# Investigation of local structural environment of complex oxide materials by employing synchrotron radiations

**M. J. Akhtar**

javeda@pinstech.org.pk

Pakistan Institute of Nuclear Science & Technoloy
Nilore, Islamabad, Pakistan

# What is Synchrotron Light (SL)?

• Synchrotron light is very ***intense*** light, including light that we cannot see
***infrared light***, ***ultraviolet light***, **&** ***X-rays***

• SL X-rays are identical with X-rays from medical and dental x-ray machines. But their intensity is more than ***one million*** times greater.

• SL enables scientists to do experiments that they have only dreamed of in the past. Experiments that would have taken months or years to perform can now be done in minutes.

• We are living through a revolution in science & technology due to this immense increase in x-ray source performance.

# Wilhelm Conrad Roentgen 1845-1923

An X-ray lab – circa 1895

Early X-ray by Roentgen. His wife's hand?

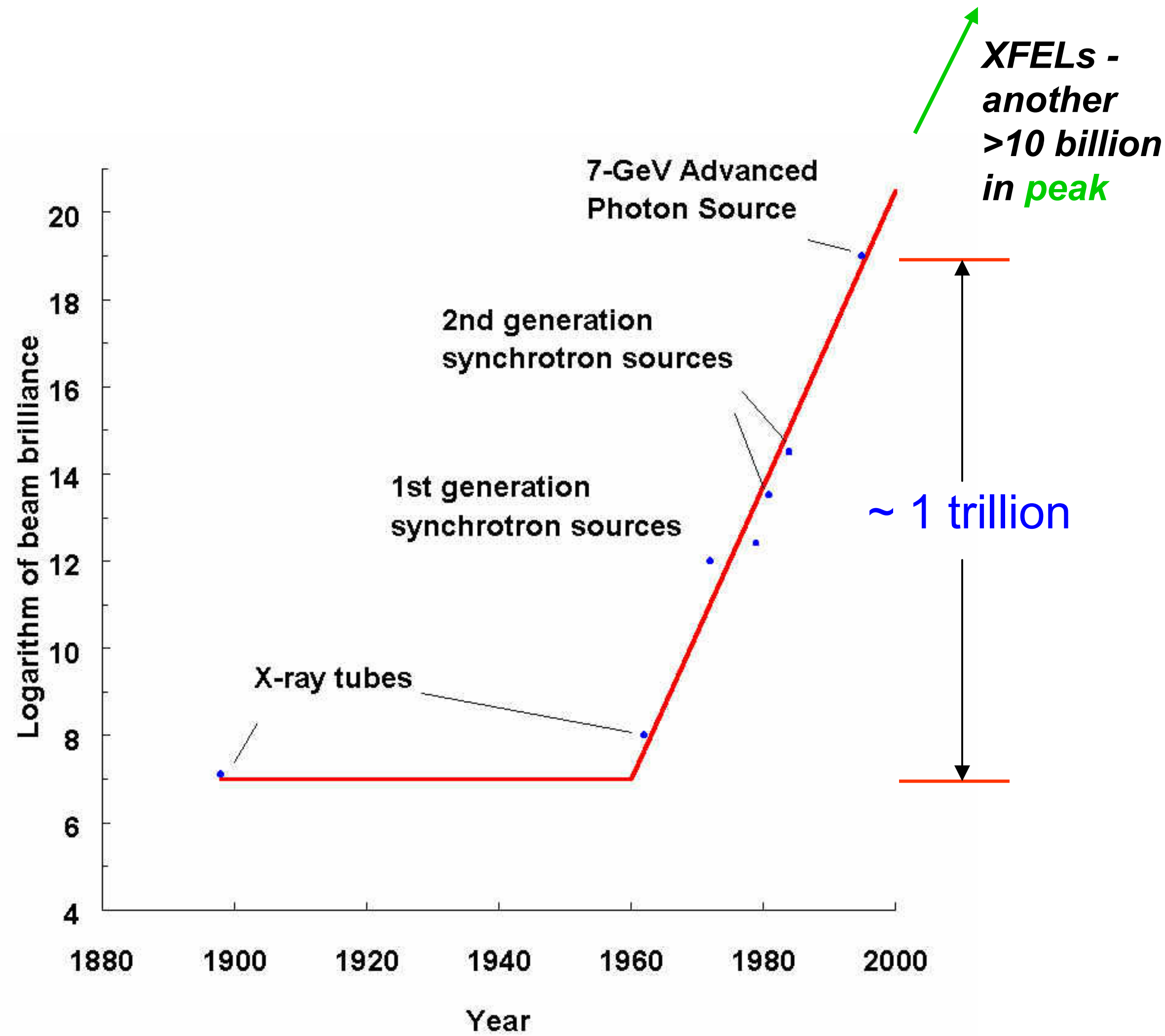
***Curiosity-driven research***

## *What Properties Make Synchrotron Radiation (SR) so Useful?*

***High brightness:***
SR is extremely intense (hundreds of thousands of times higher than conventional X-ray tubes)

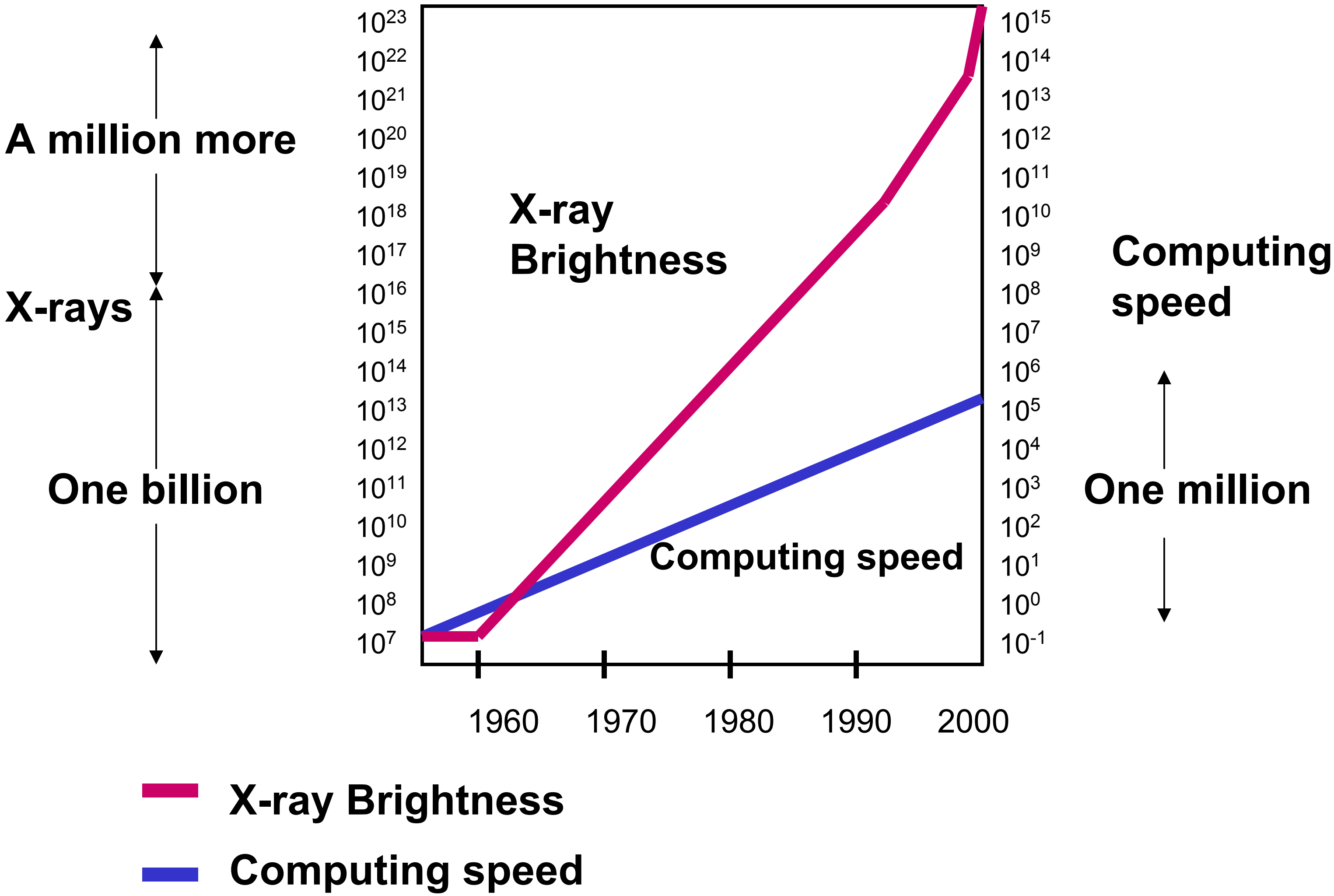
***Wide energy spectrum:***
SR is emitted with a wide range of energies

***Highly polarized and short pulses:***
SR is emitted in very short pulses, typically less that a nano-second (a billionth of a second)

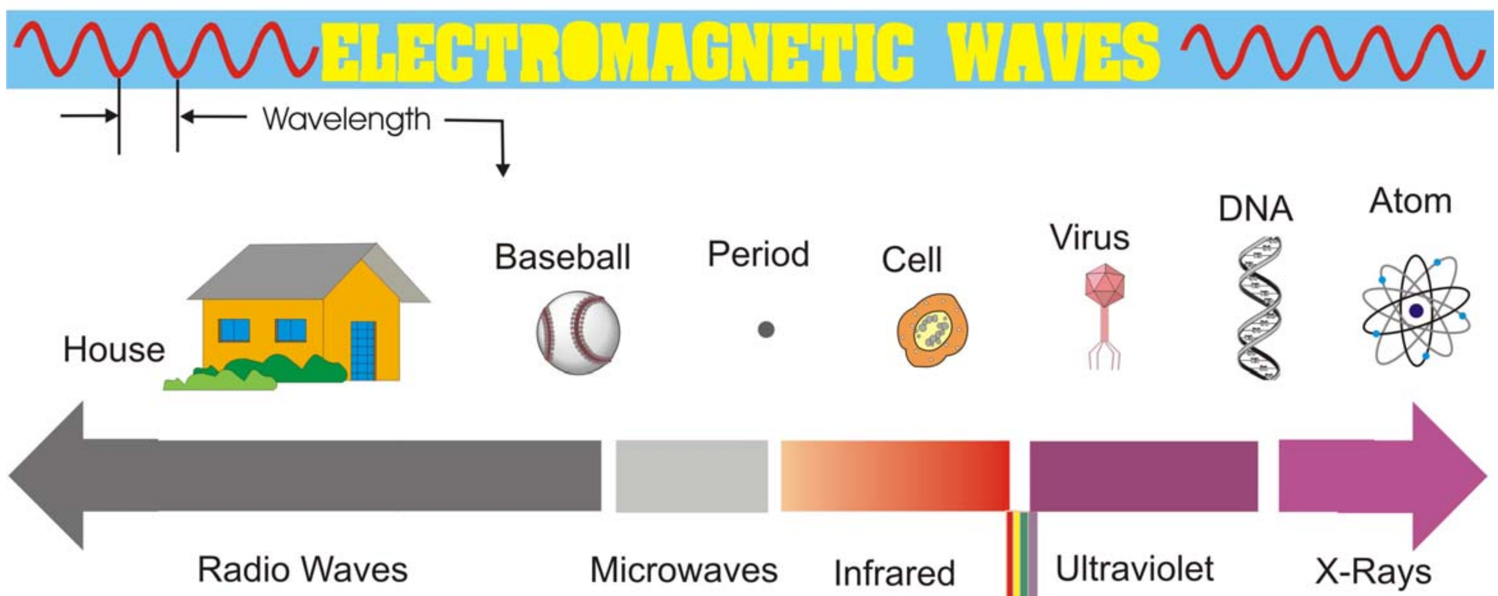



***SR offers many characteristics of visible lasers but into the x-ray regime!***

# Growth in X-ray Brightness compared to growth in Computing Speed



## *Electromagnetic Radiation - How It Relates to the World We Know*




***Seeing an object needs smaller wavelength of the light than the size of object.***
***So to study atoms or molecules, you must use light waves about their size or smaller.***

***X-ray from SYNCHROTRON RADIATION***
***- Long penetration depth in a matter***
***- Wavelengths near the size of atoms and molecules***
***- The right energies to interact with electrons in light atoms***

**Synchrotron radiation is used for experiments typically over this region**

# ***Synchrotron Radiation Facilities Around the World***

- **54 in operation in 19 countries used by more than 20,000 scientists**

  **(Brazil, China, India, Korea, Taiwan, Thailand)**

- **8 in construction**

  **Armenia, Australia, China, France, Jordan, Russia, Spain, UK**

- **11 in design/planning**

For a list of SR facilities around the world see

http://ssrl.slac.stanford.edu/SR_SOURCES.HTML

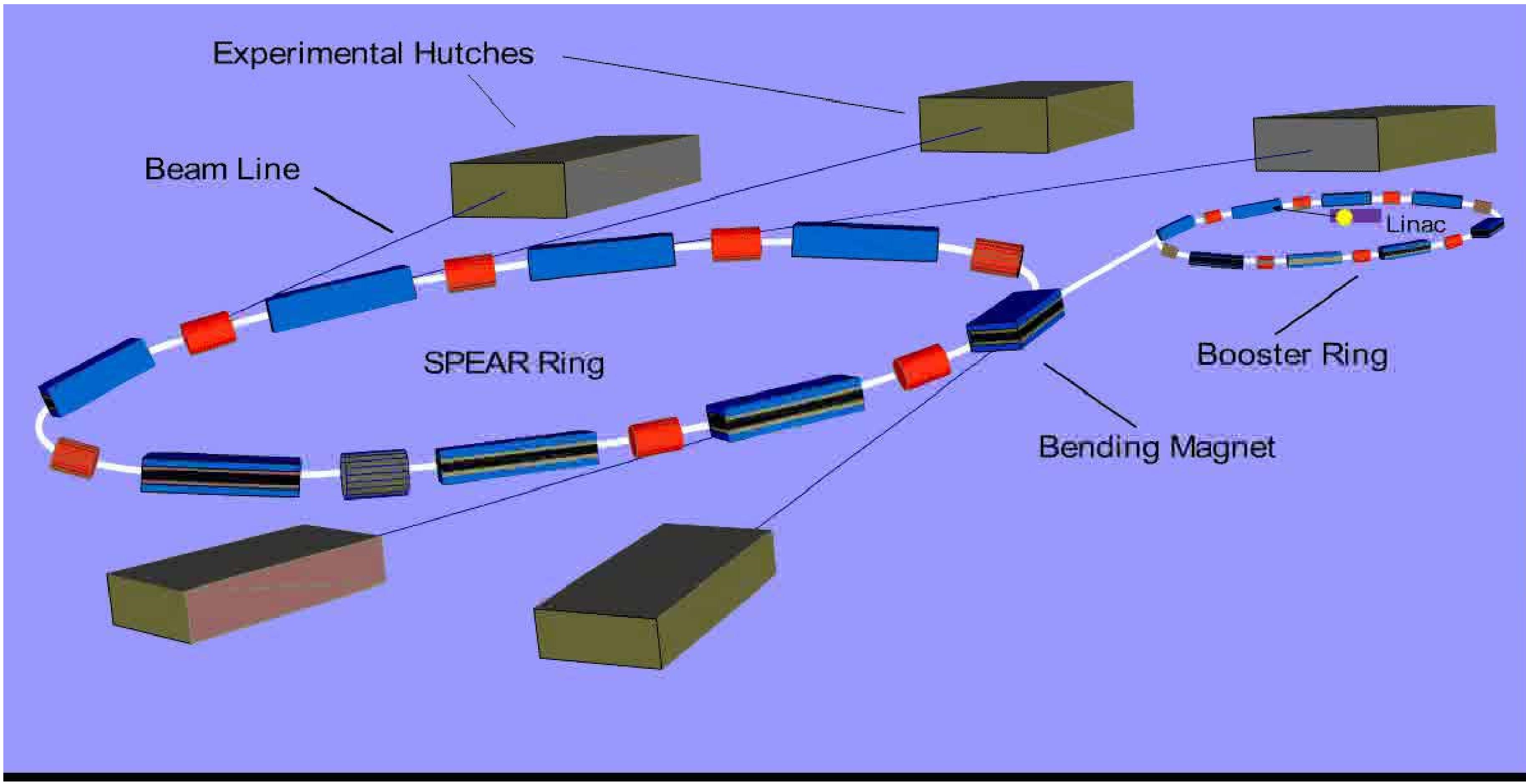
www.sesame.org.jo

# COMPARISON OF POPULATION OF SESAME MEMBER COUNTRIES WITH SOME INDUSTRIALISED COUNTRIES

| SESAME COUNTRY | POPULATION | INDUSTRIAL COUNTRY | POPULATION | SR CENTRES |
|---|---|---|---|---|
| Pakistan | 150,694,740 | USA | 290,342,554 | 8 |
| Iran | 68,278,826 | UK | 60,094,648 | 2 |
| Turkey | 68,109,469 | France | 60,180,529 | 2 |
| Israel | 6,116,533 | Germany | 82,398,326 | 3 |
| Jordan | 5,460,265 | Japan | 127,214,499 | 3(6) |
| Palestinian Authority | 3,512,062 | | | |
| UAE | 2,484,818 | | | |
| Bahrain | 667,238 | | | |
| **TOTAL** | **305,323,395** | | | |

