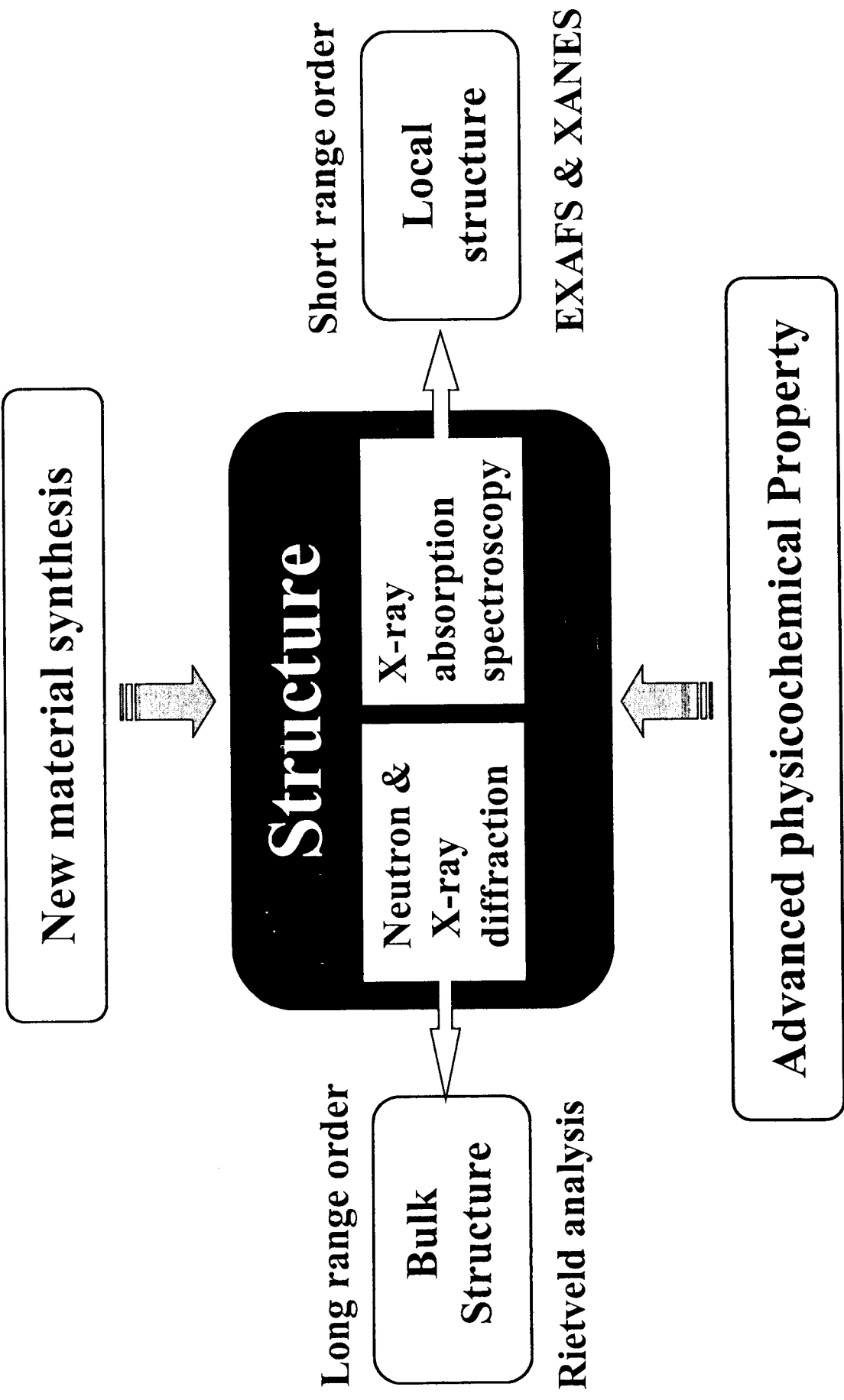




# **Spectroscopic application of X-ray absorption spectroscopy to Characterization of Geometric and Electronic Structure**

**Min Gyu Kim**

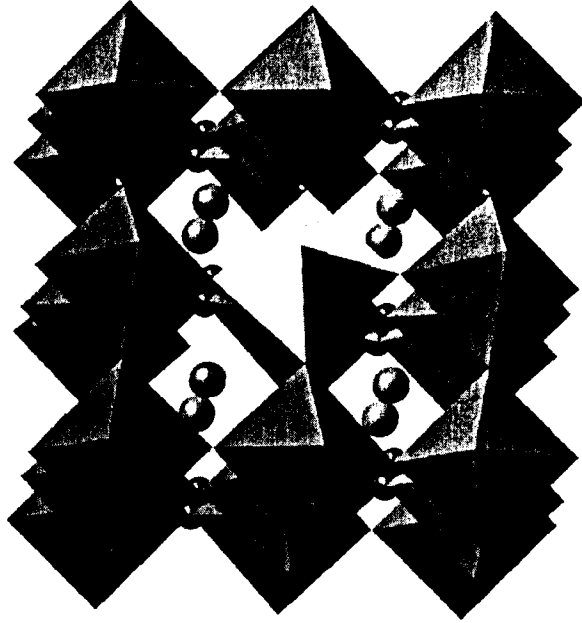
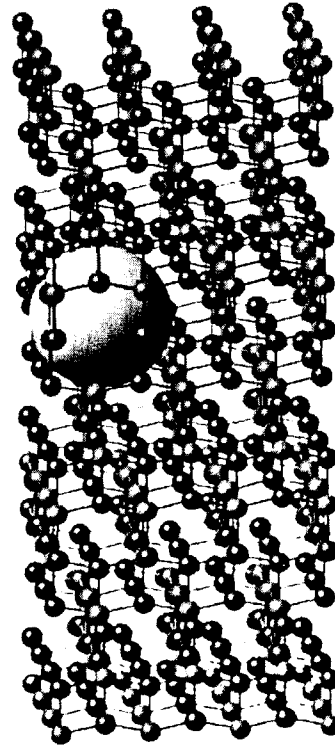
*BL3C1(EXAFS), Beamline Research Division, Pohang Accelerator Laboratory*



# Structure

?

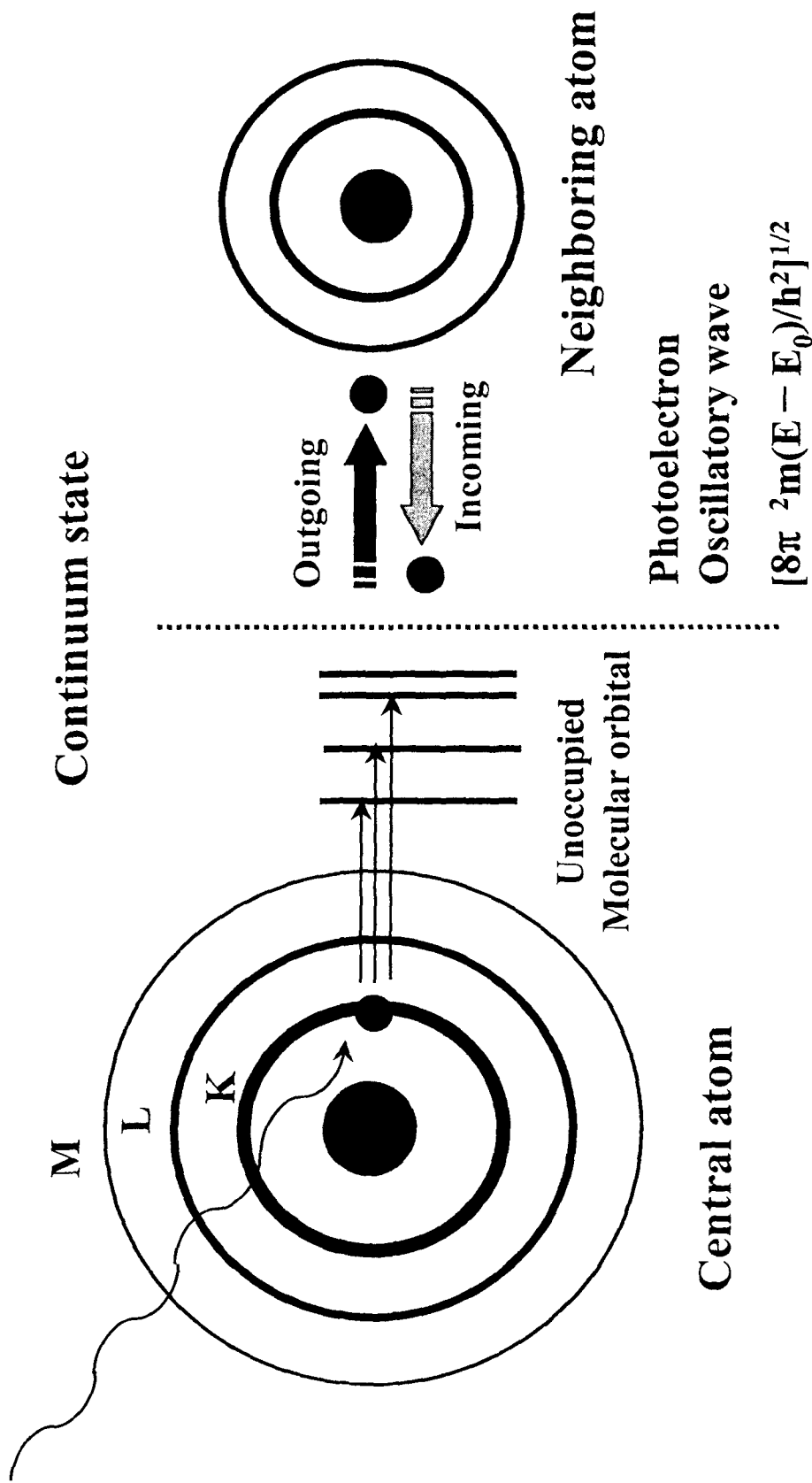
External perturbation  
ex. Potential, temperature, magnetic



# Principle of X-ray absorption



## Monochromatic X-ray



## Principle of X-ray absorption

XAS

X-ray absorption coefficient ( $\mu$ ) by the Fermi's Golden rule with the dipole approximation for the photon-induced transition of an electron from an initial state  $|i\rangle$  to a final state  $|f\rangle$

$$\mu(E) = \frac{4\pi^2 \omega e^2}{c} N_a |\langle f | \epsilon \cdot r | i \rangle|^2 \rho(E_i + \hbar\omega)$$

initial state  $|i\rangle$  : localized core electron

final state  $|f\rangle$  : core hole state with ejected photoelectron

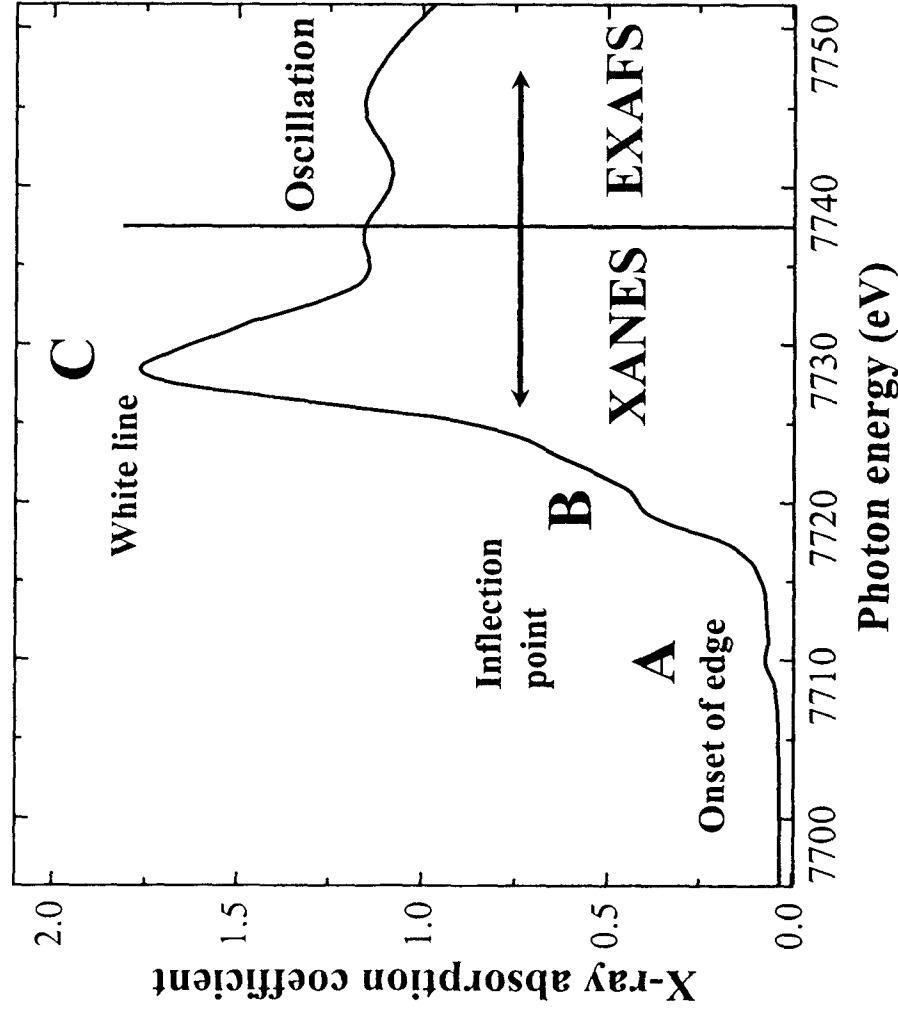
where,  $\epsilon$  is the polarization vector of the electric field,  $r$  is the electron coordinate, and  $N_a$  is the number of atoms per unit volume.

