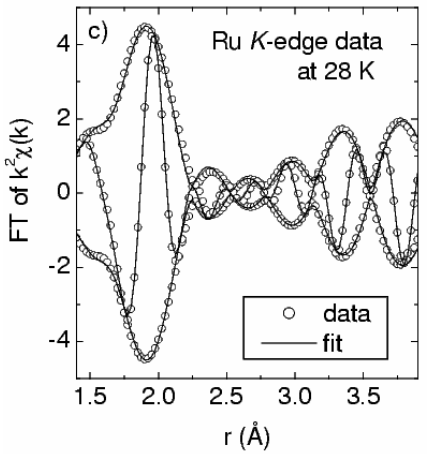


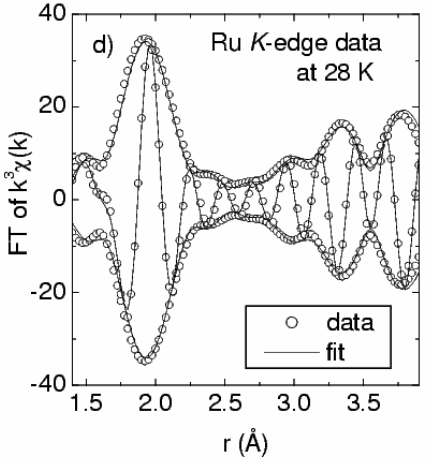
Metal/Insulator transition in $PrRu_4P_{12}$



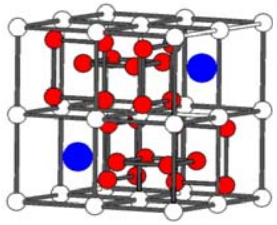








- **Nothing clearly unusual about σ^2 for Pr rattler or Ru-P distribution**
- **Unusual increase in σ^2 for Ru-Ru -- σ^2 increases below 60K!**
- **Corresponds to a small lattice distortion (rotation of RuP_6) with little distortion of Pr-Ru; two Ru sites.**
- **Confirmed by recent diffraction study**
  Iwasa etal, PRB 72, 024414 (2005)

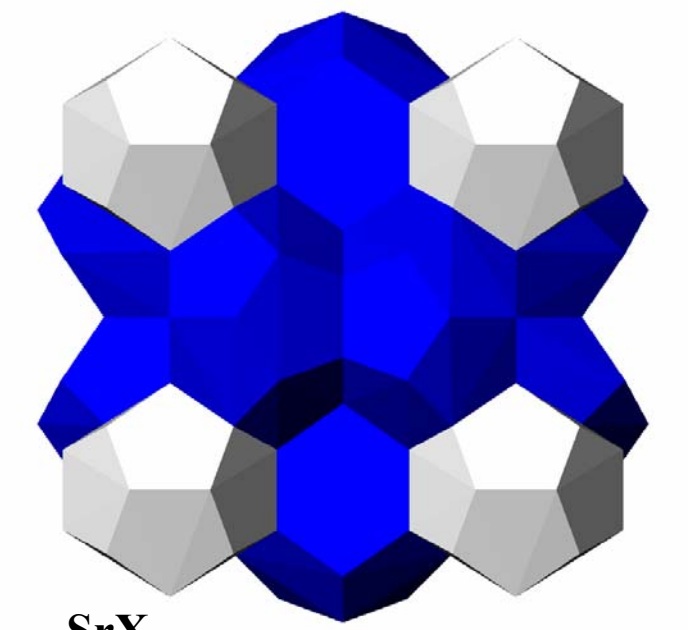


D. Cao *etal* PRL 94, 0364031 (2005).

Clathrates: -Background and Data Collection

- $Sr_8Ga_{16}Ge_{30}$ and $Eu_8Ga_{16}Ge_{30}$ Clathrates are promising thermoelectric materials – most are n-type semiconductors, with a relatively high Seebeck coefficient and are poor thermal conductors (glass-like).
- Low thermal conductivity is attributed to the "rattling" of the Sr or Eu atoms within the large cage called site 2; ie Sr2 or Eu2. Cage is SrX_{24} or EuX_{24}; X= Ga/Ge. Diffraction indicates that Sr and Eu are off-center in site 2.
- Eu and Sr on-center in smaller site 1 cage (gray).
- Data collected on beamline 4-3 at SSRL using Si <220> monochromator crystals for Sr, Ga, and Ge K-edges and Eu L_{iii}-edge.

