XAFS in Anisotropic Structures: Exploiting Angular Dependence for Better Modeling

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Outline

- **Origin of Angular dependence**

  K, L edges

- **Angular averaging**

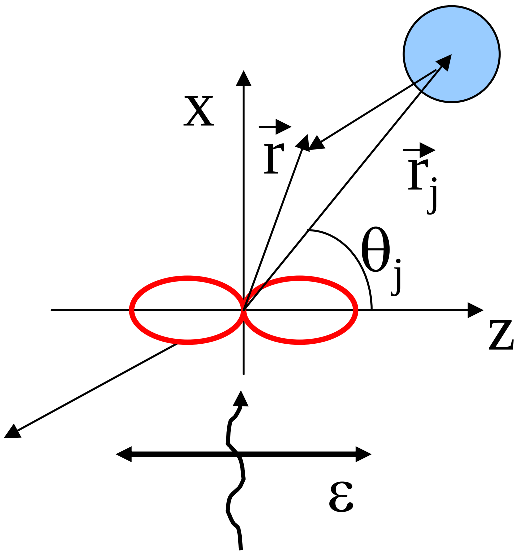
  Powders, partially oriented, crystals

  Symmetry requirements

- **Exploiting angular dependence**

  High T_c Superconductors, Manganites

Origin of Angular Dependence



$$\mu(E) \approx |\langle f\,|\,e\vec{r}\cdot\vec{\varepsilon}\,|\,i\rangle|^2$$

K-edge:

$$\begin{cases} |i\rangle = |s\rangle \quad (l = 0, P_0) \\ \vec{r}\cdot\vec{\varepsilon} \approx \cos\Theta \quad (P_1) \end{cases}$$

$$|f\rangle = |p\rangle \approx \cos\Theta \quad (l = 1, P_1)$$

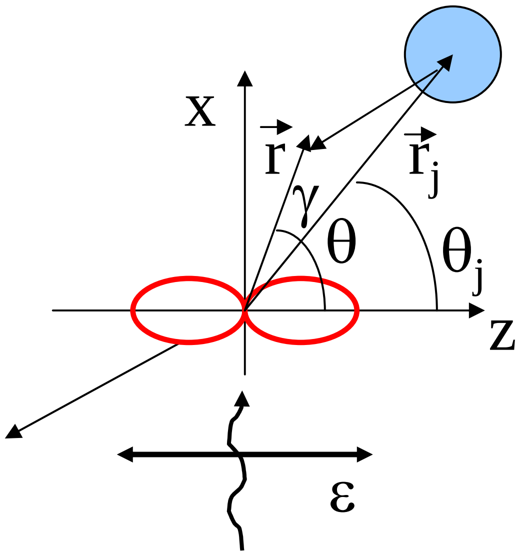
$$\int_{-1}^{1} P_{l'}(x)P_l(x)dx = \frac{2}{2l+1}\delta_{l'l}$$

$$x = \cos\Theta$$

$$\begin{cases} P_0(x) = 1 \\ P_1(x) = x \\ P_2(x) = \frac{1}{2}(3x^2 - 1) \end{cases}$$

Dipole Sel. Rules: $\Delta l = \pm 1, \Delta m_l = 0$

$$\mu(E) \approx |\langle f \,|\, e\vec{r}\cdot\vec{\varepsilon} \,|\, i\rangle|^2$$



<u>K-edge:</u> $|f\rangle = |p\rangle \approx \cos\Theta$

$$|f\rangle = |f_1\rangle + |f_2\rangle$$

$$|f_1\rangle = A(kr)\cos\Theta$$

$$|f_2\rangle = A(kr_j)\cos\Theta_j\, f(\pi)\frac{e^{ik|\vec{r}-\vec{r}_j|}}{k|\vec{r}-\vec{r}_j|}$$

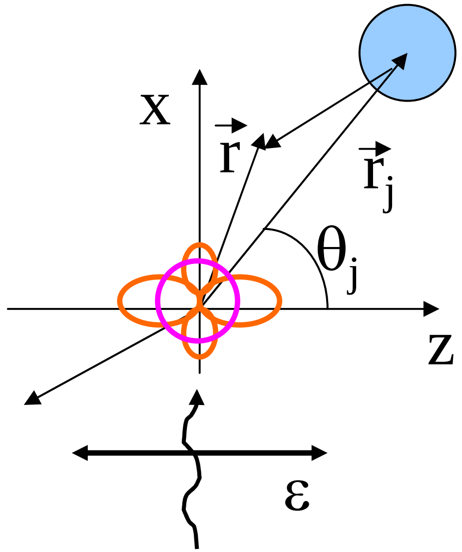
$$|\vec{r}-\vec{r}_j| = (r^2 + r_j^2 - 2rr_j\cos\gamma)^{1/2}$$

$$\cos\gamma = \cos\Theta\cos\Theta_j + \sin\Theta_j\sin\Theta\cos\phi$$

$$|f\rangle = A(kr)\cos\Theta[1 + 3i\{A(kr_j)^2\}\cos^2\Theta_j\, f(\pi)e^{2i\delta_1}]$$

$$\mu = \mu_0[1 - \mathrm{Im}\sum_j \{A(kr_j)^2\} 3\cos^2\Theta_j\, f(\pi)e^{2i\delta_1}]$$

$$\mu(E) \approx |\langle f \,|\, e\vec{r}\cdot\vec{\varepsilon} \,|\, i\rangle|^2$$