# X-ray absorption spectroscopy



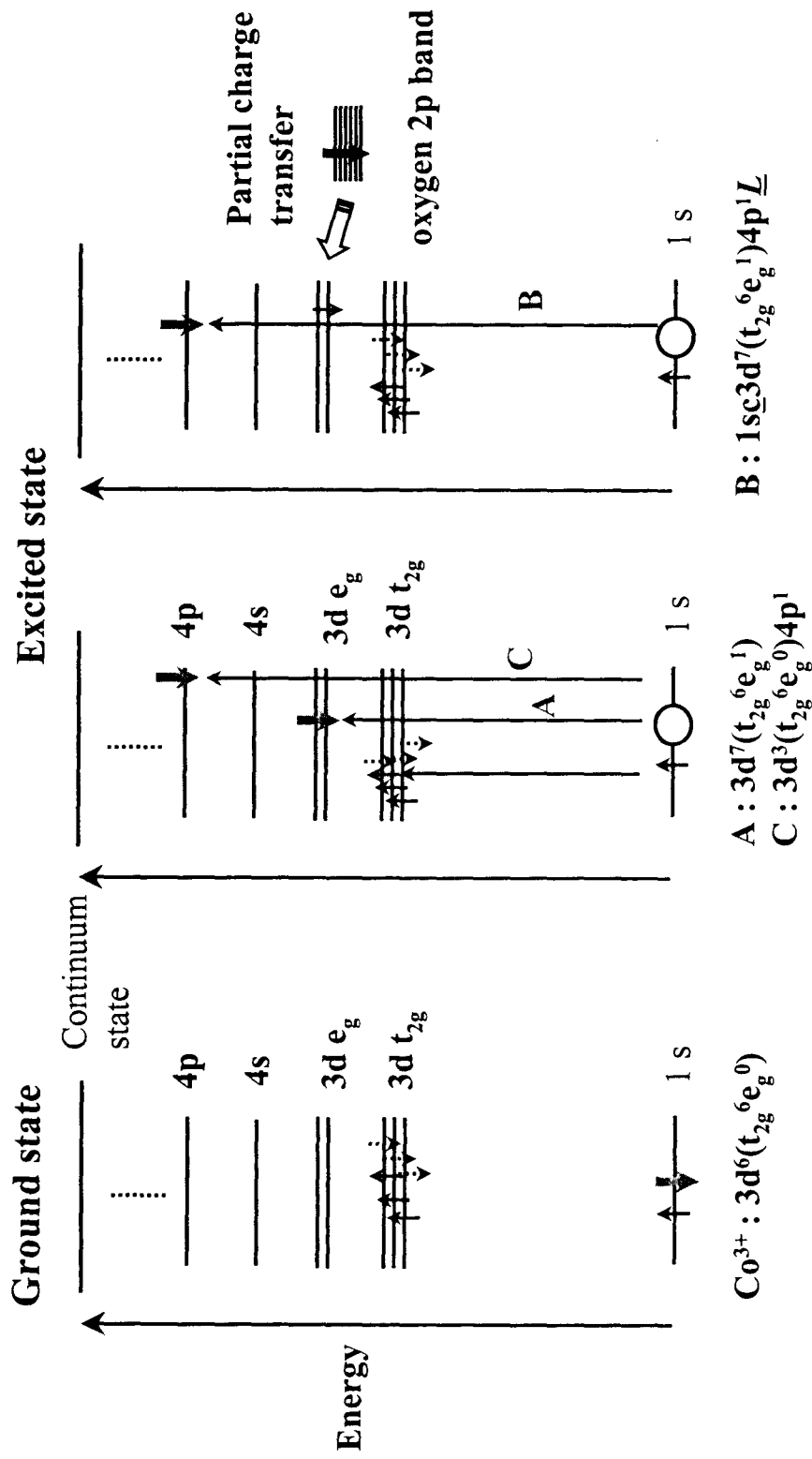
## XANES ( X-ray Absorption Near Edge Structure)

Co K-edge for LiCoO<sub>2</sub>



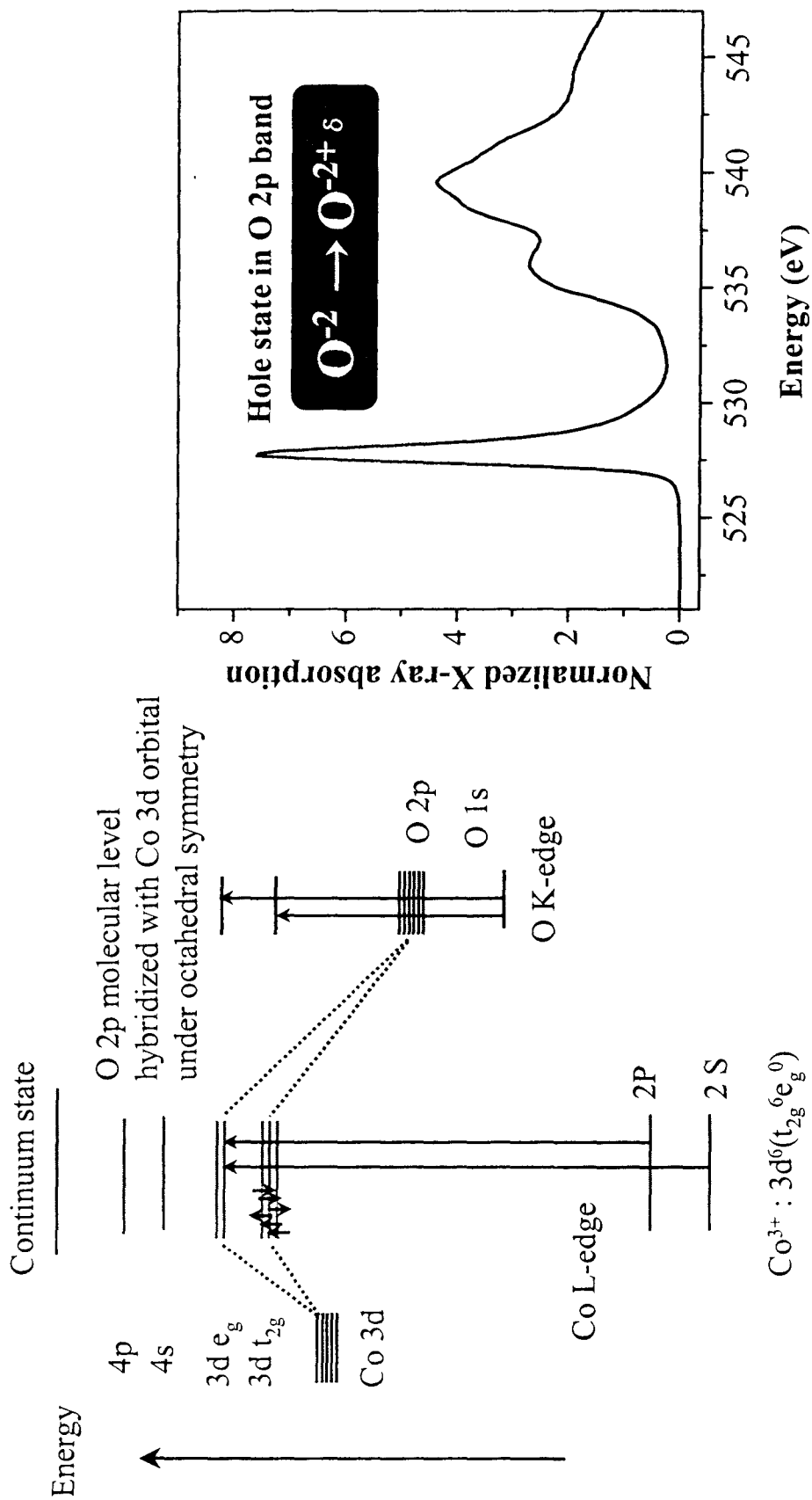
- Transition of core electron (1s, 2s, 2p..) to unoccupied energy levels,
  - K-edge (1s to np),
  - L<sub>I</sub> -edge (2s to np),
  - L<sub>II,III</sub> -edge (2p to nd, n+1 s)
  
- Electronic structure
  - Bond covalency
  - Site symmetry such as tetrahedral and octahedral,
  - Spin state (low spin or high spin)
  - 10 D<sub>q</sub> etc..

# Schematic description of electronic transition in the pre-edge region of XAS spectra



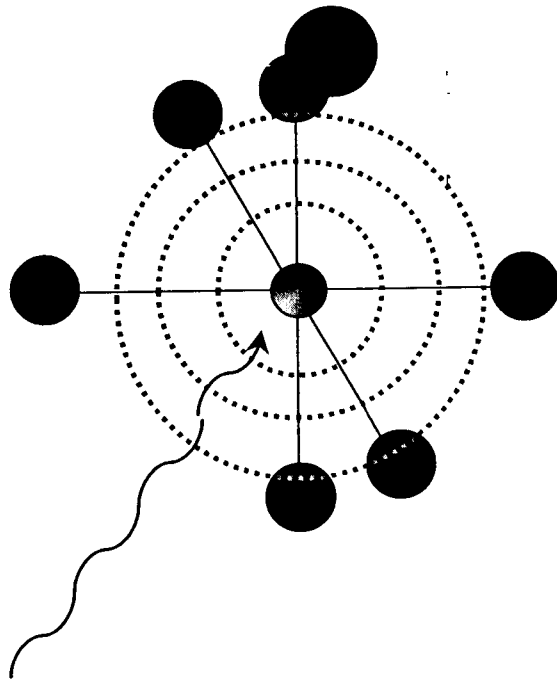
- A : Electric quadrupole-allowed transition
- B and C : Electric dipole-allowed transition with and without ligand to metal charge transfer (LMCT) process, respectively.

# Schematic description of electronic transition in Ligand K-edge XAS spectra



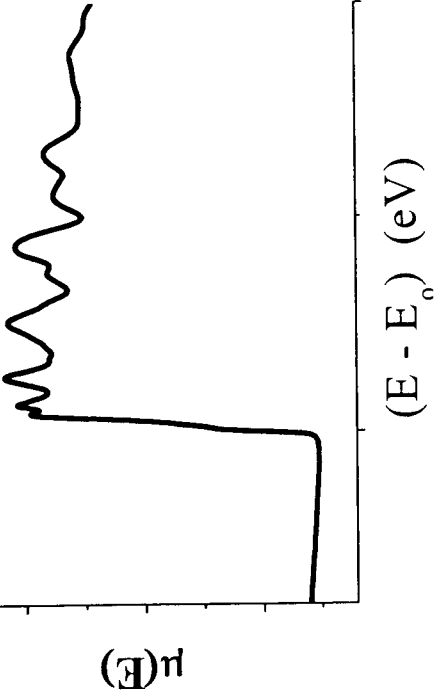


## EXAFS (Extended X-ray Absorption Fine Structure)



### Principle

- Formation of Photoelectron due to X-ray Absorption
- Outgoing spherical wave of the photoelectron from X-ray absorbing atom
- Photoelectron backscattered by the neighboring atoms : formation of the incoming wave on the absorbing atom
- Interference between the outgoing wave and the incoming wave
- Sinusoidal variation of the absorption coefficient : EXAFS



### Information

- Interatomic distance between the absorbing atom and the neighboring atoms
- Coordination number of the neighboring atoms
- Debye-Waller factor, etc..

EXAFS equation

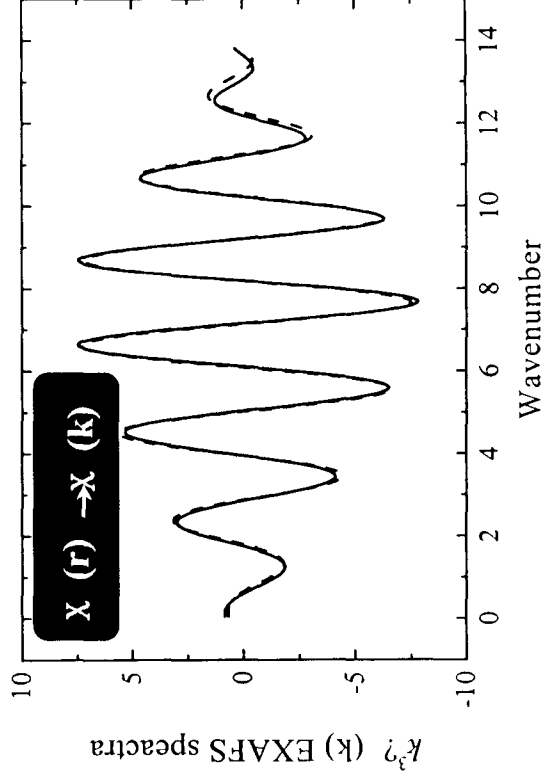
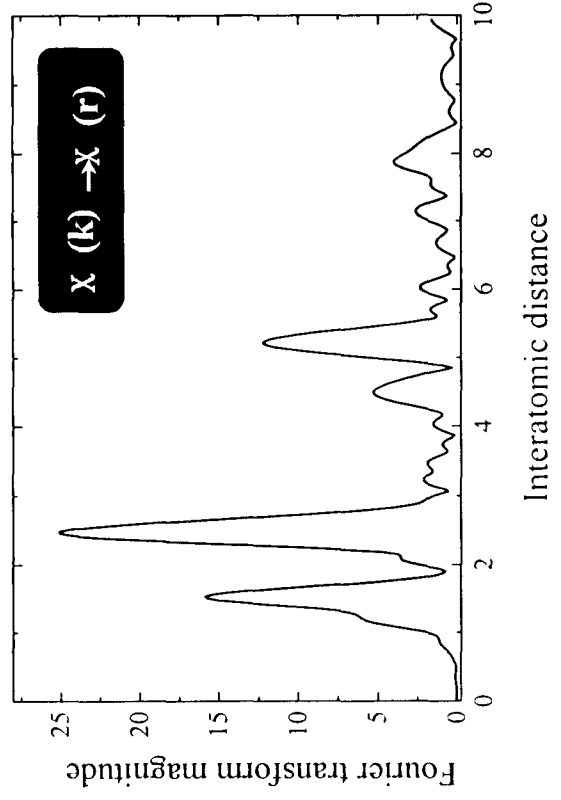
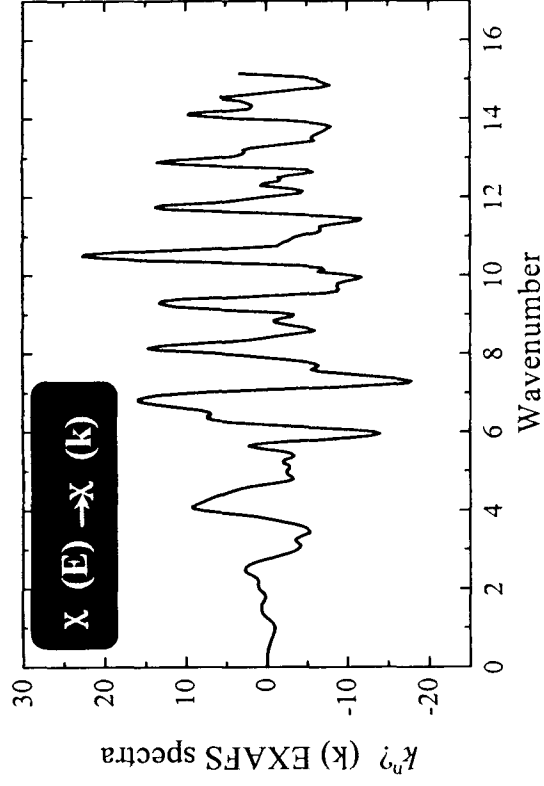
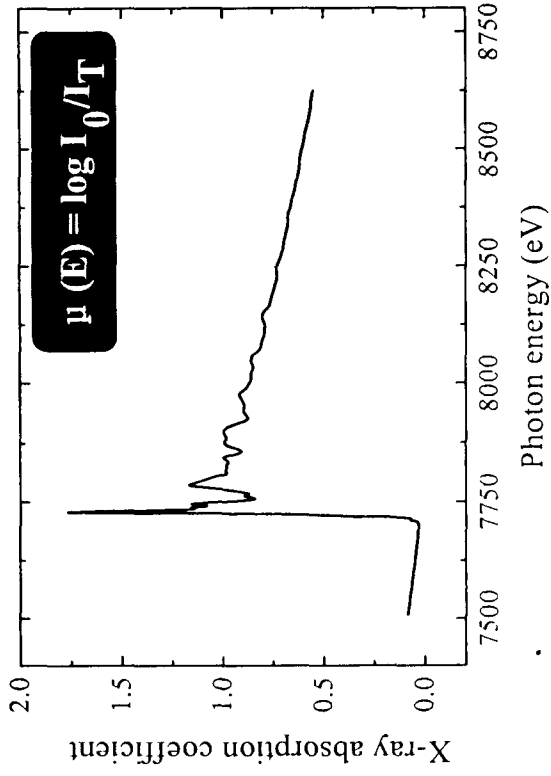
$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)}$$