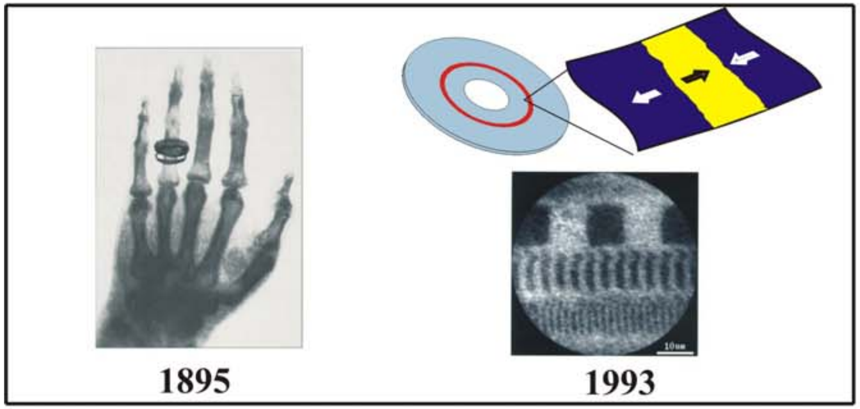
**In industrialised countries, where economies are knowledge based, there is a synchrotron radiation facility per 40M population.**

# *How a storage ring light source works*



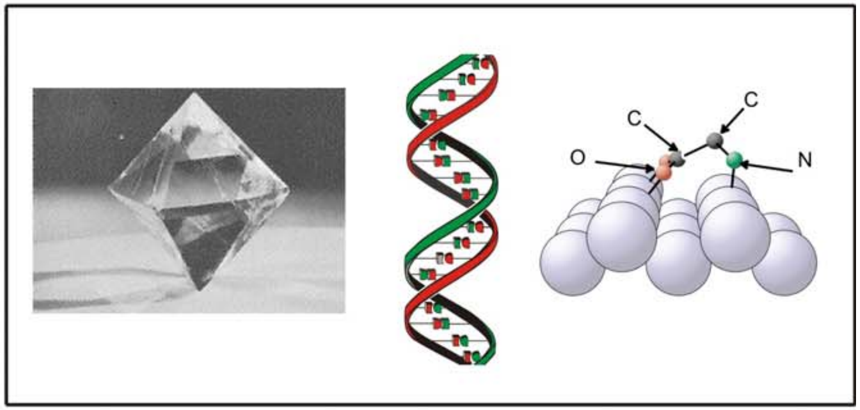
# *What we learn about matter with photons*

## Imaging - Seeing the Invisible



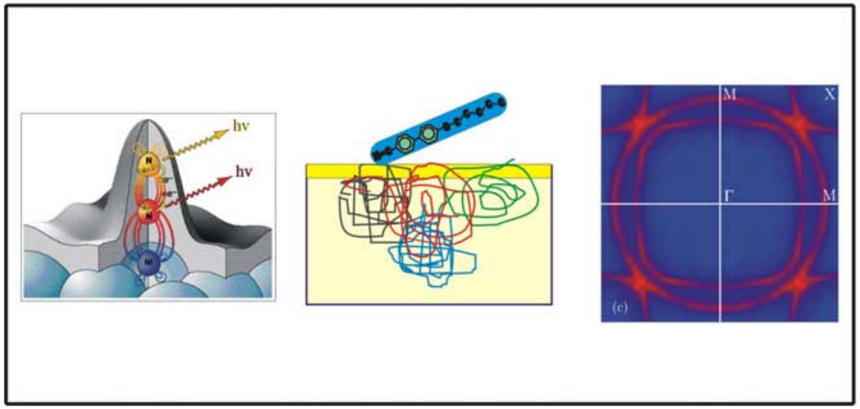

## Atomic and Molecular Structure

- where are the atoms -



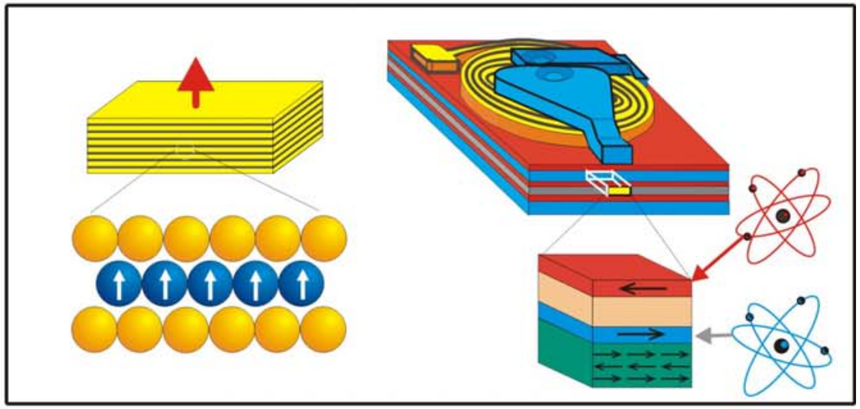

## Electronic Structure and Bonding

- where are the electrons -




## Magnetic Structure and Properties

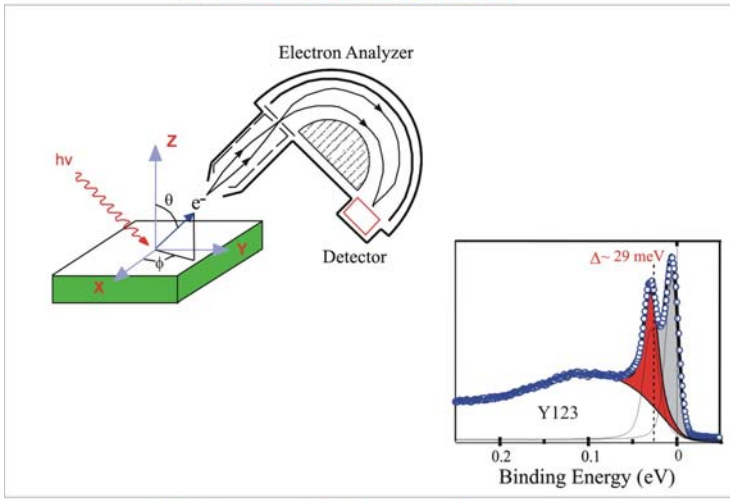
- where are the spins-



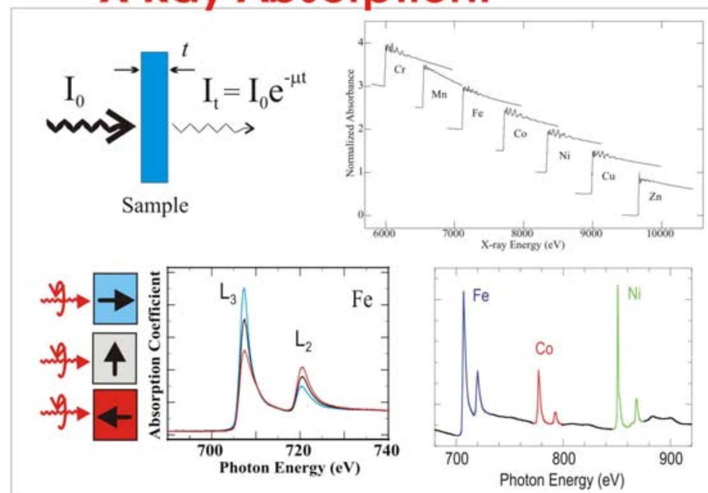
# Techniques to Study Matter with Photons

## Modern X-ray Based Techniques Include

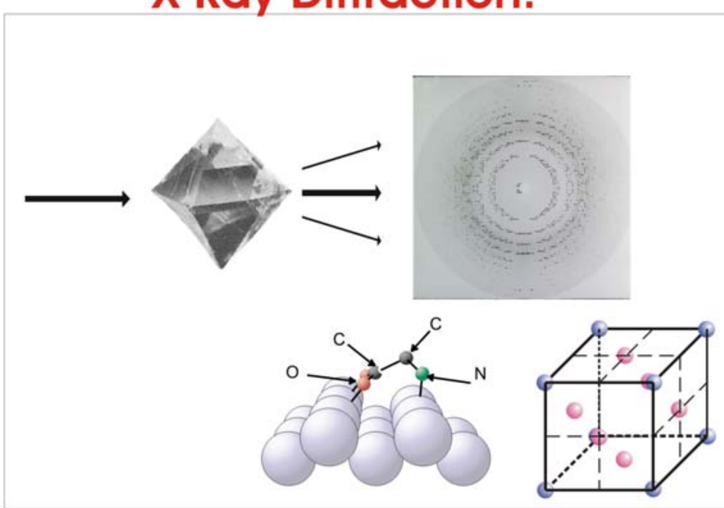
### Photoemission:



