XAS Studies of Battery Materials

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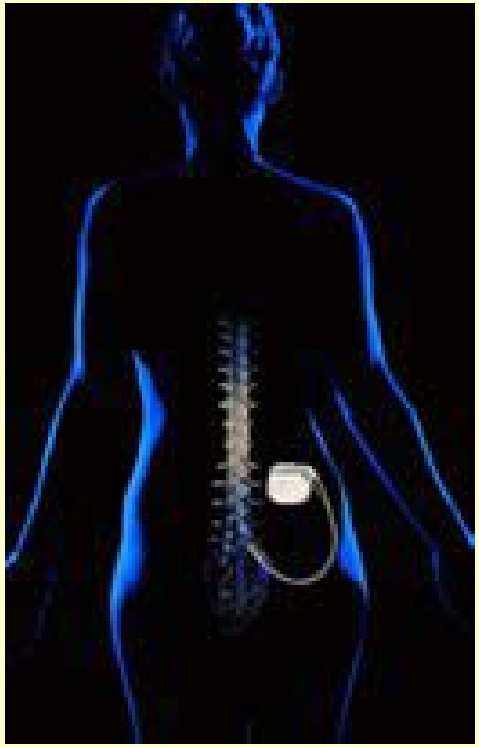
$LiCoO_2$-based Cathodes Set the Benchmark in Performance in a Variety of Uses

These ultra-compact power sources are being developed for:

- A new generation of spacecraft
- Automotive power
- Portable electronics
- Implantable medical devices, such as drug delivery systems

Uses of $Li_xAg_2V_4O_{11}$-based Batteries



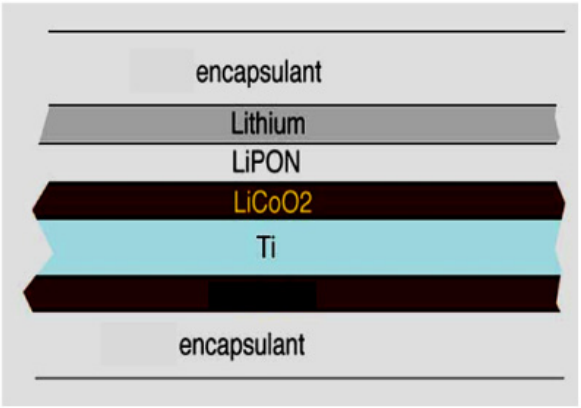
- Particularly useful in medical applications
- High power delivery
- Non-toxic

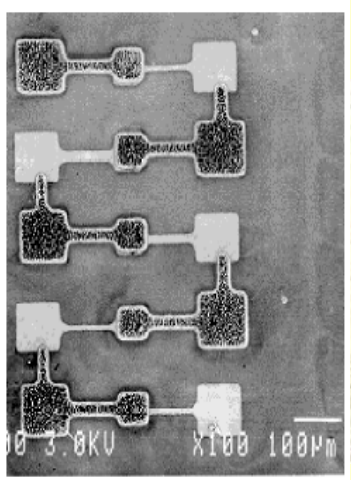
$LiCoO_2$-based Microbattery design

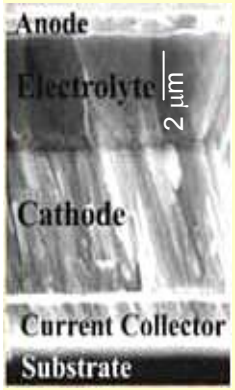
A microbattery is comprised of the following components:

- An Electrolyte - Lithium phospho-oxynitride glass (LIPON)
- Anode - Metallic Lithium
- Cathode - $LiCoO_2$
- The cathode is deposited directly onto Ti current collectors by sputtering, annealed at low temperature (~500°C compared to ~600°C for commercial batteries).

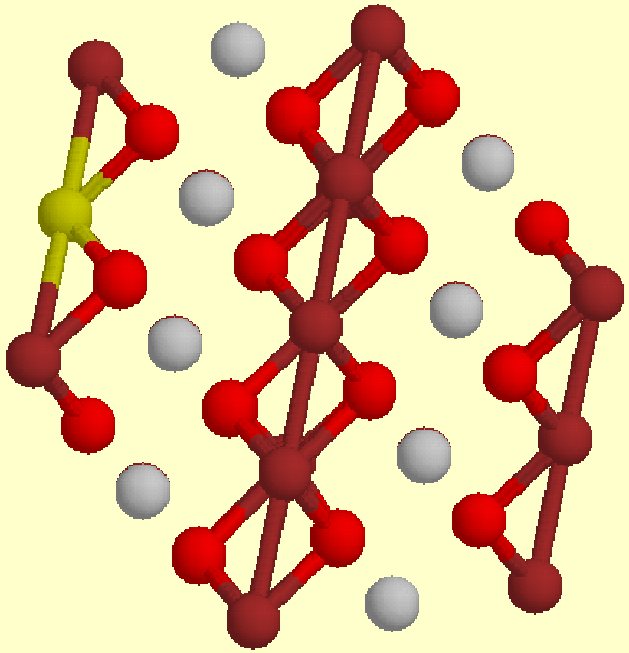
The total cell thickness is less than 20 µm.





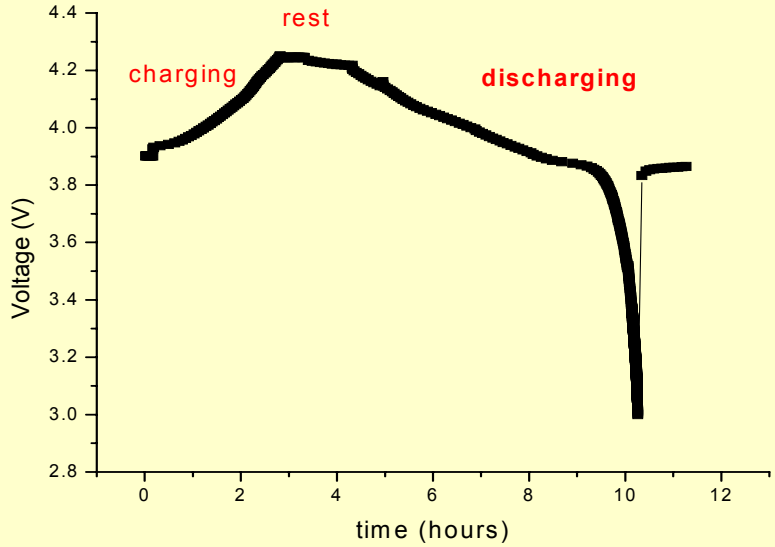


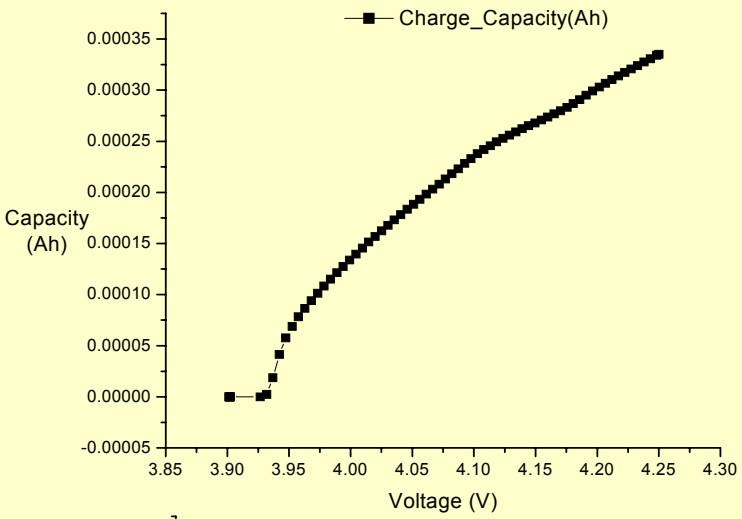
In-situ XAS of $LiCoO_2$-based Battery

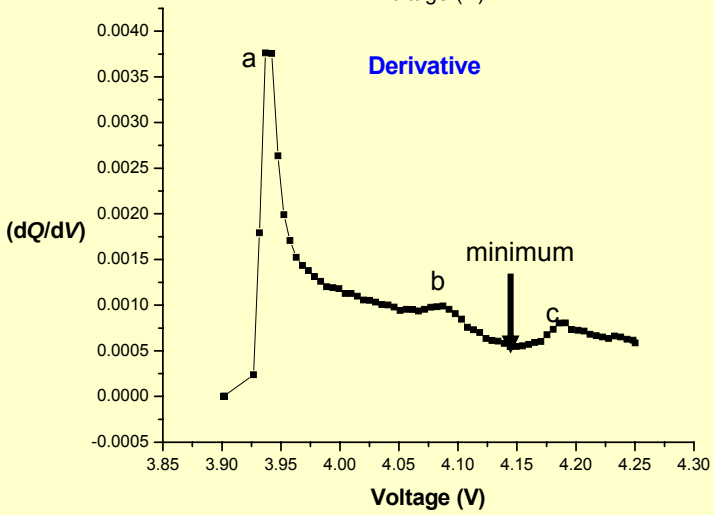


- We expect the following things to change as Li is de-intercalated:
  - Cell parameter (coupled changes in atomic positions)
  - Oxidation state of Co and/or O for charge compensation
  - Local ordering (decoupled changes in atomic positions
  - Scattering amplitude (fewer Li ions)

Electrochemical behavior



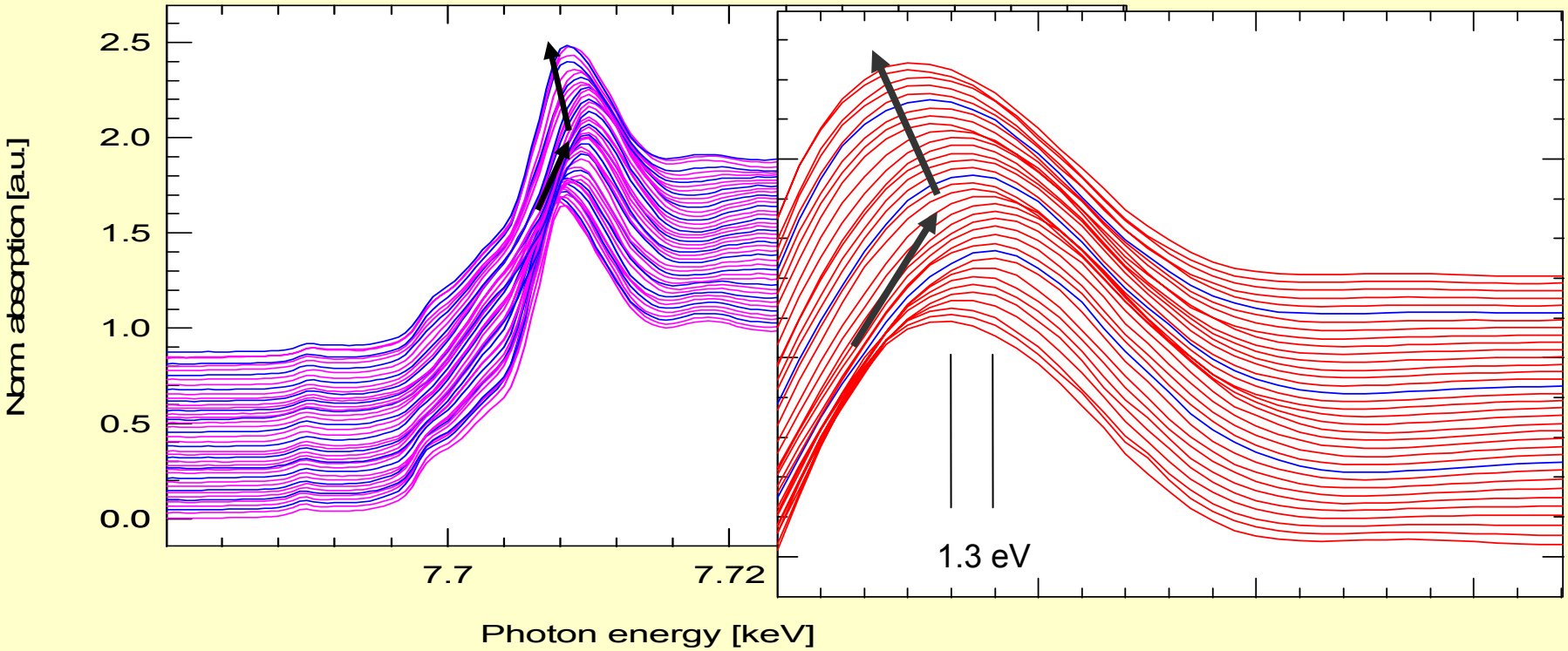




Electrochemically, the charge/discharge behavior corresponds to that of a bulk $LiCoO_2$ cell.