L$_{2,3}$-edges:

$$|i\rangle = |p\rangle \approx \cos\Theta \quad (l = 1, P_1)$$

$$\vec{r}\cdot\vec{\varepsilon} \approx \cos\Theta \quad (P_1)$$

$$|f\rangle = \begin{cases} |d\rangle & (l = 2, P_2) \\ |s\rangle & (l = 0, P_0) \end{cases}$$

$$\chi(k) = \Big\{ \langle 1|2\rangle\langle 0|1\rangle \sum_j \frac{\sin[2kr_j + \delta'_{02}(k)]}{kr_j^2} |f_j(k)| (1 - 3\cos^2\Theta_j)$$
$$+ \frac{|\langle 2|1\rangle|^2}{2} \sum_j \frac{\sin[2kr_j + \delta'_2(k)]}{kr_j^2} |f_j(k)| (1 + 3\cos^2\Theta_j)$$
$$+ \frac{|\langle 0|1\rangle|^2}{2} \sum_j \frac{\sin[2kr_j + \delta'_0(k)]}{kr_j^2} |f_j(k)| \Big\} \Big(|\langle 2|1\rangle|^2 + \frac{1}{2} |\langle 0|1\rangle|^2 \Big)^{-1}$$

$$\begin{cases} P_0(x) = 1 \\ P_1(x) = x \\ P_2(x) = \frac{1}{2}(3x^2 - 1) \end{cases}$$

$$\Delta l = \pm 1, \Delta m_l = 0$$

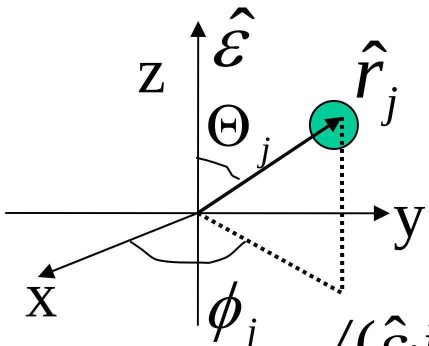
$$\frac{\langle 0|1\rangle}{\langle 1|2\rangle} = 0.2$$

Heald & Stern (1977)

Angular Averaging (K-edge, SS)

$$\chi(k) = -\sum_j 3(\hat{\varepsilon}\cdot\hat{r}_j)^2 \frac{f_j(\pi,k)}{k^2 r_j^2}\sin(2kr_j + \delta_j(k))$$

Random (powder, polycrystalline)

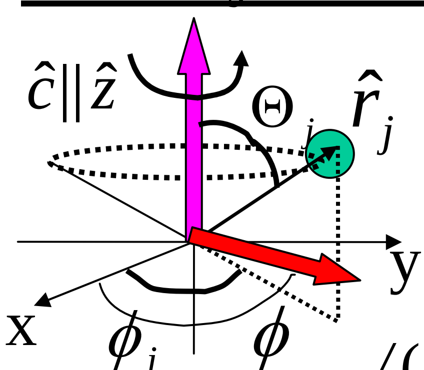


$$\hat{r}_j = (\sin\Theta_j\cos\phi_j, \sin\Theta_j\sin\phi_j, \cos\Theta_j)$$

$$\hat{\varepsilon} = (0,0,1)$$

$$\langle(\hat{\varepsilon}\cdot\hat{r}_j)^2\rangle_{\Theta_j,\phi_j} = \frac{1}{4\pi}\int d\Omega_j \cos^2\Theta_j = \frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}\sin\Theta_j d\Theta_j d\phi_j \cos^2\Theta_j = \frac{1}{3}$$

Partially oriented powder (c-axis aligned, random ab)



$$\hat{\varepsilon} = (0,0,1) \qquad \langle(\hat{\varepsilon}\cdot\hat{r}_j)^2\rangle = \cos^2\Theta_j$$

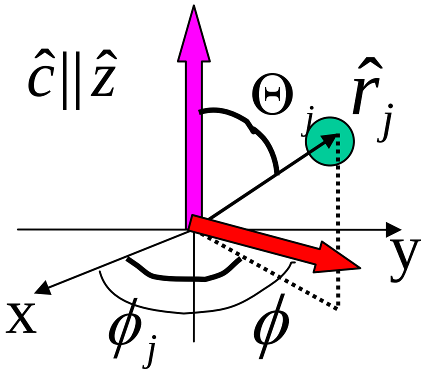
$$\hat{\varepsilon} = (\cos\phi, \sin\phi, 0)$$

$$\langle(\hat{\varepsilon}\cdot\hat{r}_j)^2\rangle = \langle(\cos\phi\sin\Theta_j\cos\phi_j + \sin\phi\sin\Theta_j\sin\phi_j)^2\rangle = \frac{\sin^2\Theta_j}{2}$$

Angular Averaging (K-edge, SS)

$$\chi(k) = -\sum_j 3(\hat{\varepsilon}\cdot\hat{r}_j)^2 \frac{f_j(\pi,k)}{k^2 r_j^2}\sin(2kr_j + \delta_j(k))$$

Single crystal



$\hat{\varepsilon} = (0,0,1)$ $\quad \langle(\hat{\varepsilon}\cdot\hat{r}_j)^2\rangle = \cos^2\Theta_j$

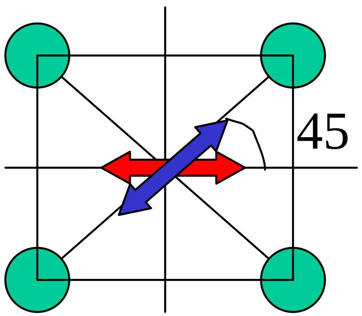
$\hat{\varepsilon} = (\cos\phi, \sin\phi, 0)$