Clathrate structure

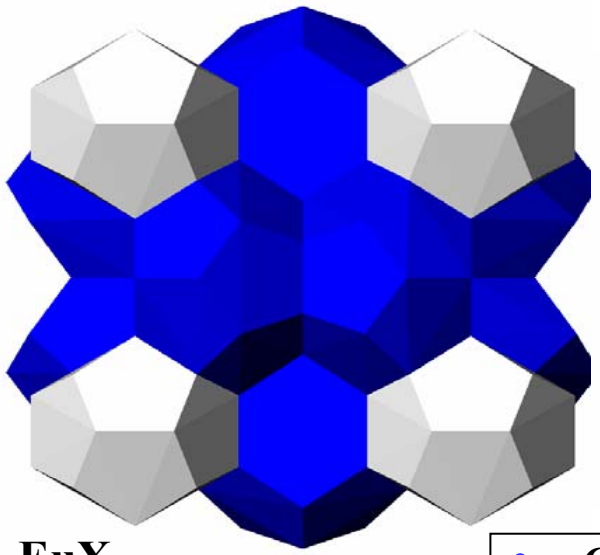


SrX_{20}

SrX_{24}

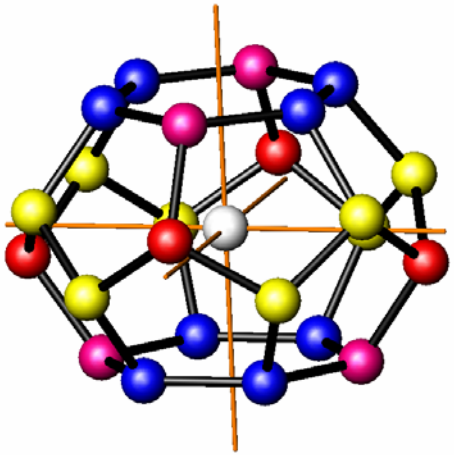
Macroscopic properties – high quality crystal, good electrical conductivity, poor thermal conductivity