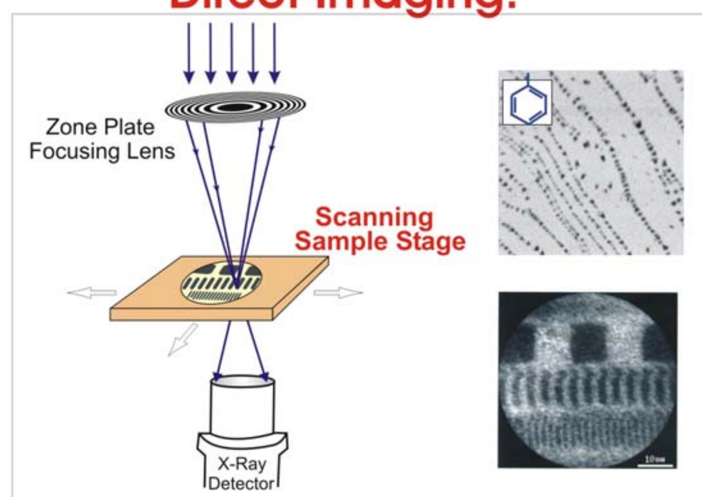

### X-Ray Absorption:




### X-Ray Diffraction:



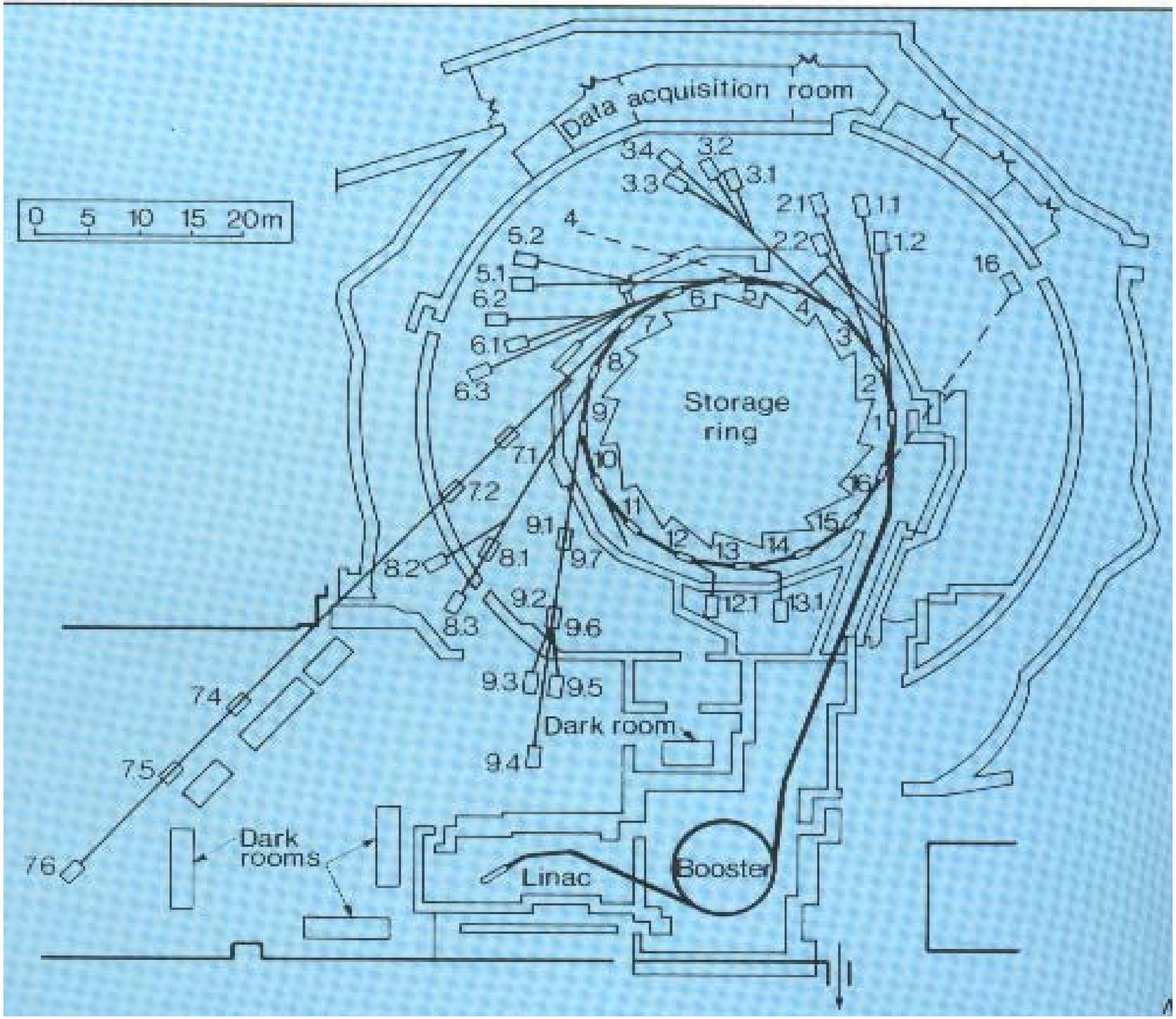

### Direct Imaging:



# SRS Daresbury Laboratory UK

- 2 GeV Synchrotron Radiation Source

# Synchrotron Radiation Source



# The basis of an X-ray absorption spectrum

**In the interaction of X-rays with matter, there are three main processes:**

**elastic scattering,**

**inelastic scattering (Compton)**

**absorption due to ionisation.**

**The absorption can be characterised by the following equation**

$$I_t = I_0 \exp(-\mu x)$$

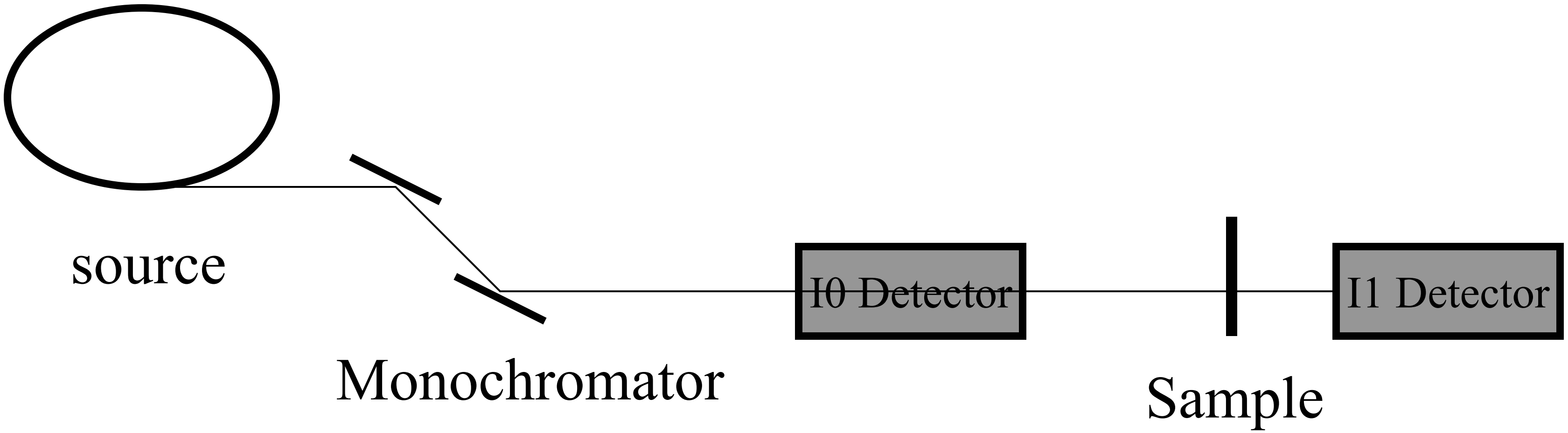
**$I_0$ is incident intensity**

**$I_t$ is the exiting intensity**

**x is the distance travelled through the material**

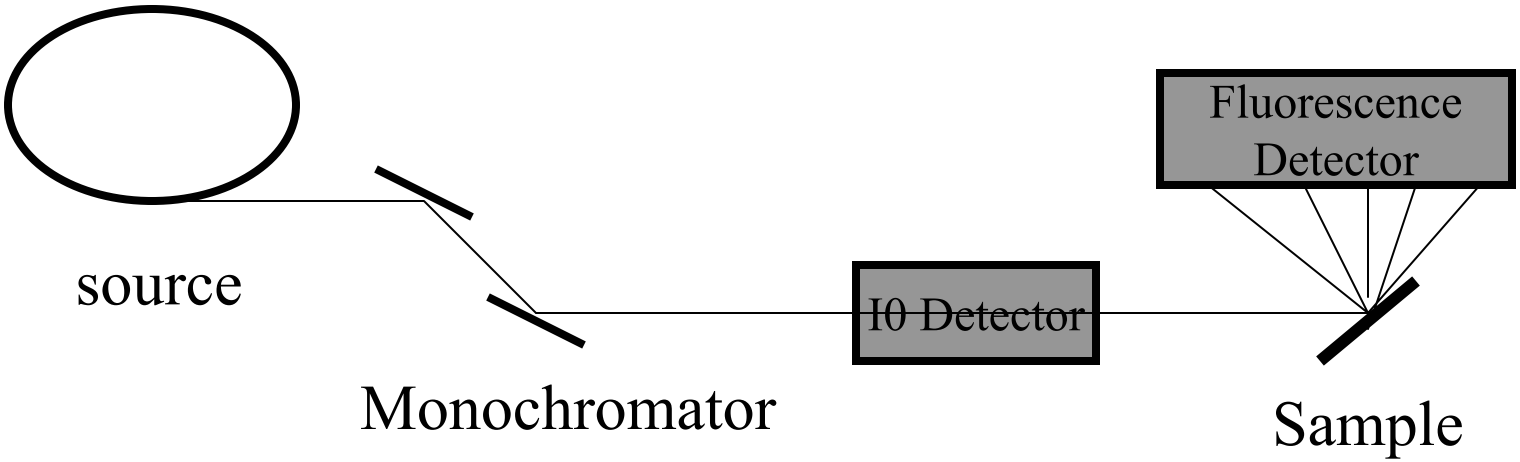
**μ is the x-ray absorption coefficient of the material**

# Transmission Mode




$$I = I_0 \exp(-\mu(E)x)$$

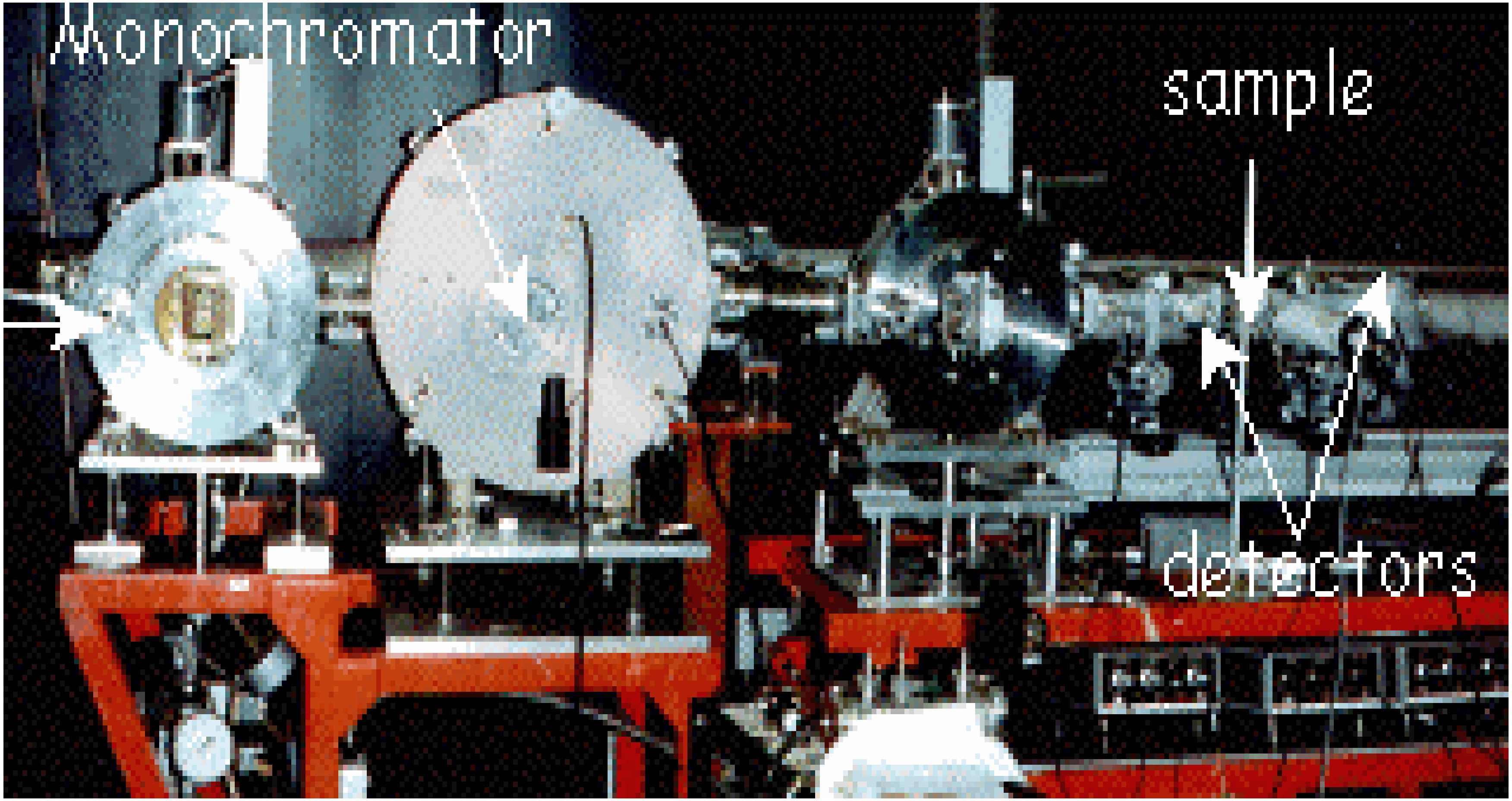
# Fluorescence Mode



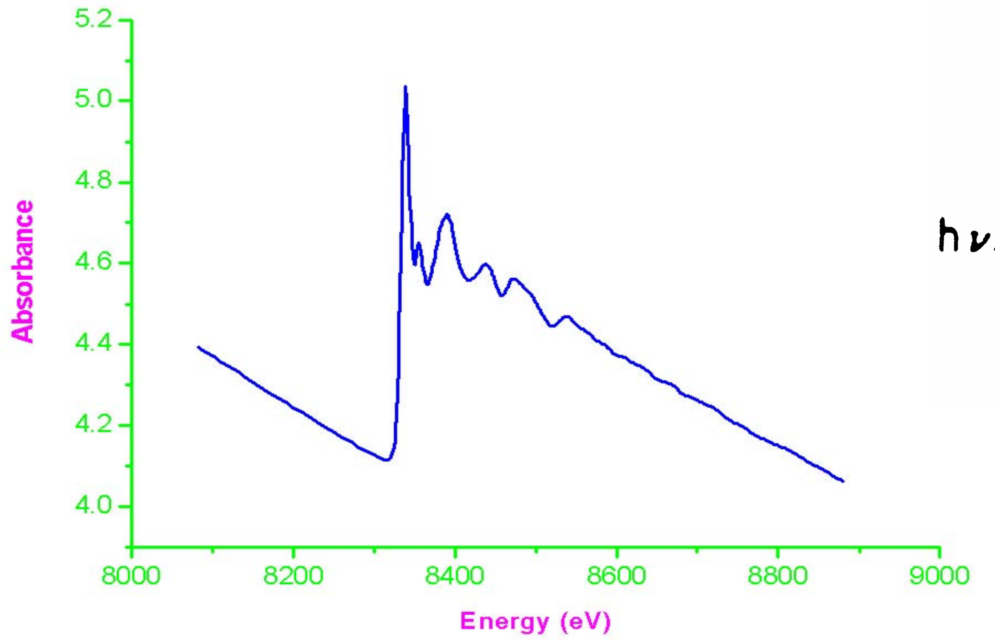

$$I \propto I_0 \mu_s(E) \left( \frac{1 - \exp(-\alpha)}{\alpha} \right)$$

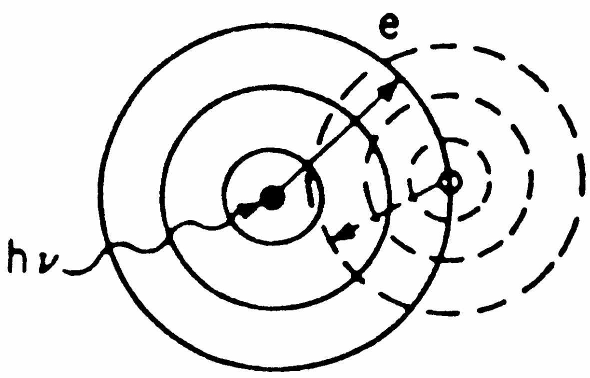
$$\alpha = (\mu_t(E) / \sin\theta + \mu_t(E_f) / \sin\phi) x$$

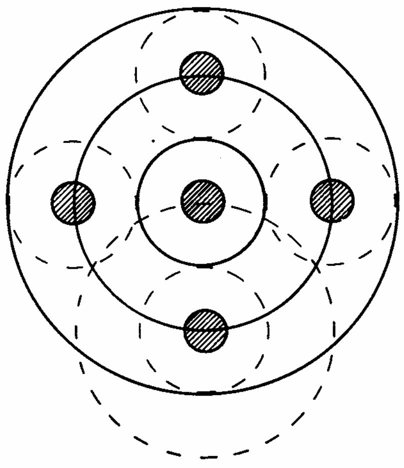
# EXAFS experimental setup



# STRUCTURAL STUDIES BY X-RAY ABSORPTION STUDIES



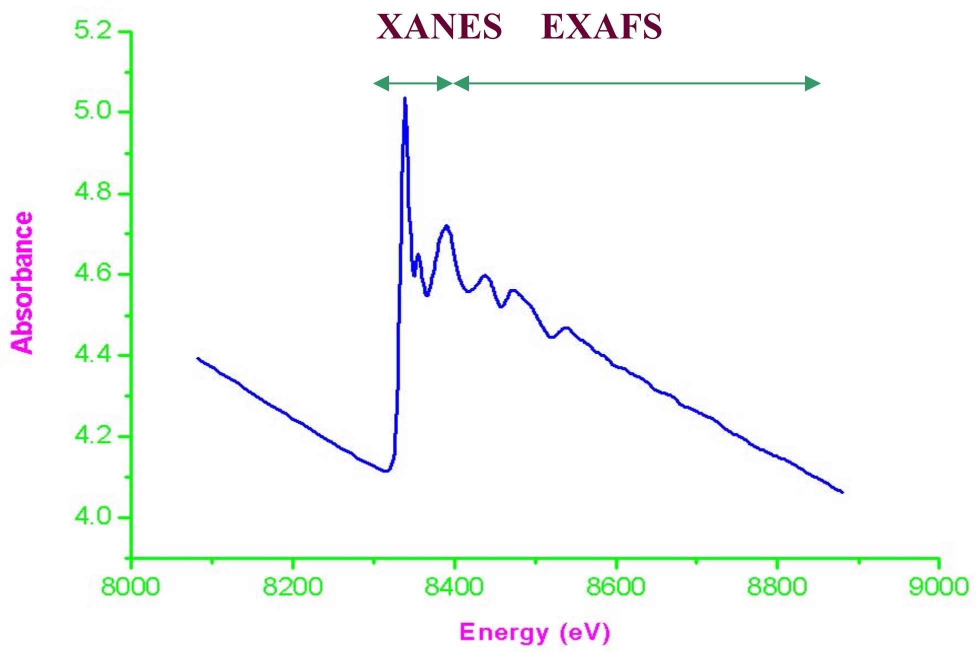



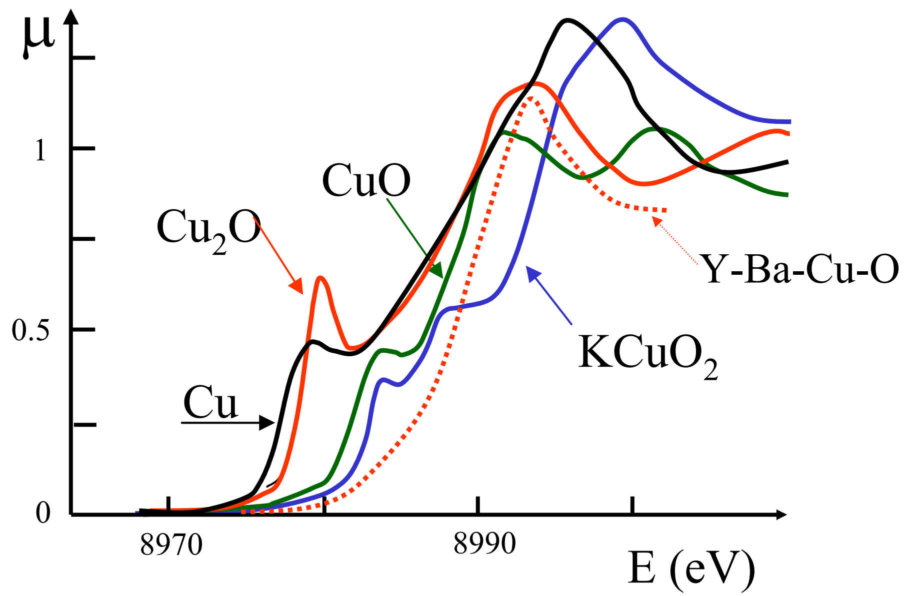
# STRUCTURAL STUDIES BY X-RAY ABSORPTION STUDIES

- **XANES:** Gives information about the ionic state of the absorbing atom.

- **EXAFS:** Provides information about the local structural environment (coordination nos and radial distances) of an absorbing atom.