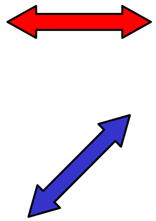
$$\langle(\hat{\varepsilon}\cdot\hat{r}_j)^2\rangle = \langle(\cos\phi\sin\Theta_j\cos\phi_j + \sin\phi\sin\Theta_j\sin\phi_j)^2\rangle$$

$$= \sin^2\Theta_j\cos^2(\phi - \phi_j)$$

Symmetry requirements

$$\chi(k) \approx \sum_j (\hat{\varepsilon} \cdot \hat{r}_j)^2 \ldots$$

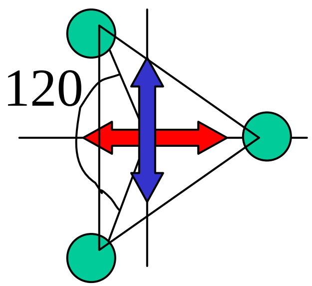


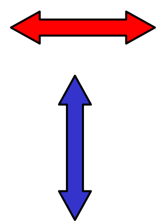


$$\sum_{j=1}^{4} \cos^2 45 = 2$$

$$2 + 0 = 2$$

Same for 4-fold rot. axis

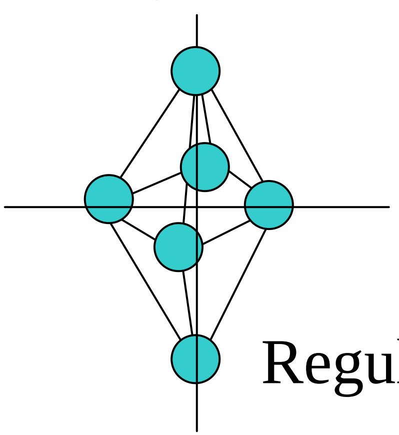




$$1 + \cos^2 120 + \cos^2 120 = 1.5$$

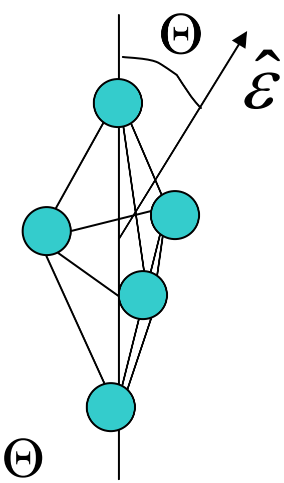
$$\cos^2 30 + \cos^2 30 + 0 = 1.5$$

Same for 3-fold



Regular Octahedron

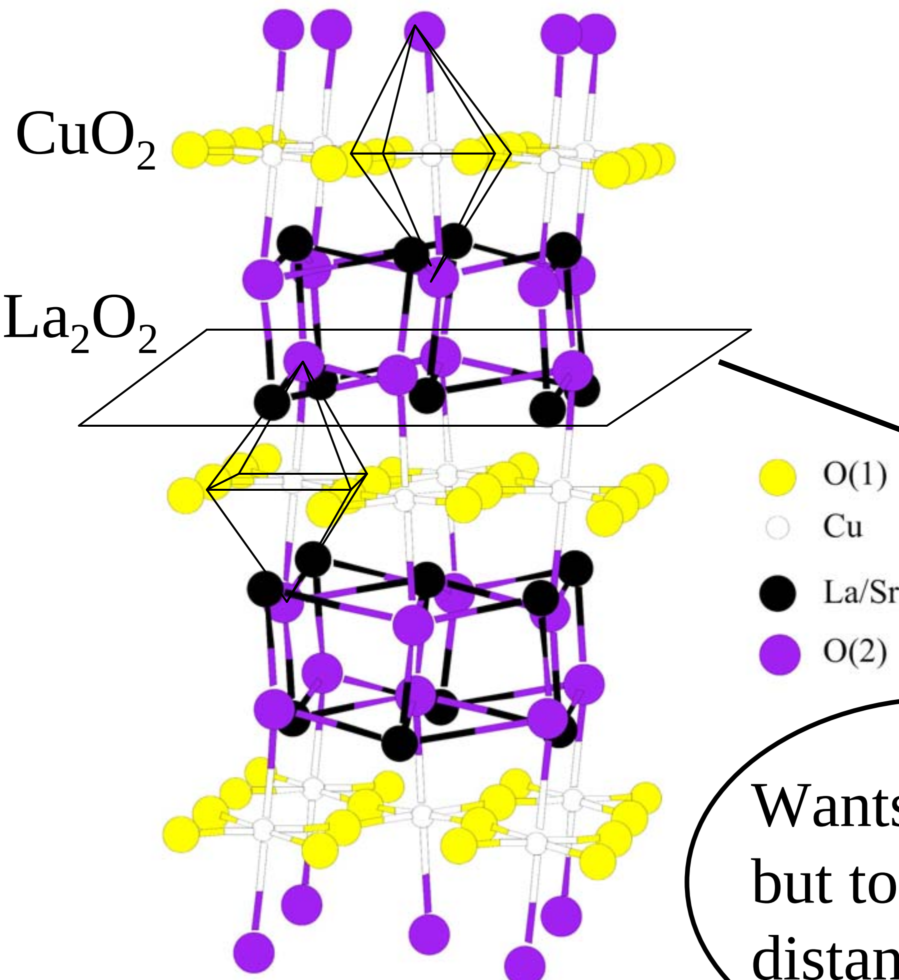
Needs lower than cubic symmetry to see angular dependence