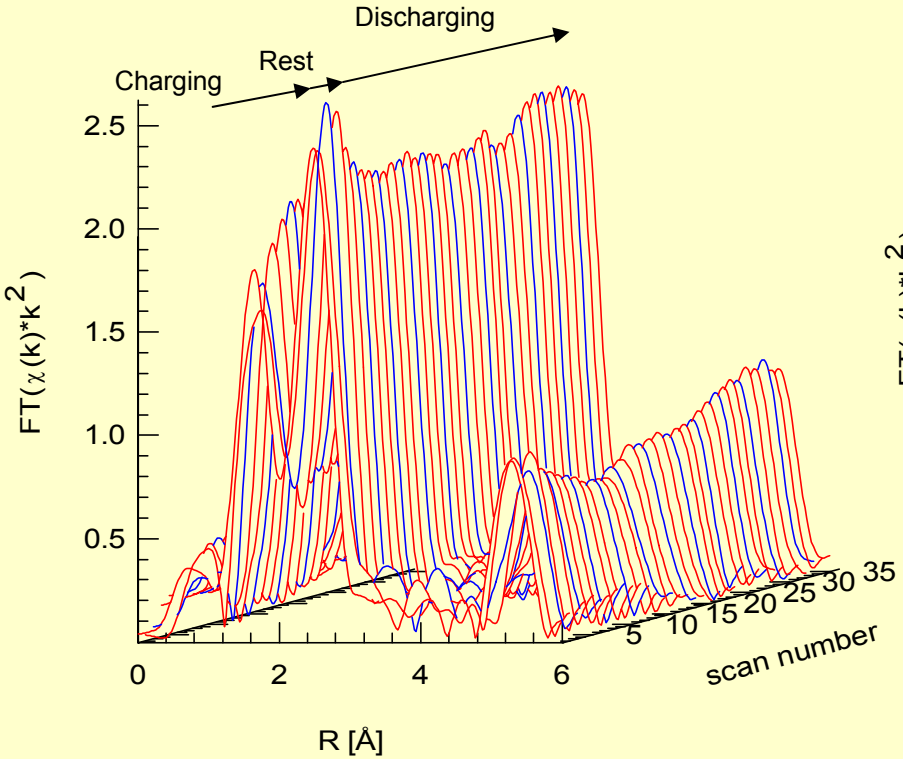
For example, we find the same features on the *d*Q/*d*V vs. V plot that has been reported by Reimers et al.

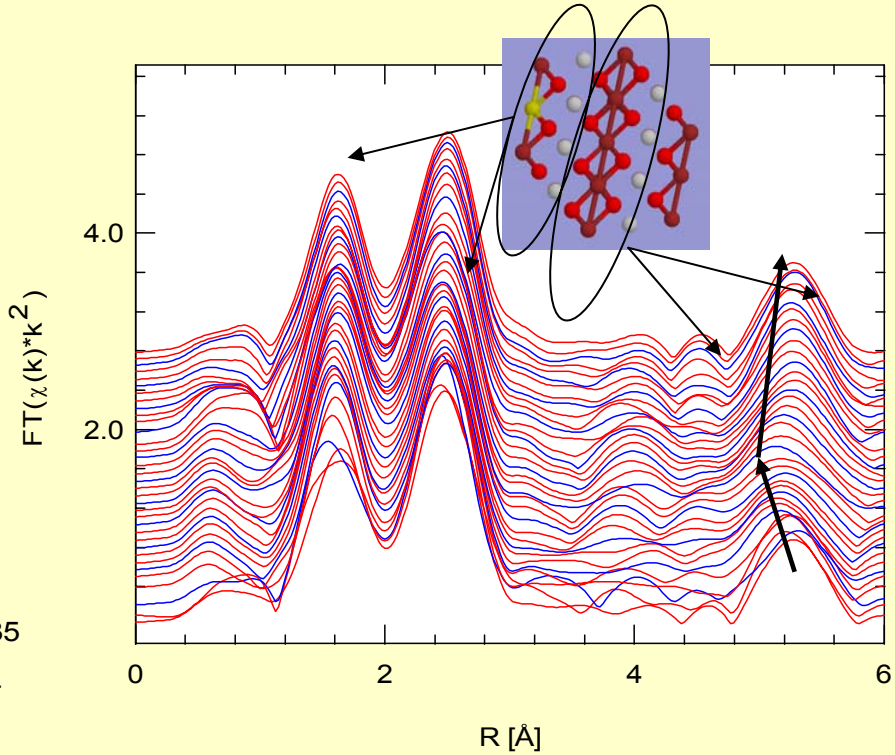
X-ray absorption near-edge structure of Co



- The white line of the near-edge undergoes a shift of ~1.3 eV
- similar shift for a $Li_xNi_{0.8}Co_{0.2}O_2$ cell has been reported [Johnson and Kropf].

Real-space manifestation of cycling





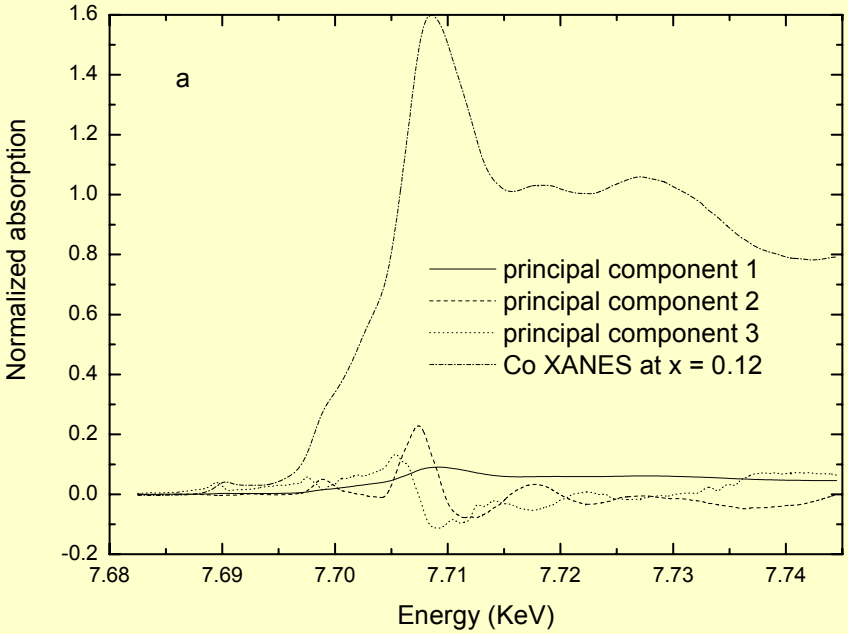
- **The amplitude of the Fourier transform peaks change as a function of charge/discharge**
- **The two ovals in the inset show the regions of the layered structure that correspond to the peaks.**
- **The inter-/intra-layer atoms distances contract as a function of charging.**

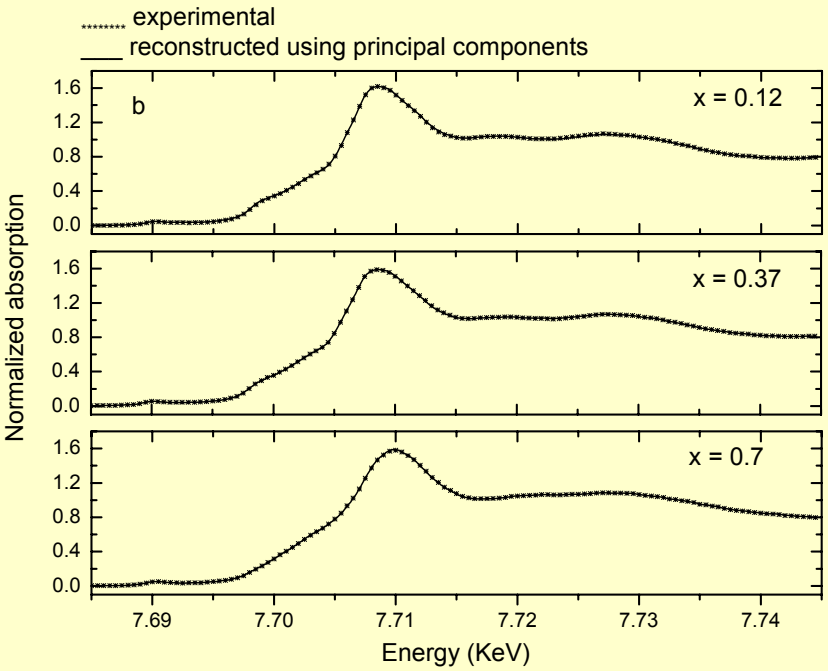
PCA Formulation

$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & . & . & \alpha_{1n} \\ \beta_{21} & \beta_{22} & . & . & \beta_{2n} \\ \chi_{31} & \chi_{32} & . & . & \chi_{3n} \\ . & . & . & . & . \\ . & . & . & . & . \\ \mu_{m1} & \mu_{m2} & . & . & \mu_{mn} \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & . & . & a_{1n} \\ b_{21} & b_{22} & . & . & b_{2n} \\ c_{31} & c_{32} & . & . & c_{3n} \\ . & . & . & . & . \\ . & . & . & . & . \\ m_{m1} & m_{m2} & . & . & m_{mn} \end{bmatrix} \bullet \begin{bmatrix} v_{11} & 0 & . & 0 \\ 0 & v_{22} & . & 0 \\ . & . & v_{ij} & . \\ 0 & 0 & . & v_{nn} \end{bmatrix} \bullet \begin{bmatrix} w_{11} & w_{12} & . & w_{1n} \\ w_{21} & w_{22} & . & w_{2n} \\ . & . & . & . \\ w_{n1} & w_{n2} & . & w_{nn} \end{bmatrix}$$