# XANES
## Chemical information: oxidation state




Oxidation Numbers (formal valences)

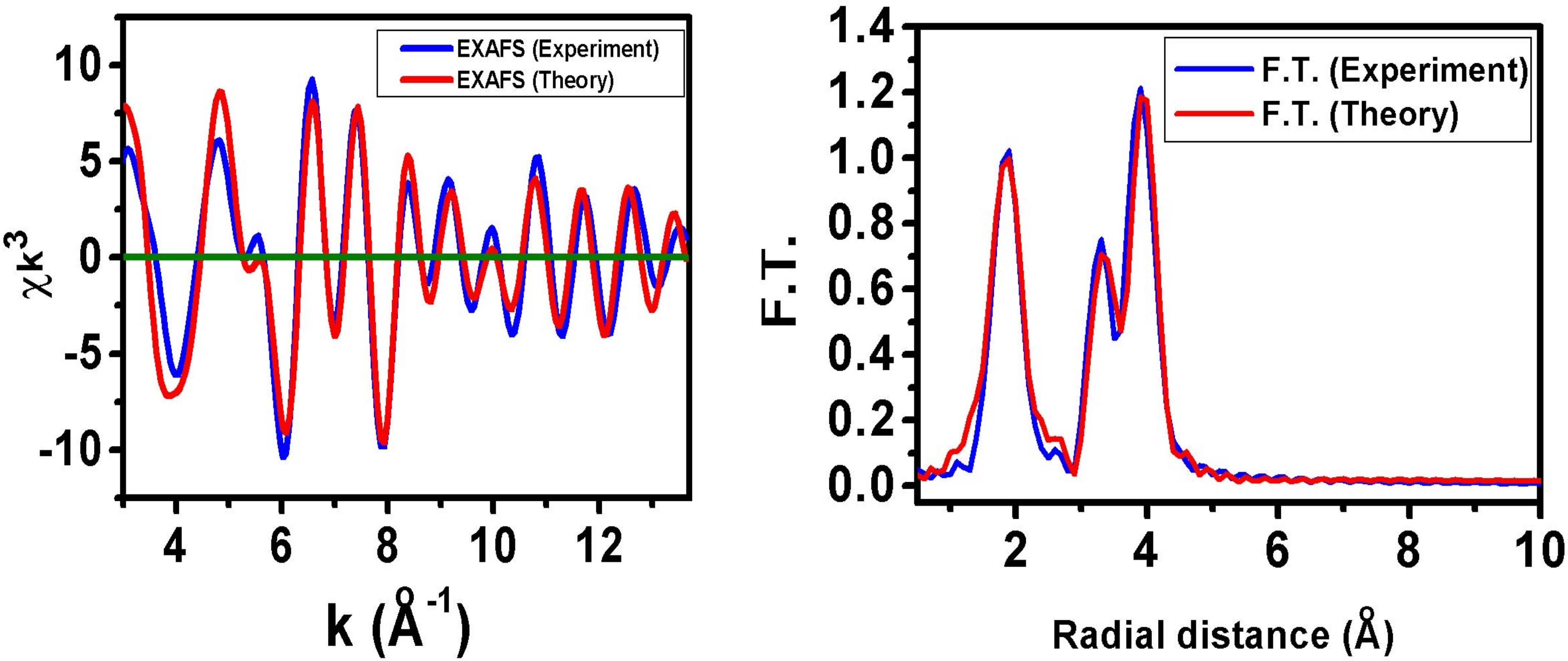
I $Cu_2O$

II CuO

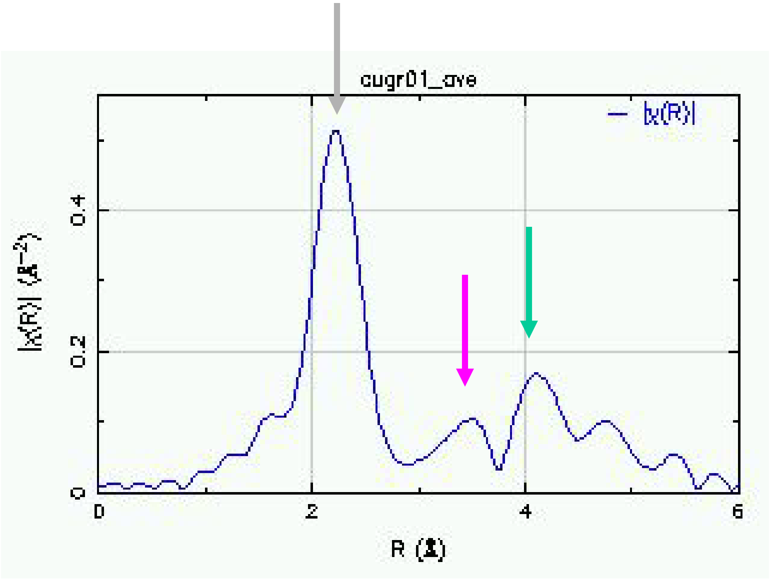
III $KCuO_2$

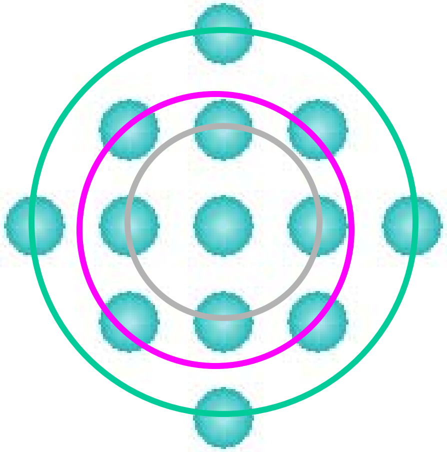
Higher transitions energy are expected for higher valence states.

# EXAFS spectra and Fourier transforms of the Fe K-edge in $SrFeO_3$



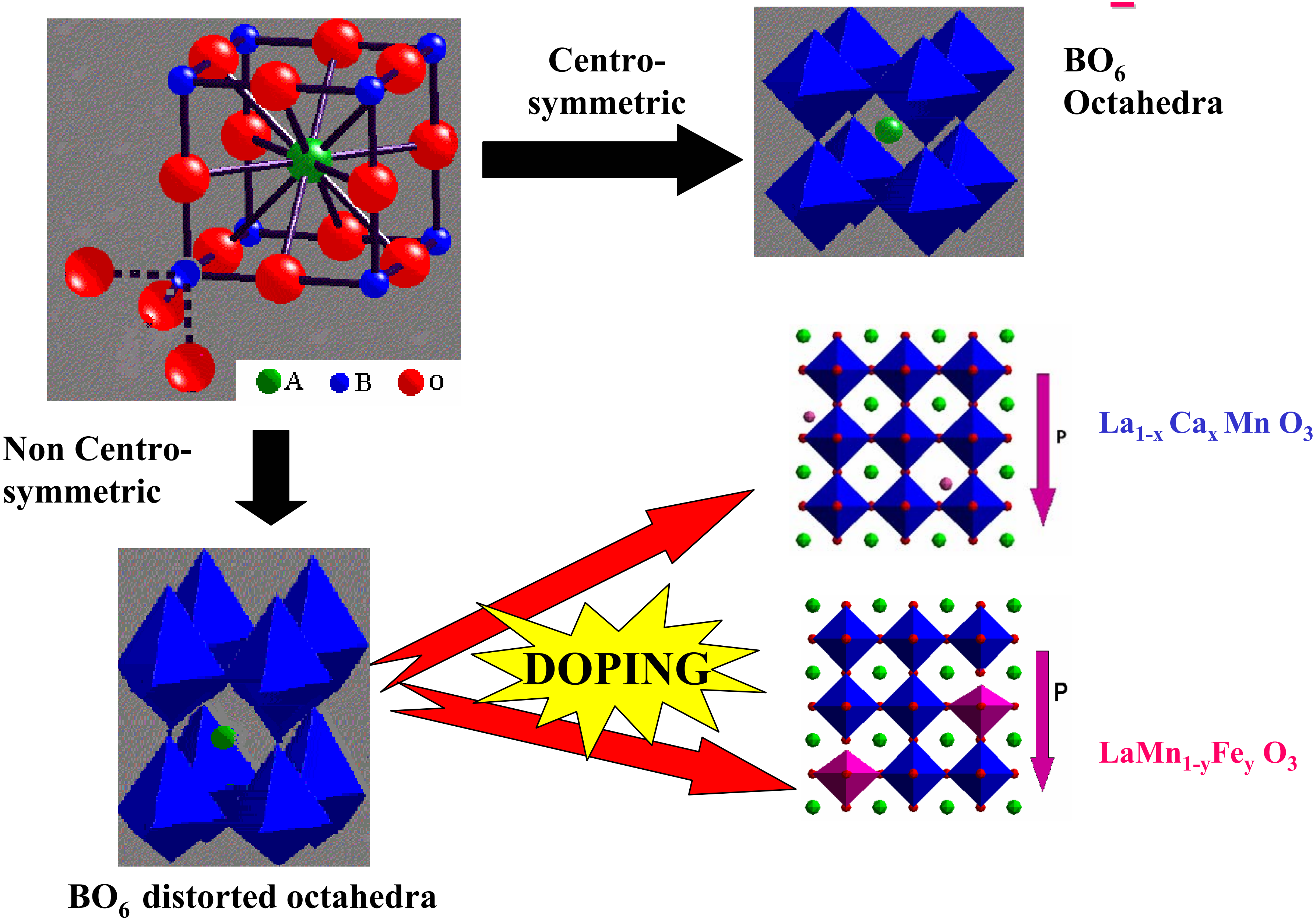
# Fourier Transform of χ(k)



- **Similar to an atomic radial distribution function**
  - **Distance**
  - **Number**
  - **Type**
  - **Structural disorder**

# Defects in Perovskites ($ABO_3$)



# Present Studies

- $BaBiO_3$ (K & Pb doping)
- $YBa_2Cu_3O_7$ (Sb doping)
- $BaFeO_3$ & $SrFeO_3$ (Nb doping)

# $BaBiO_3$

- $BaBi_{1-x}Pb_xO_3$ $T_c$ 13K
- $Ba_{1-x}K_xBiO_3$ $T_c$ 30K

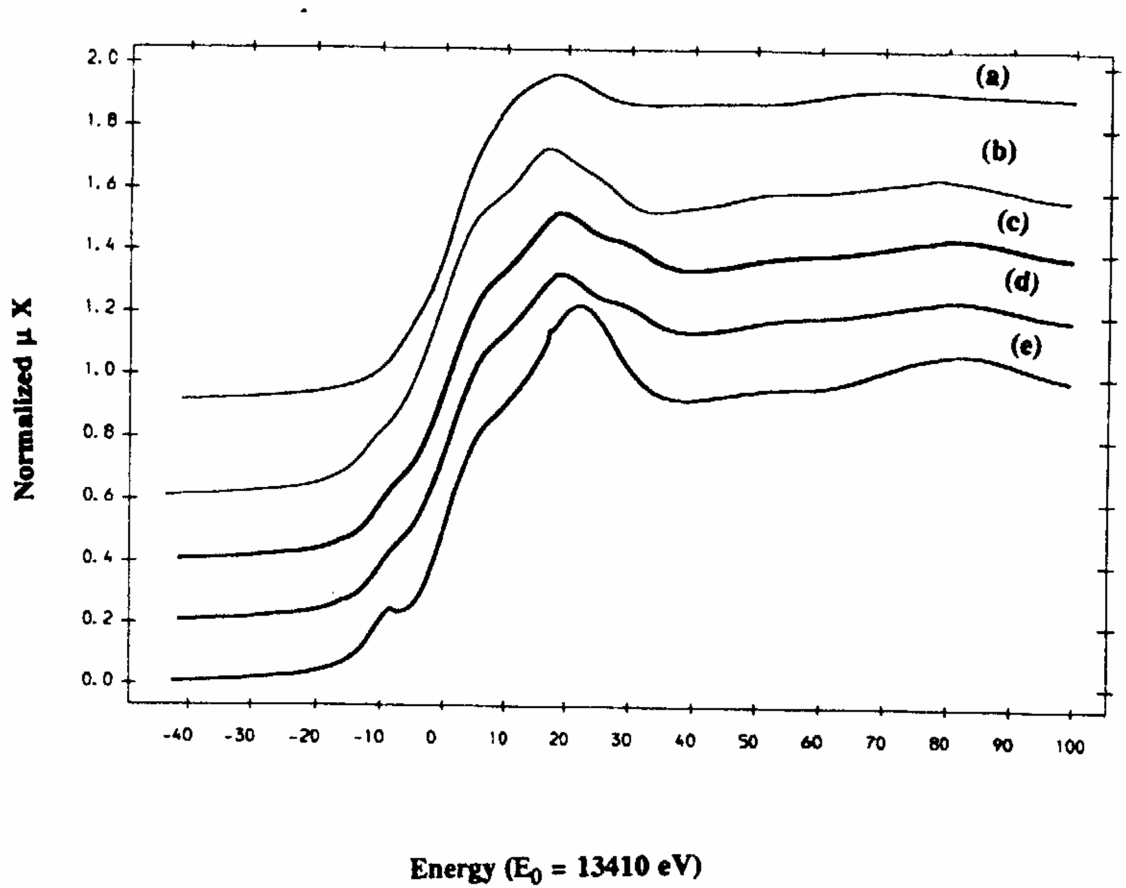
- Dispute about the valence state of Bi in pure & doped $BaBiO_3$

- $BaBi^{4+}O_3$

- $BaBi_{0.5}^{3+}Bi_{0.5}^{5+}O_3$

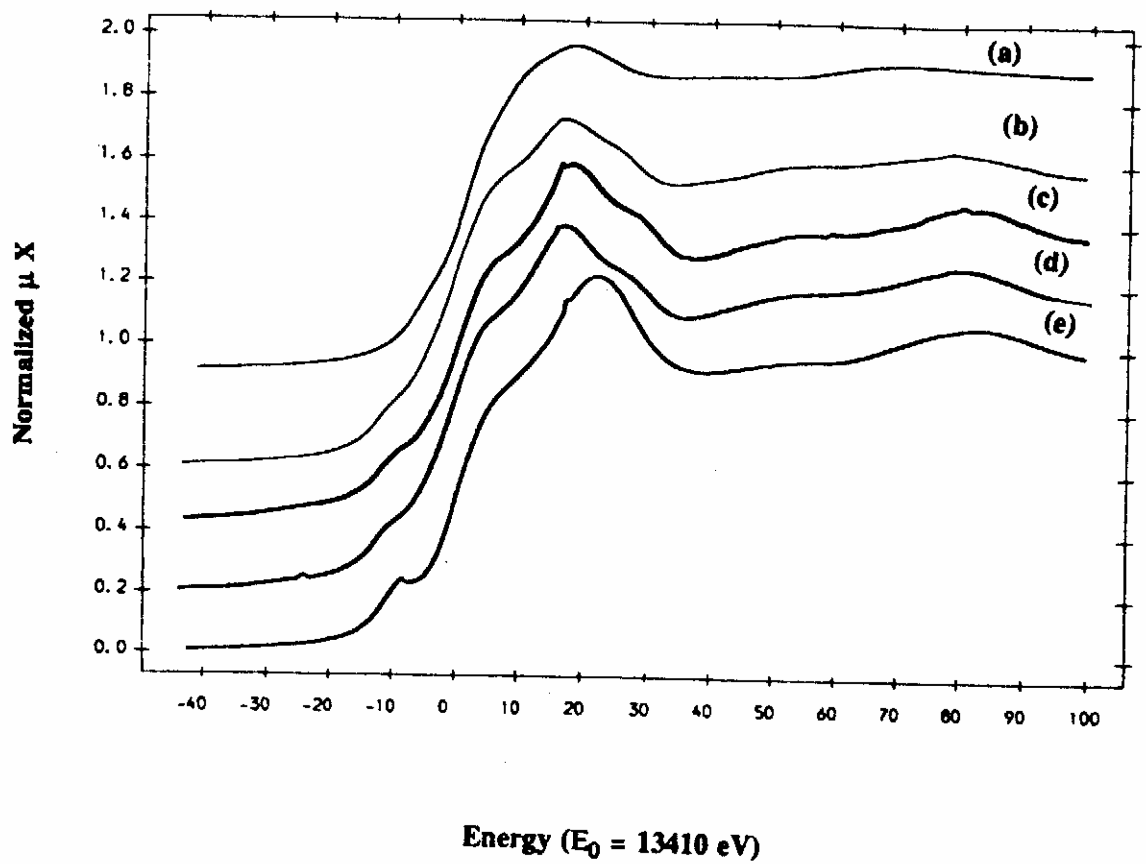
# XANES Spectra of $Ba_{1-x}K_xBiO_3$

- (a) $Bi_2O_3$
- (b) $BaBiO_3$
- (c) $Ba_{0.6}K_{0.4}BiO_3$
- (d) $Ba_{0.5}K_{0.5}BiO_3$
- (e) $NaBiO_3$