To convert energy E into the photoelectron wavevector k with  $[8\pi^2 m(E - E_0)/h^2]^{1/2}$ , where  $E_0$  is threshold energy of absorption edge

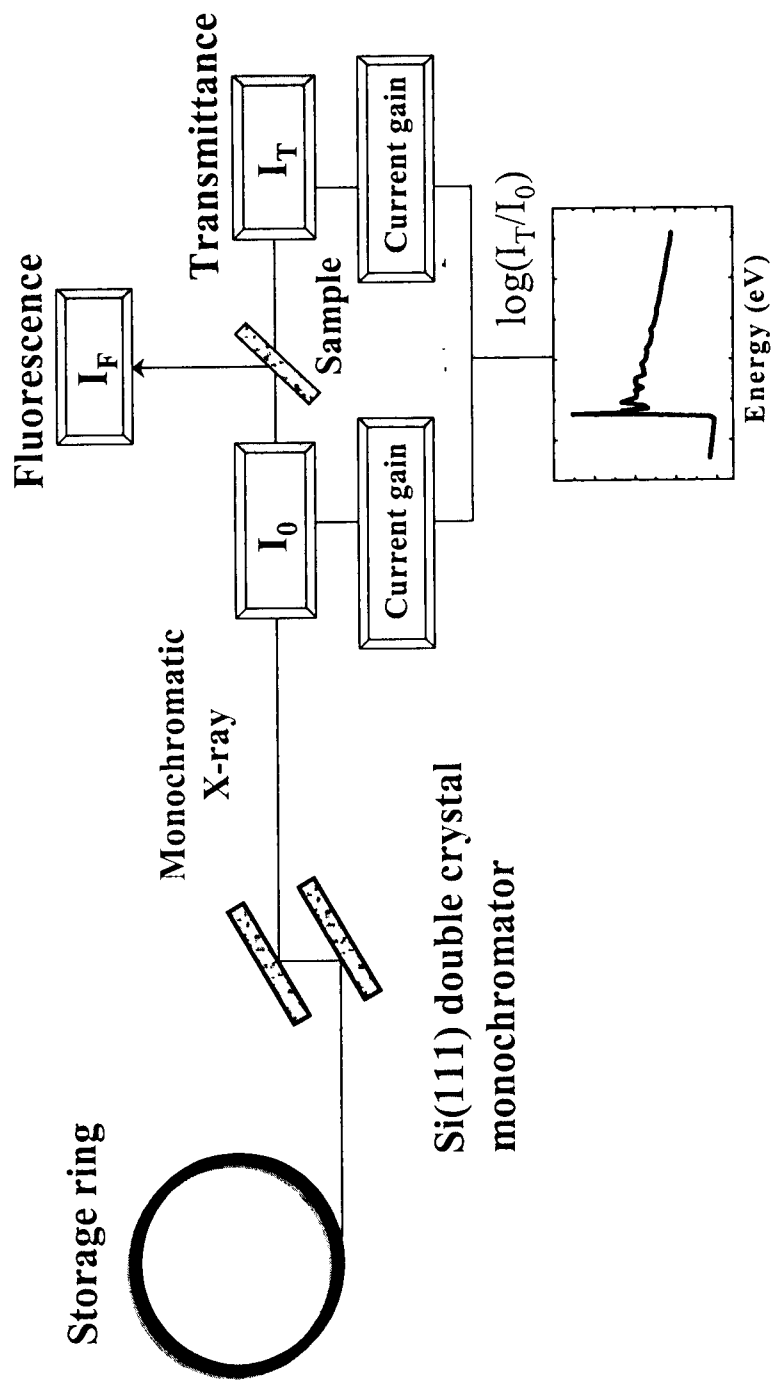
$$\chi(k) = \sum N_j S_j(k) F_j(k) \exp(-2\sigma_j^2 k^2) \exp(-2r_j/\lambda_j(k)) \frac{\sin(2kr_j + \phi_{ij}(k))}{kr_j^2}$$

- r : Interatomic distance from absorbing atom
- N<sub>j</sub> : i<sup>th</sup> coordination number on absorbing atom
- S<sub>j</sub>(k) : Amplitude reduction factor due to many-body effects such as shake up/off process at the absorbing atom
- F<sub>j</sub>(k) : Backscattering amplitude from N<sub>j</sub> neighboring atoms
- σ : Debye-Waller factor (due to thermal vibration and static disorder)
- λ : Electron mean free path
- φ<sub>ij</sub>(k) : Total phase shift experienced by photoelectron

# Standard EXAFS analysis procedure



# Block diagram of X-ray absorption spectroscopic measurement

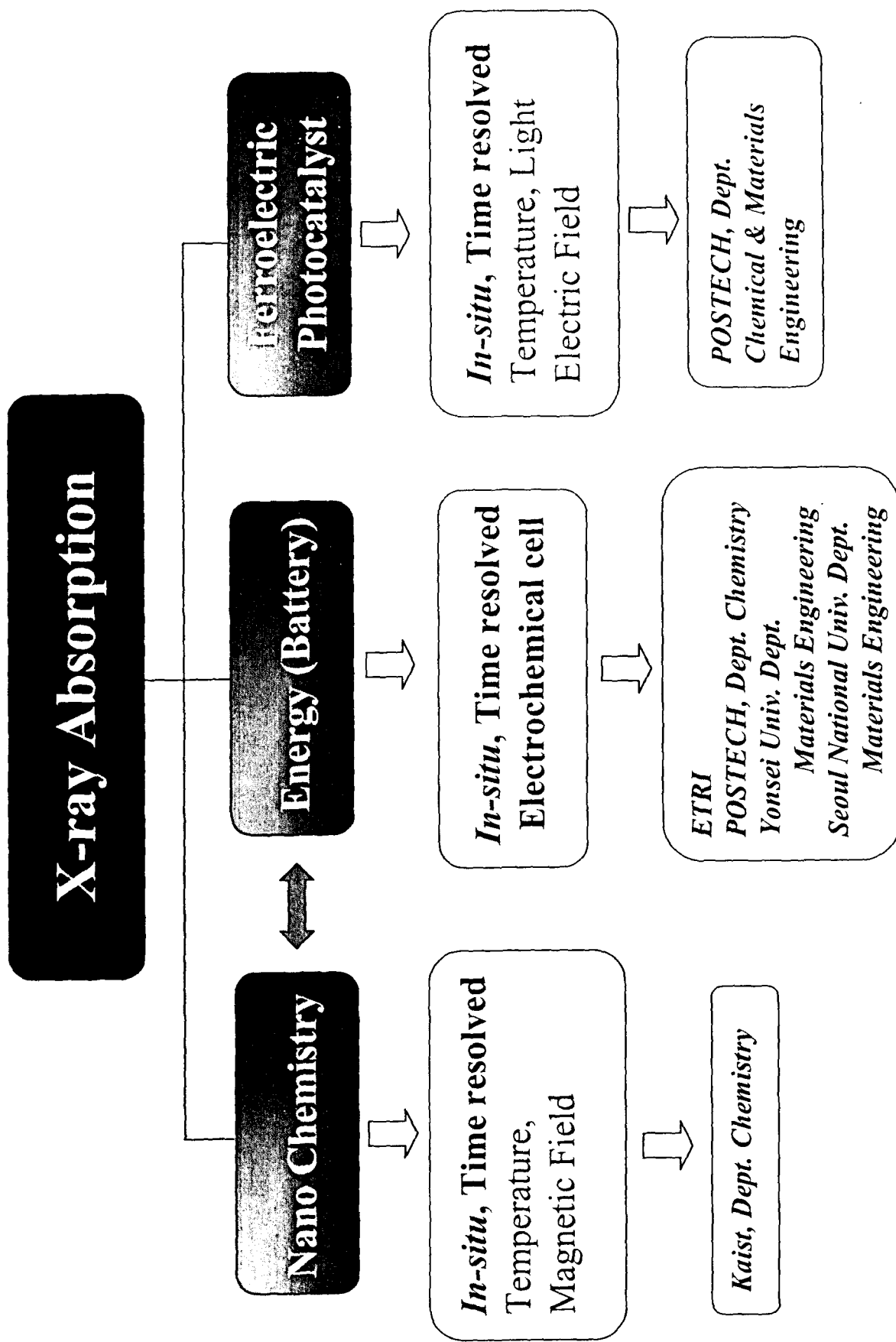


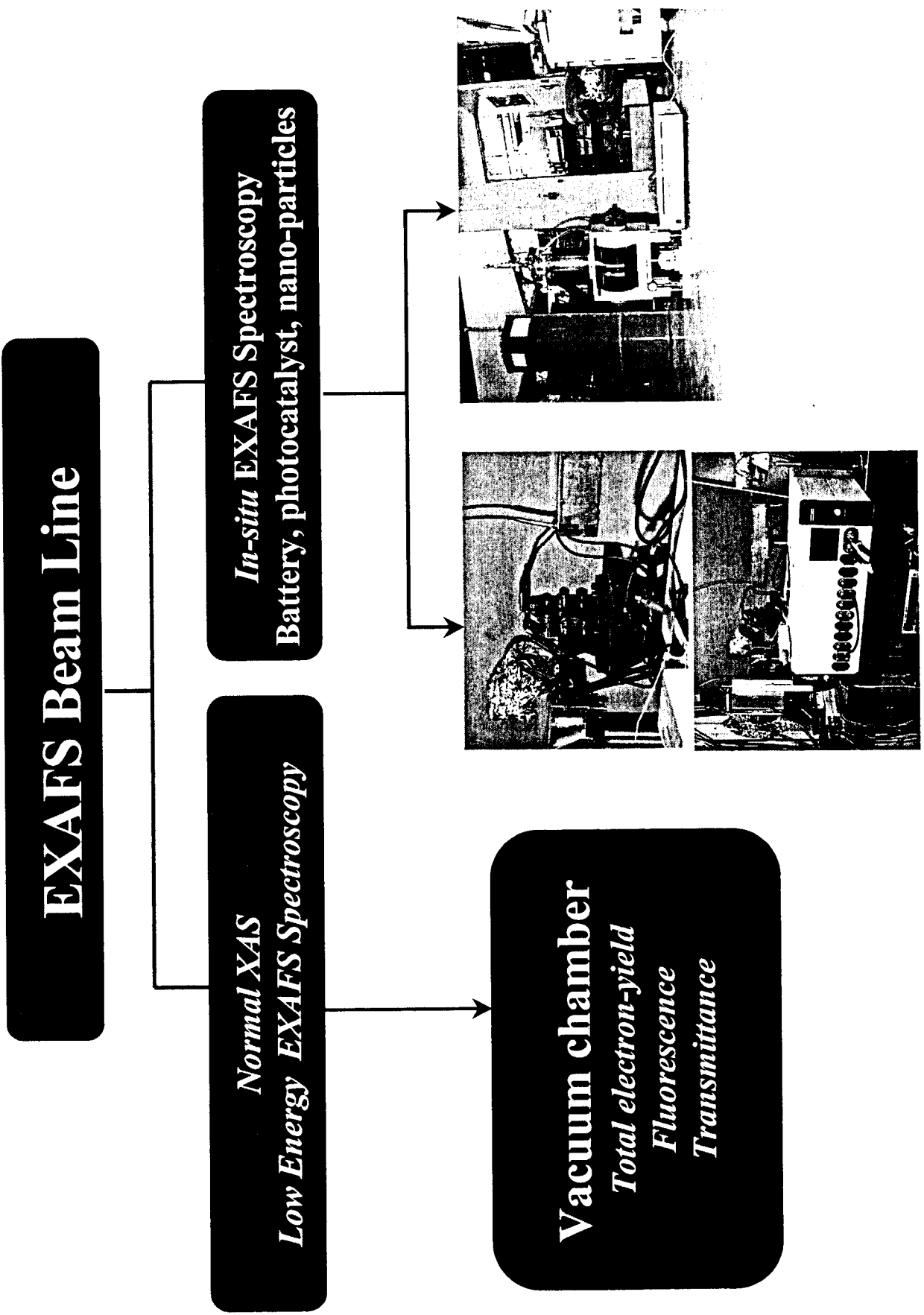
## Possible experiments

- Transmission mode's XAFS
- Fluorescence mode's XAFS
- Total electron-yield XAFS
- In-situ*, time-resolved XAFS