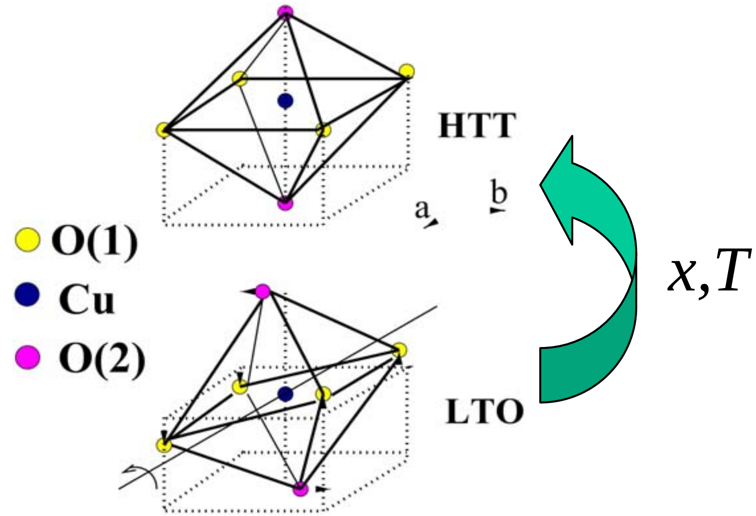


$$\mu(\Theta) = \mu_{\parallel} \sin^2\Theta + \mu_{\perp} \cos^2\Theta$$

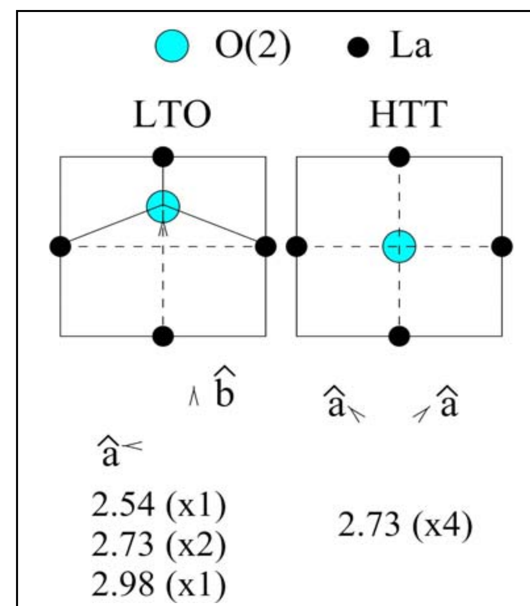
Example 1

High T_c superconductor $La_{2-x}Sr_xCuO_4$

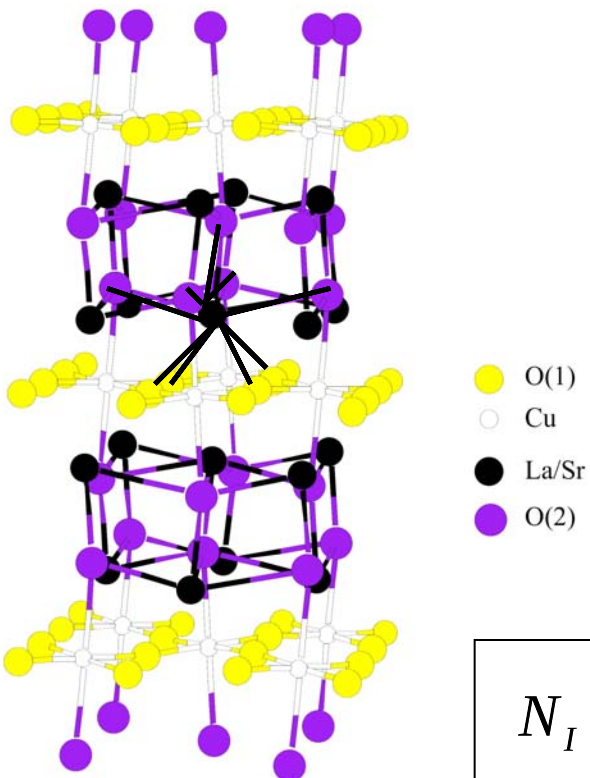




Wants the plane, but too many distances…



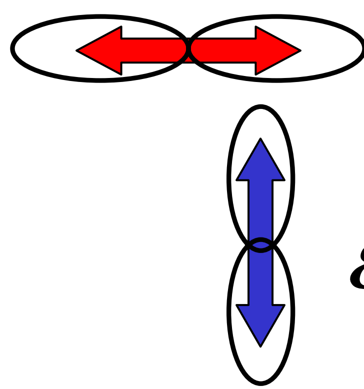
High T_c superconductor $La_{2-x}Sr_xCuO_4$



Distance (Å)		Angle w/c-axis
La-O(2)(1X)	2.35	5
La-O(1)(2X)	2.59	48
La-O(1)(2X)	2.68	44
La-O(2)(1X)	2.54	76
La-O(2)(2X)	2.73	77
La-O(2)(1X)	2.97	78

$$N_I = \frac{2\Delta k \Delta r}{\pi} \approx 6-8$$

$$(\hat{\varepsilon}\cdot\hat{r}_j)^2 = \cos^2\Theta_j$$



$\hat{\varepsilon} \| ab$

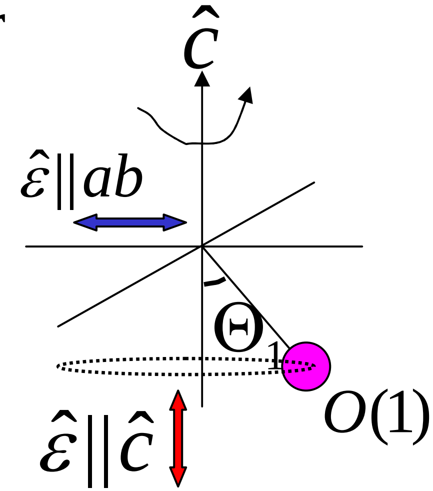
$\hat{\varepsilon} \| \hat{c}$

High T_c Superconductor $La_{2-x}Sr_xCuO_4$

Approach 1:

1. *Trust angles* (use polarized theory)
2. Analyze c-pol, ab-pol *separately*

{ Analyze c-pol → La-O(1) distances →
  set them in ab-pol → get La-O(2) planar



Approach 2:

1. *Trust angles* (use polarized theory)
2. Analyze c-pol and ab-pol *simultaneously* constraining "inclined" La-O(1) distances

C-pol data set + Ab-pol data set

R(La-O(1))=R1 R(La-O(1))=R1

"global" variable

$$\chi_c \approx \cos^2 \Theta_1$$

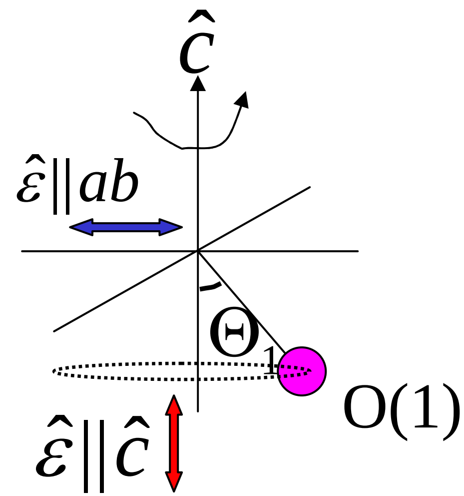
$$\chi_{ab} \approx \frac{\sin^2 \Theta_1}{2}$$