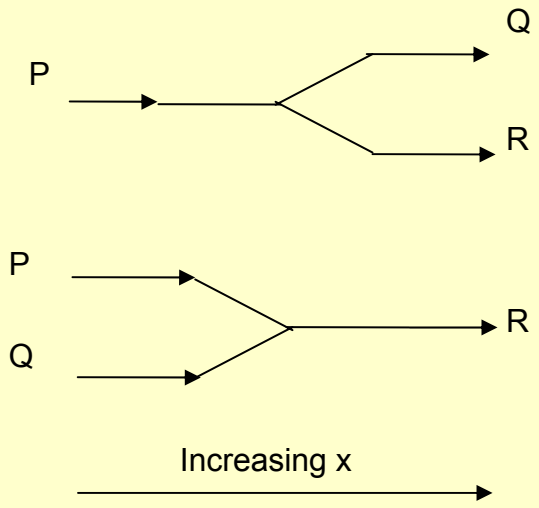
[A] = **[B]** • **[V]** • **[w]**^{t}

PCA: Components and Reconstruction





PCA: Possible Reaction Pathways



Co K-edge in $Li_{(1-x)}CoO_2$

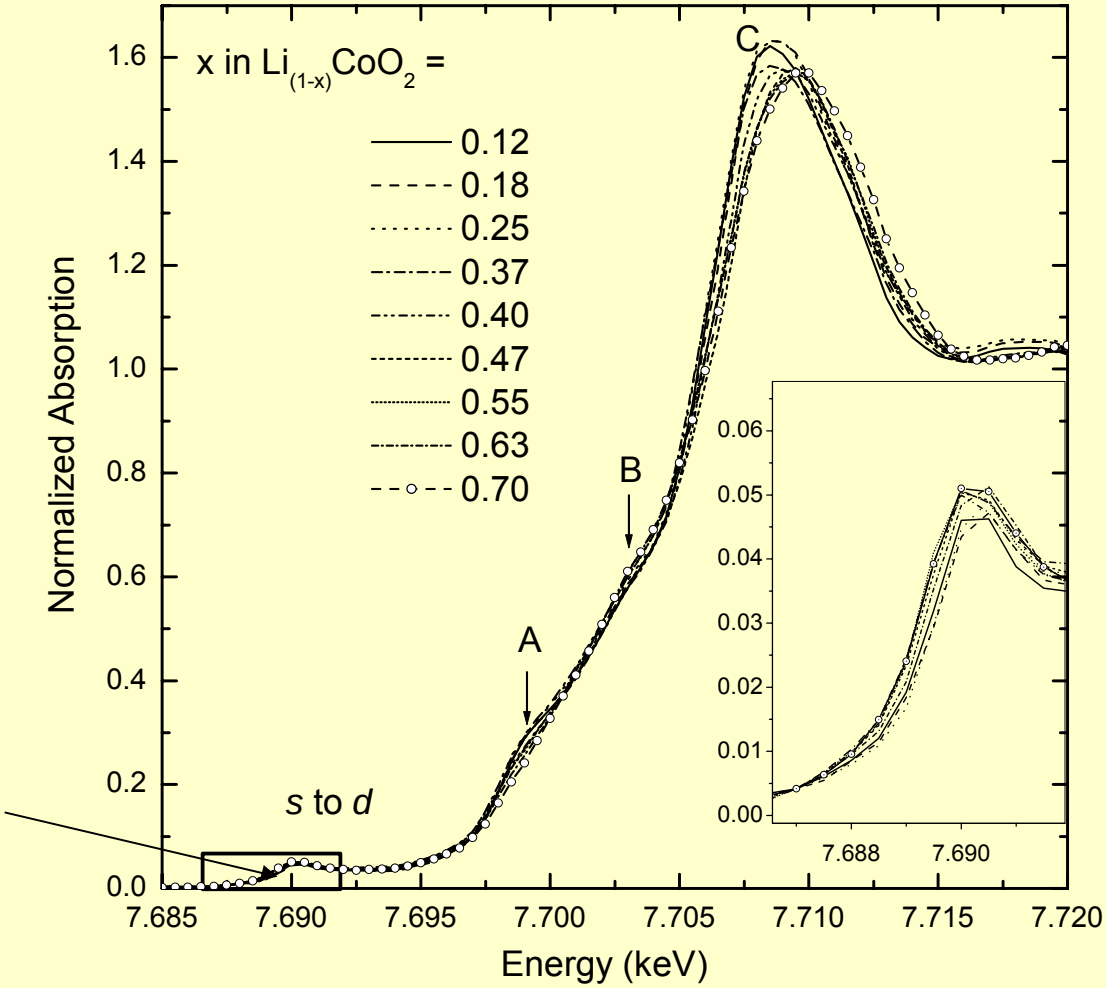
The Co K-edge XANES in $Li_{(1-x)}CoO_2$ as a function of x.

The *s to d* transition and *s to p* transition (A, B and C) are labeled.

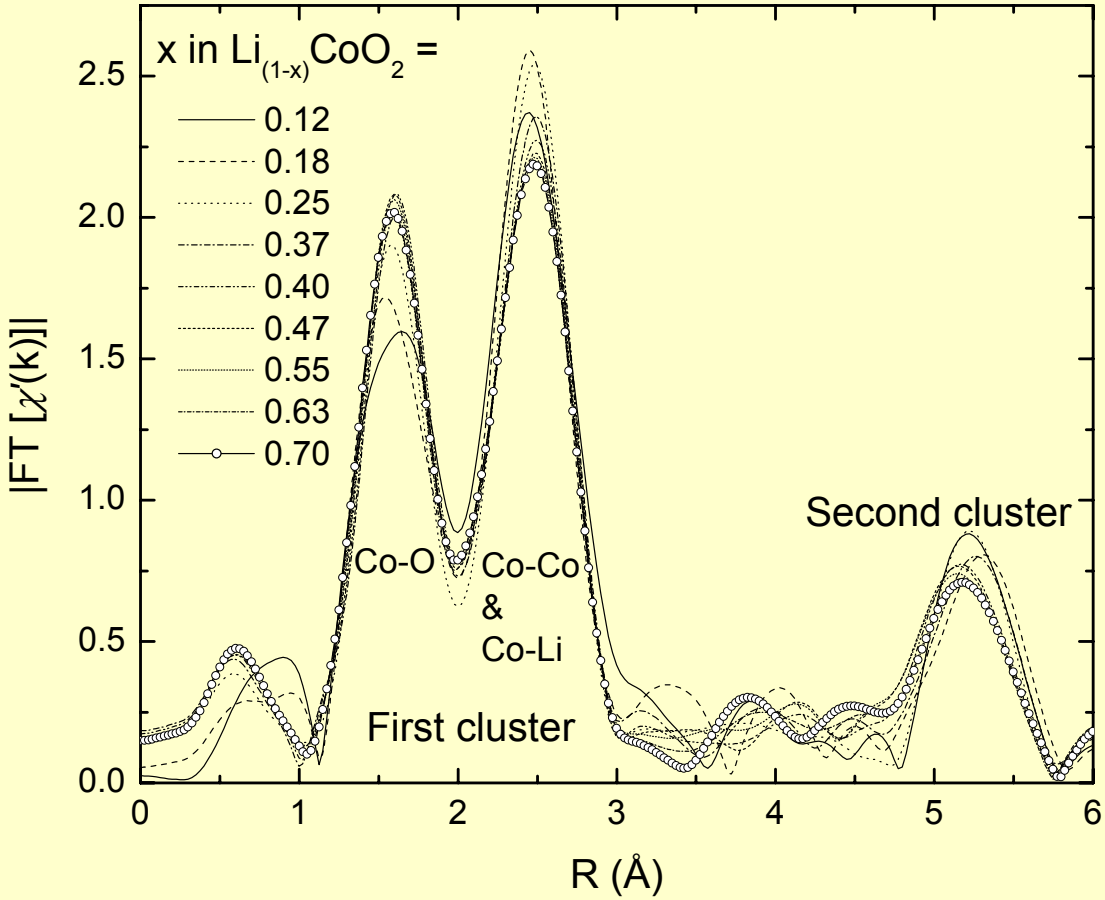
Co does appears to be involved in charge recompensation

…because

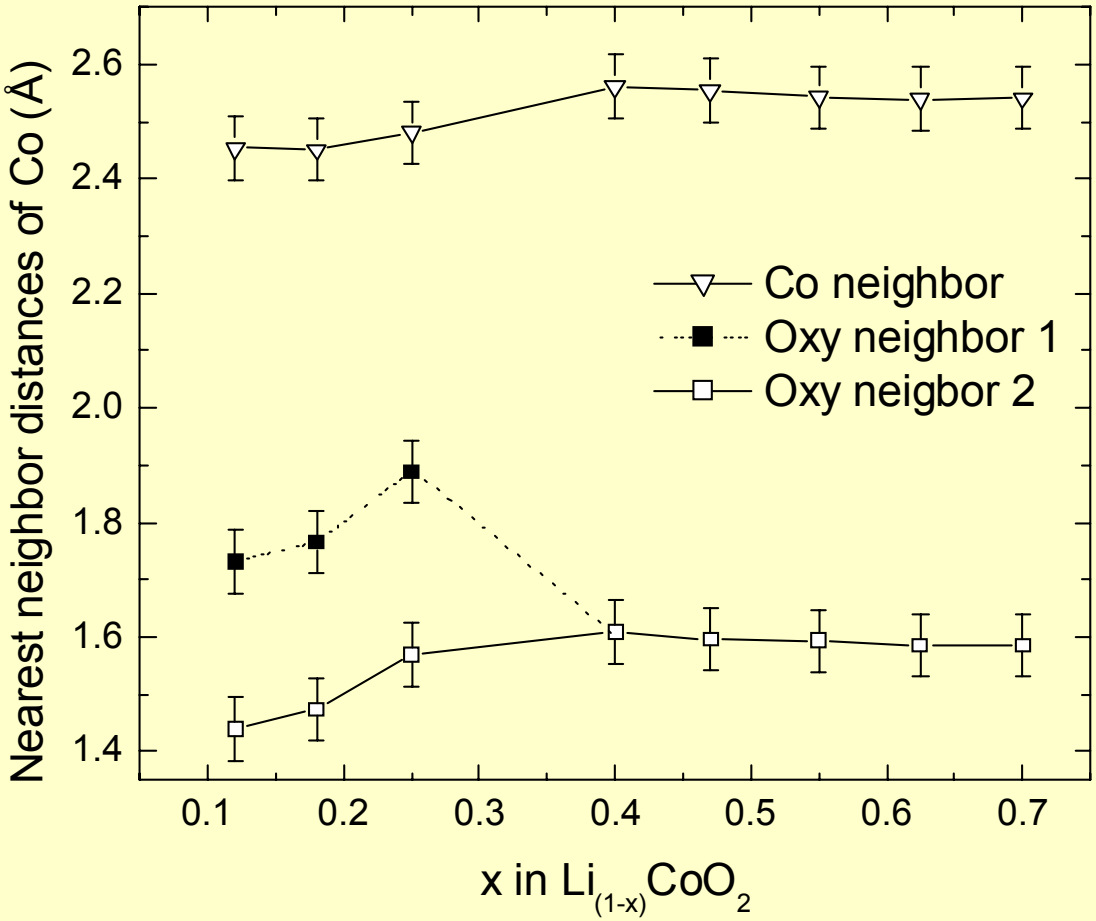
if the d-band occupancy of Co changes with increased delithiation, then this peak amplitude should increase



Theoretical fit to real-space data



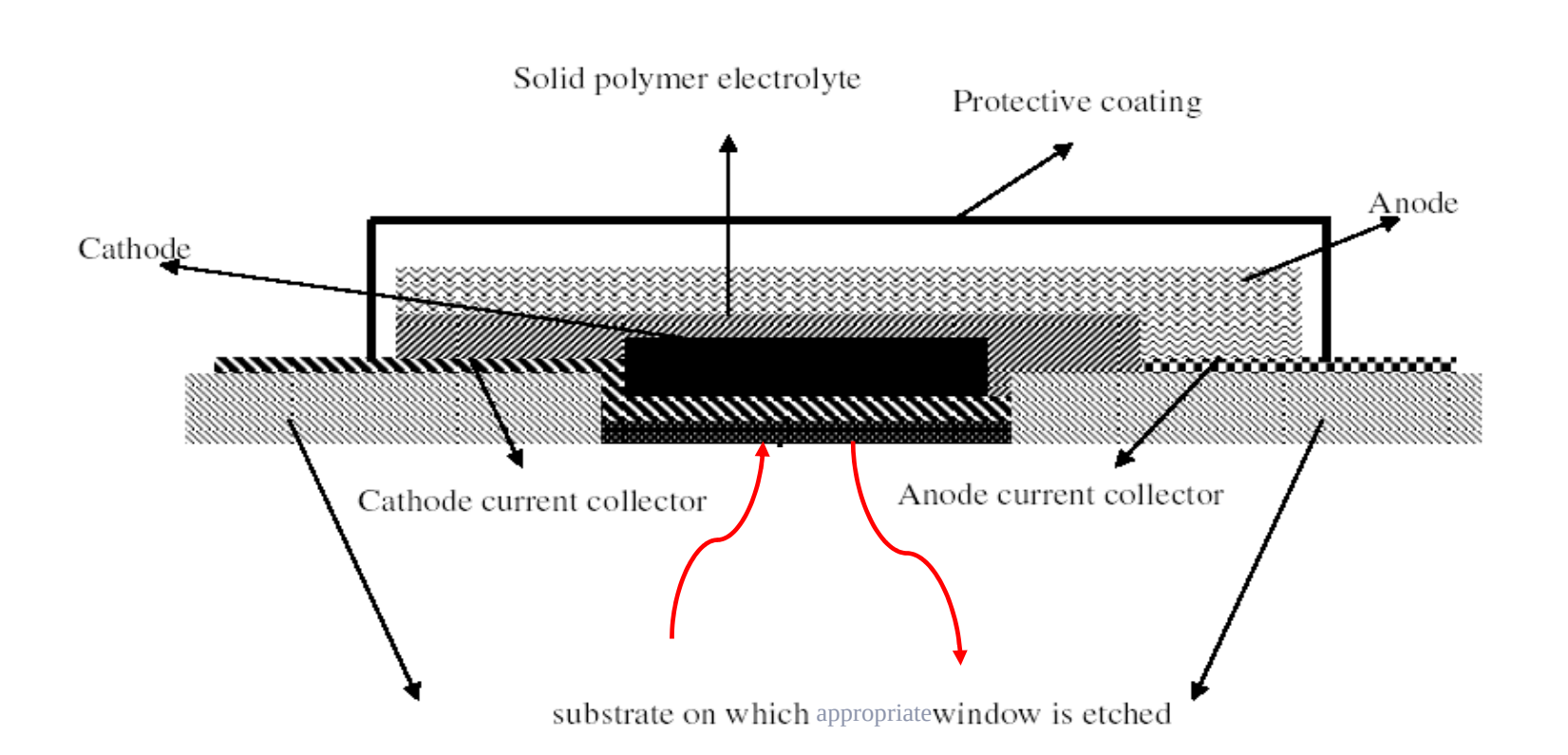
Theoretical fit to real-space data



The atomic structure around Co shows charge compensation occurs first by formation of O holes (for x<0.25).