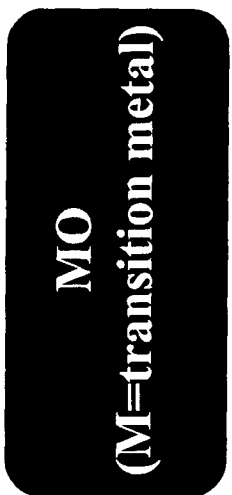
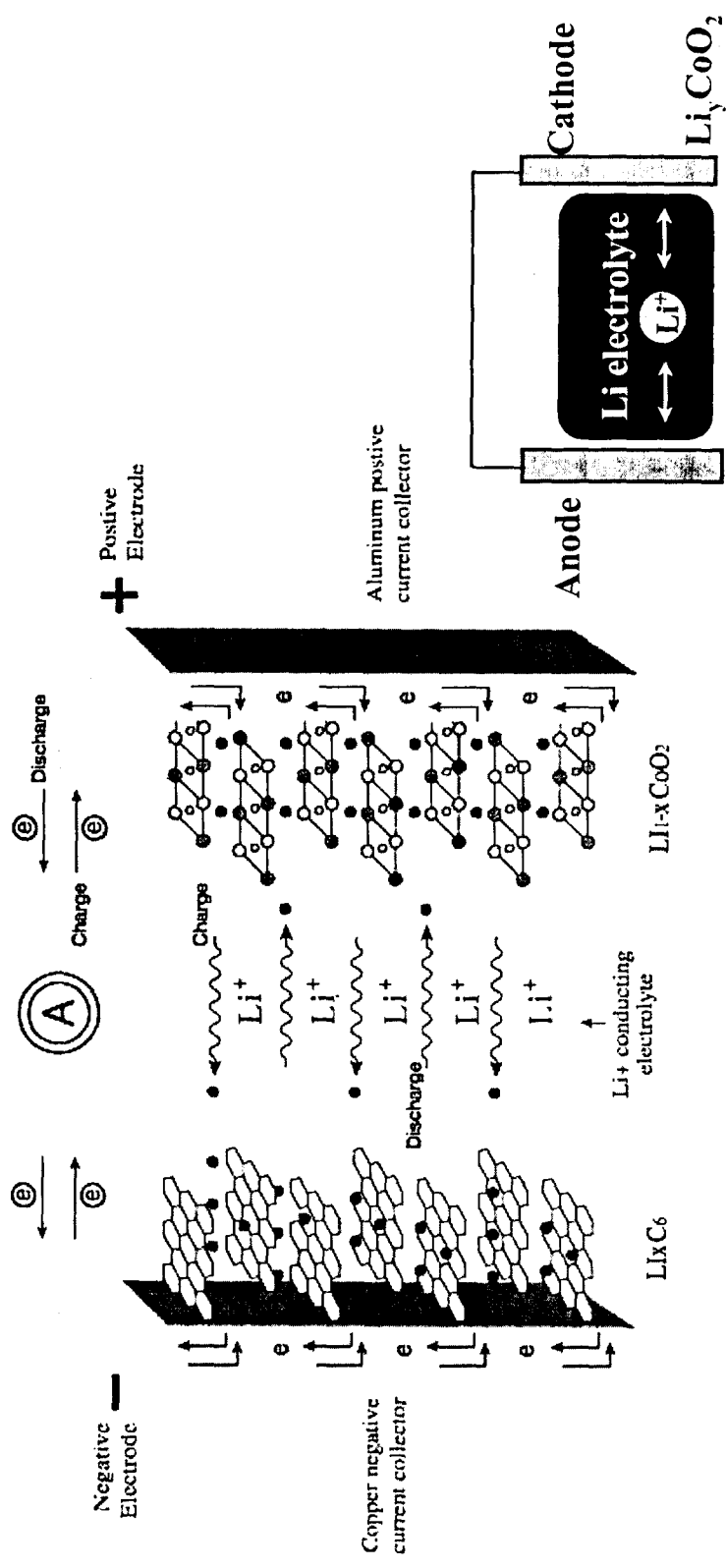
## Equipments in experimental station

- Gas-flow ion chambers
- Silicon detector at room-temp operation
- Low-Temp cryostat (JANIS VPF100, 77~300K)
- Graze Incidence angle sample-position stage
- Magnet (>1.5T) in Low temperature

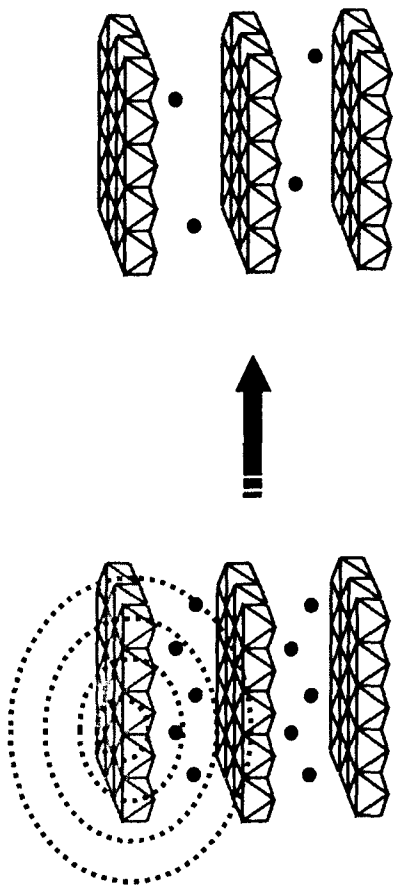




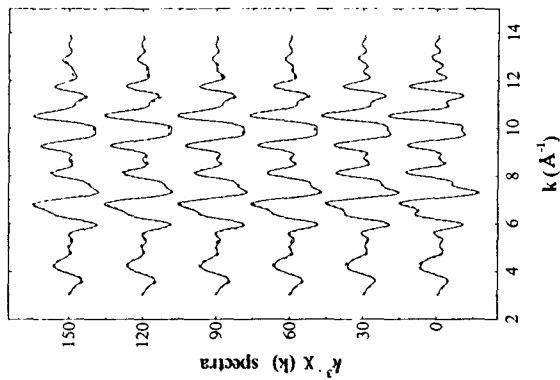
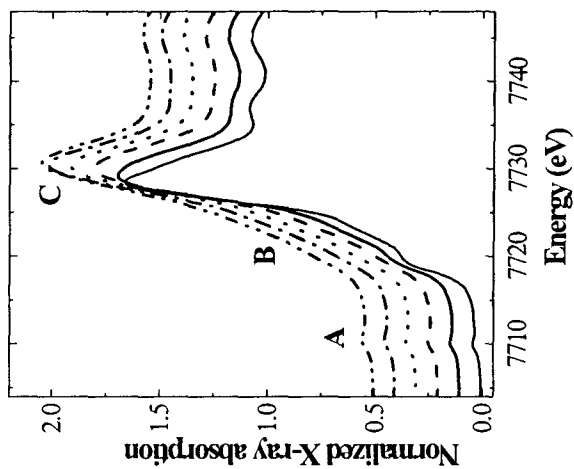
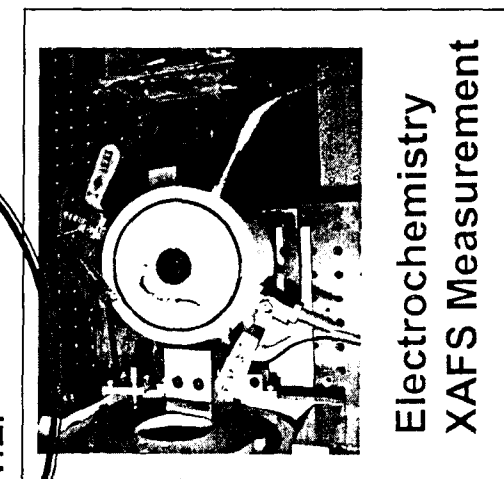
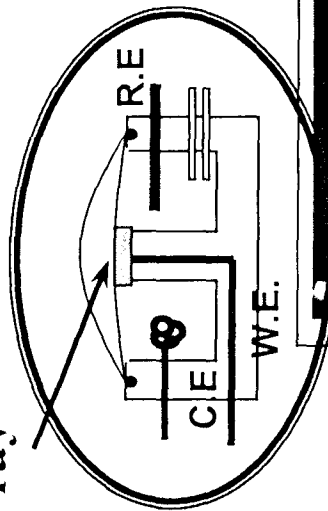
# Secondary Li-ion rechargeable Battery



XAFS Study of Li ion rechargeable battery



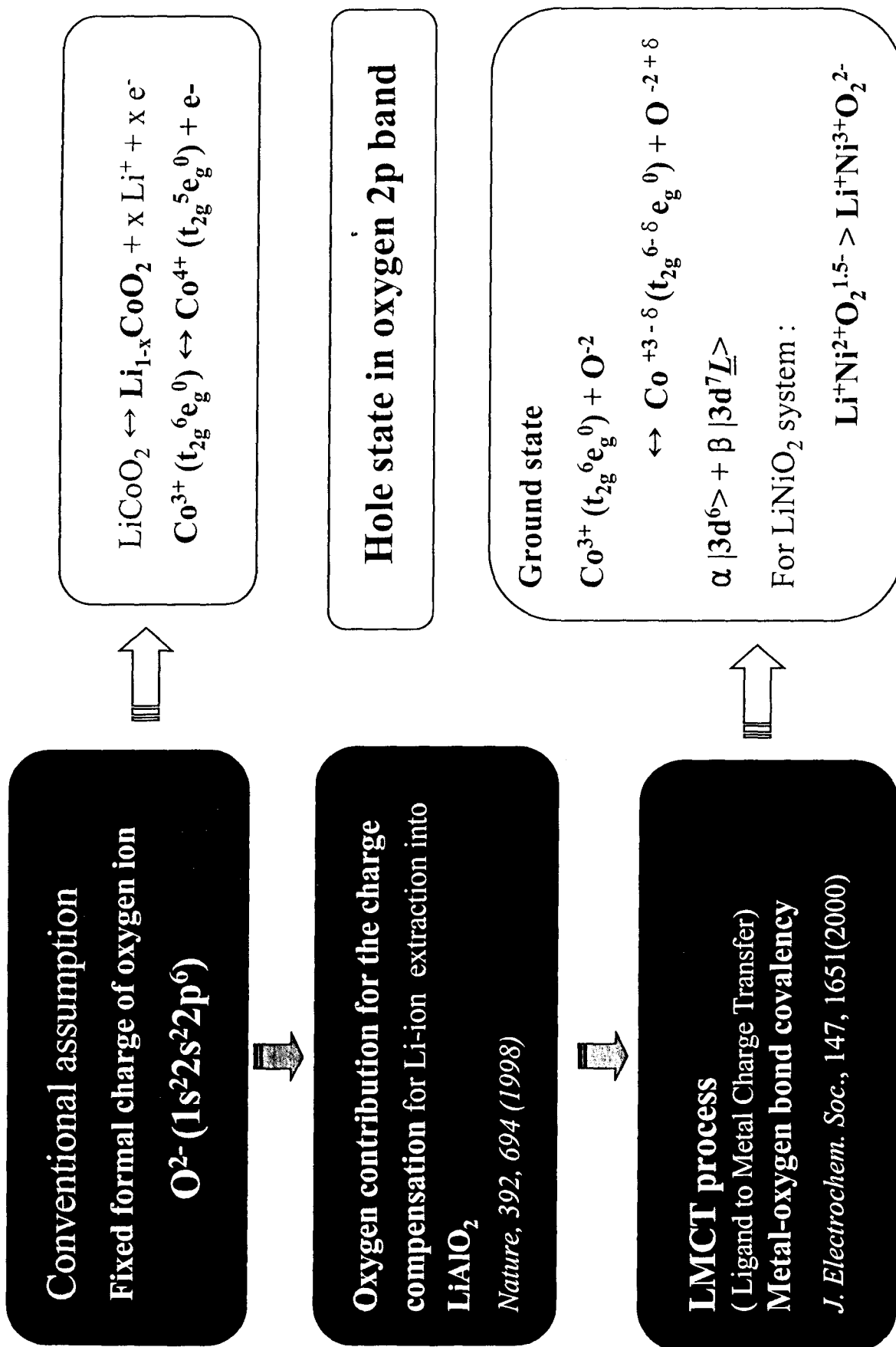
X-ray



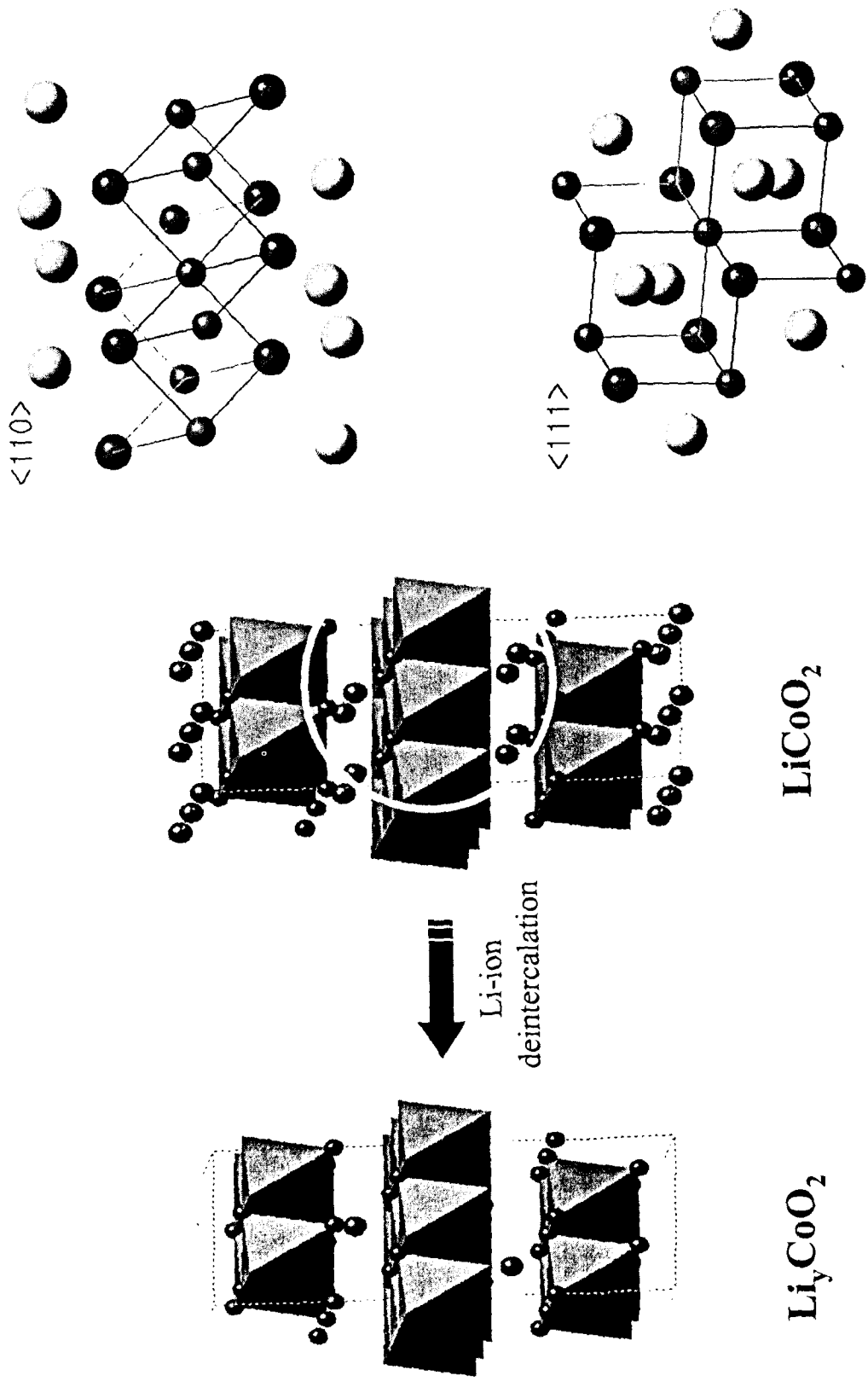
M. G. Kim, et al., *J. Phys. Chem. B*, 1999, 103, 6457.  
W. S. Yoon, et al., *J. Electrochem. Soc.*, 2000, 147, 2023.