High T_c superconductor $La_{2-x}Sr_xCuO_4$

Approach 3:

1. *Fit angles* (use random theory)
2. Analyze c-pol, ab-pol *simultaneously*

$\chi_{ran} \approx 1/3$



c-pol data set

R(La-O(1)) = R1

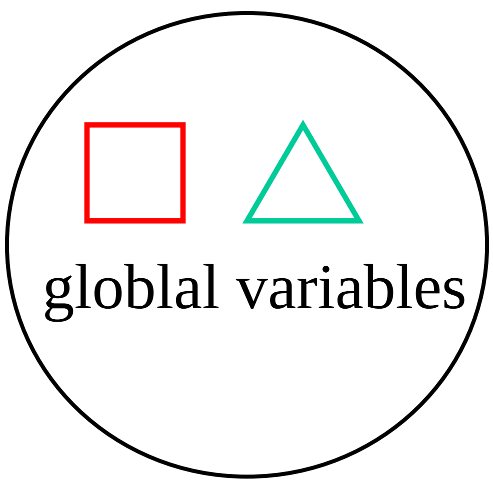
$$A_c(La-O(1)) = A_{ran} 3\cos^2\Theta_1$$

+

ab-pol data set

R(La-O(1)) = R1

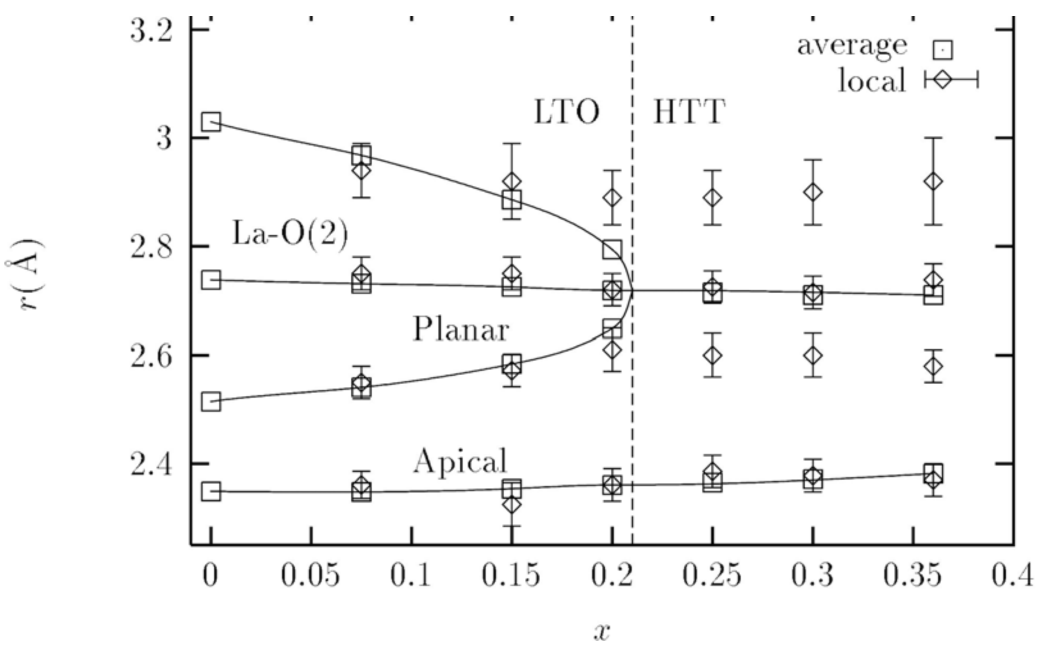
$$A_{ab}(La-O(1)) = A_{ran} 3\frac{\sin^2\Theta_1}{2}$$