XANES shows us that for x>0.25, charge compensation occurs through Co d-hole formation.

Spectro-electrochemical Cell



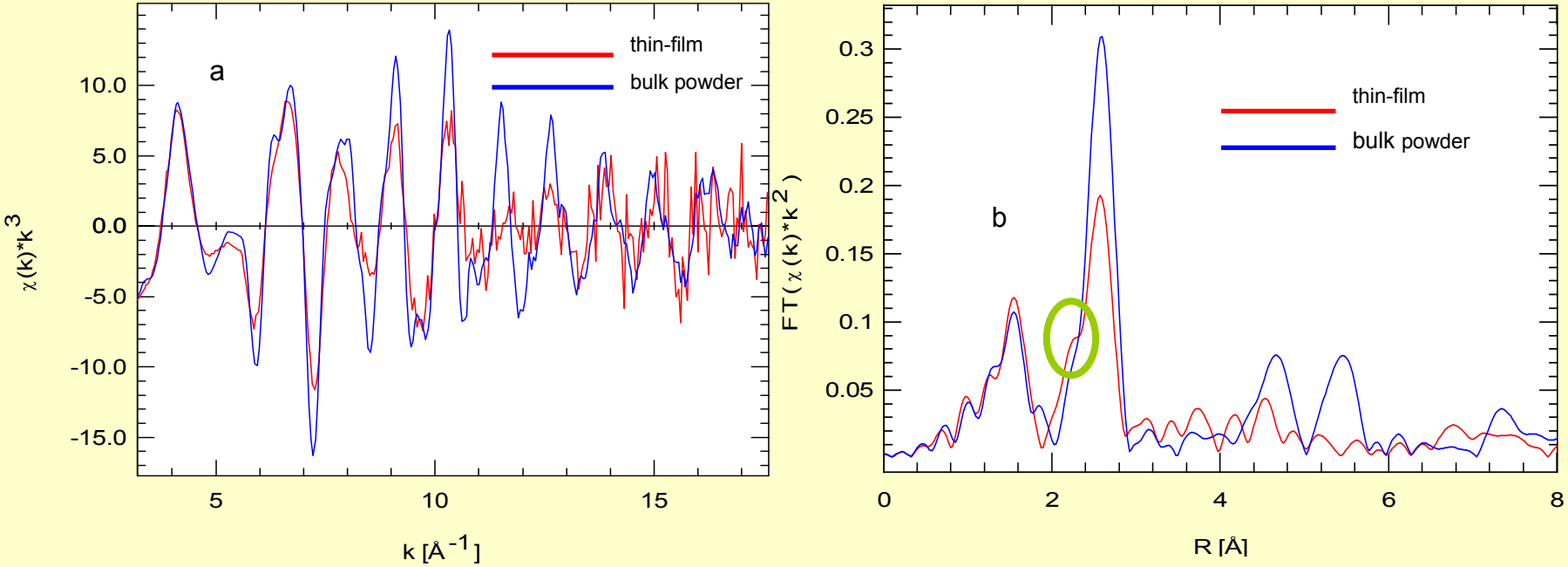
Spectro-electrochemical cell for in-situ XAS at the **O K-edge** being developed.

Half-cell built and tested.

How Optimal is the Structure in Thin-film $LiMCoO_2$ Cathode?

- The process of thin-film deposition may render the structure to be far from equilibrium.
- Non-equilibrium structure will affect the performance of the cell.

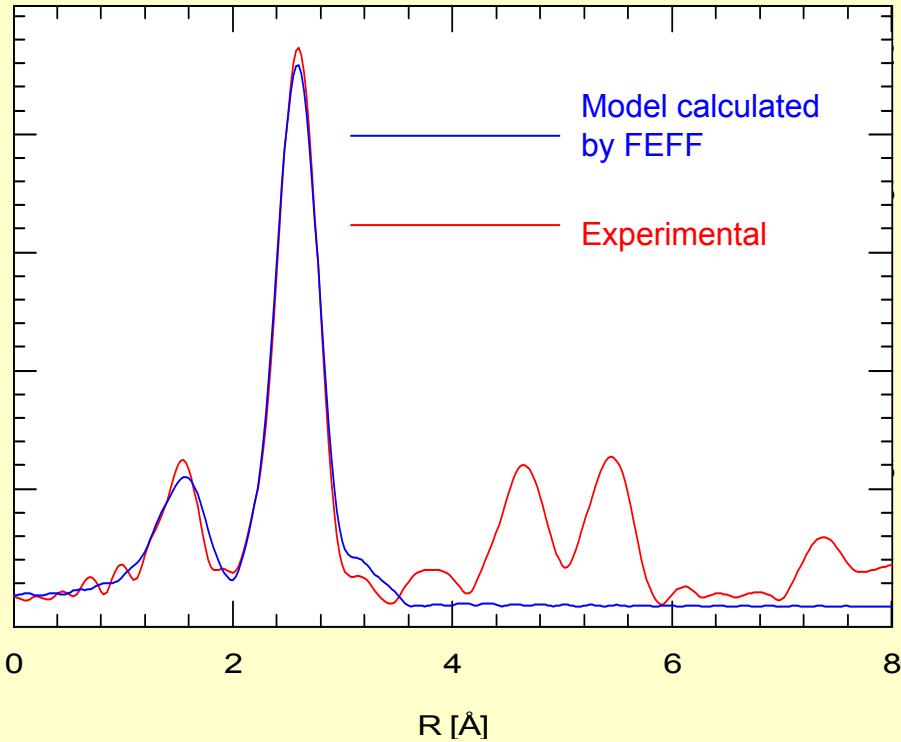
$LiNiO_2$ cathodes: thin-film and bulk

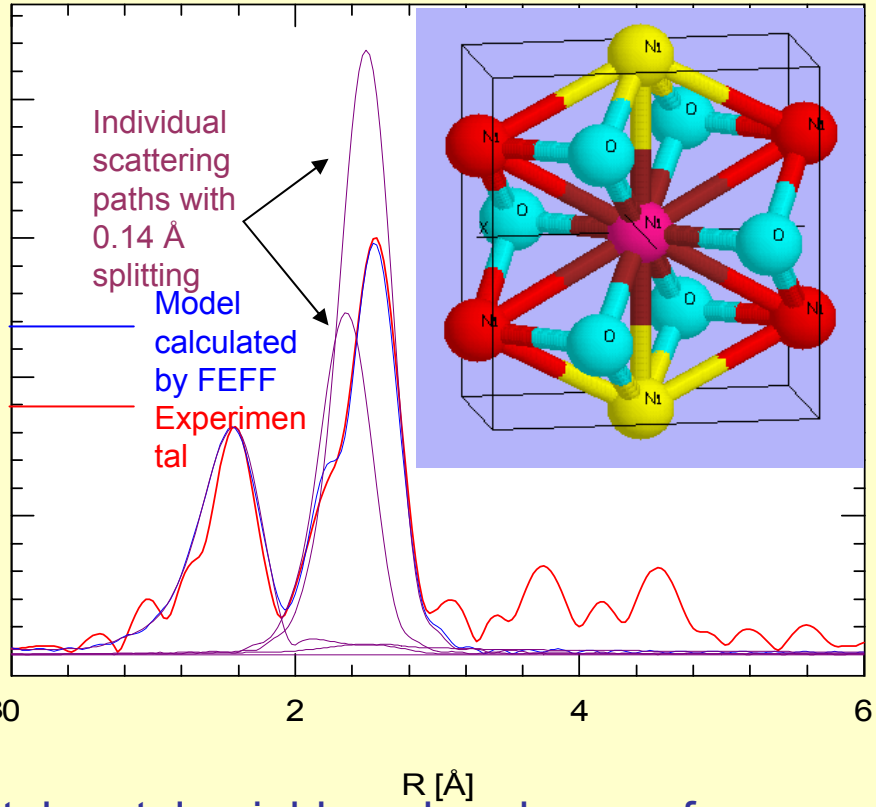


- The a) oscillating function $\chi(k)$ and its Fourier transform, b) FT[$\chi(k)*k^2$] function for $LiNiO_2$, as we go from bulk (blue) to thin-film (red).
- The amplitude of the Ni-Ni peak of the thin-film (in the plane of the substrate) is reduced and a shoulder is observed. This total effect cannot be explained by Jahn-Teller distortions.

Theoretical simulation of metal environment

Ni Environment in LiNiO2 bulk powder





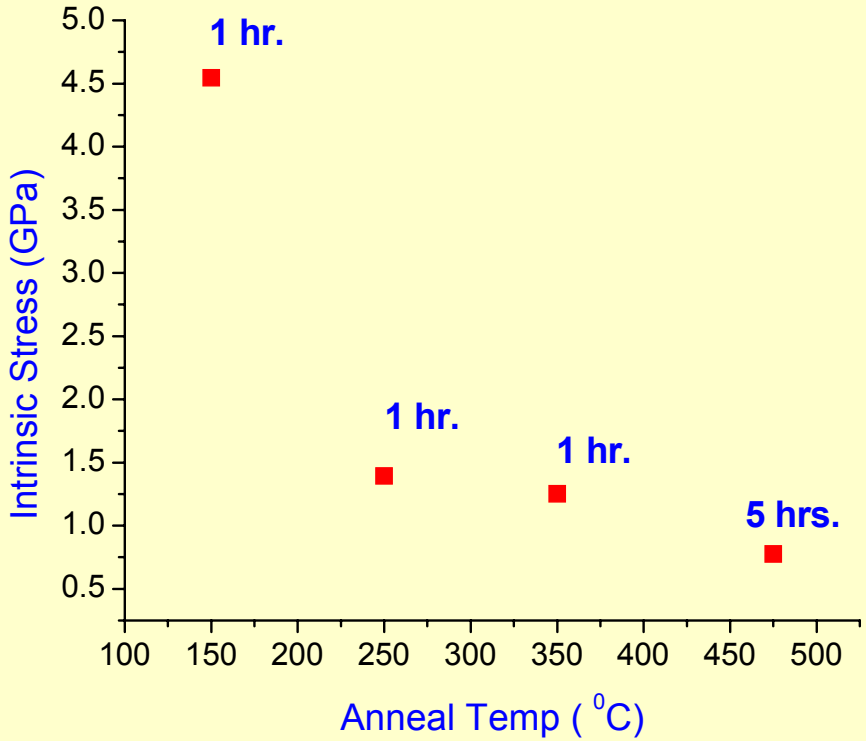
- Our simulation shows that the set of metal-metal neighbors break away from a six-fold symmetry to a two-fold symmetry; i.e., the six atoms are split into a set of two (**at a slightly shorter distance**) and four (**at slightly larger distance**).
- **The same effect is observed in $LiCoO_2$ thin films.**

EXAFS Experiments Designed to Study the Local Strain in $LiCoO_2$ Thin Films

Samples:

- Multiple 700nm of LiCoO2 was deposited on 2” Si wafer
- Samples annealed to different temperatures
- Fluorescence EXAFS data collected at X23B and X11B

Bulk Stress Relaxation With Annealing on Isostructural $LiCoO_2$



Wafer curvature measurement of stress, shows bulk stress being annealed out with heat treatment

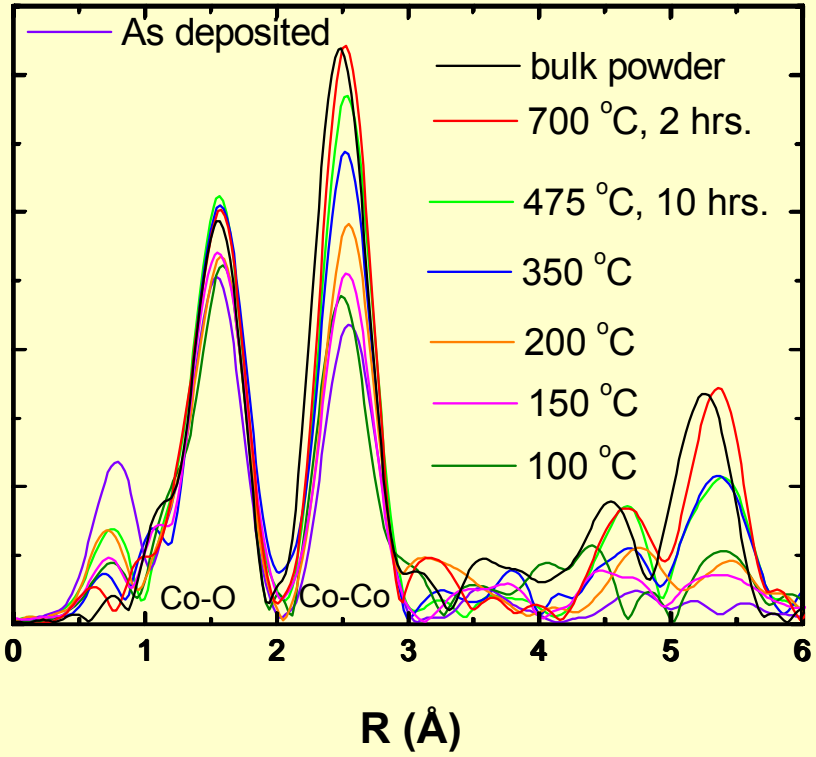
Co Atomic Neighborhood with Annealing

Relaxation of stress takes place in a complex set of steps.