Thermal conductivity in filled clathrates

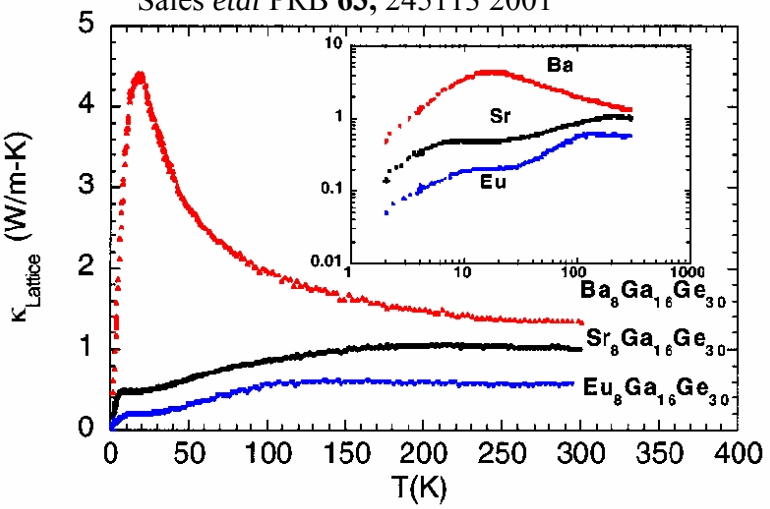


EuX_{20} EuX_{24}

Site 2 cage; EuX_{24}



Sales *etal* PRB **63**, 245113 2001



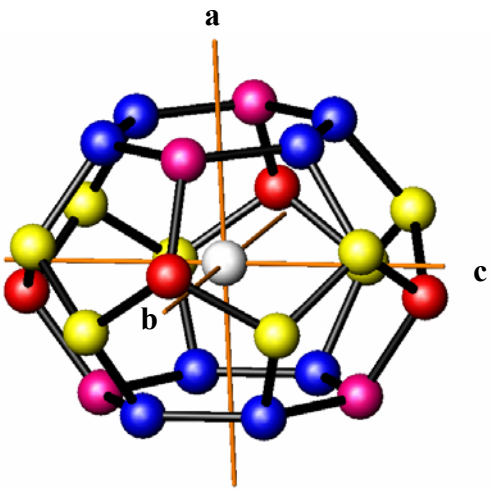
- Central atom is Eu2 or Sr2.
- Blue atoms – nearest neighbor M3 sites ~ 3.6Å
- Purple atoms – M1 sites ~ 3.78Å.
- Yellow atoms – M2 sites ~ 3.98Å.
- Red atoms – further neighbor M3 sites ~ 4.15Å

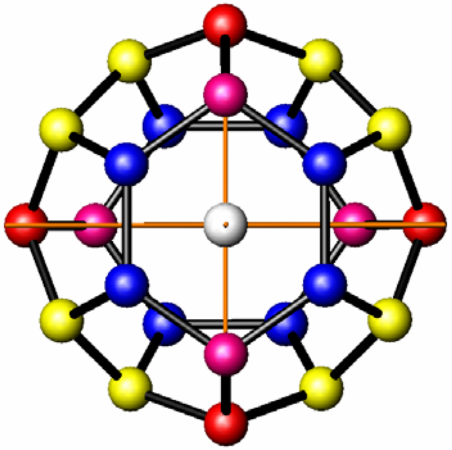
In n-type material

- Low thermal conductivity is attributed to the "rattling" of the Sr or Eu atoms within the large cage called site 2; Cages are SrX_{24} or EuX_{24}; X= Ga/Ge. Sr and Eu are off-center in site 2; κ is suppressed - good for thermoelectrics
- Eu and Sr are on-center in smaller site 1 cage (gray).

UCSC

Structure of the Sr2 (or Eu2) site





Top View

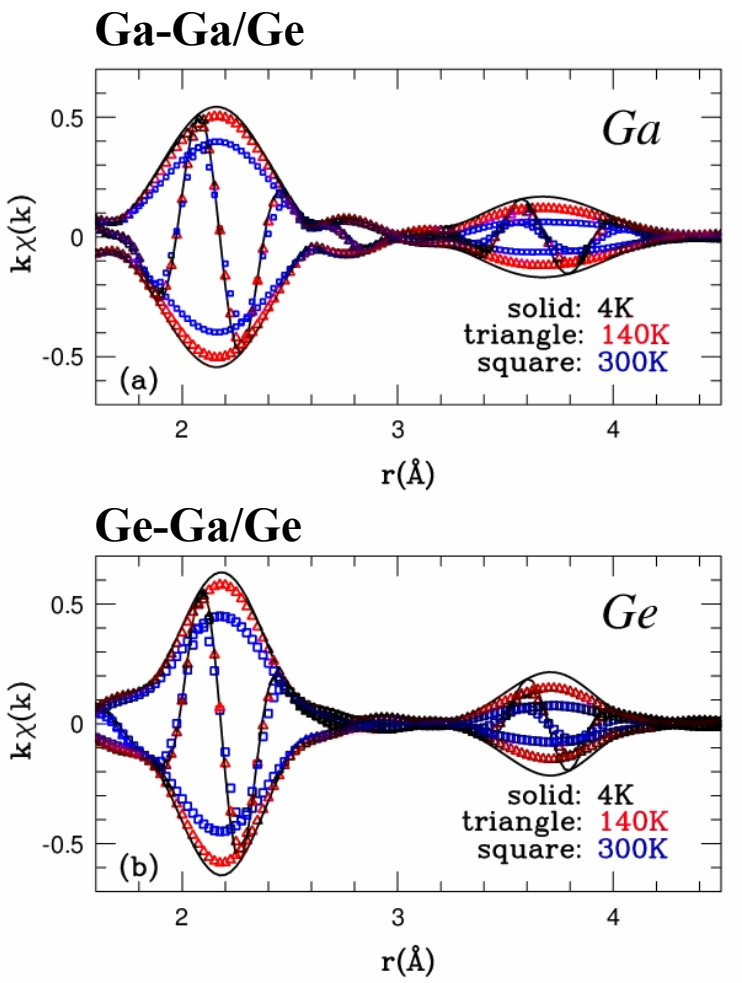
- **Central atom is Sr.**
- **Blue atoms – nearest neighbor M3 sites ~ 3.6Å**
- **Purple atoms – M1 sites ~ 3.78Å.**
- **Yellow atoms – M2 sites ~ 3.98Å.**
- **Red atoms – further neighbor M3 sites ~ 4.15Å**