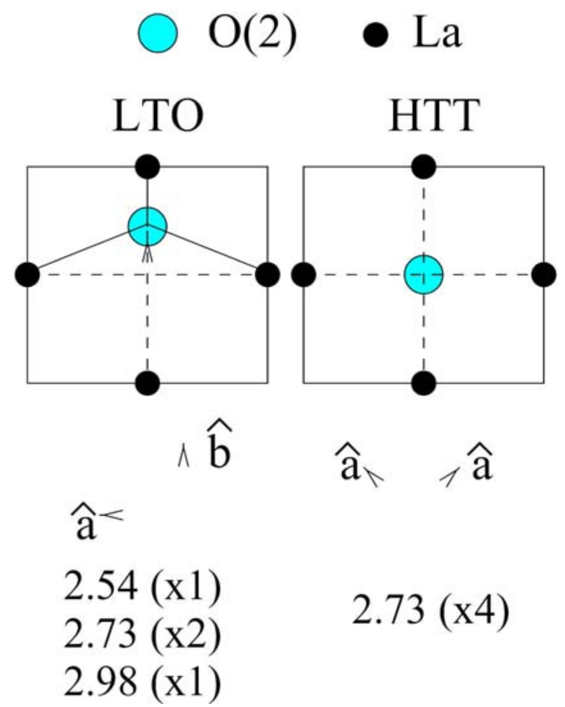


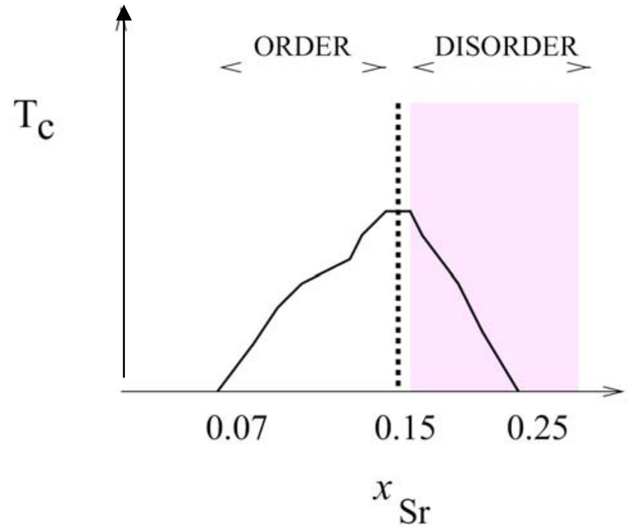
$\chi_c \approx \cos^2\Theta_1$

$\chi_{ab} \approx \frac{\sin^2\Theta_1}{2}$

High T_c superconductor $La_{2-x}Sr_xCuO_4$



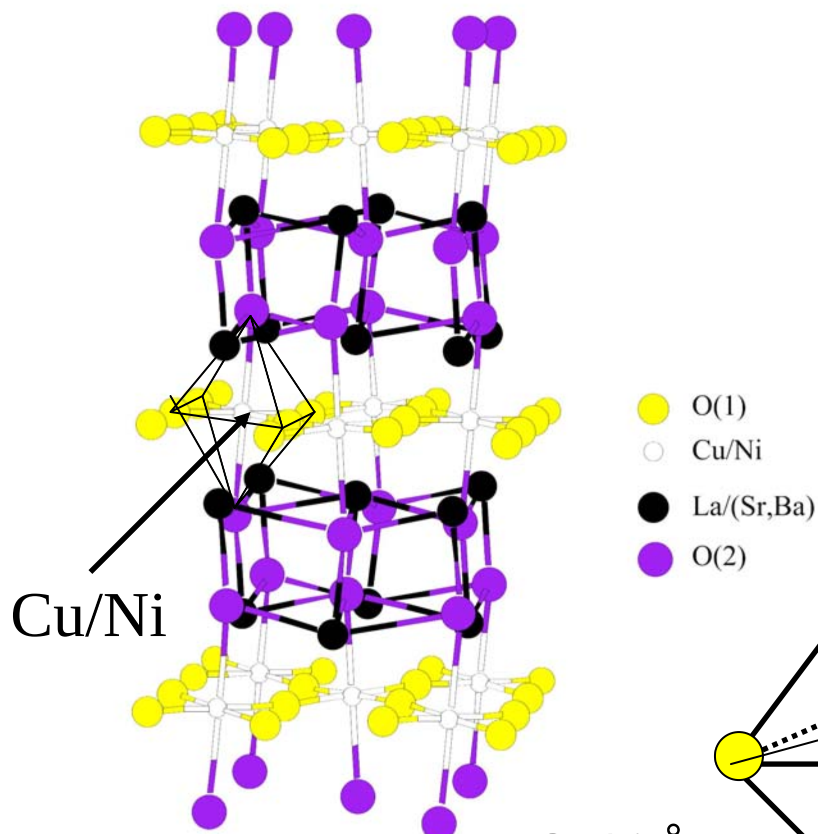


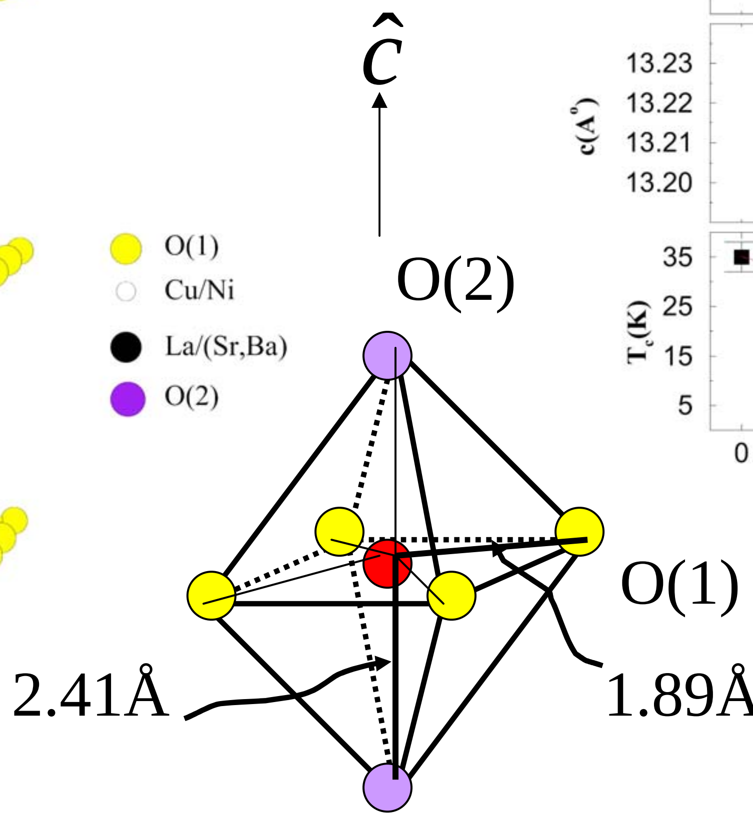


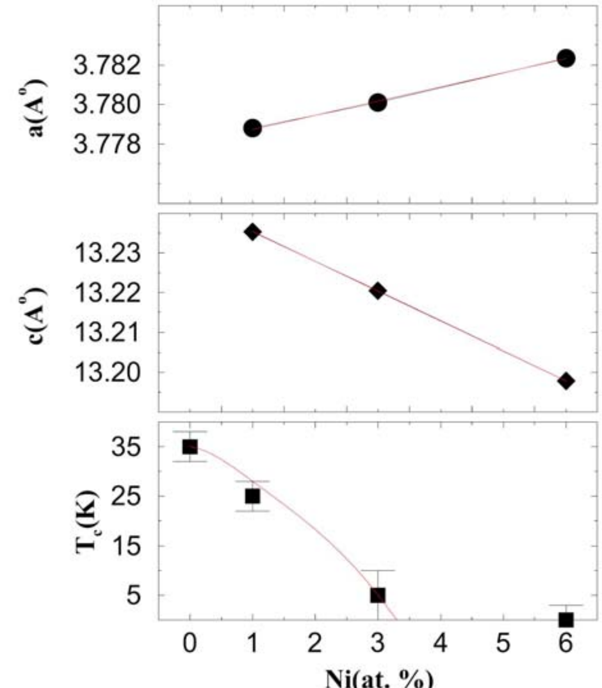
PRL **76**, 439 (1996)
PRB **56**, R521 (1997)
PRB **61**, 7055 (2000)