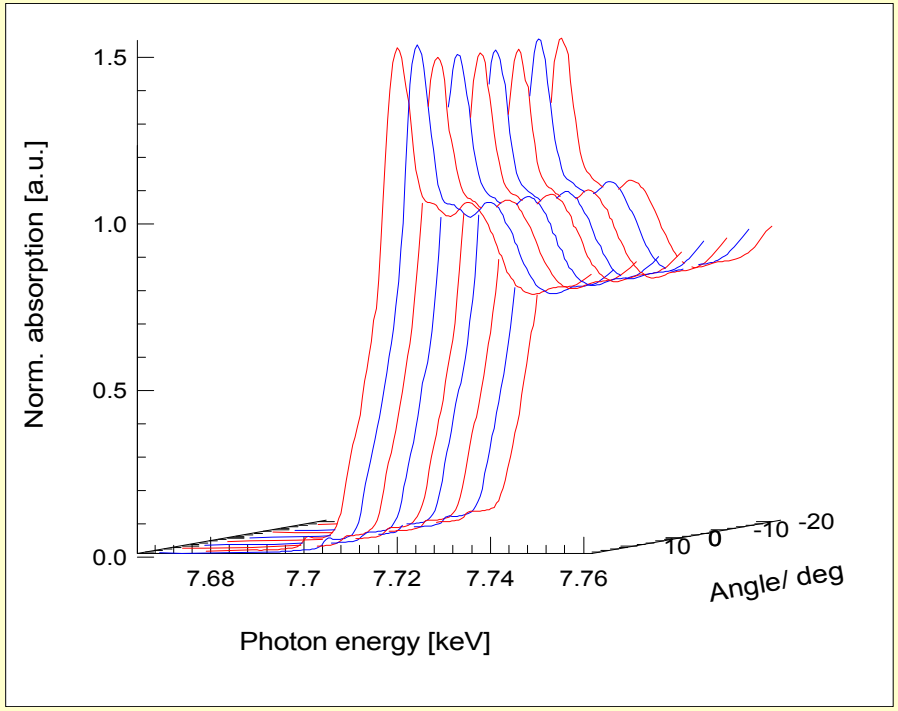
Stress on the Co-O bonds relaxed by 10 hrs. anneal at 475 ^{0}C

Stress remains on the Co-Co plane after annealing for 10 hrs at 475 ^{0}C.

Stress released by annealing at 700 ^{0}C for 2 hrs. However a c-axis expansion remains.

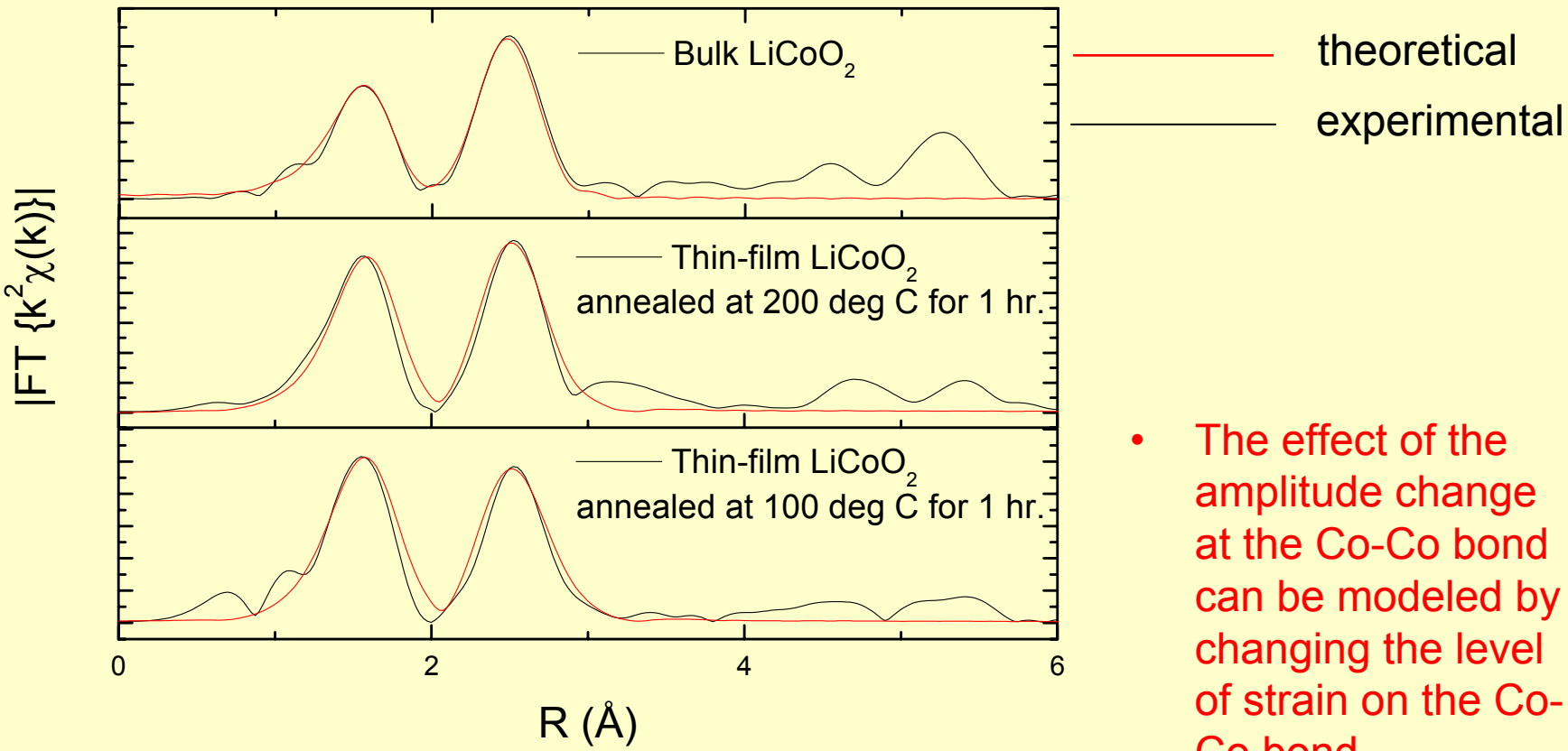


Angle-resolved XAS



- No texturing effect picked up by the plane-polarized X-rays.
- Orientation of the thin film with respect to the polarized X-ray beam is not the cause of this effect.

The same effect is observed in $LiCoO_2$



- The effect of the amplitude change at the Co-Co bond can be modeled by changing the level of strain on the Co-Co bond.

Experiments at the O K-edge

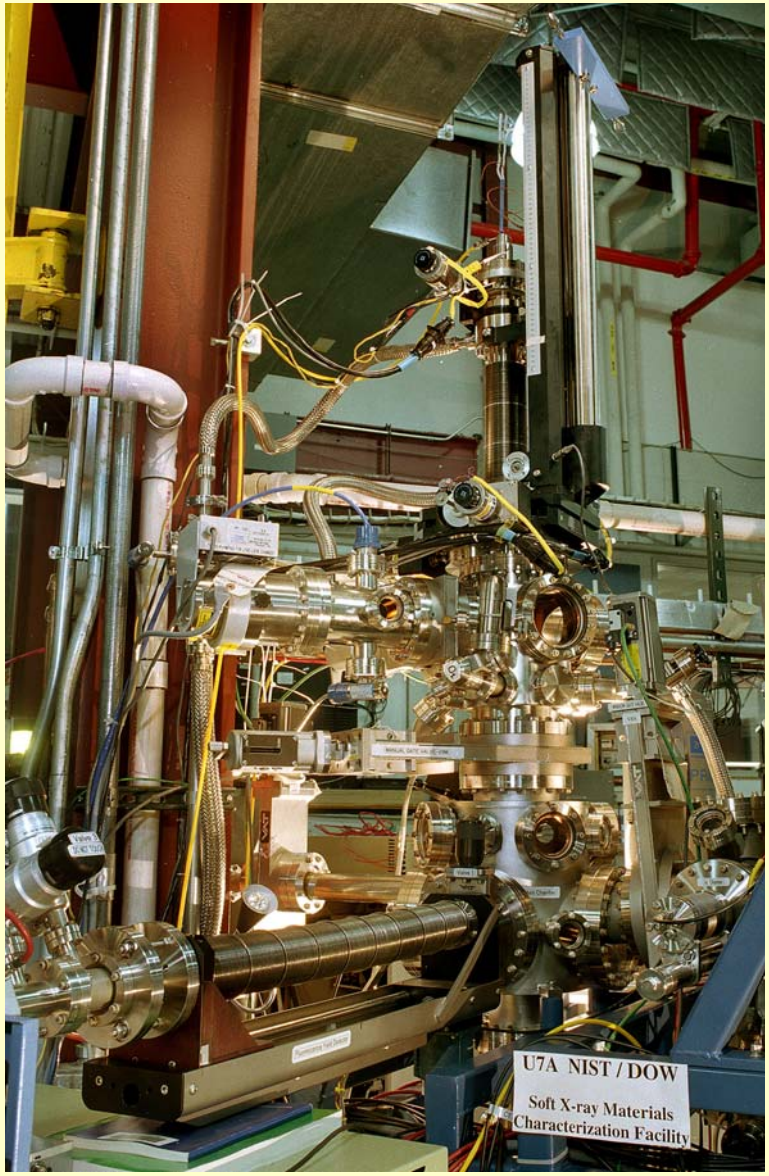
U7 endstation at the NSLS:

•1200 line grating mono;

•Focused beam (~1.5mm x1.5mm);

•Fluor. and P.E.Y. detector;

•motorized sample manipulator (4 degrees of motional freedom)