Off-center directions (four sites)

- **24k sites – along the b or c axes, (0,Δ,0) or (0,0, Δ).**
- **modified "24k"site; off-center towards most distant M3 site (red atoms) - (δ,Δ,0) .**
- **24j sites – along (0, Δ, Δ); midpoint between two M2 sites (yellow atoms). Poor fit for EXAFS and diffraction.**

UCSC

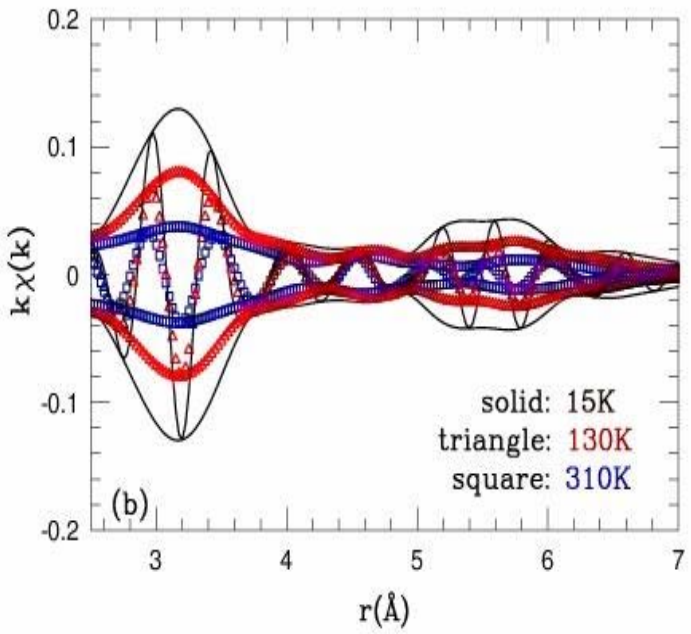
Ga and Ge EXAFS of $Eu_8Ga_{16}Ge_{30}$



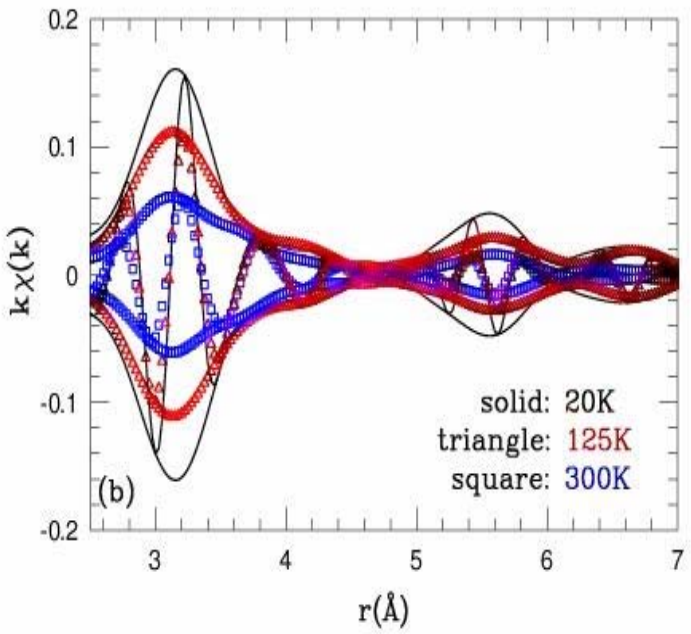
- Ga and Ge k-edge EXAFS very similar
- Weak T-dependence of 1st peak
  - → Stiff Eu1 and Eu2 cages
  - → High Debye Temperature, 400K
- Nearly identical results for $Sr_8Ga_{16}Ge_{30}$