Example2

Ni impurities in $La_{1.85}Sr_{0.15}Cu_{1-y}Ni_yO_4$







Planar O(1) 4X, rigid
Apical O(2) 2X, soft

→ Dominate powder XAFS

Example2

Ni impurities in $La_{1.85}Sr_{0.15}Cu_{1-y}Ni_yO_4$

c-pol data set

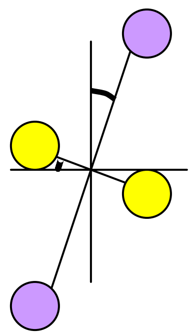
$R(Ni\text{-}O(2))=R2$ } O(2)
$A_{ran}3\cos^2\Theta_2$

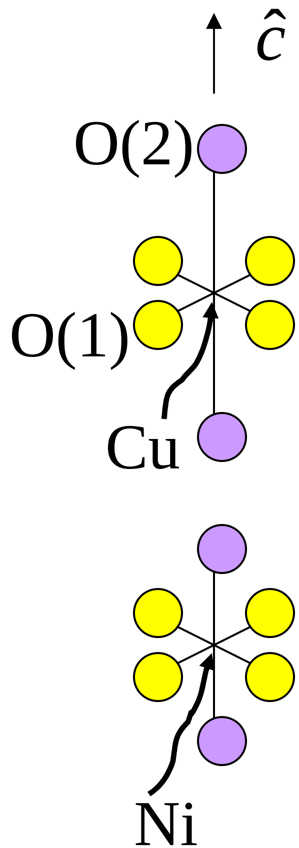
$R(Ni\text{-}O(1))=R1$
$A_{ran}3\cos^2\Theta_1$

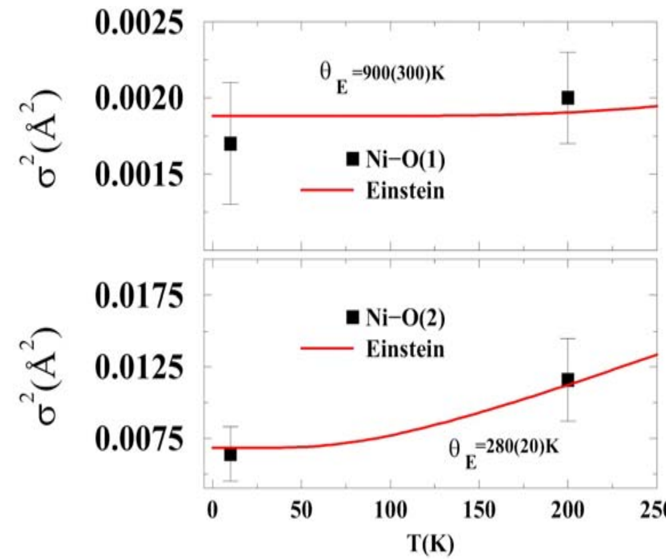
ab-pol data set

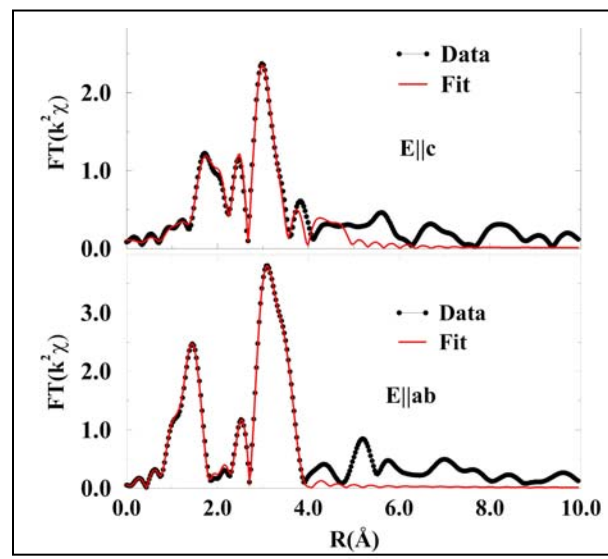
$R(Ni\text{-}O(1))=R1$ } O(1)
$A_{ran}3\frac{\sin^2\Theta_1}{2}$