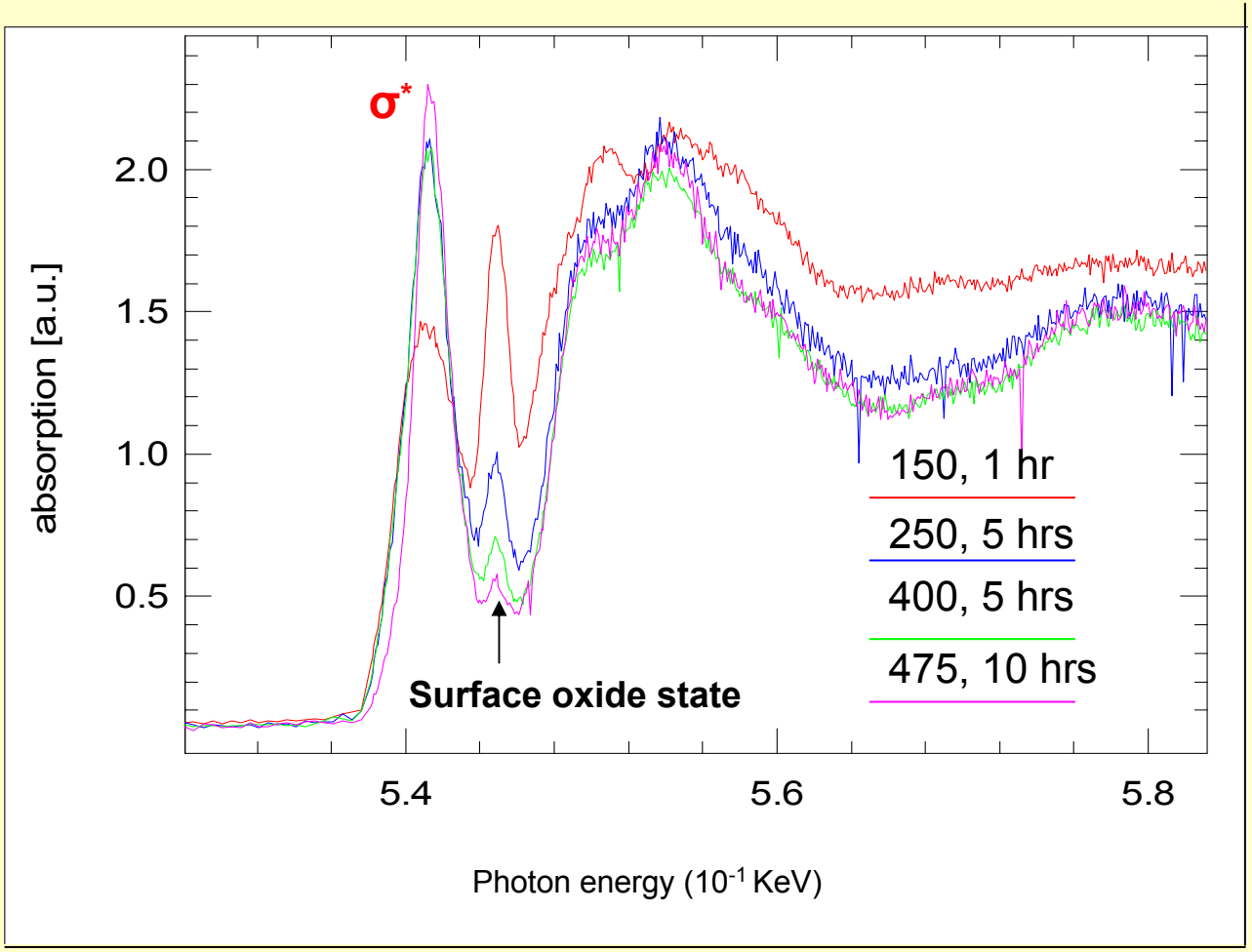


O K Fluorescence Yield from $LiCoO_2$ on Si wafer

The degree of covalent σ^* bonding increases with annealing

at the expense of

surface oxide states.

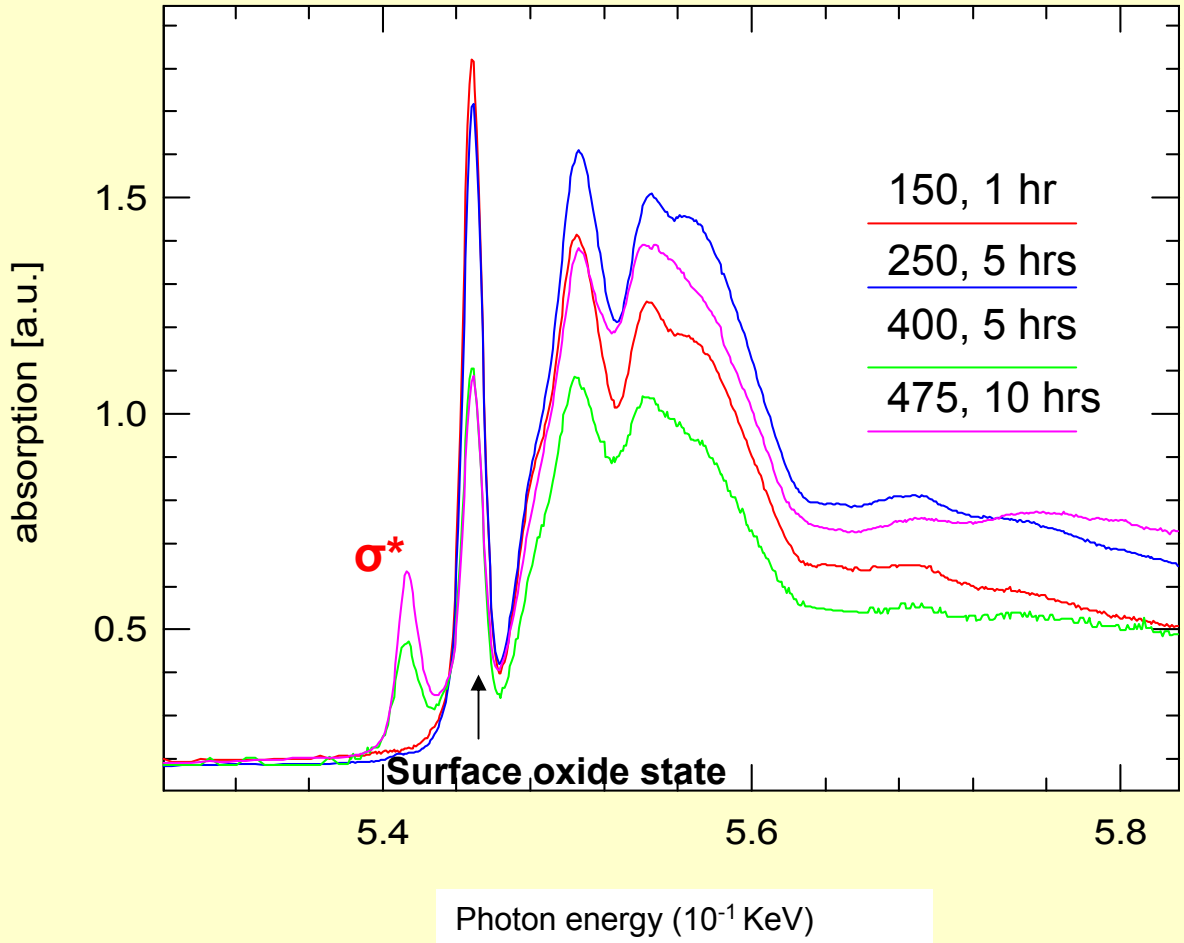


O K Electron Yield from $LiCoO_2$ on Si wafer

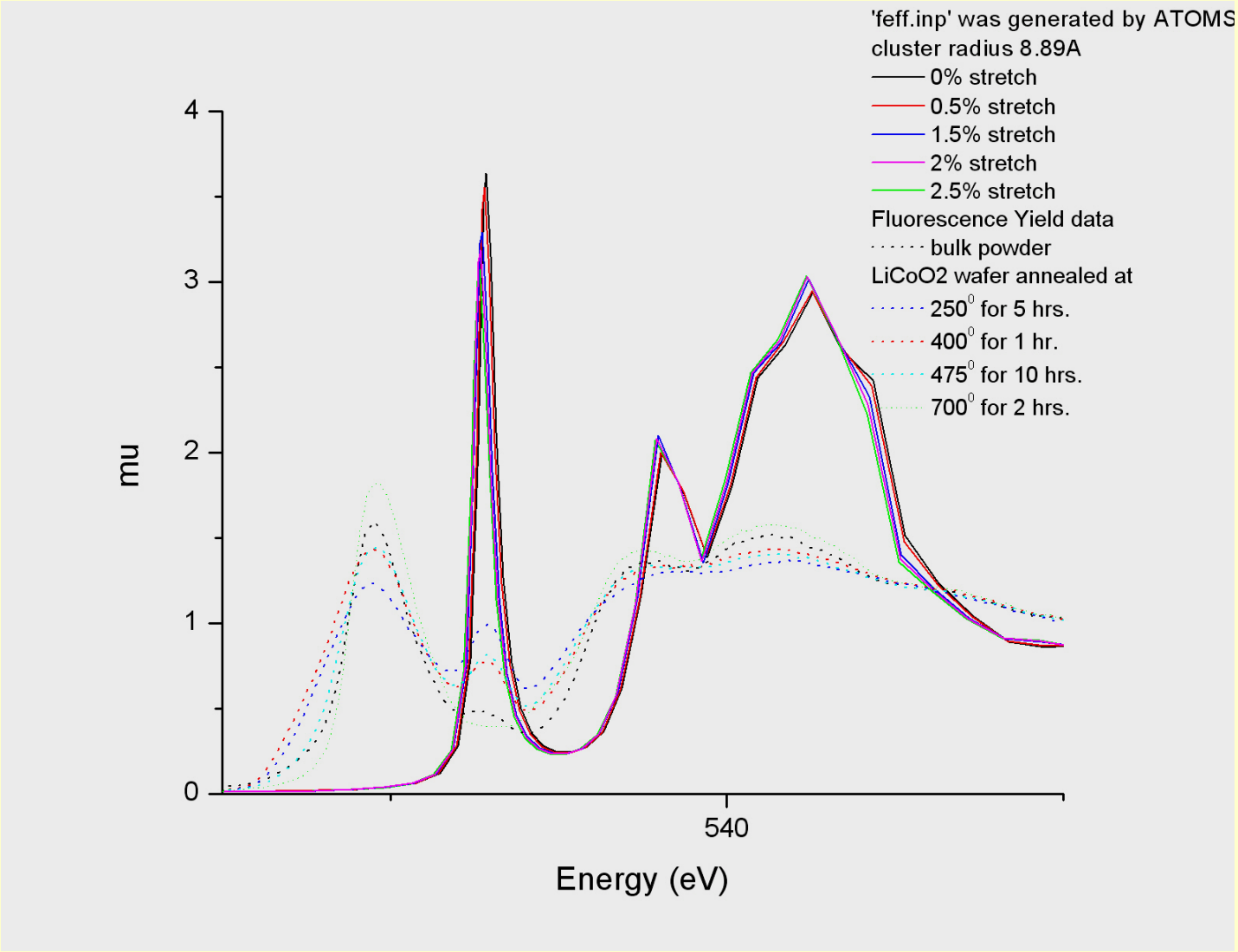
Surface oxide states dominate the electron yield signal. They diminish with annealing

while

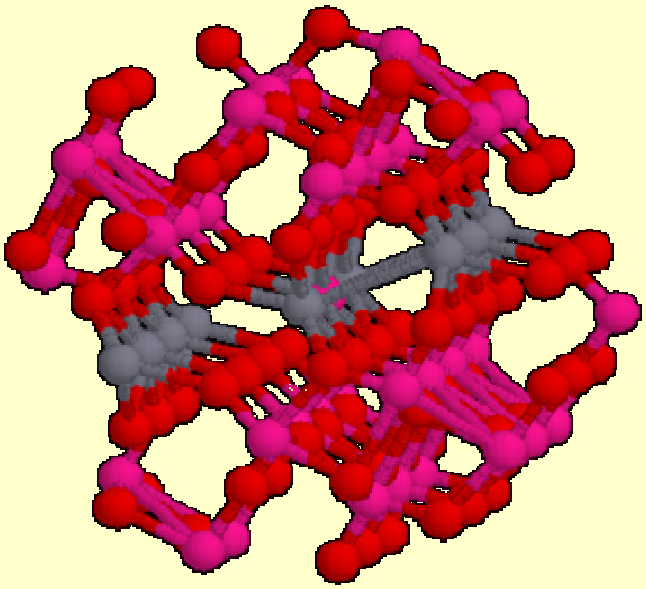
the degree of covalent σ^* bonding increases with annealing.