EXAFS of rattler atoms Eu and Sr

$Eu_8Ga_{16}Ge_{30}$ – Eu L_{III}-edge



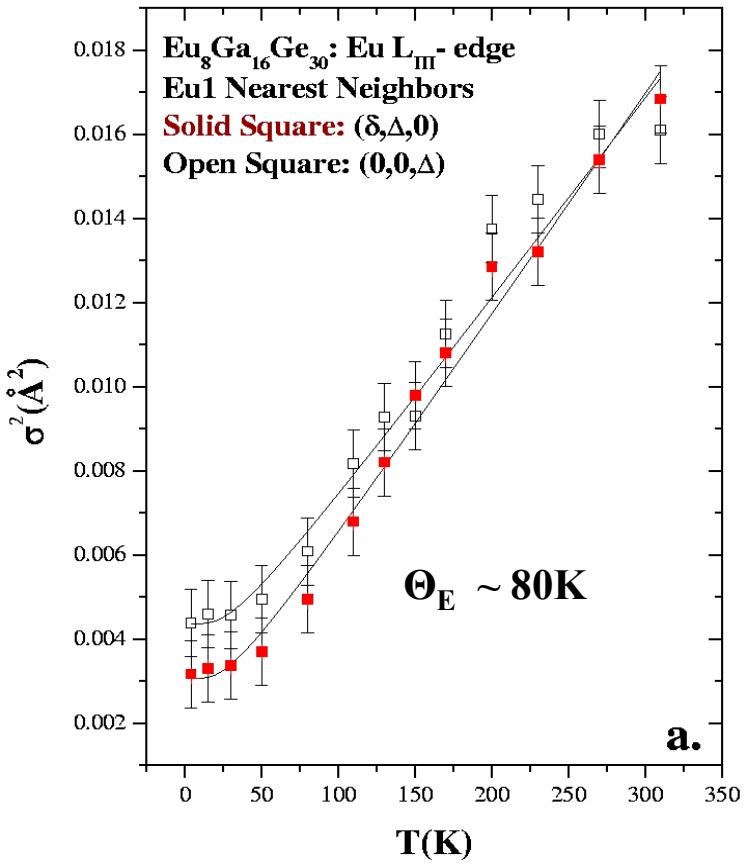
$Sr_8Ga_{16}Ge_{30}$ – Sr k-edge



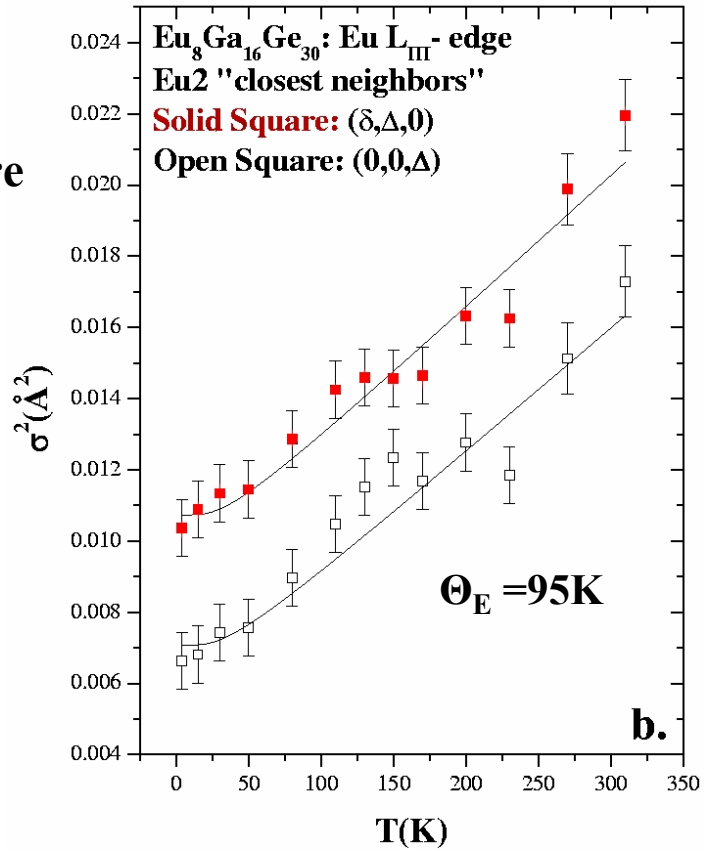
Baumbach *etal* PRB 2005

- **Eu and Sr EXAFS strongly T dependent**
- **First peak mostly near 3.2 Å -- but expect it to extend to ~4 Å**
- **To fit Eu2 use 4 groups of neighbors with different σ^2's**
- **Requires that near neighbors have small σ, more distant neighbors within cage have a large σ**
- **Off-center Eu2 or Sr2 bonded to side of cage!!**