$R(Ni\text{-}O(2))=R2$
$A_{ran}3\frac{\sin^2\Theta_2}{2}$



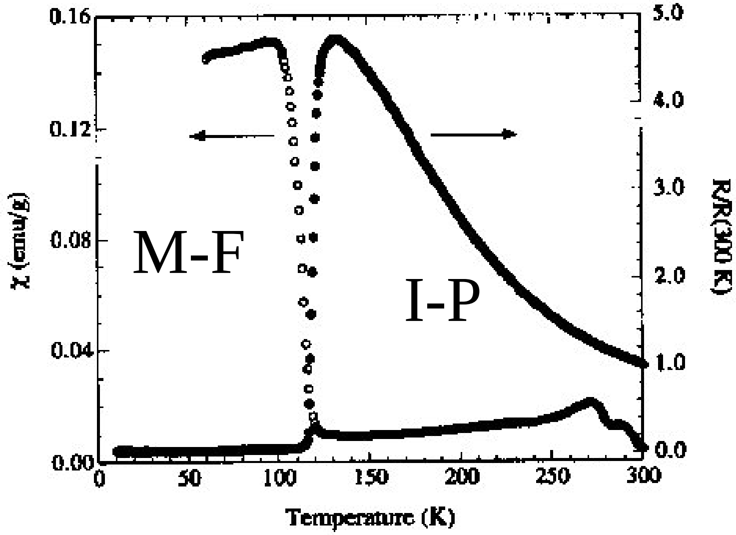


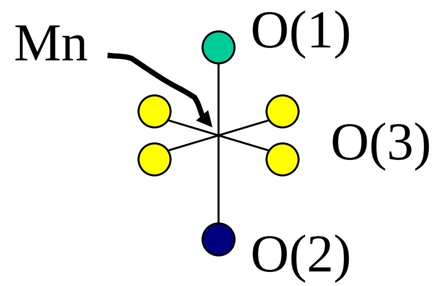


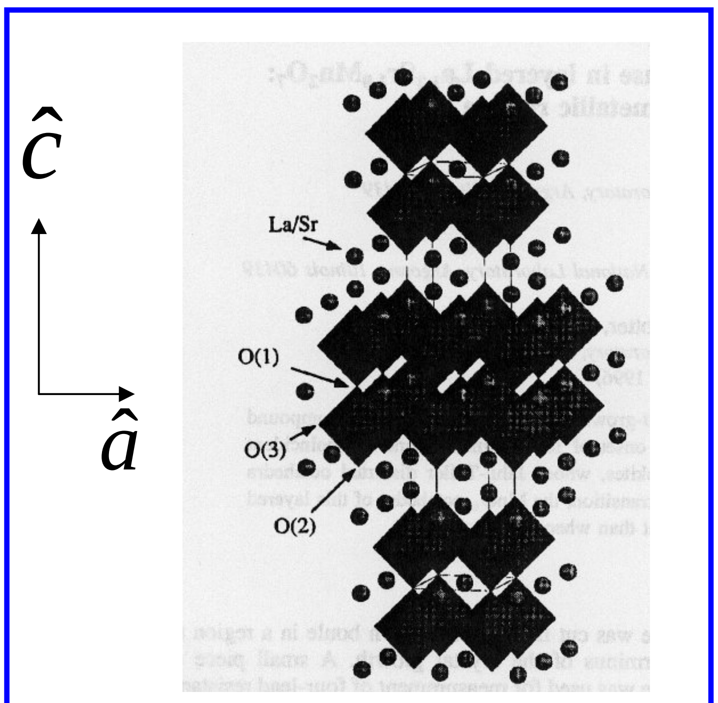


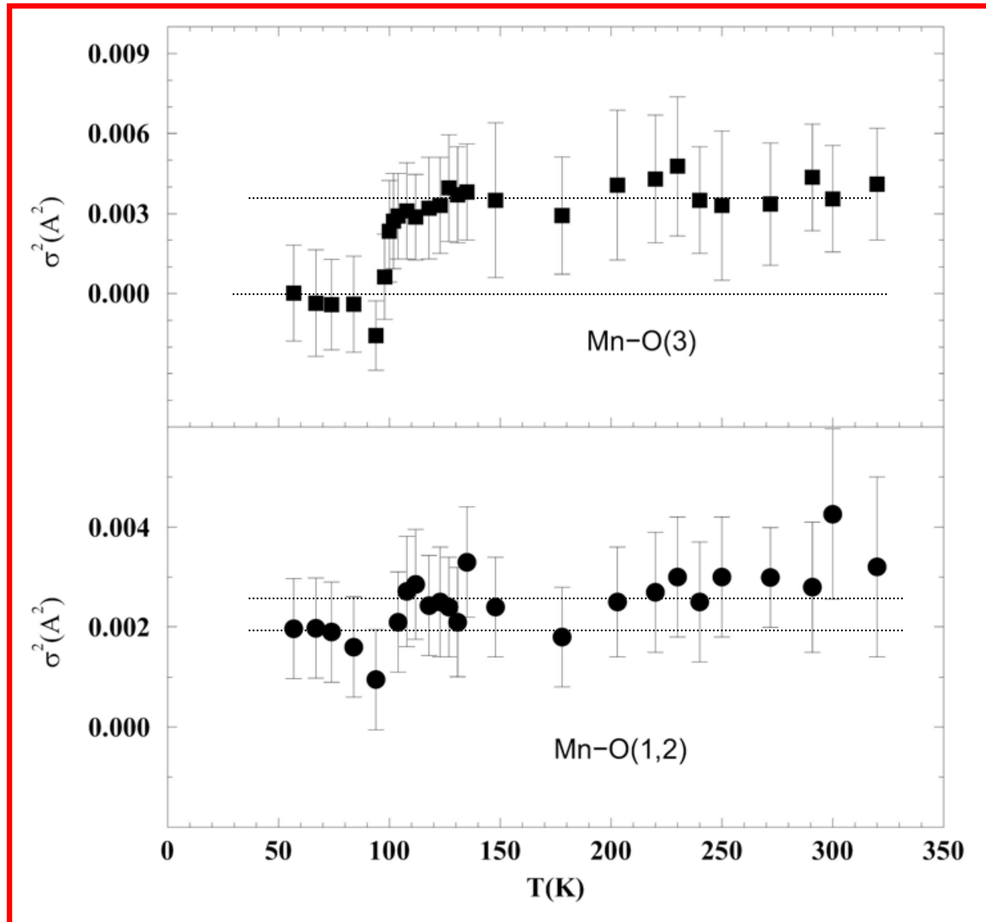
	XAFS	Diffraction
O(1)	1.882(8)Å	1.888Å
O(2)	2.25(1)Å	2.414Å

Example3 CMR $La_{1.2}Sr_{1.8}Mn_2O_7(x=0.4)$









Conclusions

- *Angular resolved XAFS increases "effective" number of independent points in data* N_I / N_P

Allowing:

- *Solving otherwise unsolvable local structures*
- *Increased sensitivity to small lattice anomalies*