The electrochemical properties of the materials are highly related to electronic structure ~~XAS~~



Crystal Structure of  $\text{Li}_y\text{CoO}_2$  System



# Characterization of $\text{Li}_y\text{CoO}_2$ system

XAS

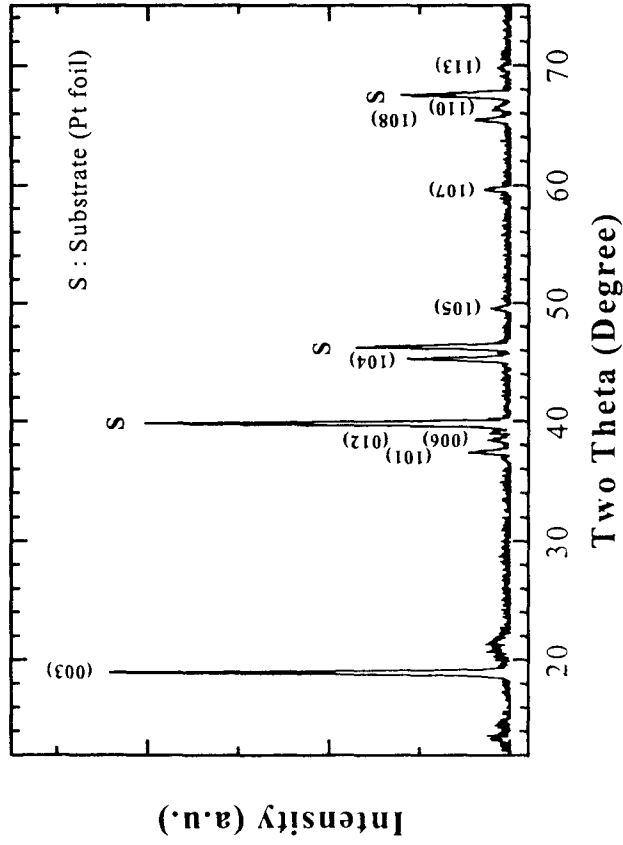
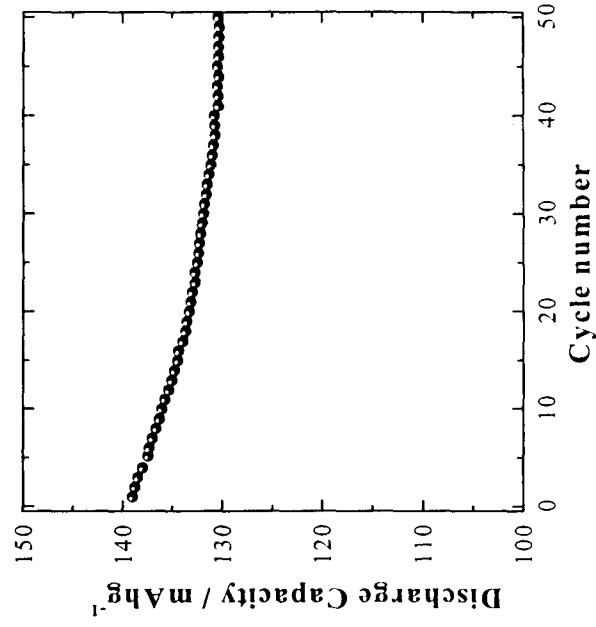
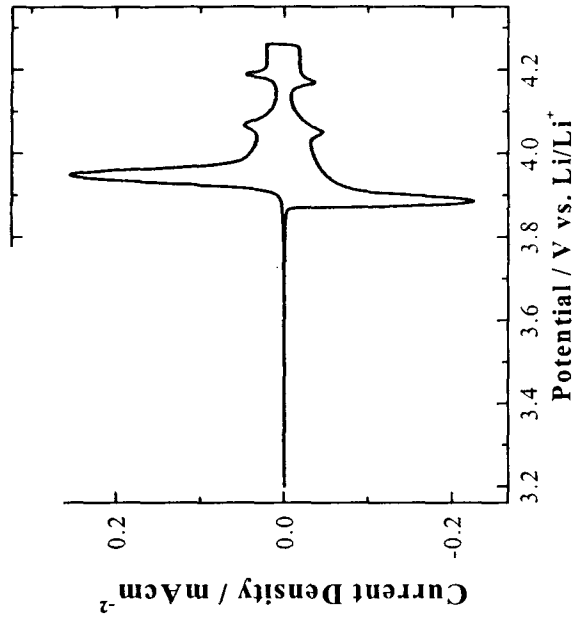


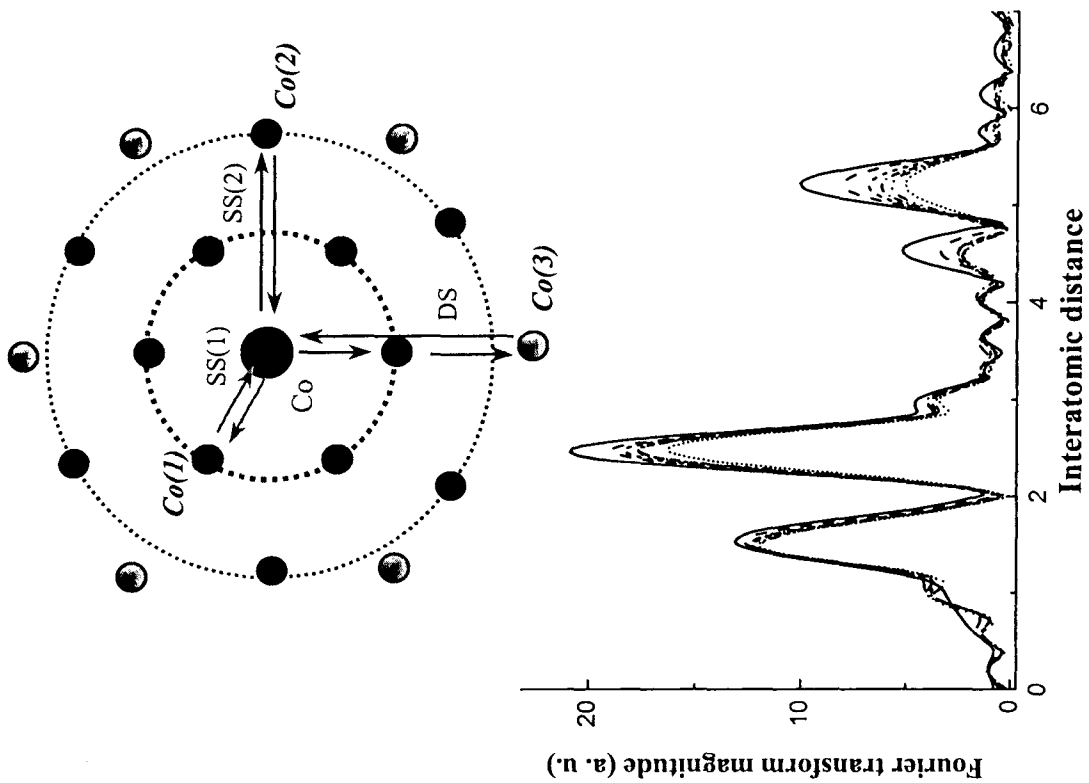
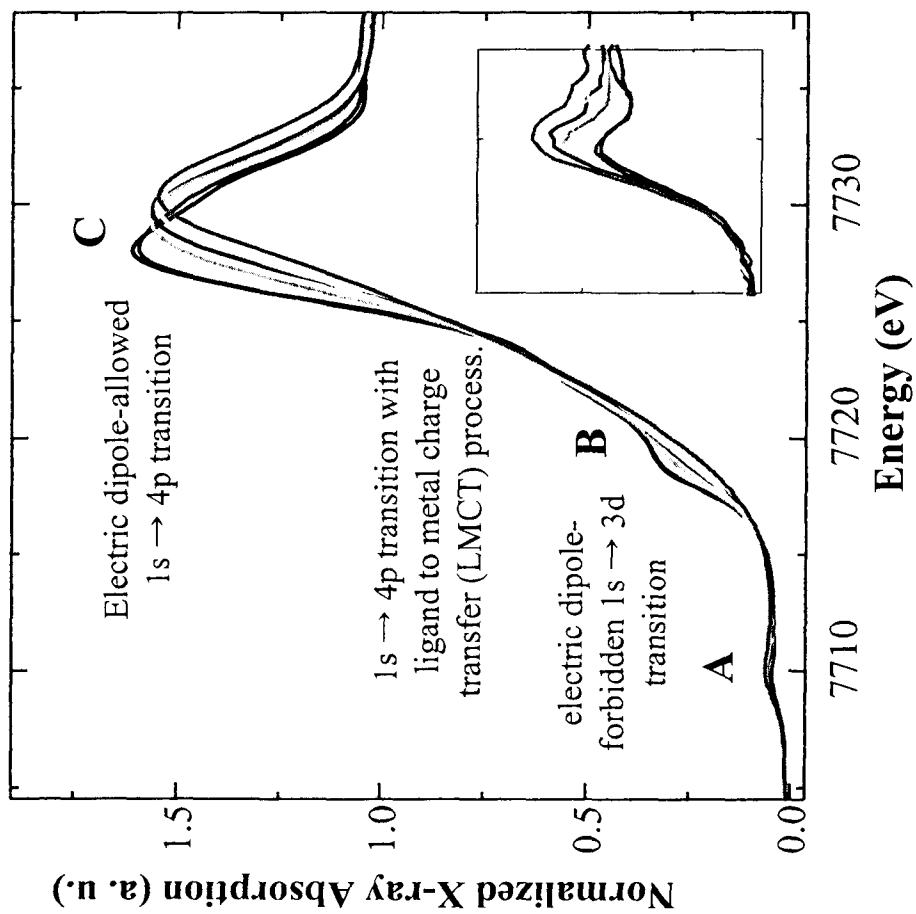
Figure 1. XRD pattern of  $\text{LiCoO}_2$  film on Pt substrate annealed at  $800^\circ\text{C}$  in air for 30 minutes

Figure 2. Cyclic Voltammogram of  $\text{LiCoO}_2$  film at a scan rate of  $0.1 \text{ mV/s}$ .

Figure 3. Discharge capacity vs. cyclic number of  $\text{LiCoO}_2$  film electrochemically cycled at the current density of  $50 \mu\text{A}/\text{cm}^2$  in the voltage range between 3.0 and 4.2 V.

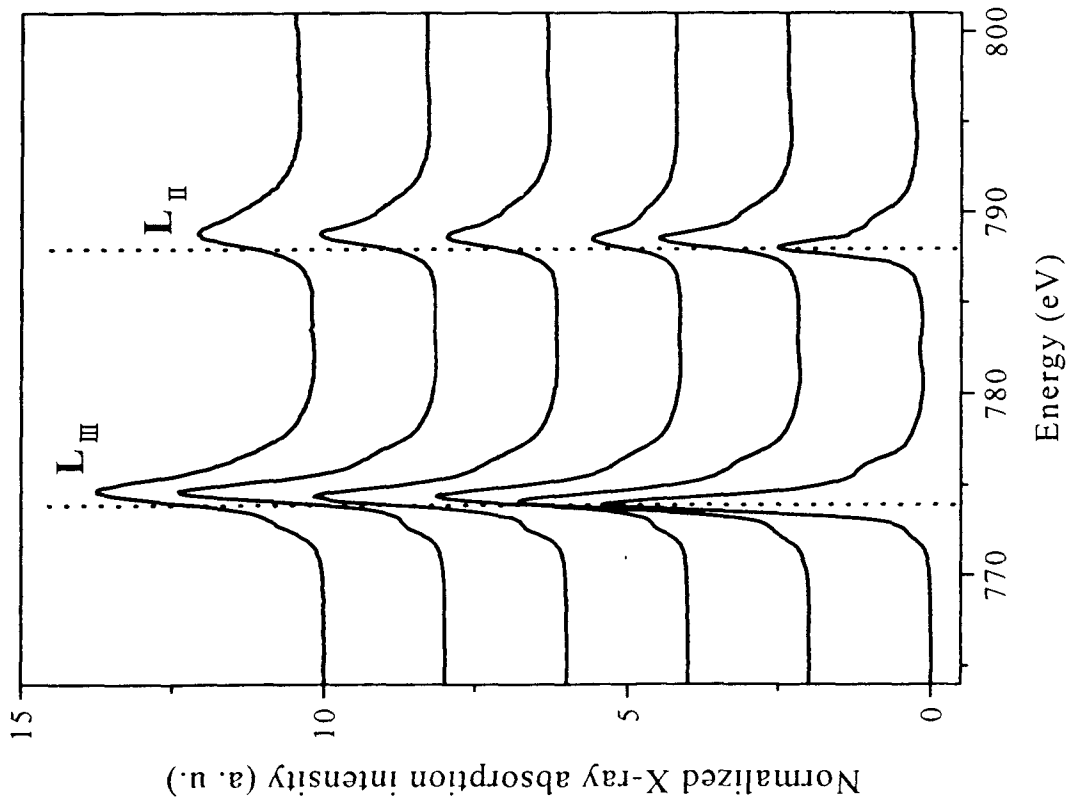


# Local Structure of $\text{Li}_y\text{CoO}_2$ System by Co K-edge XANES and EXAFS



FT magnitudes of Co K-edge  $k^3$ -weighted EXAFS spectra as a function of interatomic distance for the electrochemical Li ion extracted  $\text{LiCoO}_2$