Einstein model for Eu1 and Eu2



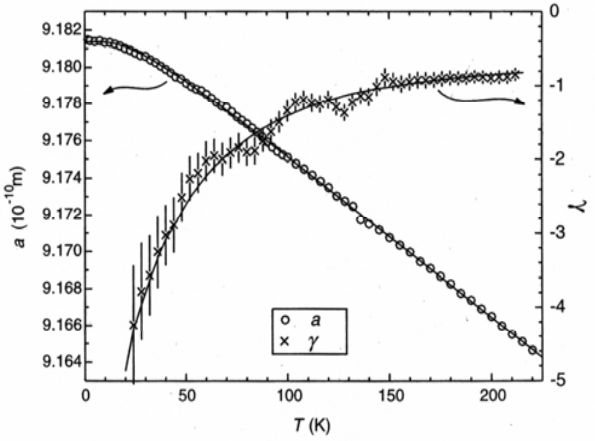
Eu1 and Eu2 are both rattlers



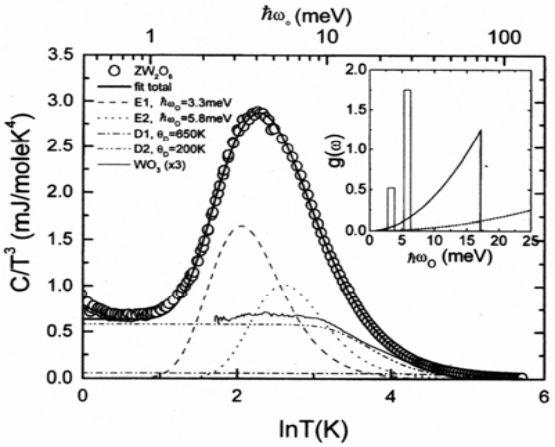
Einstein temperature for Eu2 nearest neighbors higher than for Eu1! This is a measure of radial vibrations – quite different than the low average Einstein temperature from diffraction thermal parameters.

Eu2 off-center ~ 0.44Å

Background: ZrW_2O_8



Ernst *et al, Nature* **396, 1998**



Ramirez *et al, Physical Review Letters* **80, 1998**

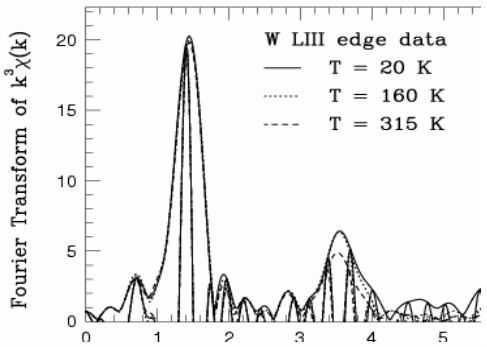
Cubic crystal structure

- ZrO_6 (yellow) octahedra and WO_4 (red) tetrahedra corner linked; two types of W-- (W(1)with O(1) and O(4) neighbors and W(2) with O(2) and O(3) neighbors).
- Zr-Zr distance determines lattice constant.
- $W(1)O_4$ and $W(2)O_4$ tetrahedral units not constrained along <111> axis. The O3 or O4 along the <111> axis is not connected to another unit.
- WO_4 tetrahedra are very stiff – Raman measurements yield ~ 1000 cm^{-1} (~ 1500K) for the compression mode.

Example of unusual correlations

Large motions of WO_4 tetrahedra (and ZrO_6 octahedra) but very small vibrations of W-O!