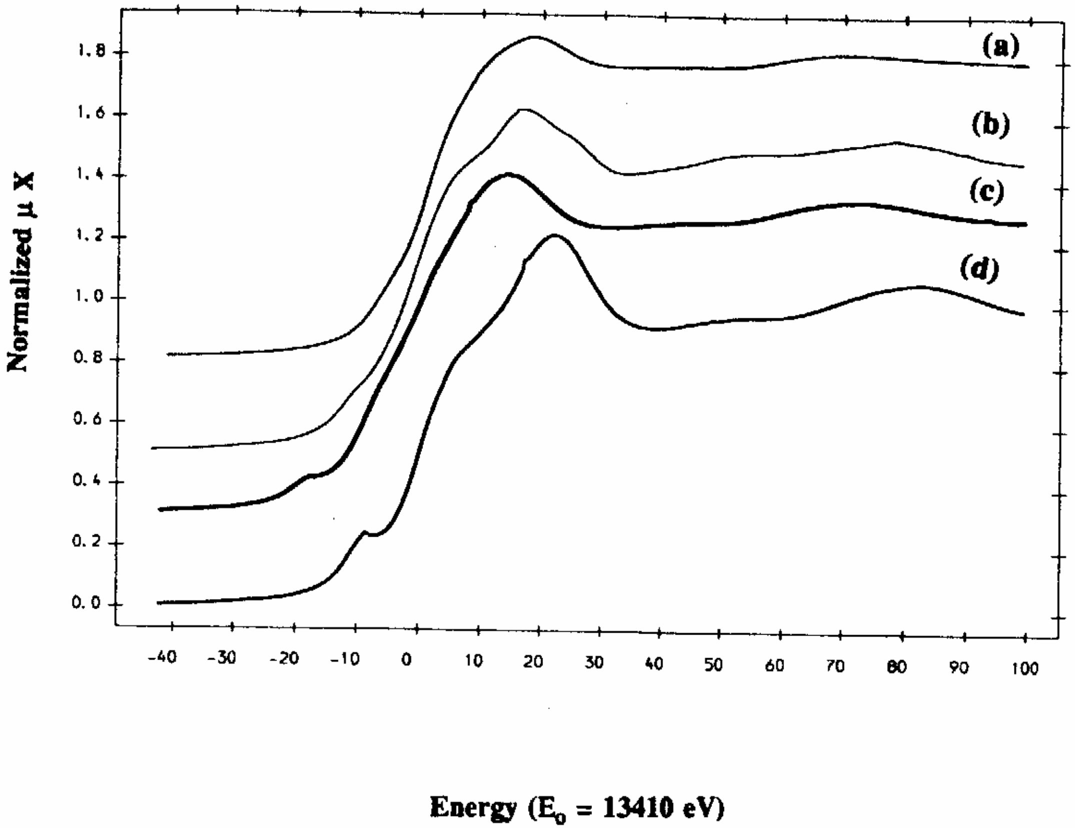
# XANES Spectra of $BaBi_{1-x}Pb_xO_3$

- (a) $Bi_2O_3$
- (b) $BaBiO_3$
- (c) $BaBi_{0.25}Pb_{0.75}O_3$
- (d) $BaBi_{0.3}Pb_{0.7}O_3$
- (e) $NaBiO_3$



# XANES Spectra of $BaBiO_3$

- (a) $Bi_2O_3$
- (b) $BaBiO_3$
- (c) spectrum produced by linear combination of $Bi_2O_3$ & $NaBiO_3$
- (d) $NaBiO_3$




Akhtar et al, J. Mater. Chem. 4 (1994) 1081

# Properties of $SrFeO_3$

- Shows interesting properties:
  - Catalyst
  - Metals-Insulator transitions
  - Toxic gas sensors
  - Magnetoresistance

# Motivation for present study

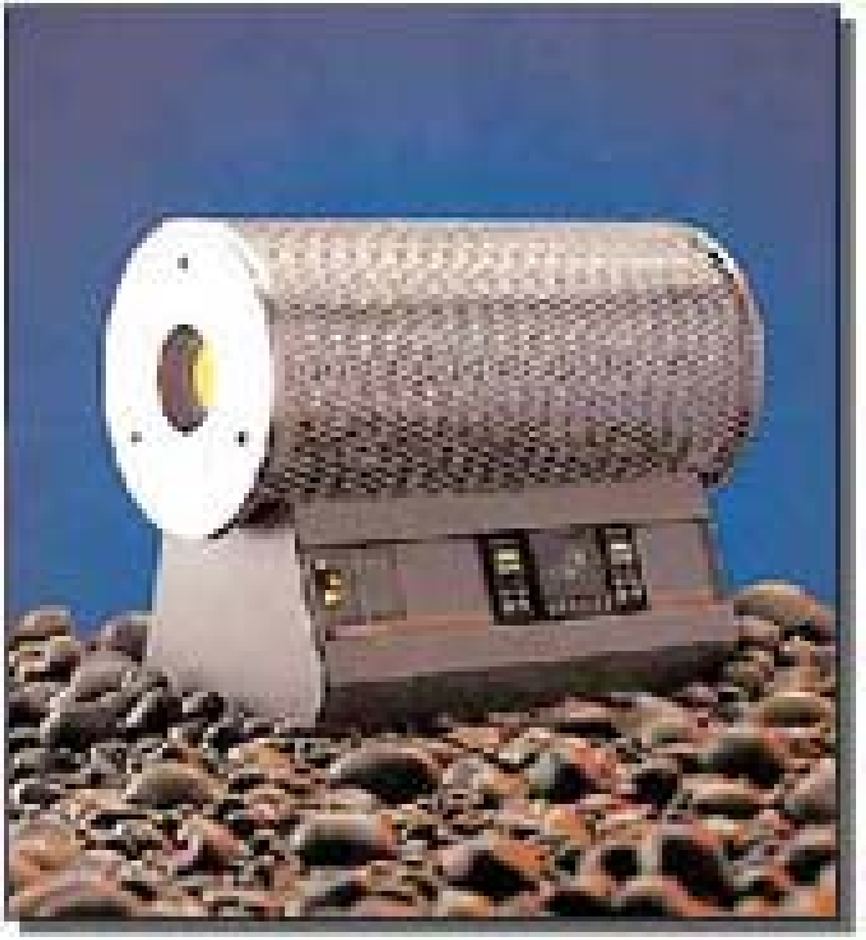
– $SrFeO_3$ ($Fe^{4+}$ valence state)

– $SrFeO_{2.5}$ ($Fe^{3+}$ valence state)

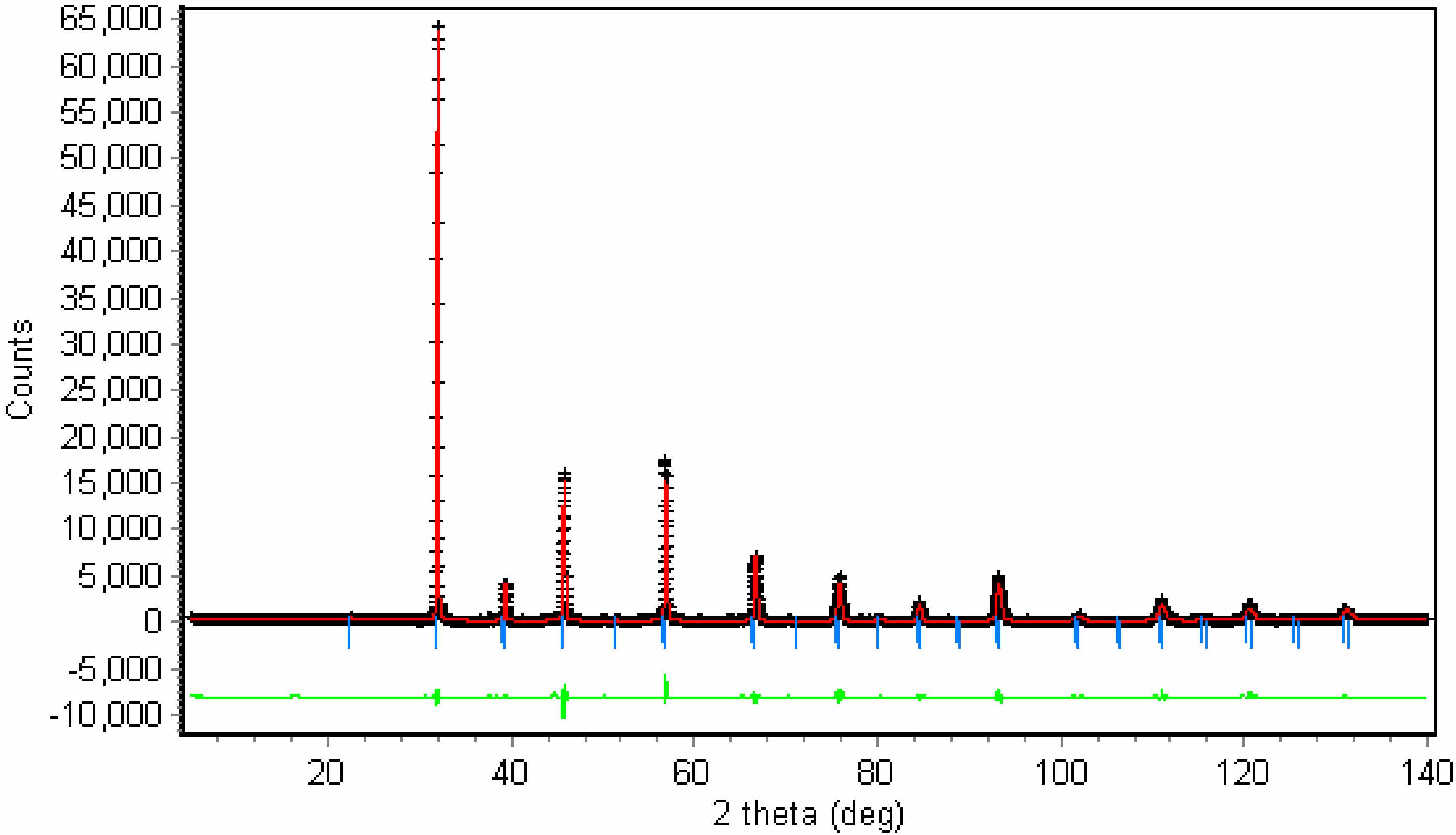
- $SrFeO_3$ $SrFe_{0.5}Nb_{0.5}O_3$

# Synthesis of $SrFe_{1-x}Nb_xO_3$

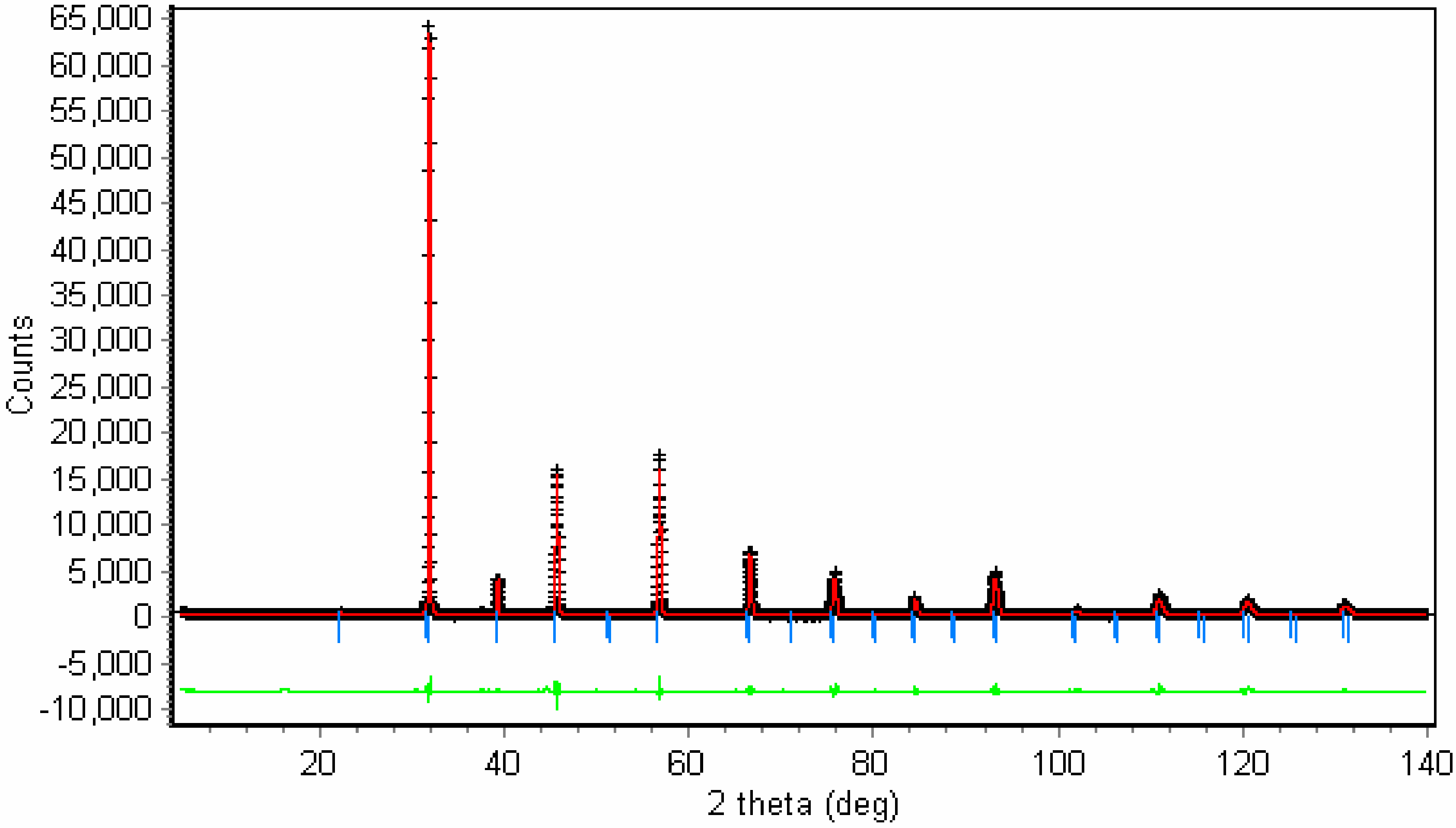
- **Solid State Methods**
- **Appropriate amount of oxides were mixed in stoichiometric ratio.**
- **Heated at 1450 ºC for 72 hours in air.**