Comparison of O K FY data with FEFF8 Theory



Ex-situ Study of Li Intercalation in $Ag_2V_4O_{11}$

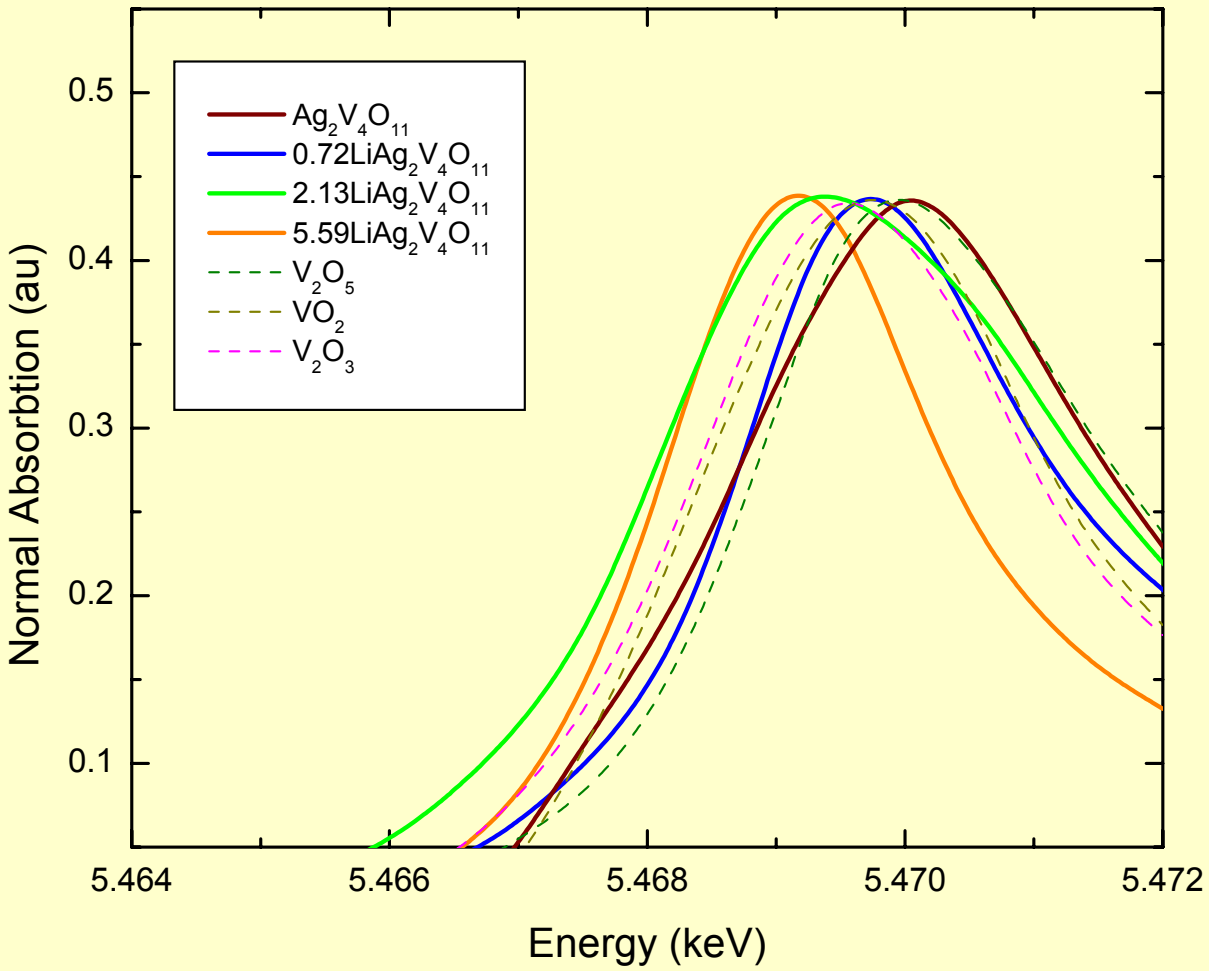


Ag and V K-edges are well separated in energy and this cathode is not optimized for in-situ studies.

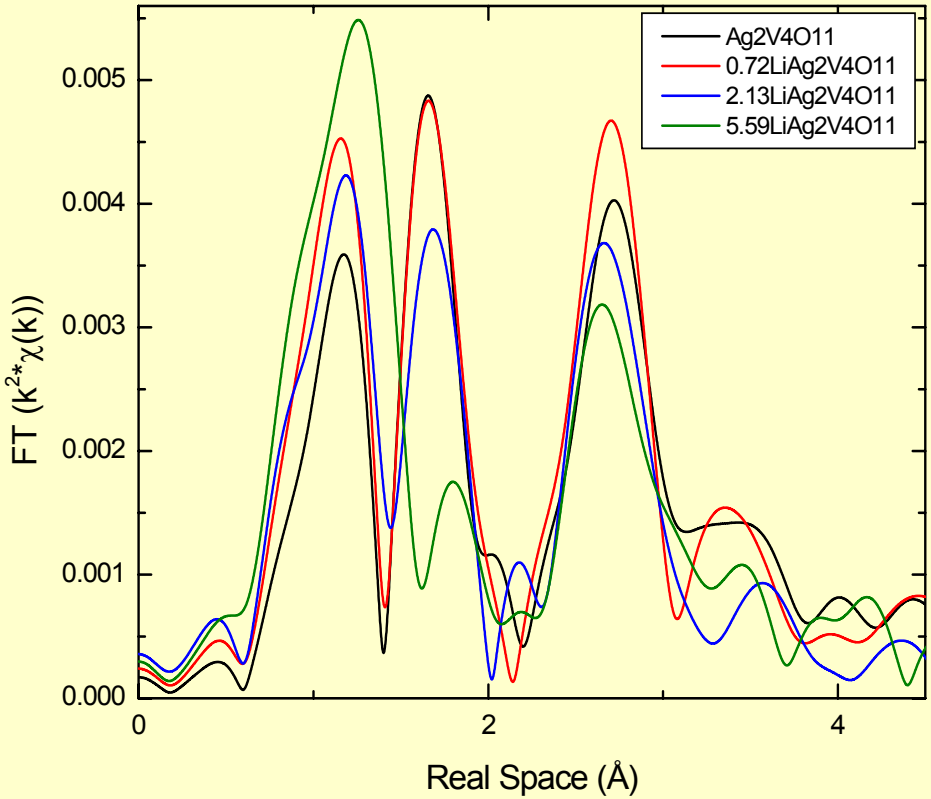
We expect the following things to change as Li is intercalated:

- atomic positions (coupled/de-coupled)
- oxidation state of V and Ag with charge compensation

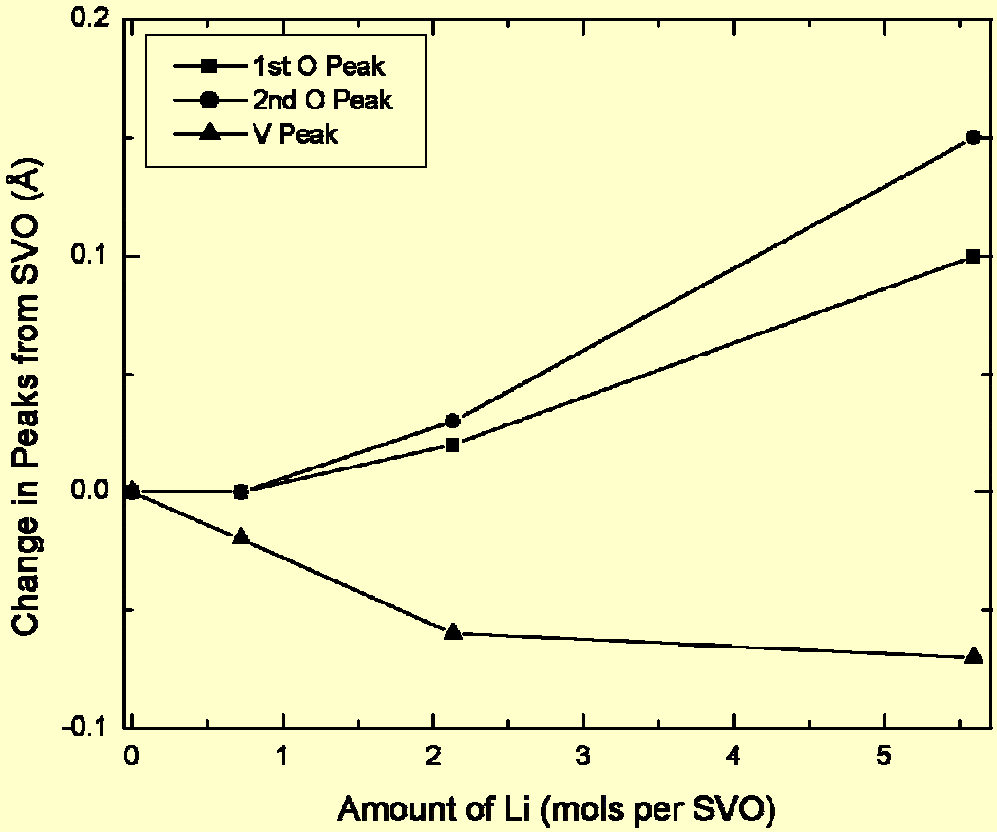
Change in the Oxidation State of V



Changes in V Atomic Neighborhood



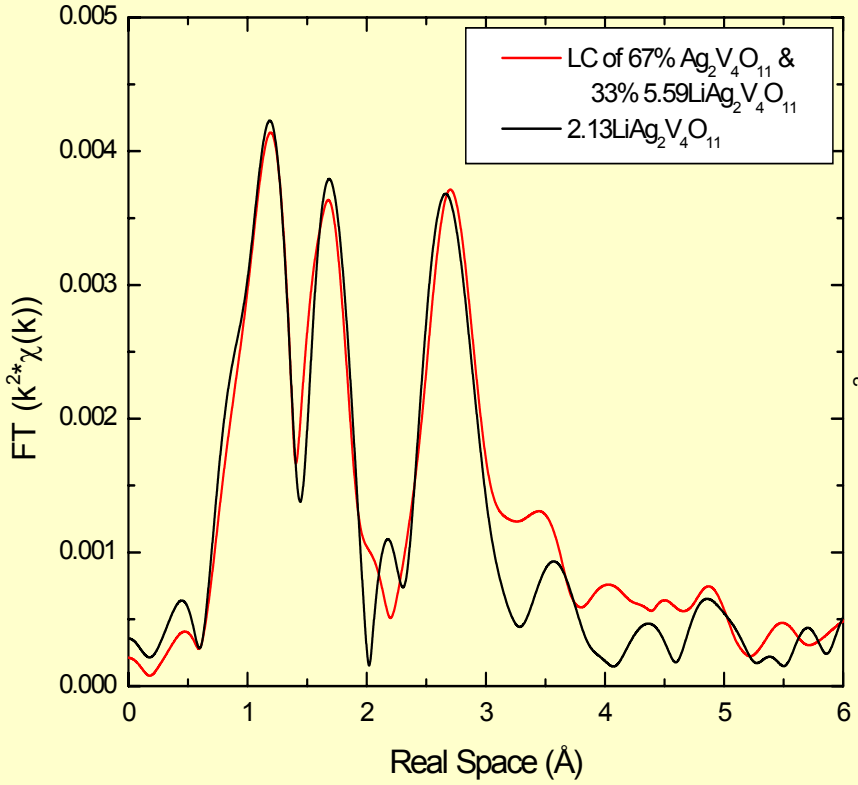
Ionic Neighbor Distances Around Vanadium

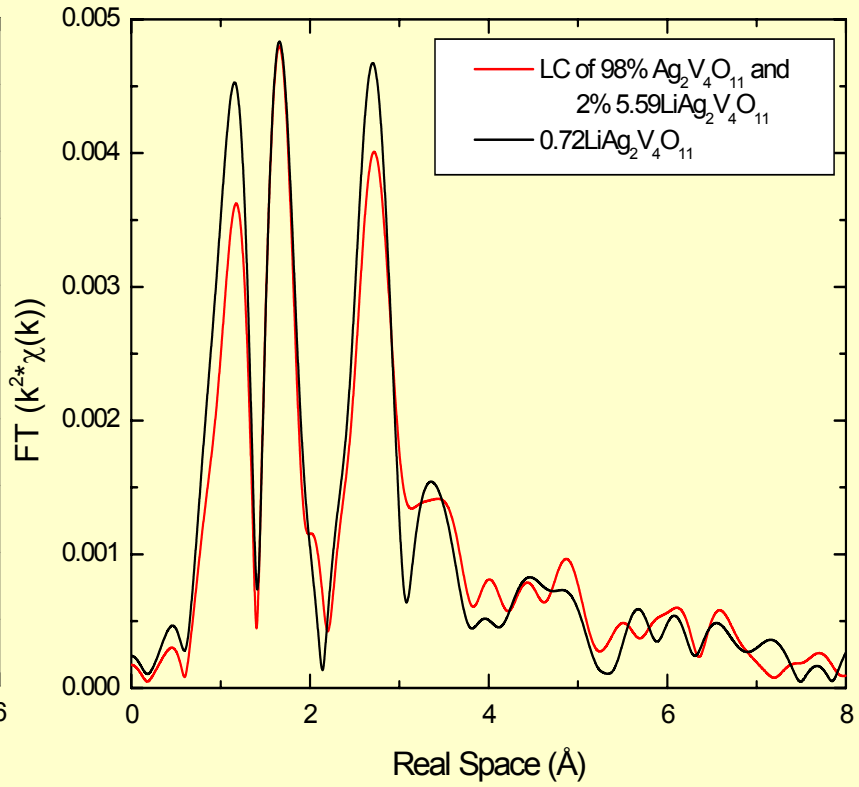


Equilibrium ionic distances will be a function of the local Coulumbic interactions