UCSC



σ^2 vs. T for ZrW_2O_8

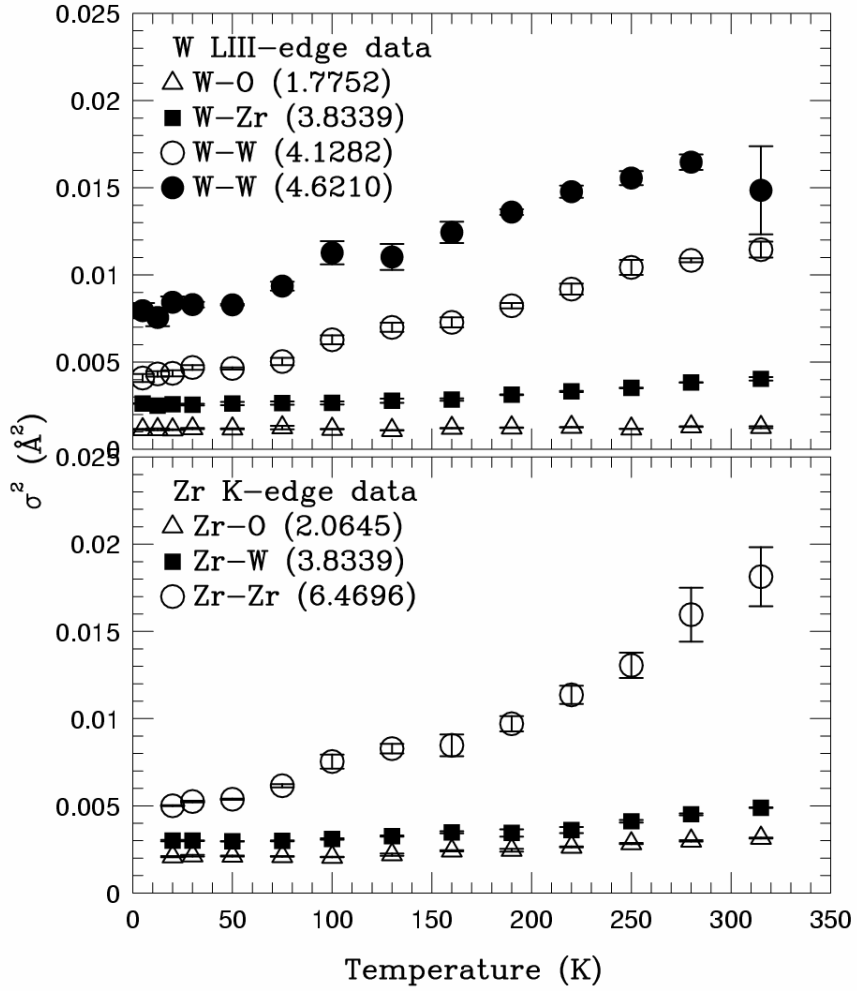
- σ^2 for W-O nearly independent of T
- Very small zero-point motion (0.0012Å²)
  zero-point motion from Raman energies ~ 0.0011Å²
- σ^2 for W-W has a strong T dependence
- Large zero-point motion contribution (0.0045Å²)
- σ^2 for Zr-O weak T dependence
- σ^2 for Zr-Zr very strong T dependence