# XRD data of $SrFeO_3$



# XRD data of $SrFe_{0.5}Nb_{0.5}O_3$

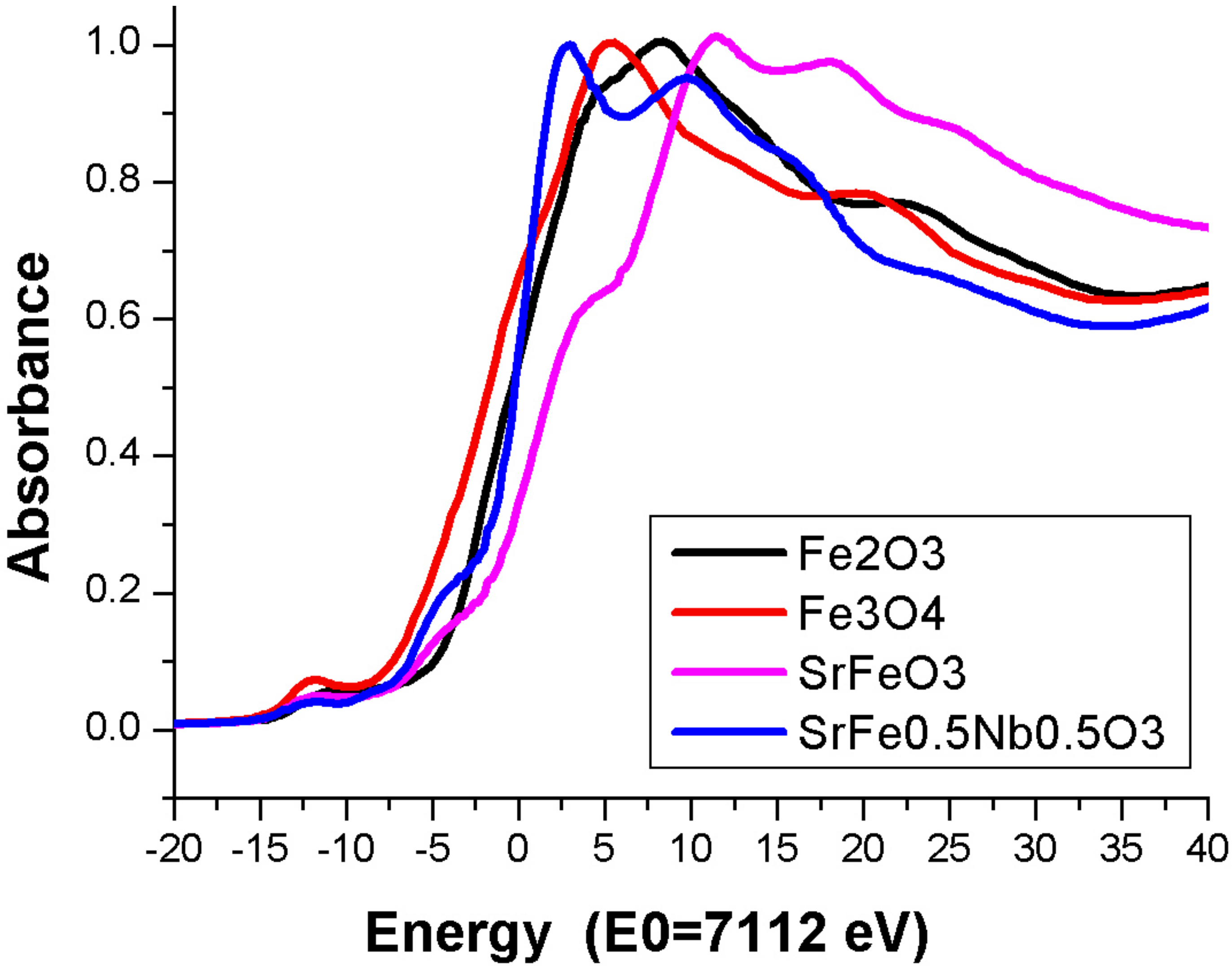


# XRD Data Analysis Results

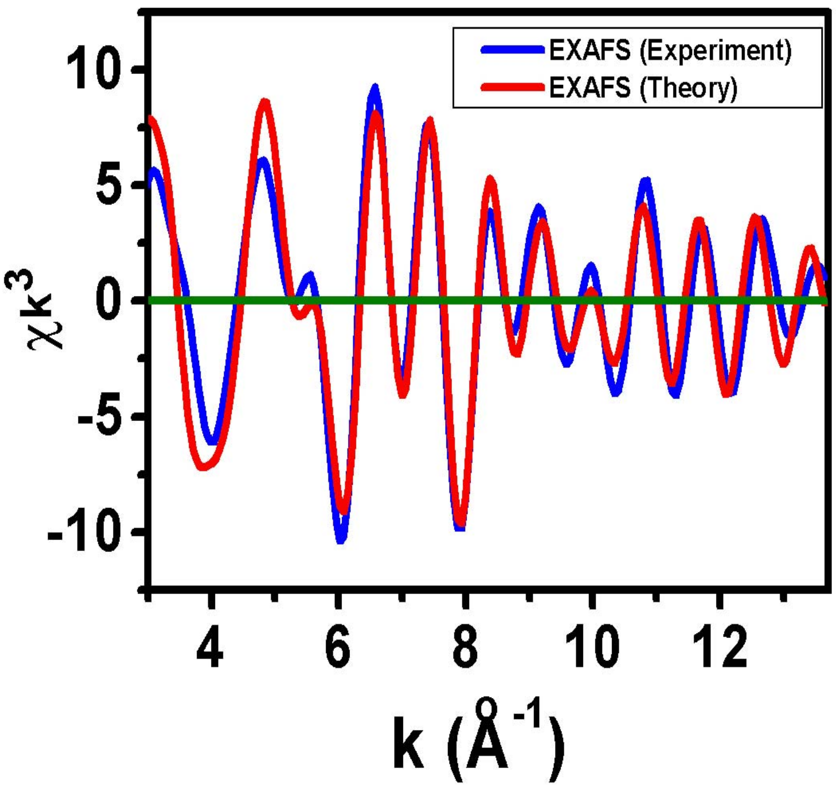
| | $SrFeO_3$ | $SrFe_{0.5}Nb_{0.5}O_3$ |
|---|---|---|
| a (Å) | 3.87000(5) | 3.96804(3) |

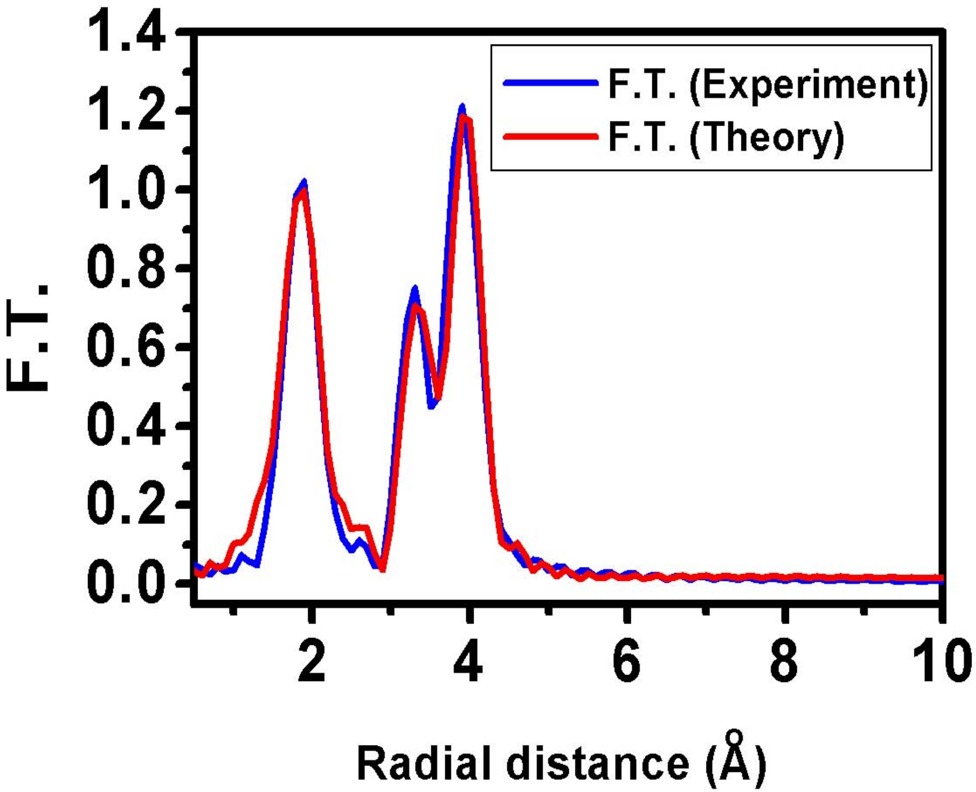
- No oxygen vacancies are found

# XANES Spectra of Fe K-edge in $SrFe_{1-x}Nb_xO_3$

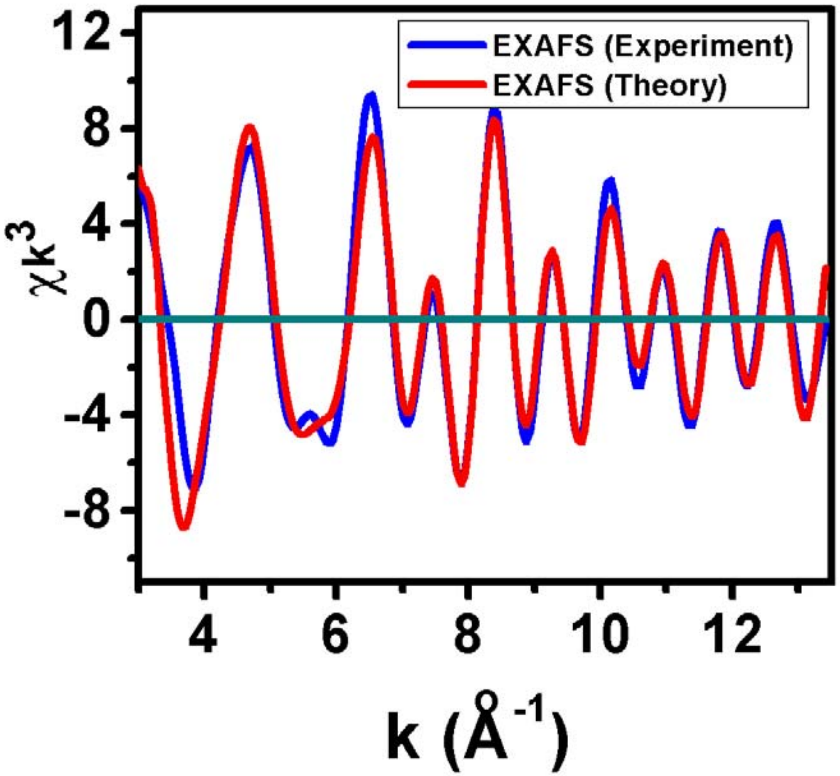


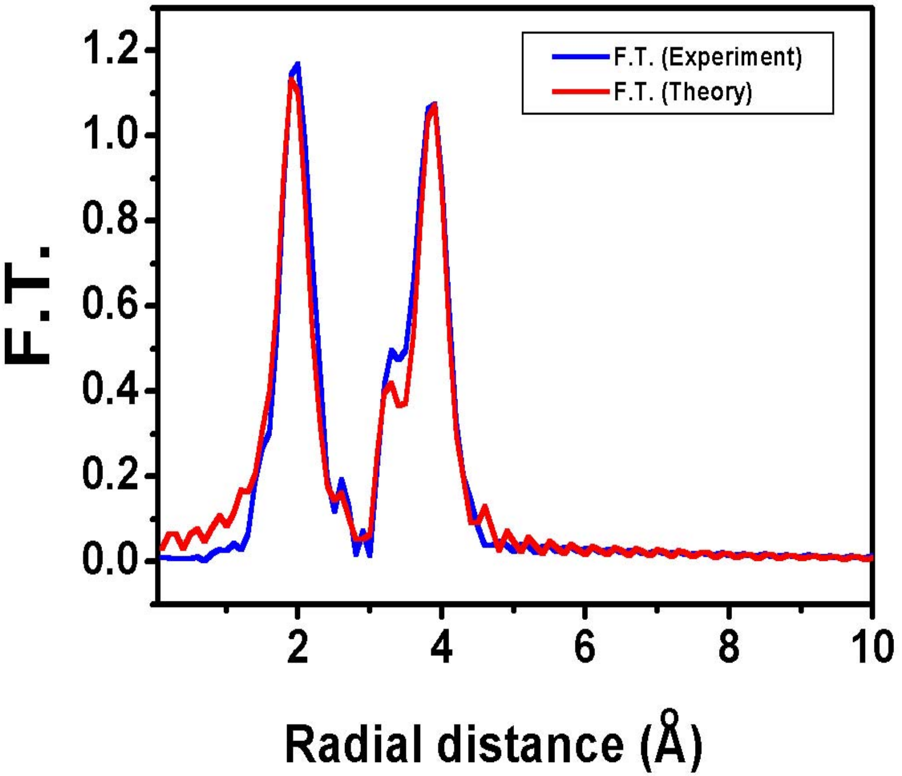
# EXAFS spectra and Fourier transforms of the Fe K-edge in $SrFeO_3$