We observe that V-V ionic distance decreases with even 0.79 mol Li/ mol SVO

LC of V Ionic Neighborhood

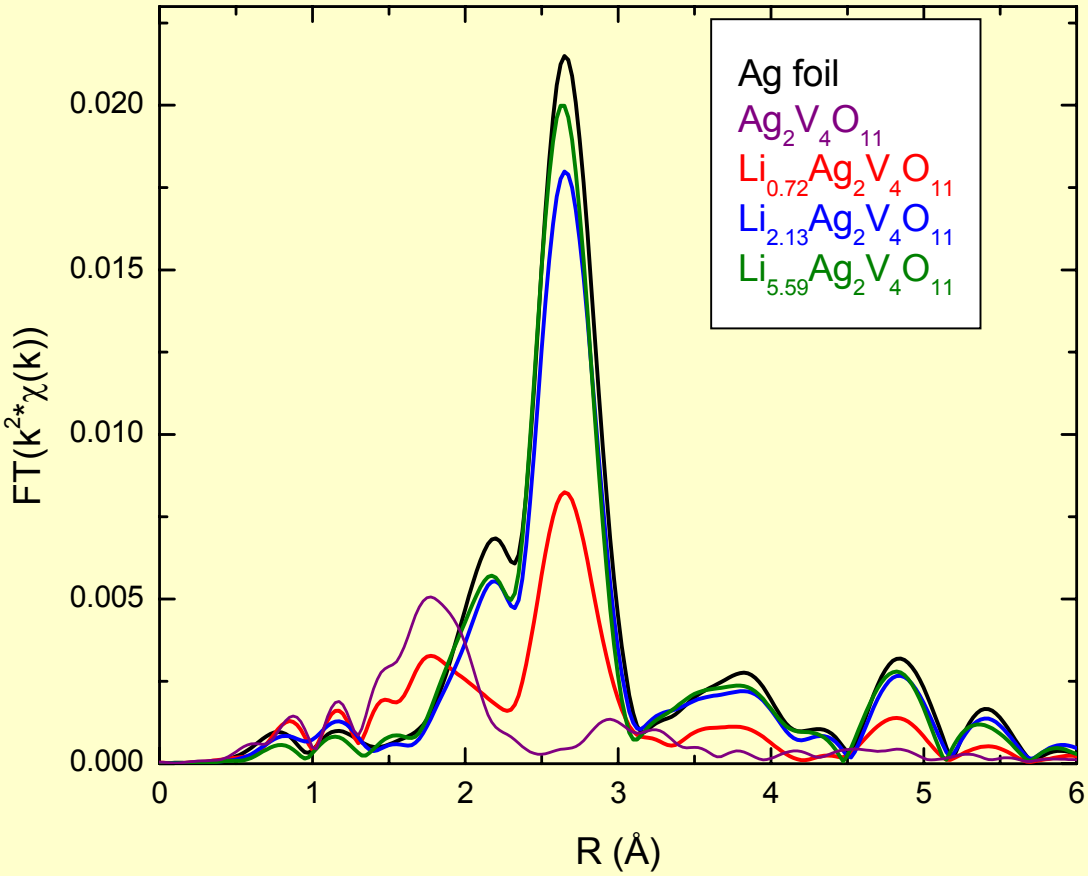




Phase segregation between SVO and the phase at 5.59 mol Li/ mol SVO

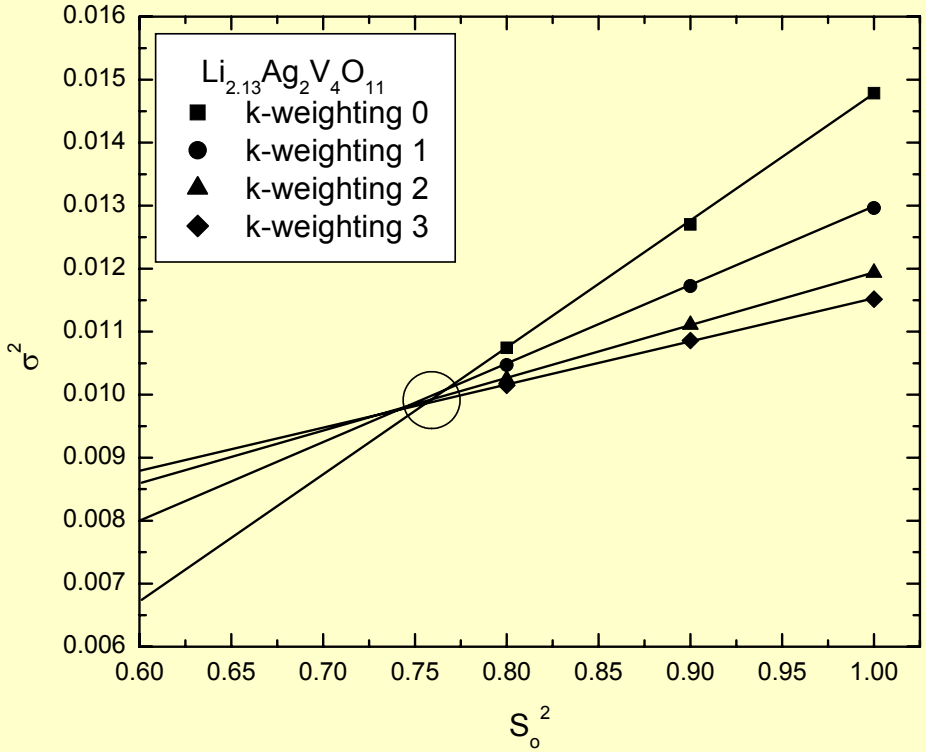
However, this phase segregation not observed at lower lithiation

Ag K-edge analysis of $Li_xAg_2V_4O_{11}$



- **FT {χ′} at the silver k-edge of the samples. Features of SVO are well resolved from those of metallic Ag.**

S_0^2 Determination in $Li_xAg_2V_4O_{11}$



S_0^2 (fcc Ag) = 0.79

S_0^2 ($Li_{5.59}Ag_2V_4O_{11}$) = 0.77

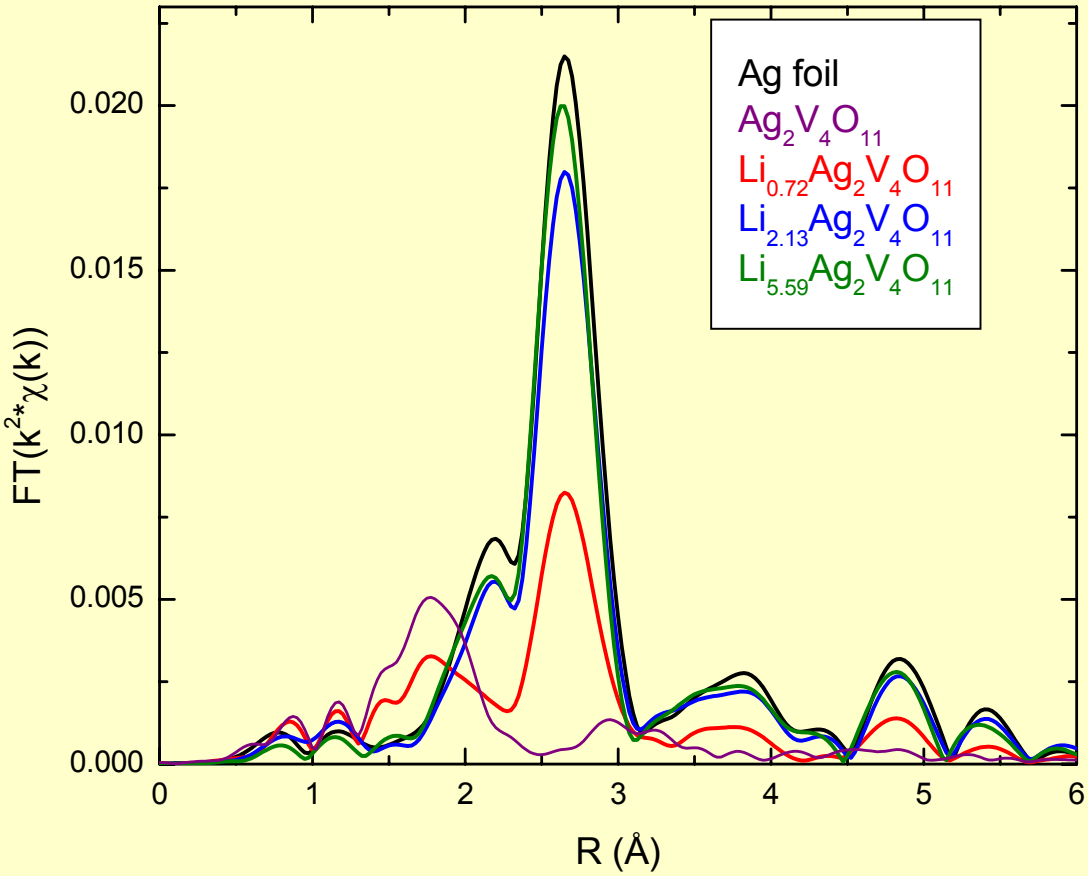
S_0^2 ($Li_{2.13}Ag_2V_4O_{11}$) = 0.76

N (fcc Ag) = 12

N ($Li_{5.59}Ag_2V_4O_{11}$) = 11.3

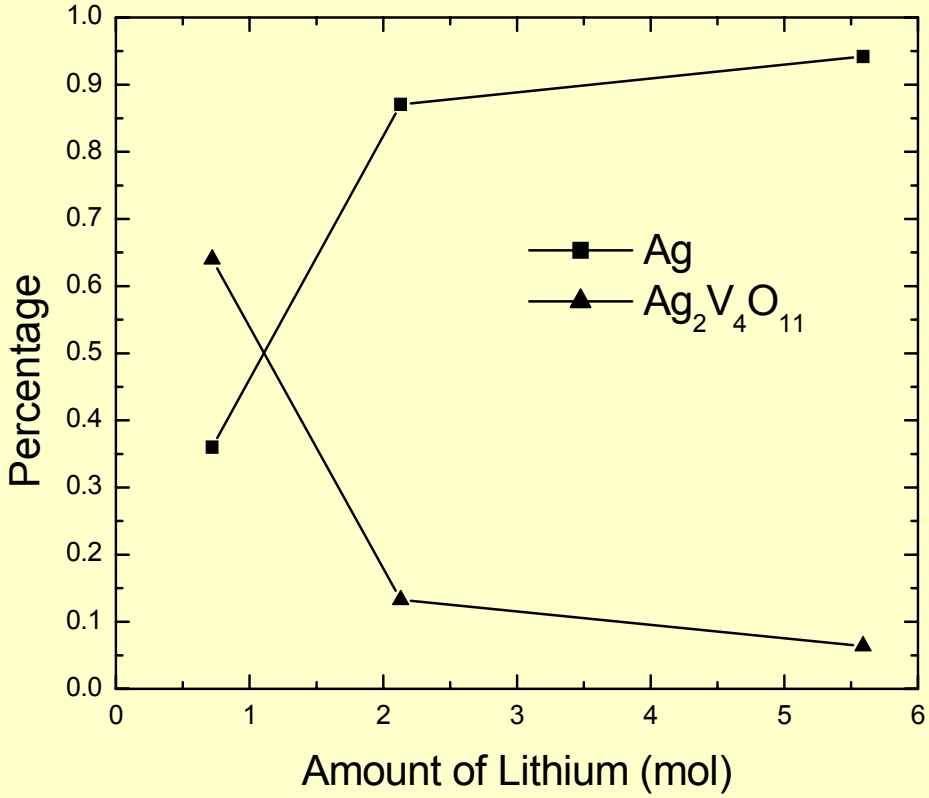
N ($Li_{2.13}Ag_2V_4O_{11}$) = 11.25

Disorder: Ag K-edge analysis of $Li_xAg_2V_4O_{11}$



The remaining difference in amplitude at the Ag-Ag bond is from disorder:
σ^2 (fcc Ag) = 89% σ^2 ($Li_{2.13}Ag_2V_4O_{11}$)

LC XANES Using SVO and Ag as Endpoints



- A different story from Ag EXAFS

Concluding Remarks

- XANES and EXAFS tell complementary stories
  - Interpretation of XANES and EXAFS data should be internally consistent
- PCA is very useful in providing objective global picture prior to more subjective analysis of XANES and EXAFS
- Attempt should be made to look at all the relevant atomic species in your system
  - Low energy excitations can provide some very useful information, e.g. 3d transition metal L-edge data.
- Linear Combination approaches can simplify an otherwise complicated picture
  - Especially useful for systems where the correct structural model is not known.
- In EXAFS analysis, de-coupling steps should be taken to extract information about correlated properties.