## Co L<sub>II,III</sub>-edge X-ray absorption spectra



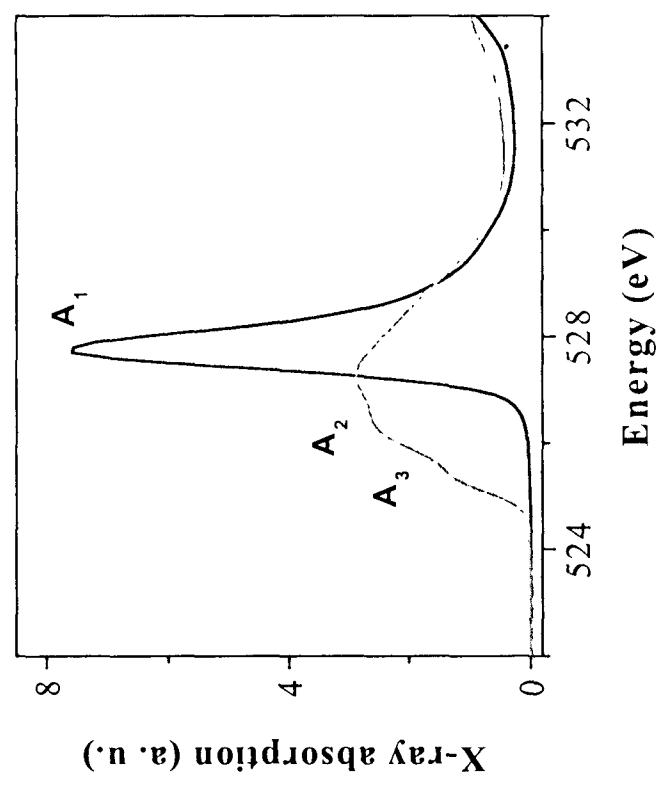
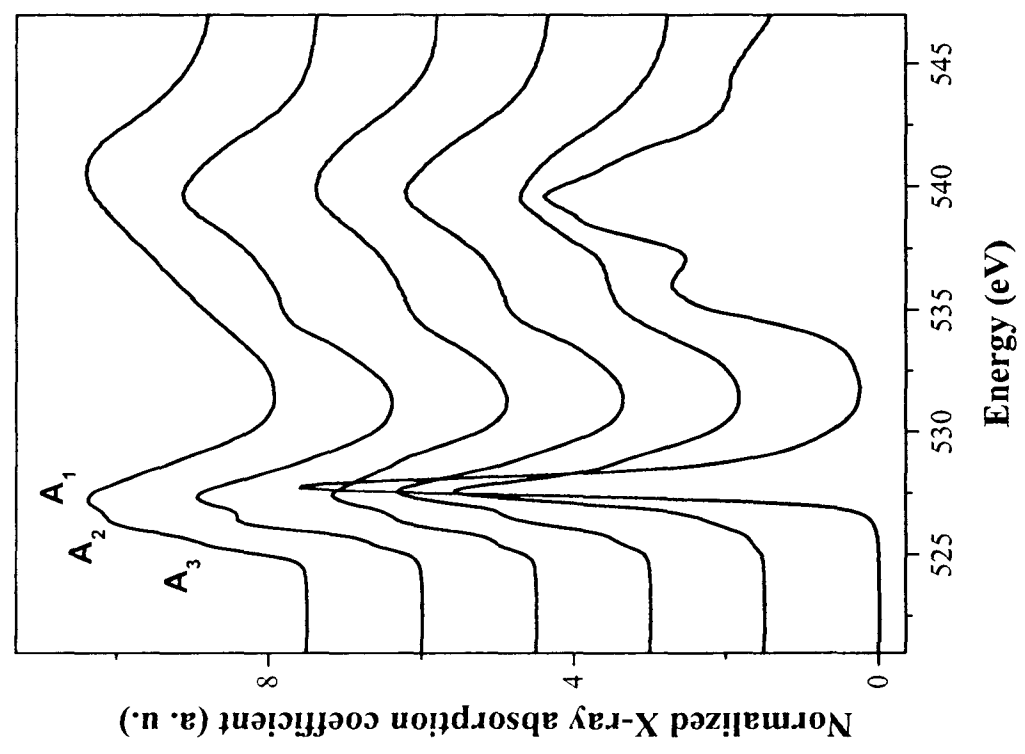
□ Two main peaks of L<sub>III</sub> and L<sub>II</sub> edges : electronic transitions of Co 2p<sub>3/2</sub> and 2p<sub>1/2</sub> core electrons to an unoccupied 3d level highly hybridized with oxygen 2p orbital, respectively.

□ As the Li-ion extraction increases, the peaks are broaden toward higher energy region and its main peak intensity decreases.

□ Systematic variation of the peak position and intensity

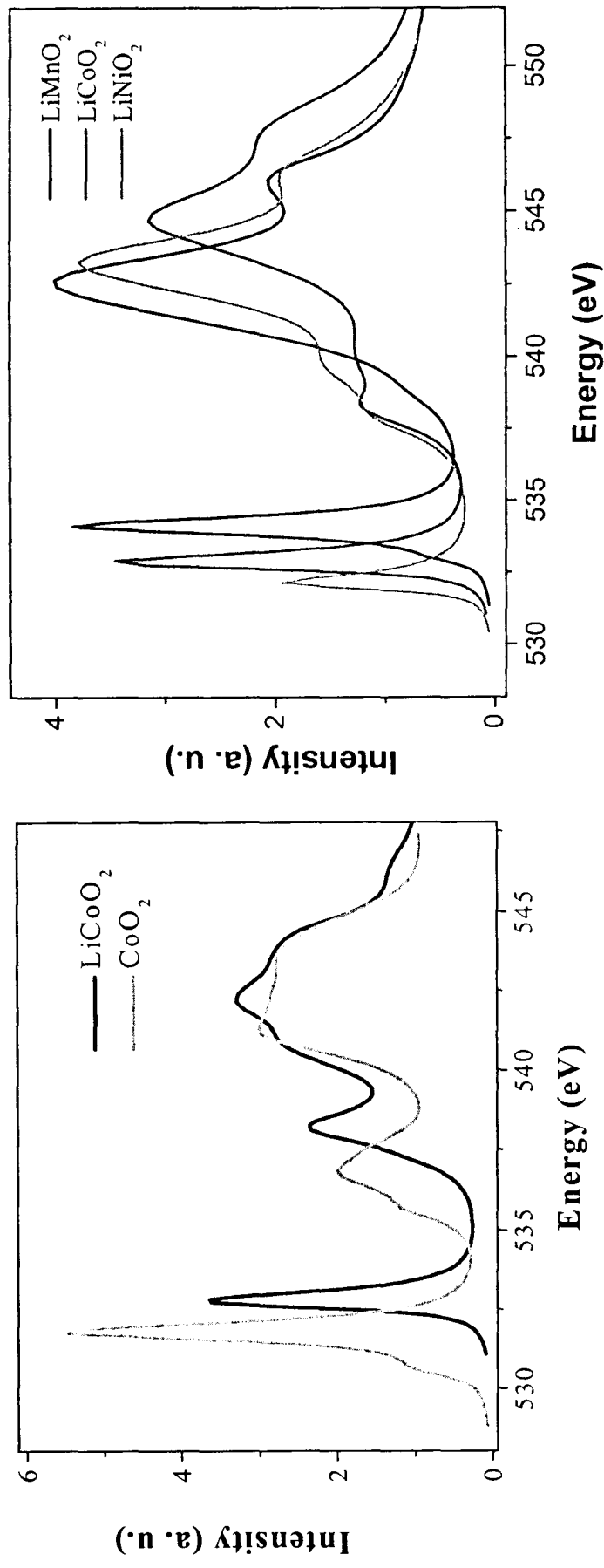
**Increase of the average oxidation state of Co ion with Li-ion deintercalation**  
**Rehybridization of Co-O molecular orbital by local structural distortion of CoO<sub>6</sub> octahedral sites**

# Oxygen K-edge X-ray absorption spectra



- A<sub>1</sub> peak at ~ 527.8 eV : the transition of oxygen 1s to an unoccupied 2p orbital (the hybridization of Co 3d and oxygen 2p orbitals)  
:  $O1s^2 + Co\ 3d^6 (t_{2g}^6 e_g^0) \leftrightarrow O1s^1 \underline{c} + Co\ 3d^7 (t_{2g}^6 e_g^1)$
- The higher energy peaks above 536 eV : transition to unoccupied Co 4s and 4p orbitals hybridized with oxygen 2p orbital.
- The weak absorption peaks, A<sub>2</sub> and A<sub>3</sub> peaks at ~ 525.8 eV and ~ 526.3 eV, are due to the formation of Co<sup>4+</sup> by Li-ion extraction.  
A<sub>2</sub> :  $O1s^2 + Co\ 3d^5 (t_{2g}^5 e_g^0) \leftrightarrow O1s^1 \underline{c} + Co\ 3d^6 (t_{2g}^6 e_g^0)$   
A<sub>3</sub> :  $O1s^2 + Co\ 3d^5 (t_{2g}^5 e_g^0) \leftrightarrow O1s^1 \underline{c} + Co\ 3d^6 (t_{2g}^5 e_g^1)$

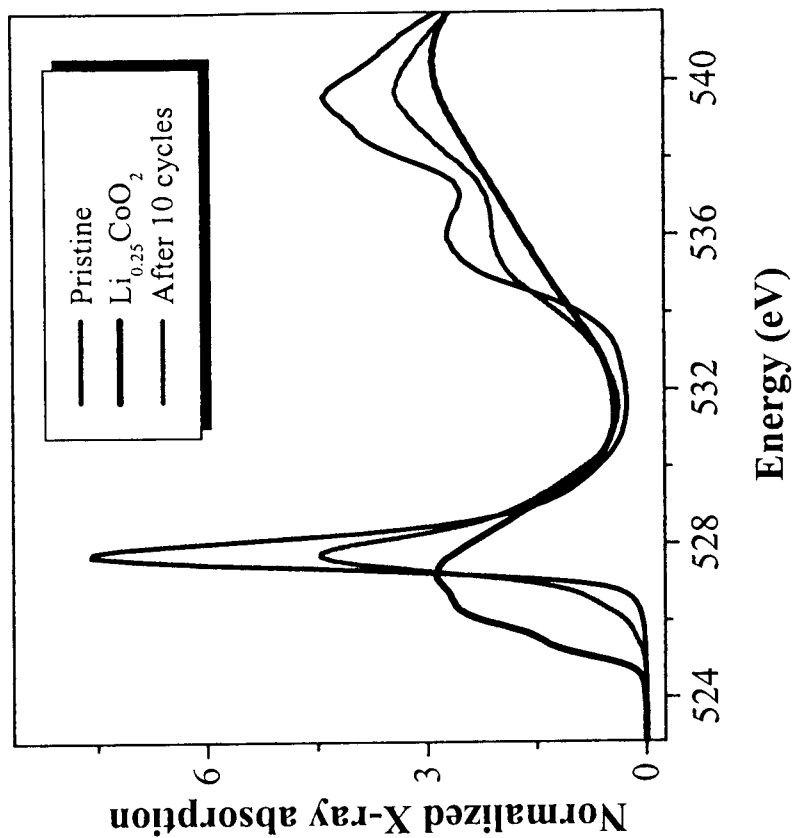
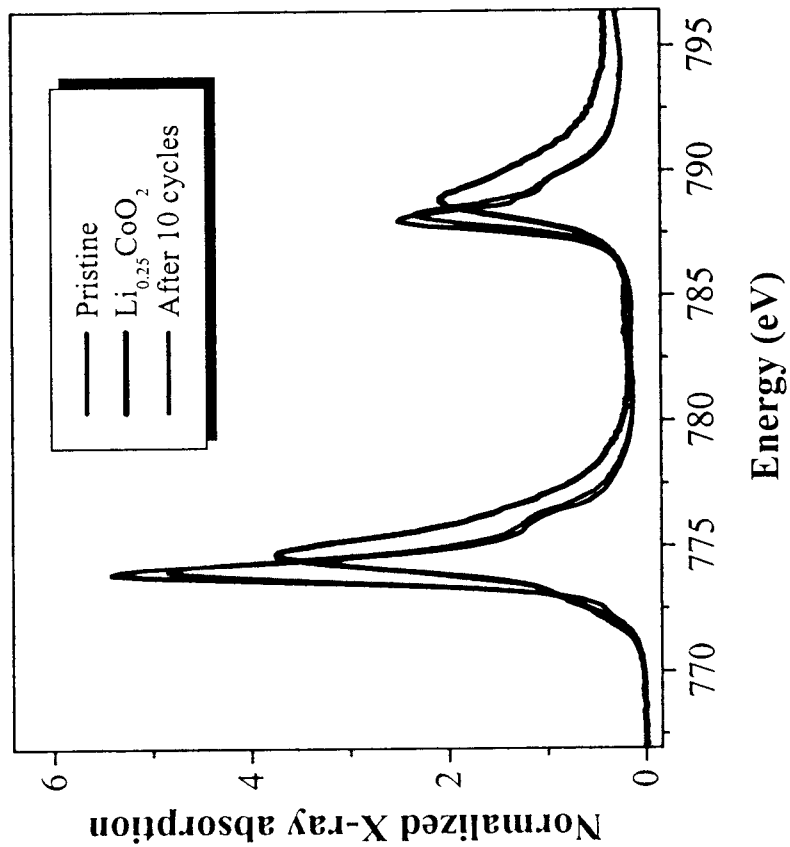
# Ab initio calculation of oxygen K-edge X-ray absorption spectra



The O K-edge XAS for  $\text{Li}_x\text{CoO}_2$  system have been calculated with *FEFF8* module in *UWXCXAFS* package. The structural parameters have been used as input parameters for calculation, where the same lattice parameter is used for comparison of spectral variation of O K-edge XAS with and without Li-ion.

# Oxygen K-edge XAS of $\text{Li}_x\text{Co}_{0.50}\text{Ni}_{0.50}\text{O}_2$ System

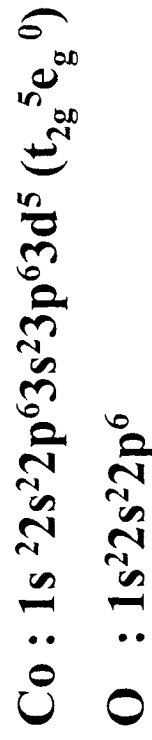
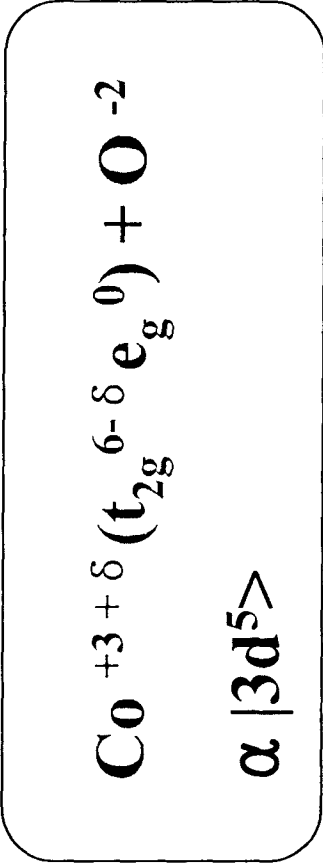
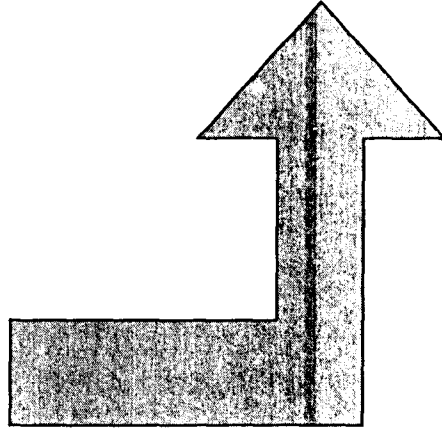
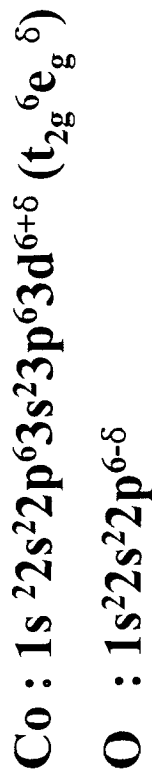
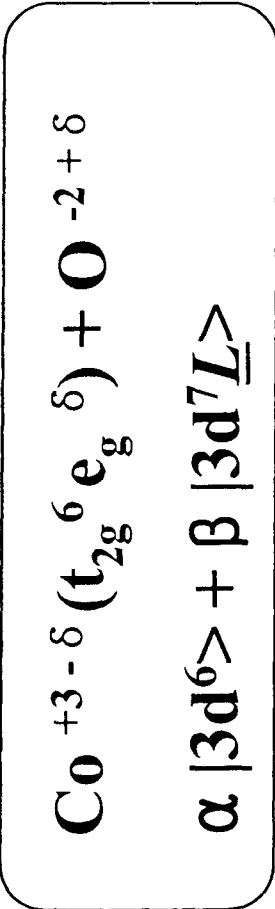
XAS