# EXAFS spectra and Fourier transforms of the Fe K-edge in $SrFe_{0.5}Nb_{0.5}O_3$

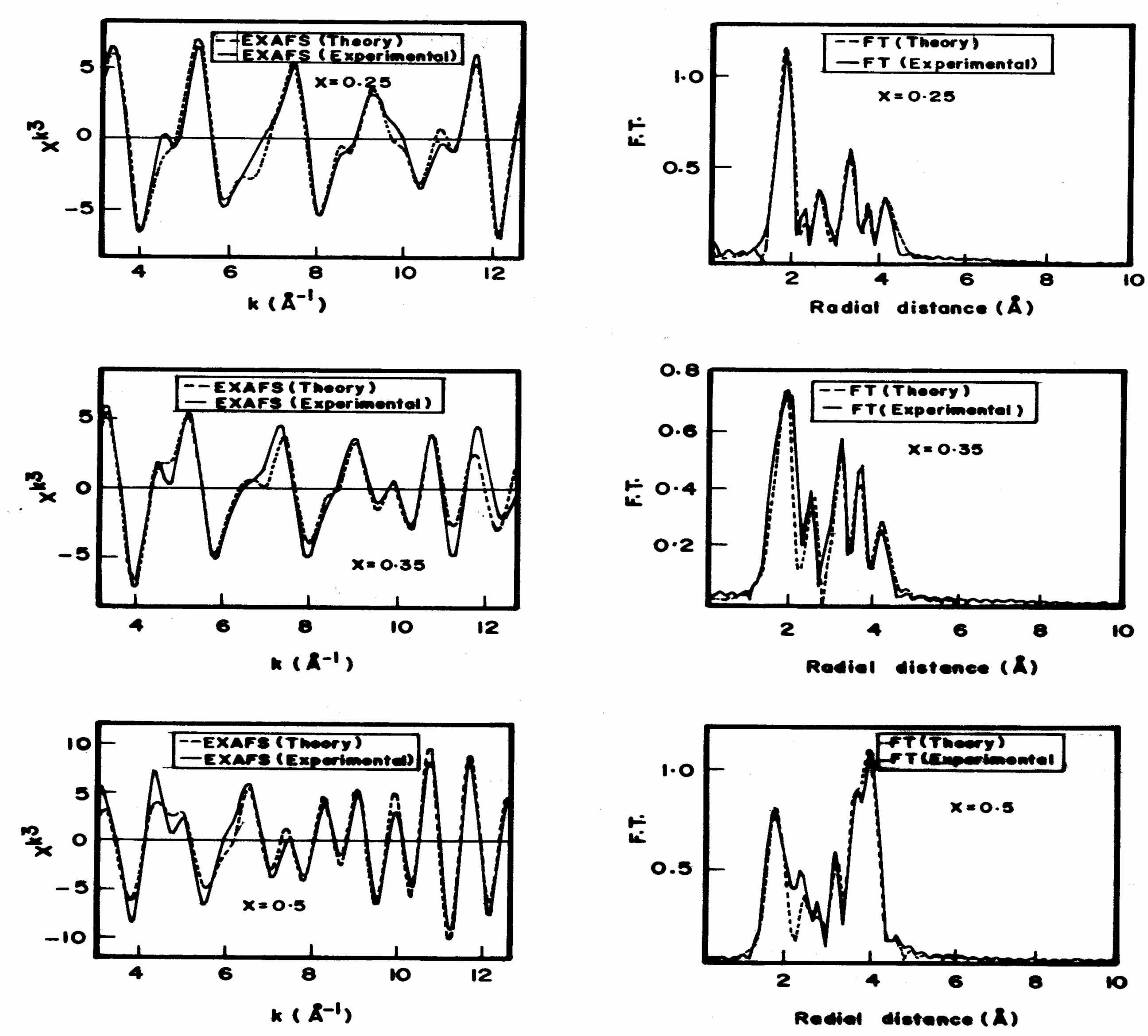


# EXAFS Structural data for the Fe K-edge in $SrFe_{1-x}Nb_xO_3$

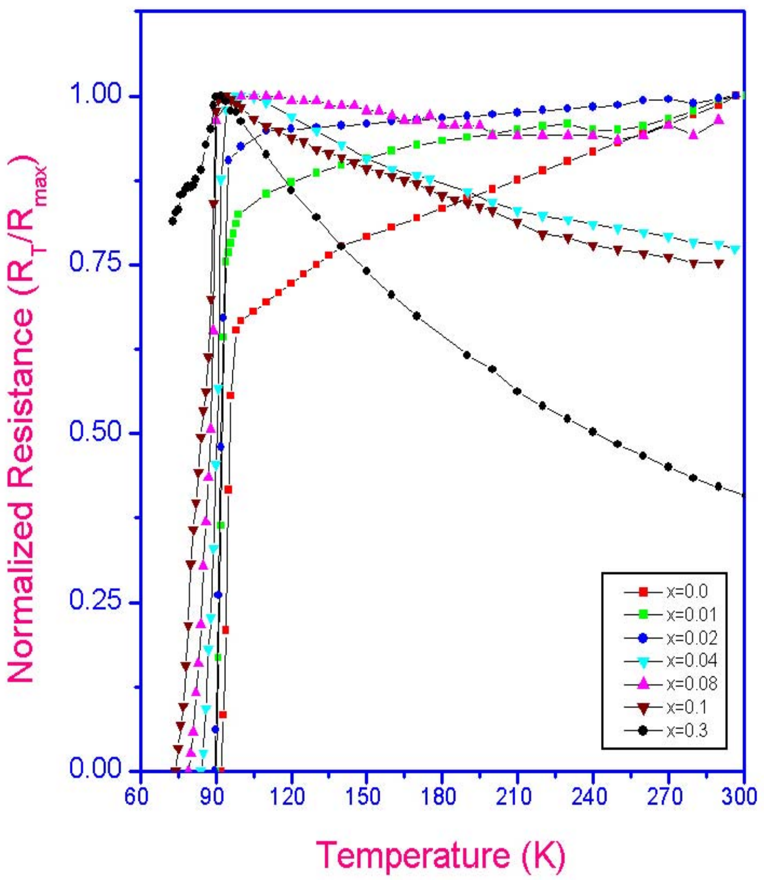
| Shell | $SrFeO_3$ | | | $SrFe_{0.5}Nb_{0.5}O_3$ | | |
|---|---|---|---|---|---|---|
| | CN | RD(Å) | DWF(Å$^2$) | CN | RD(Å) | DWF(Å$^2$) |
| Fe-O | 6 | 1.92 | 0.021 | 6 | 1.98 | 0.016 |
| Fe-Sr | 8 | 3.34 | 0.023 | 8 | 3.38 | 0.029 |
| Fe-Fe | 6 | 3.89 | 0.011 | 3 | 3.91 | 0.004 |
| Fe-Nb | - | - | - | 3 | 3.99 | 0.040 |

# EXAFS spectra and Fourier transforms of the Fe K-edge in $BaFe_{1-x}Nb_xO_3$

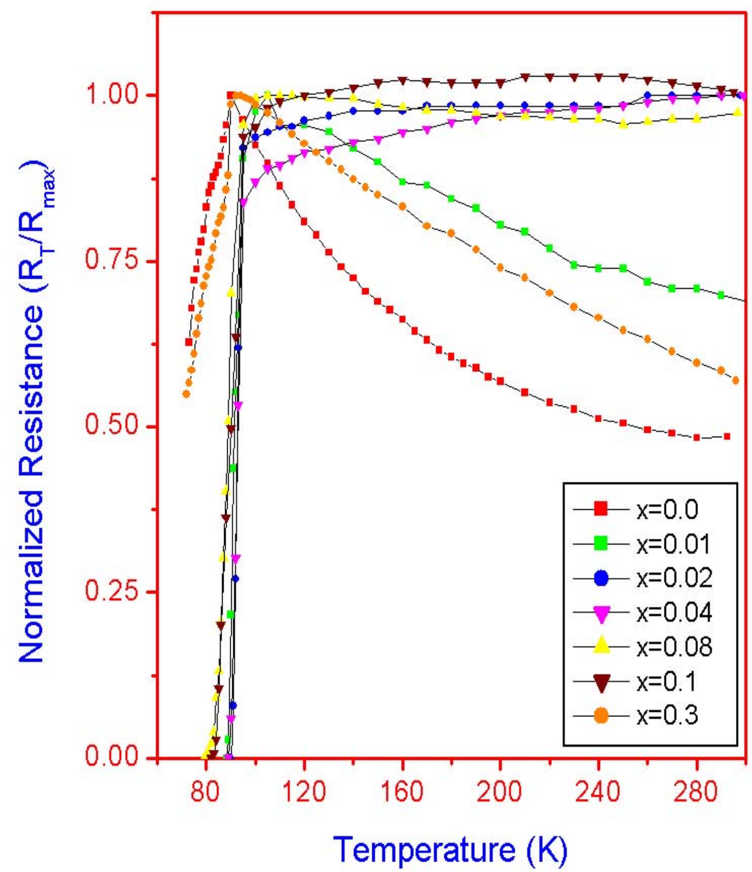


# The Effects of Sb doping on $YBa_2Cu_{3-x}Sb_xO_7$

# Effects of doping & sintering conditions on $YBa_2Cu_{3-x}Sb_xO_3$

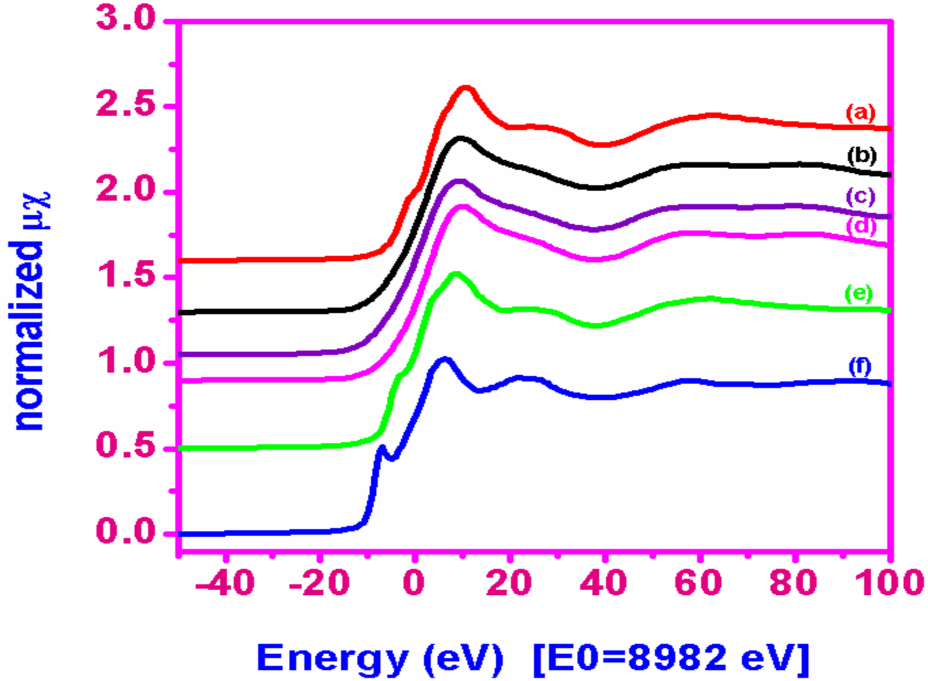



Resistance vs. temperature measurements for furnace cooled $YBa_2Cu_{3-x}Sb_xO_{7-\delta}$



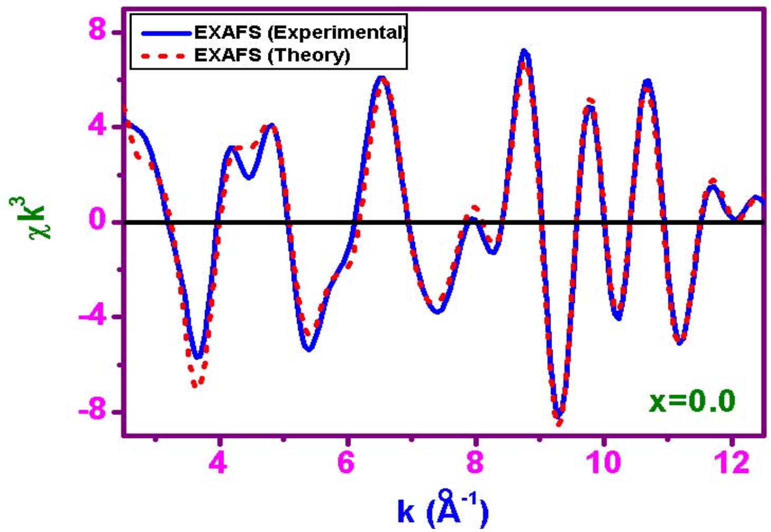

Resistance vs. temperature measurements for air quenched $YBa_2Cu_{3-x}Sb_xO_{7-\delta}$

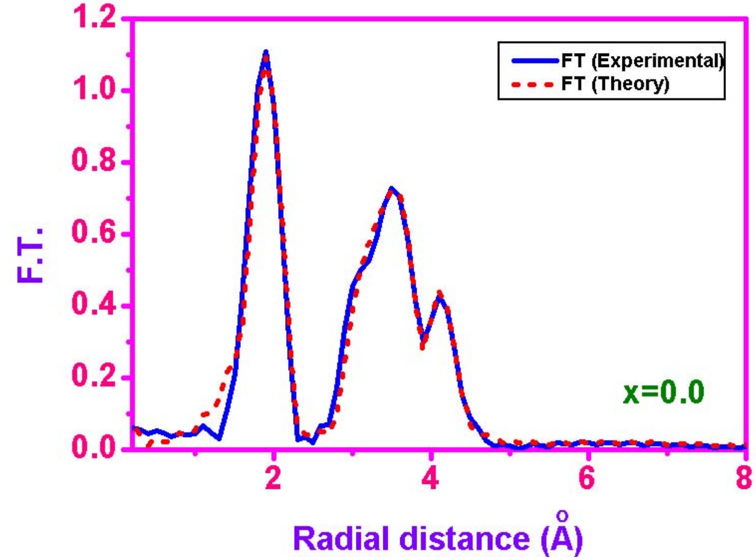
# XANES Spectra of Cu K-edge in $YBa_2Cu_{3-x}Sb_xO_7$

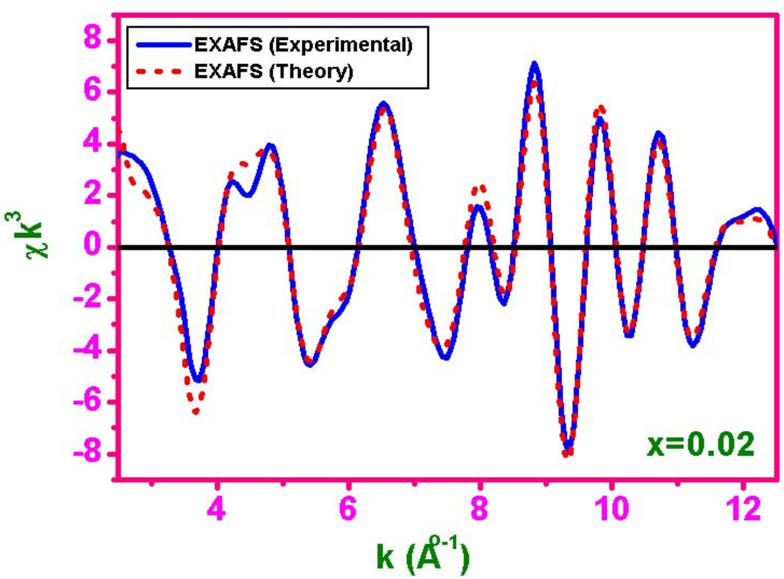


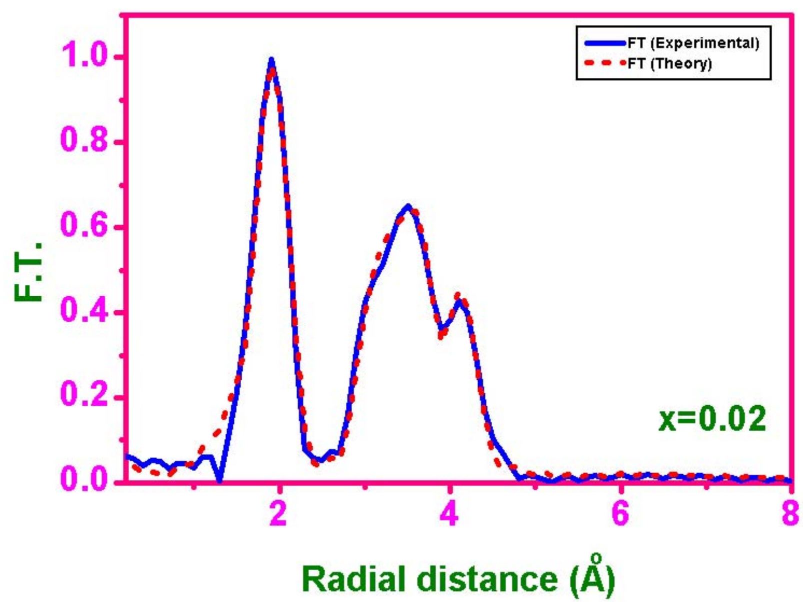

XANES spectra at the Cu K-edge of (a) $KCuO_2$, (b) $YBa_2Cu_{2.98}Sb_{0.02}O_{7-\delta}$, (c) $YBa_2Cu_{2.99}Sb_{0.01}O_{7-\delta}$, (d) $YBa_2Cu_3O_{7-\delta}$, (e) CuO and (f) $Cu_2O$