Strong Correlations

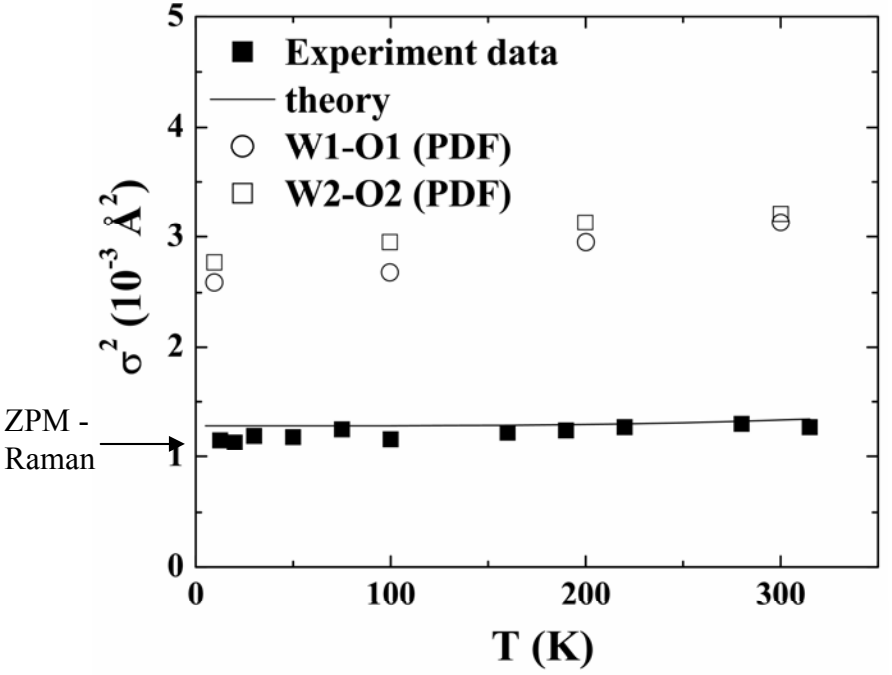
W – involved in small amplitude (high frequency) W-O mode and large amplitude (low frequency) WO_4–WO_4 mode.

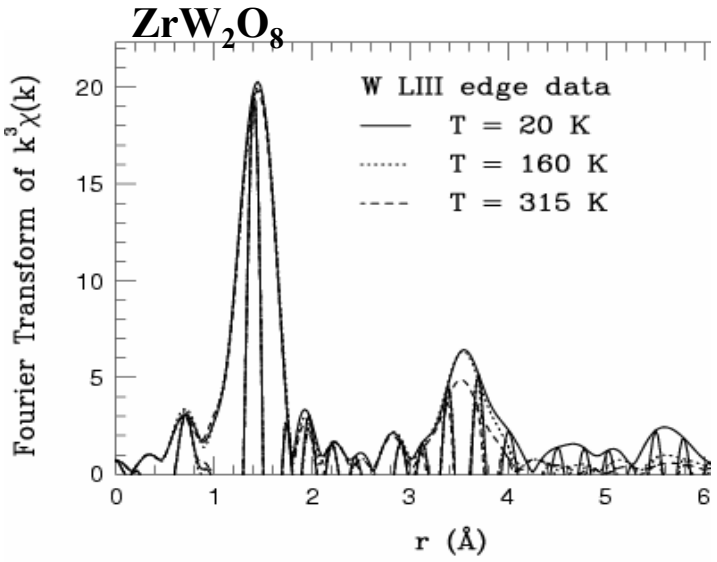
$\sigma^2_{EXAFS} = U^2_A + U^2_B - 2U_AU_B\phi$

where U_A and U_B are atomic displacement parameters from diffraction, but need good anisotropic parameters



Controversy with PDF





- Structure has two WO_4 tetrahedra, W-O bonds - strongest in structure.
- 4 closely spaced W-O peaks.
- σ^2_{EXAFS} for W-O nearly independent of T
- Very small zero-point motion (ZPM) value - 0.0012Å^2;
  ZPM from highest Raman energies ~ 0.0011Å^2
- $\sigma^2_{cluster}$ calculation; comparable to σ^2_{EXAFS} ZPM value ~ 0.0013Å^2.

Strong Correlations

W – involved in small amplitude (high frequency – 125 meV) W-O mode and large amplitude (low frequency) WO_4 –WO_4 mode.

Neutron PDF needs to integrate over a large enough energy range to probe high frequency correlations.

Need joint EXAFS/PDF studies on same sample material

Conclusions

- In complex structures, σ^2 can arise from a combination of mechanisms – a T dependence can help separate them.
- In some systems there are several characteristic temperatures- often associated with different parts of the unit cell.
- Significant correlation effects can be observed in addition to the often used, correlated Debye model.
- For large open unit cells, molecular clusters can behavior much like large atoms in low energy vibrations.
- In some cases the same atom can be involved in a low frequency Einstein mode and also a very high frequency Einstein mode.
- When several mechanisms operative, only parts of the displacements are correlated.
- Shown that for uniform powder samples and unfocused beamline can obtain very high reproducibility in EXAFS data [not usually attainable using focused beamlines].

UCSC