Comparison of X-ray absorption spectra for the charge-discharge cycling property in (left)  $\text{Co L}_{III,II}$ -edge and (right) oxygen K-edge

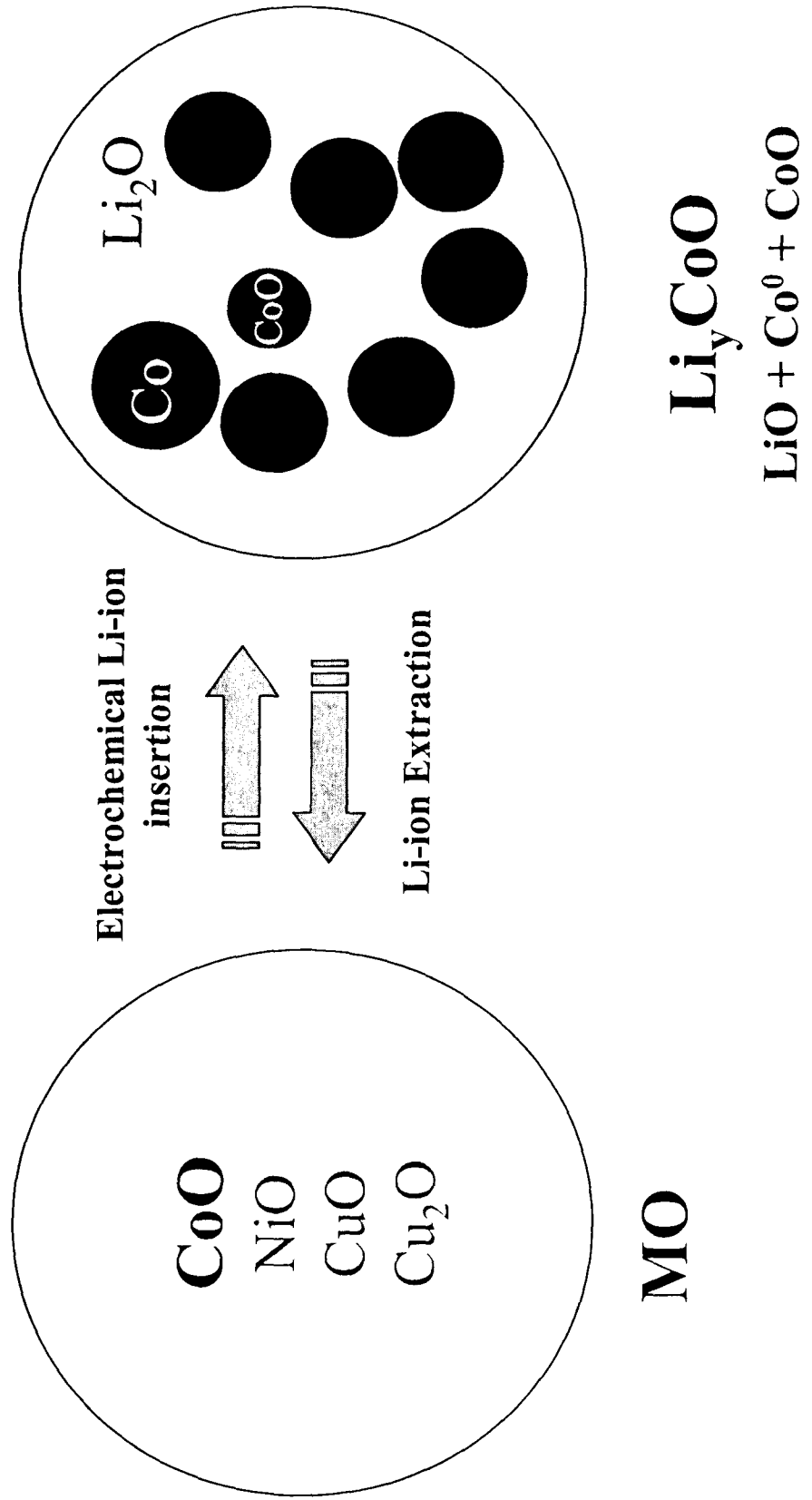


# Variation of electronic structure

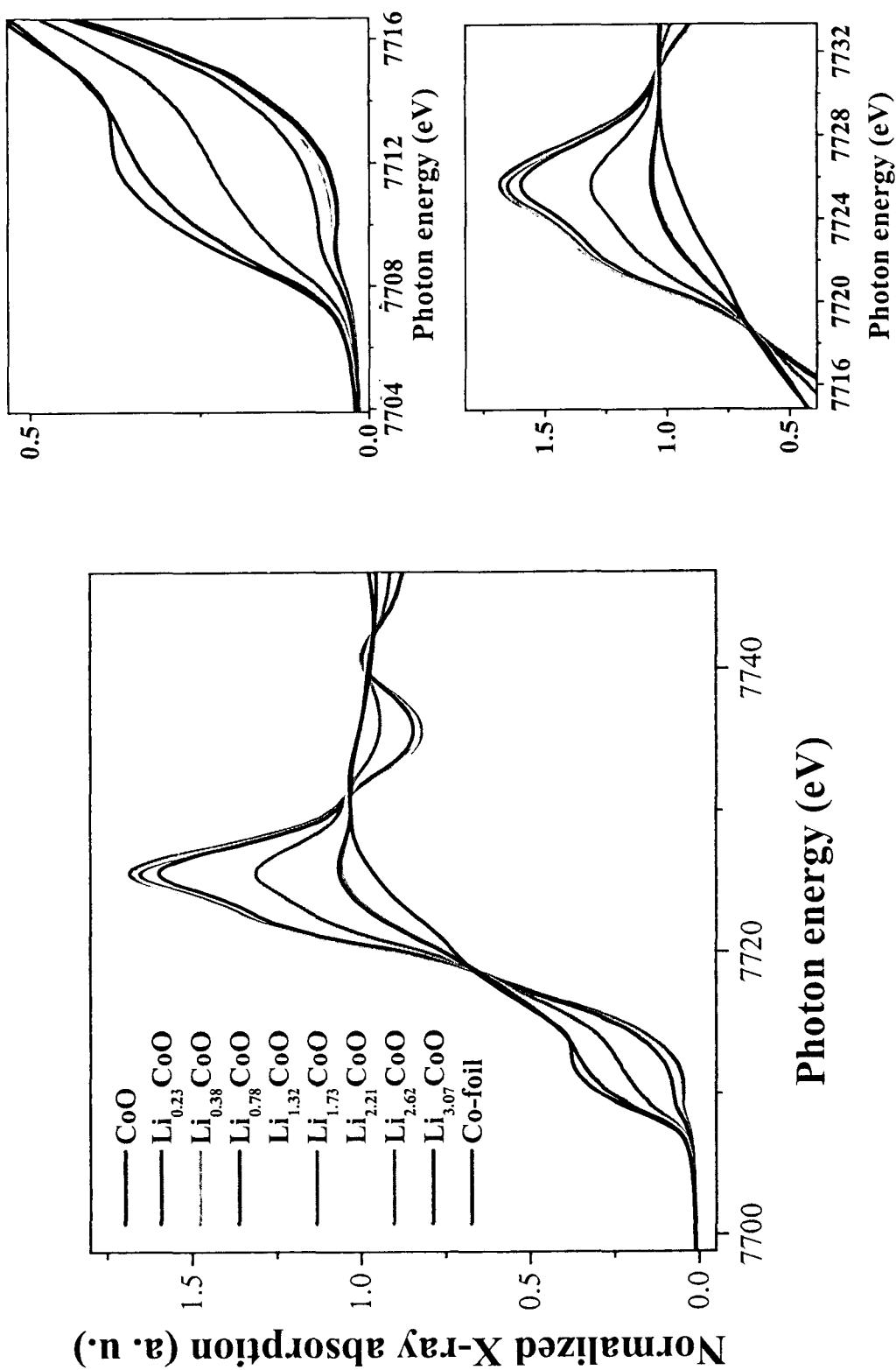


- In the pristine  $\text{LiCoO}_2$ , the electronic ground state of  $\text{Co}^{3+}$  represents the coexistence of  $3d^6$  and  $3d^7\bar{L}$  states
- For the Co L-edges, the broad peak feature to higher energy means the increase of average oxidation state of Co ion and rehybridization of Co-O molecular orbital by local structural distortion of  $\text{CoO}_6$  octahedral sites
- For the oxygen K-edge, the Li-ion deintercalation gives rise to peak shift towards lower energy region and the formation of two additional absorption peaks below the threshold energy corresponding to oxygen 2p hole state hybridized with 3d orbital of  $\text{Co}^{4+}$  ion.
- The lower peak intensities increase with the Li-ion deintercalation, indicating transfer into the hole state ( $\bar{L}$ ) in oxygen 2p of  $\text{Co}(t_{2g})$  - O molecular level by the formation of  $\text{Co}^{4+}$  ion.
- The Li-ion re-intercalation results in reversible transfer of hole state into the oxygen atomic site.
- The charge compensation for the electron exchange in the Li-ion deintercalation-intercalation process can be achieved in oxygen site as well as Co metal atomic site.

**Li<sub>y</sub>CoO System investigated by Co K-edge X-ray Absorption spectroscopy **

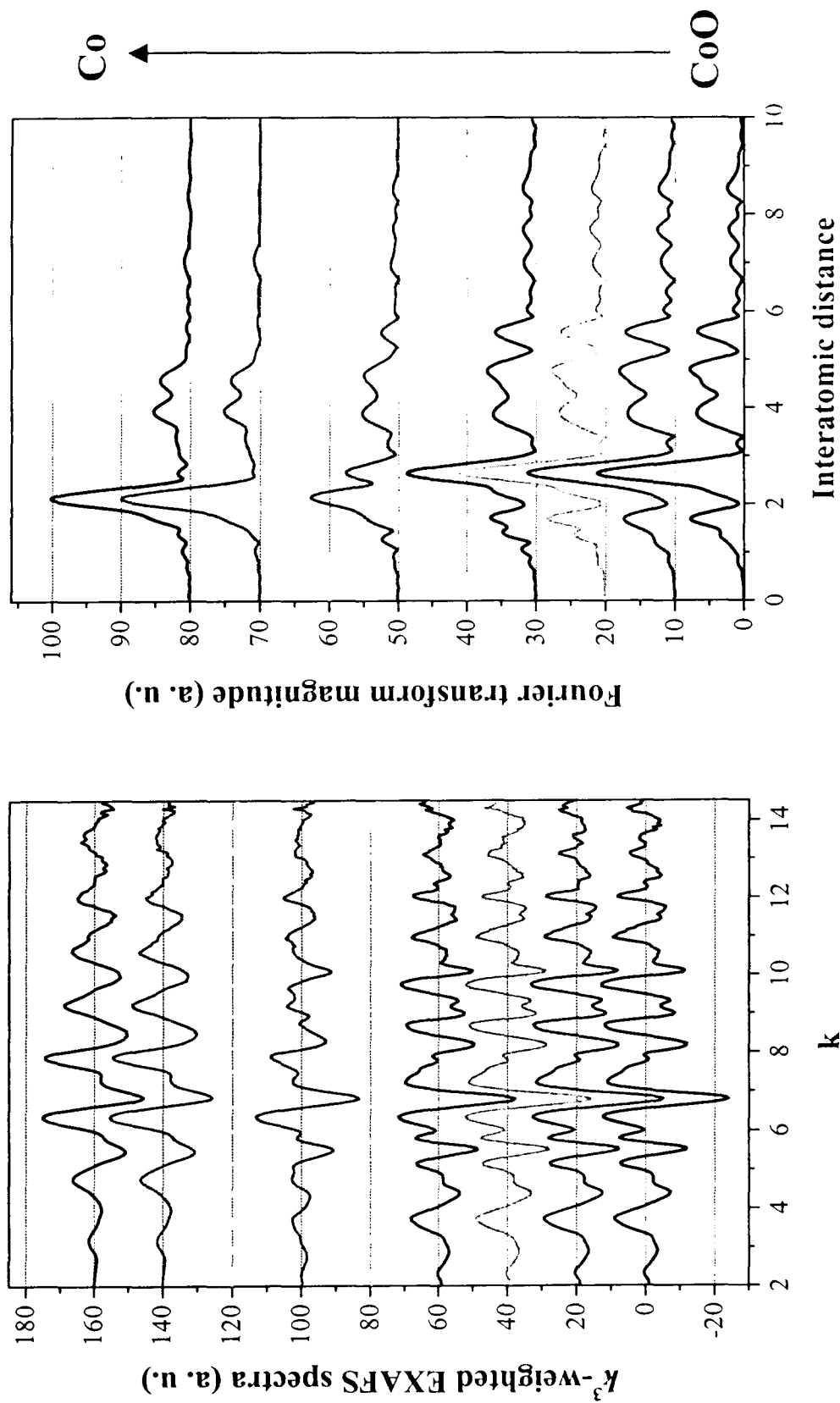


# Li<sub>y</sub>CoO System investigated by Co K-edge X-ray Absorption spectroscopy ~~XAS~~



Co K-edge X-ray absorption spectra for CoO anode (Li<sub>y</sub>CoO) in the discharge processes