# EXAFS spectra and Fourier transforms of the Cu K-edge in $YBa_2Cu_{3-x}Sb_xO_7$



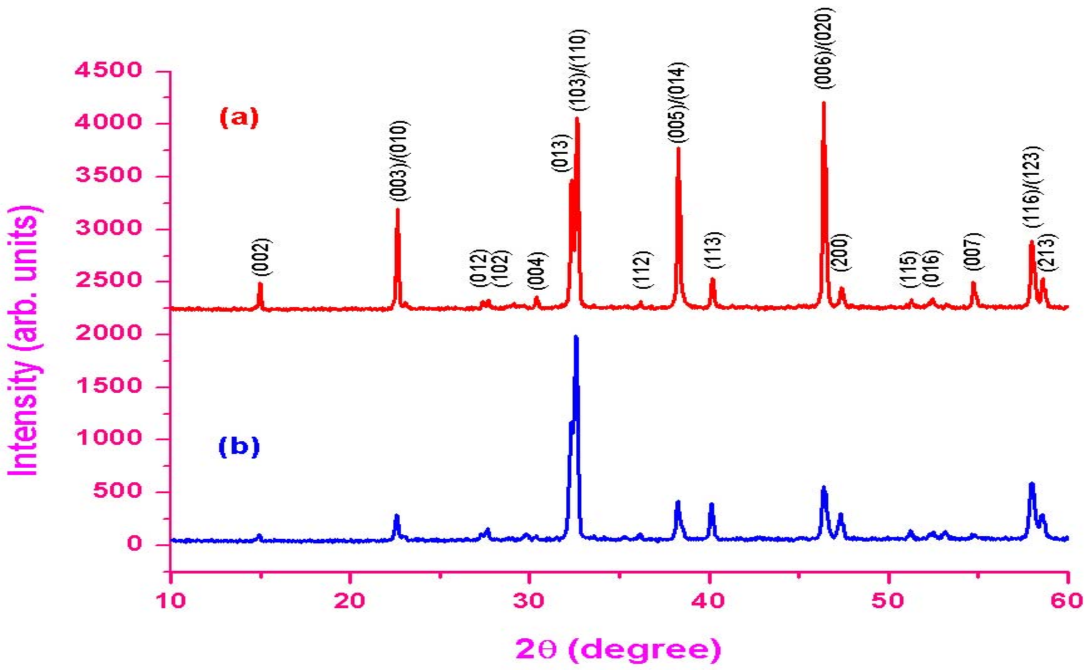



# EXAFS Structural data for the Cu K-edge in $YBa_2Cu_{3-x}Sb_xO_7$

| Shell | $YBa_2Cu_3O_7$ | | | $YBa_2Cu_{2.99}Sb_{0.01}O_7$ | | | $YBa_2Cu_{2.98}Sb_{0.02}O_7$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | CN | RD(Å) | DWF($Å^2$) | CN | RD(Å) | DWF($Å^2$) | CN | RD(Å) | DWF($Å^2$) |
| Cu-O | 4.0(3.7) | 1.95 | 0.010(0.009) | 4.0(3.6) | 1.96 | 0.014(0.011) | 4.0(3.6) | 1.95 | 0.013(0.010) |
| Cu-O | 1.0(0.9) | 2.33 | 0.021(0.022) | 1.0(0.9) | 2.38 | 0.021(0.024) | 1.0(0.9) | 2.40 | 0.022(0.022) |
| Cu-Y | 4.0(3.9) | 3.24 | 0.016(0.015) | 4.0(3.8) | 3.23 | 0.016(0.016) | 4.0(3.6) | 3.22 | 0.016(0.015) |
| Cu-Ba | 4.0(3.5) | 3.46 | 0.036(0.031) | 4.0(3.4) | 3.42 | 0.049(0.038) | 4.0(3.3) | 3.41 | 0.050(0.039) |
| Cu-Cu | 1.0(1.1) | 3.68 | 0.003(0.004) | 1.0(1.1) | 3.68 | 0.004(0.006) | 1.0(1.1) | 3.68 | 0.004(0.005) |
| Cu-Cu | 4.0(4.1) | 4.00 | 0.015(0.016) | 4.0(3.8) | 4.00 | 0.014(0.014) | 4.0(4.0) | 4.00 | 0.015(0.015) |

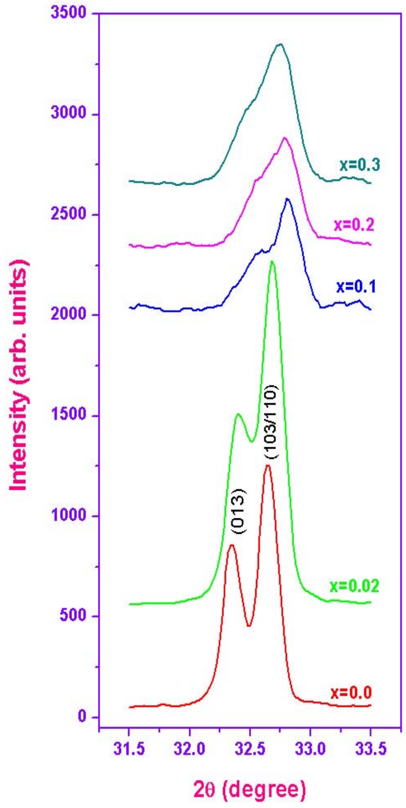
Akhtar et al, Supercond. Sci. Technol., 13 (2000) 1612

# XRD data

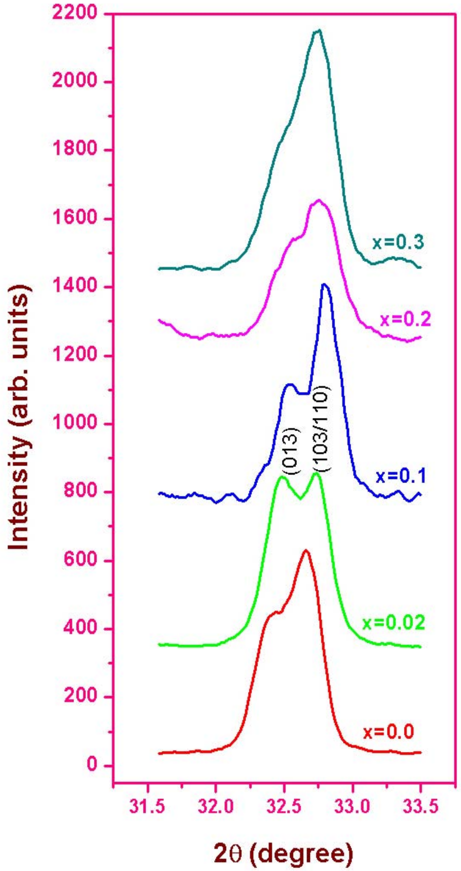



XRD patterns of furnace cooled (a) $YBa_2Cu_3O_{7-\delta}$ and (b) $YBa_2Cu_{2.98}Sb_{0.02}O_{7-\delta}$

# XRD data

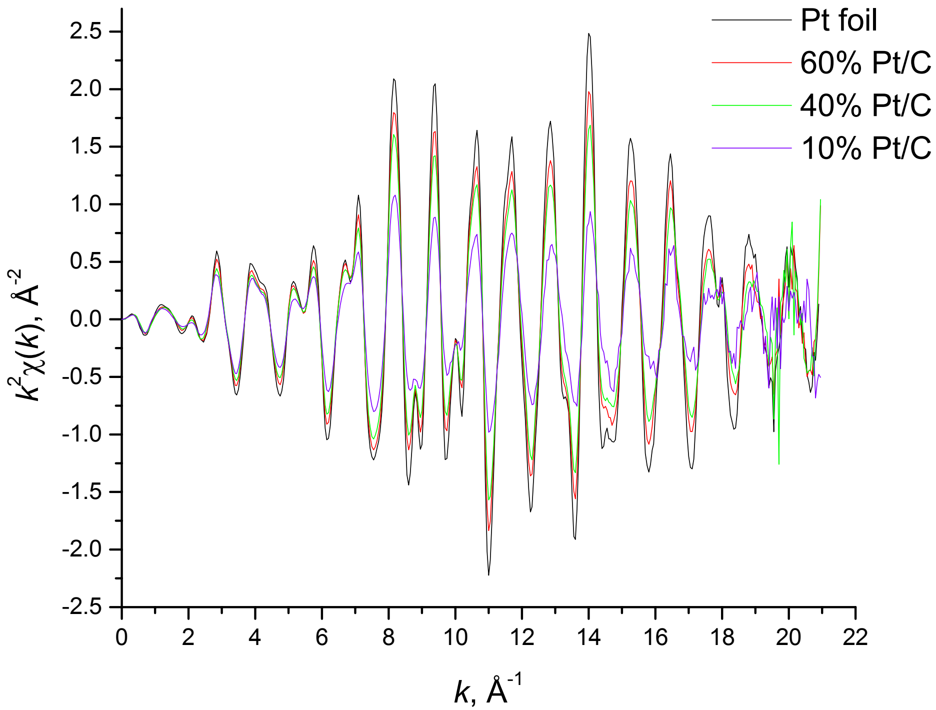


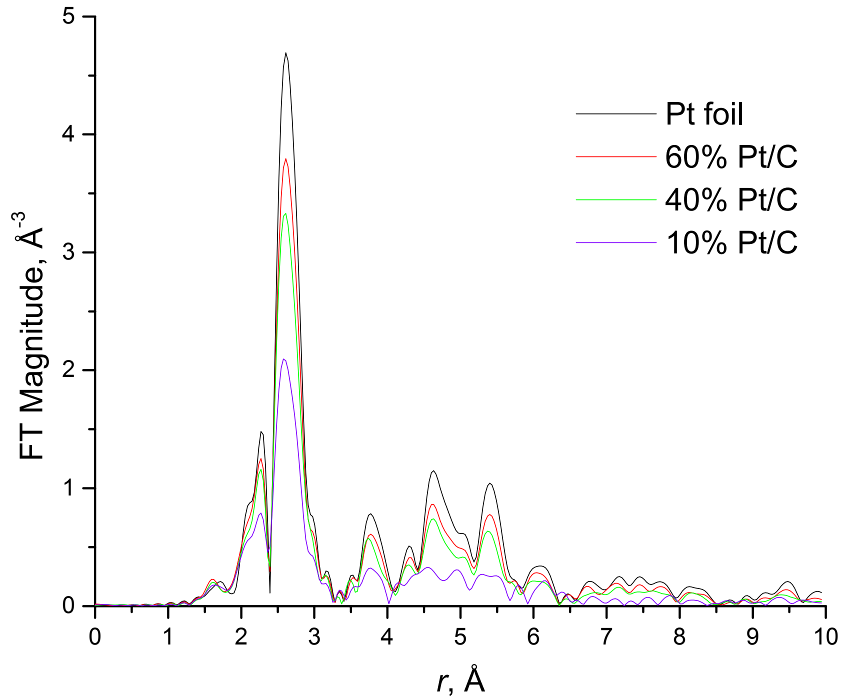

XRD patterns of furnace cooled $YBa_2Cu_{3-x}Sb_xO_{7-\delta}$ (effects of doping)




XRD patterns of air quenched $YBa_2Cu_{3-x}Sb_xO_{7-\delta}$ (effects of doping)

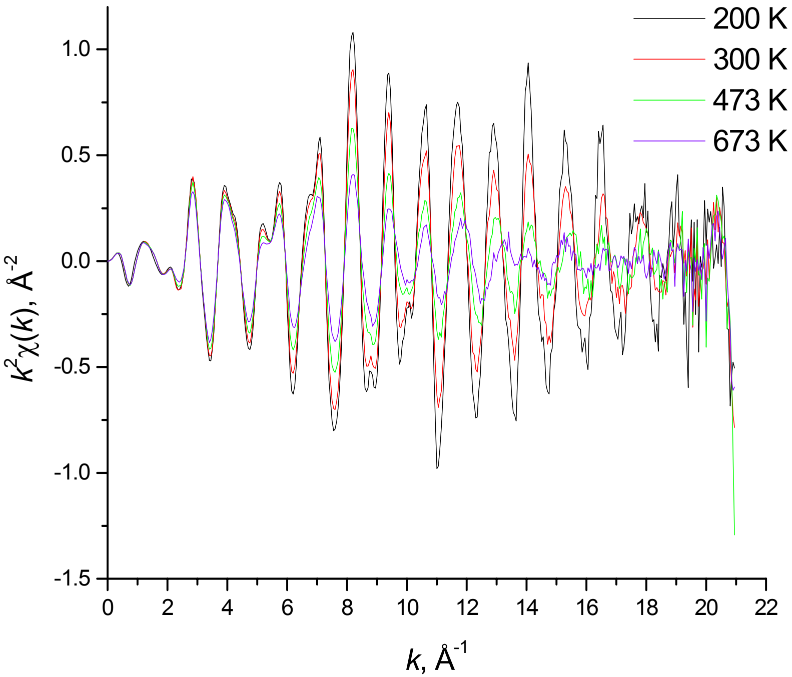
# Size Dependence

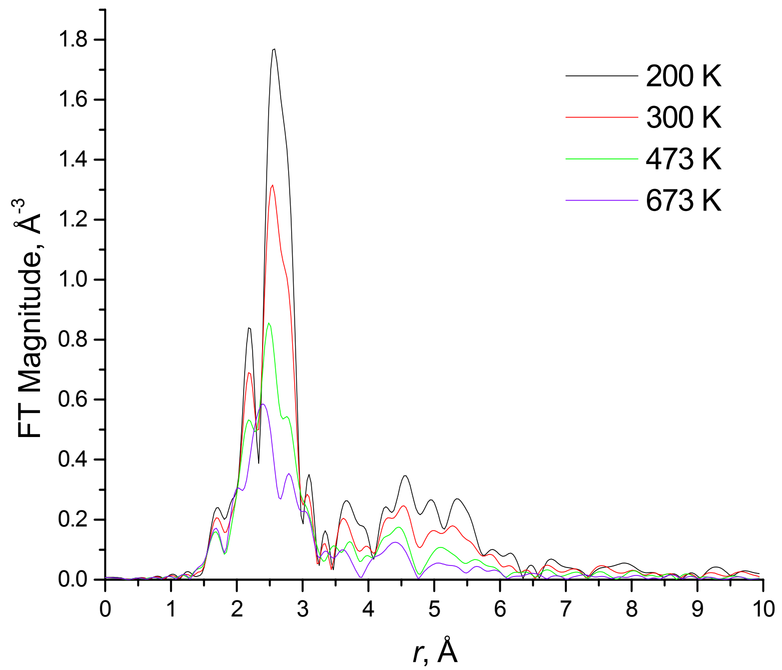



Size dependence on the extended x-ray absorption spectra. The amplitude of the EXAFS signal is directly proportional to the coordination numbers for each shell; therefore, as the cluster size increases, the amplitude also will increase.

# Temperature Dependence



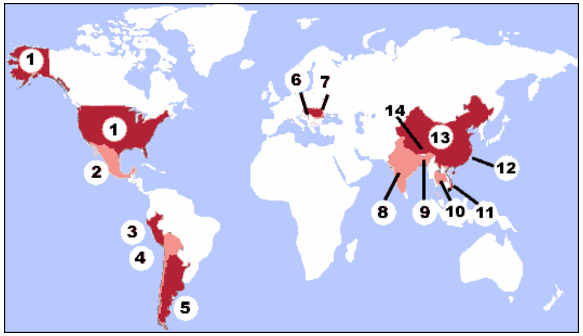




Temperature dependence on the extended x-ray absorption spectra for 10% Pt/C. As the temperature increases, the dynamic disorder ($\sigma_D^2$) increases, causing the amplitude to decrease.

# Role of metal-reducing bacteria in arsenic release from Bengal sediments (Islam et al., Nature, 430, 68-71, 2004)

As-contaminated drinking water a global problem – hundreds of millions now at risk

As(III) more toxic and more mobile than As(V); As causes skin lesions and cancers; tube wells sample contaminated water at depth

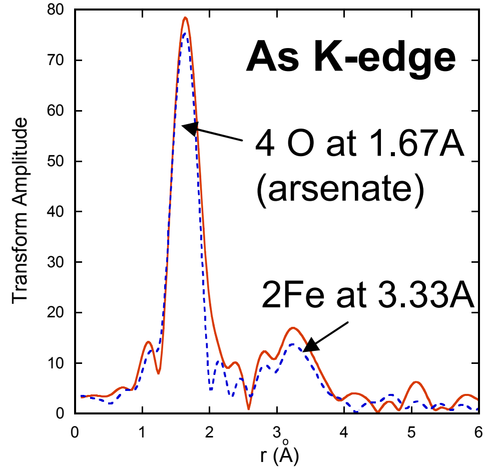



Researchers from Manchester University and Daresbury have studied sediments from Bengal and shown:

Anaerobic bacteria release As from sediments as water soluble As(III) via redox reactions
As(V) – As(III) reduction follows Fe(III) – Fe(II) reduction

As K-edge EXAFS shows >90% sediment As is As(V) (arsenate) adsorbed on Fe oxides both **before and after** reaction with bacteria – only ~10% As is bioavailable.

This fundamental work will help development of 'clean-up' technologies



# Phase One Beamlines

| No. | Beamline | Energy Range | Source type |
|---|---|---|---|
| 1 | MAD Protein Crystallogphy | 5 – 15 keV | MPW (In-vacuum undulator in phase 2) |
| 2 | PES and Photoabsorption spectroscopy | 5-1000 eV | Undulator |
| 3 | SAX/WAXS | 10 keV | Undulator |
| 4 | XAFS/XRF | 3-30 keV | 2.5 Tesla MPW |
| 5 | Powder Diffraction | 3-25 keV | 2.5 Tesla MPW |
| 6 | IR Spectromicroscopy | 0.01-1 eV | Large Aperture Bending magnet |

# EXAFS Users Group at SESAME

- http://www.sesame.org.jo
- Dr. M. Javed Akhtar (PINSTCH)

    javeda@pinstech.org.pk

# Thank you