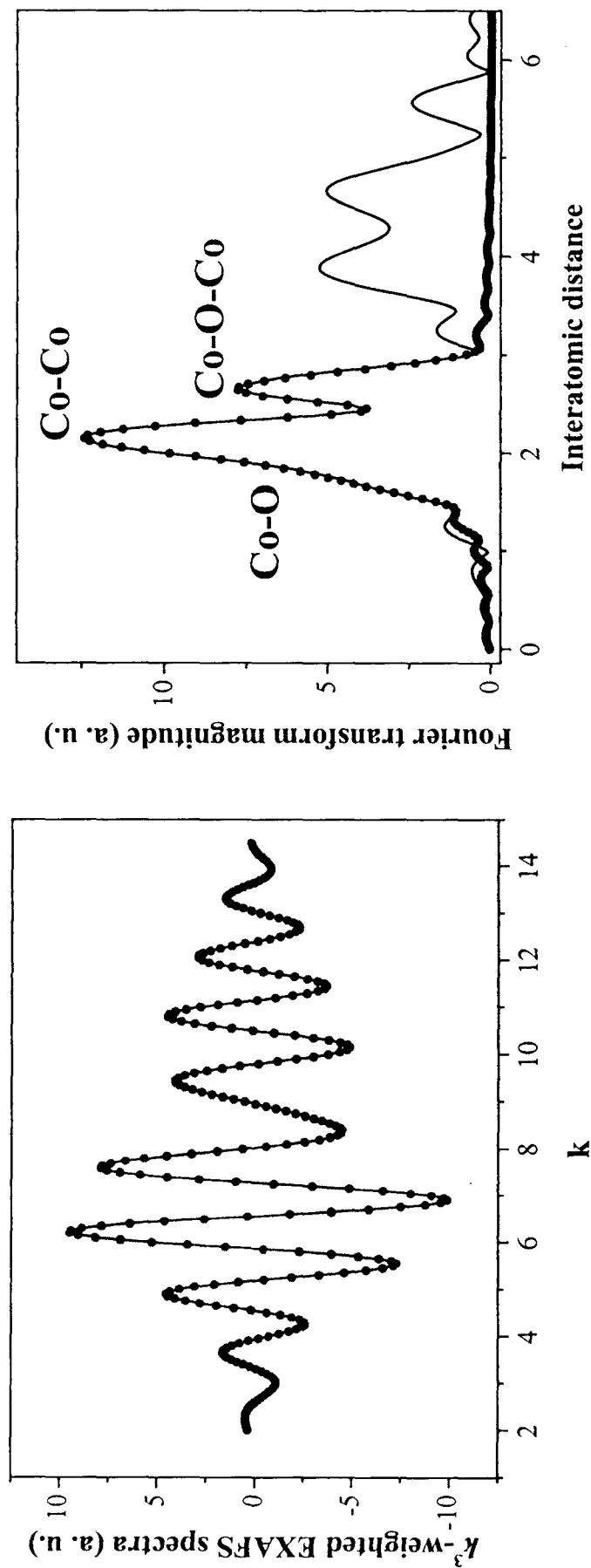
# Li<sub>y</sub>CoO System investigated by Co K-edge X-ray Absorption spectroscopy $\int$ XAS



$k^3$ -weighted Co K-edge EXAFS spectra and corresponding FT for CoO anode (Li<sub>y</sub>CoO) in the discharge process

# Li<sub>y</sub>CoO System investigated by Co K-edge X-ray Absorption spectroscopy

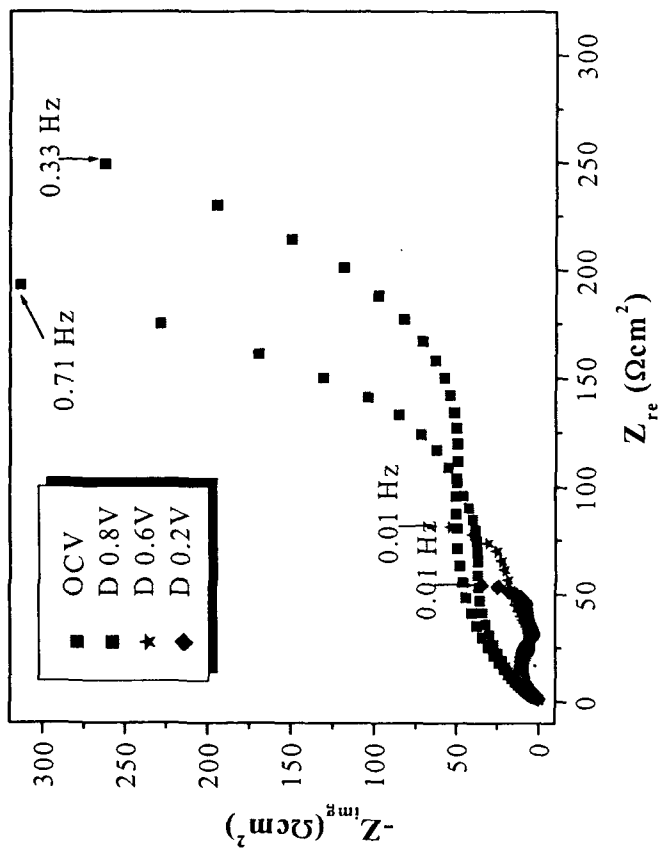
- Co-O : r=2.114 Å, N = 1.81 (6),  $\delta^2=2.71(10^{-3})$  Å
- Co-Co : r=2.509 Å, N = 6.12 (12),  $\delta^2=6.22(10^{-3})$  Å
- Co-O : r=3.009 Å, N = 3.60 (24),  $\delta^2=9.21(10^{-3})$  Å



## Experimental Fourier-filtered (solid line) and best-fitted (circle) $k^3X$ (k) spectra and Fourier transforms for the Li<sub>1.74</sub>CoO.

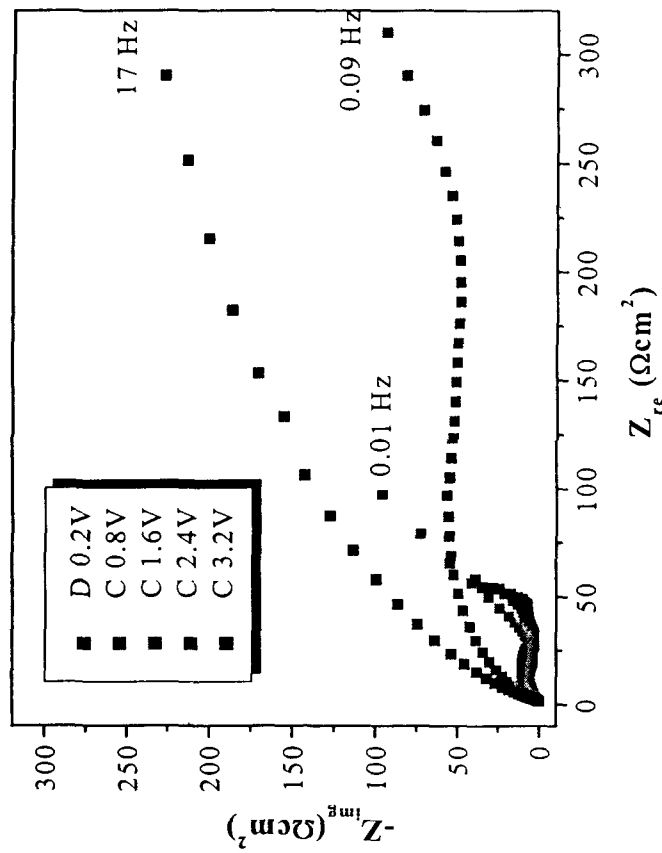
In all curve fitting process, the goodness of fit by  $\{\sum (k^3X_{\text{data}} - k^3X_{\text{model}})^2\} / \sum (k^3X_{\text{data}})^2$  has been estimated within allowed error range. The estimated errors are within  $\pm 0.02$  Å for the interatomic distance and about 15% for the Debye-Waller factor.

# Impedance spectroscopy for $\text{Li}_y\text{CoO}$ System



**Impedance in discharge**

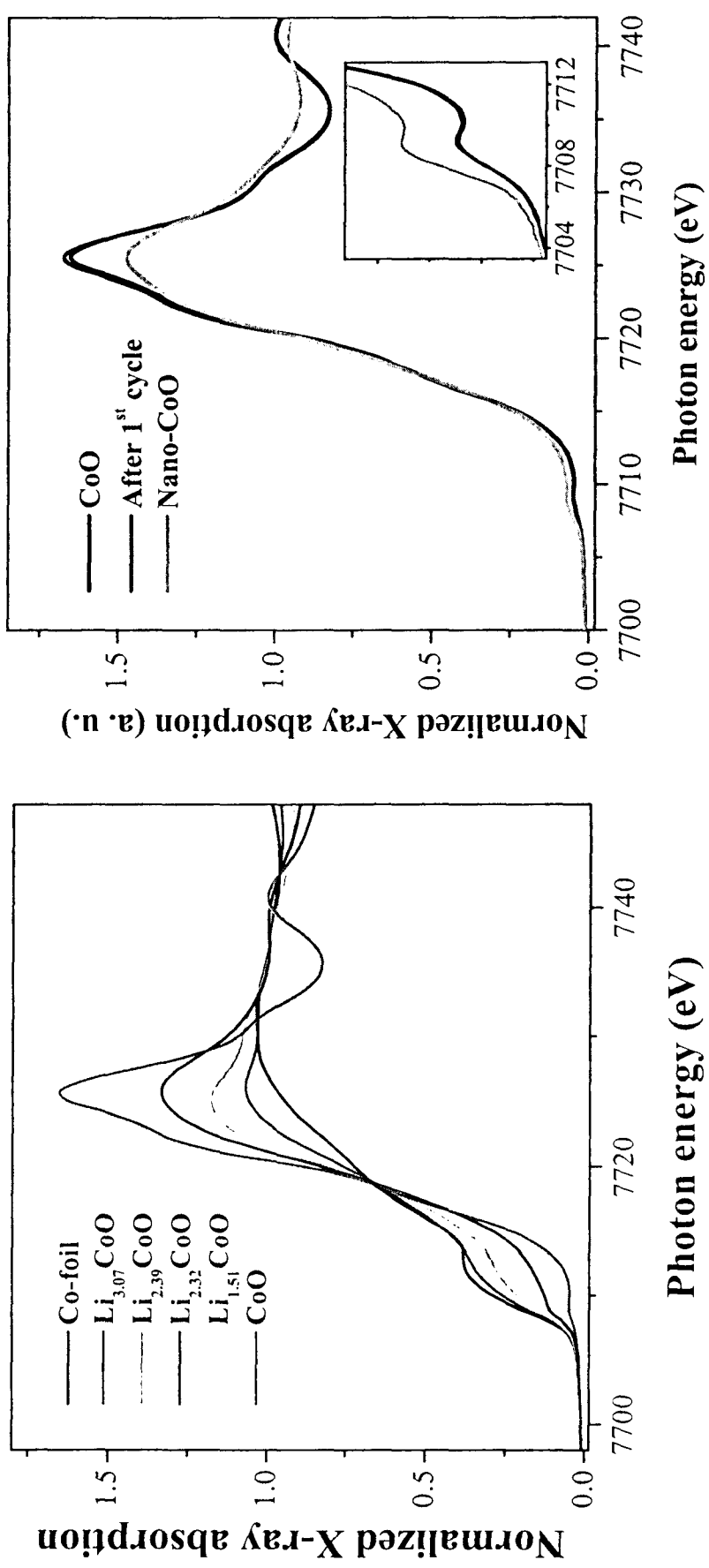
**Li-ion insertion :  
new phases evolution**



**Impedance in charge**

**Li-ion extraction :  
return to an original phase**

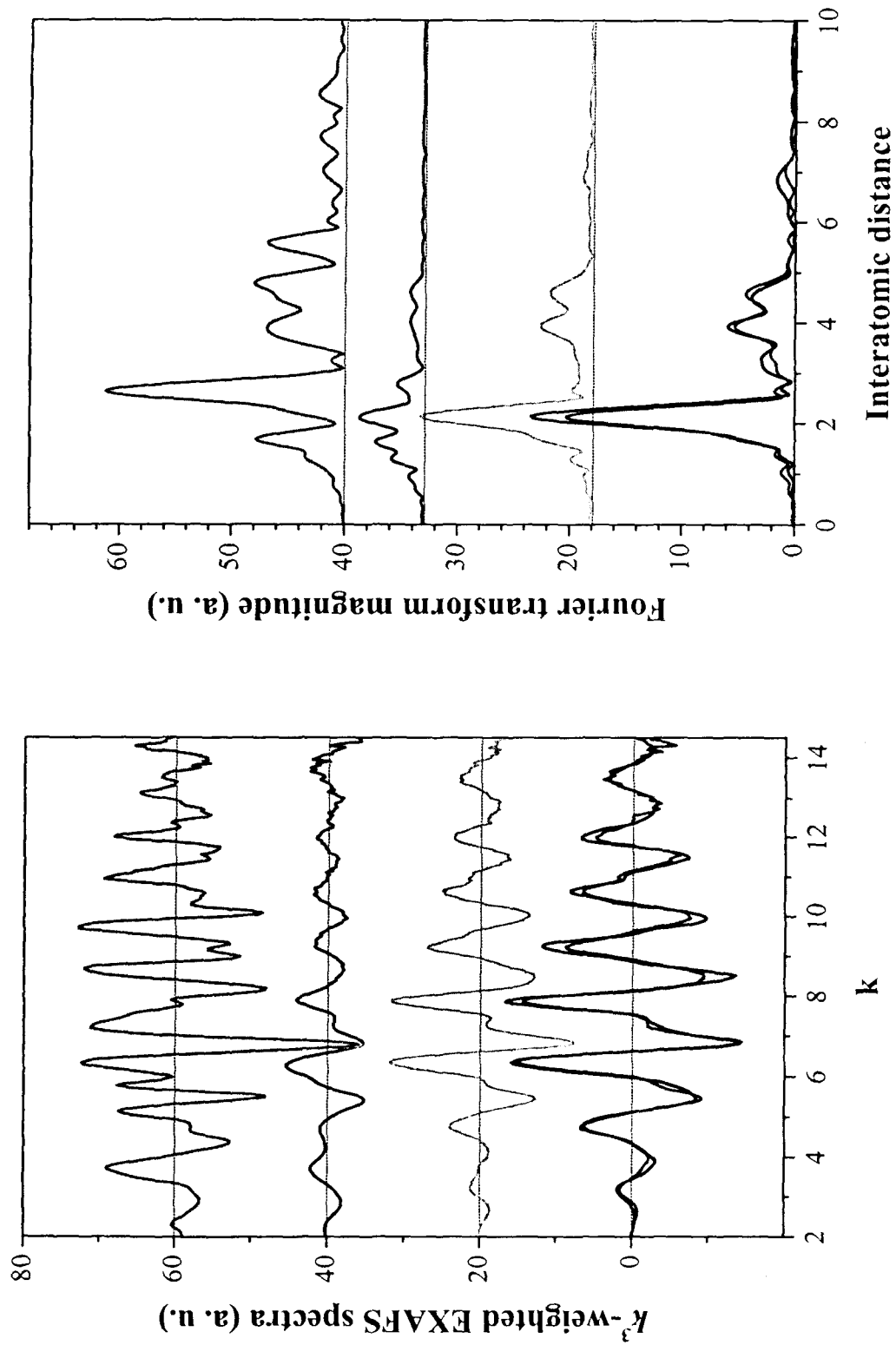
# Li<sub>y</sub>CoO System investigated by Co K-edge X-ray Absorption spectroscopy



Co K-edge X-ray absorption spectra for CoO anode (Li<sub>y</sub>CoO) in the charge processes

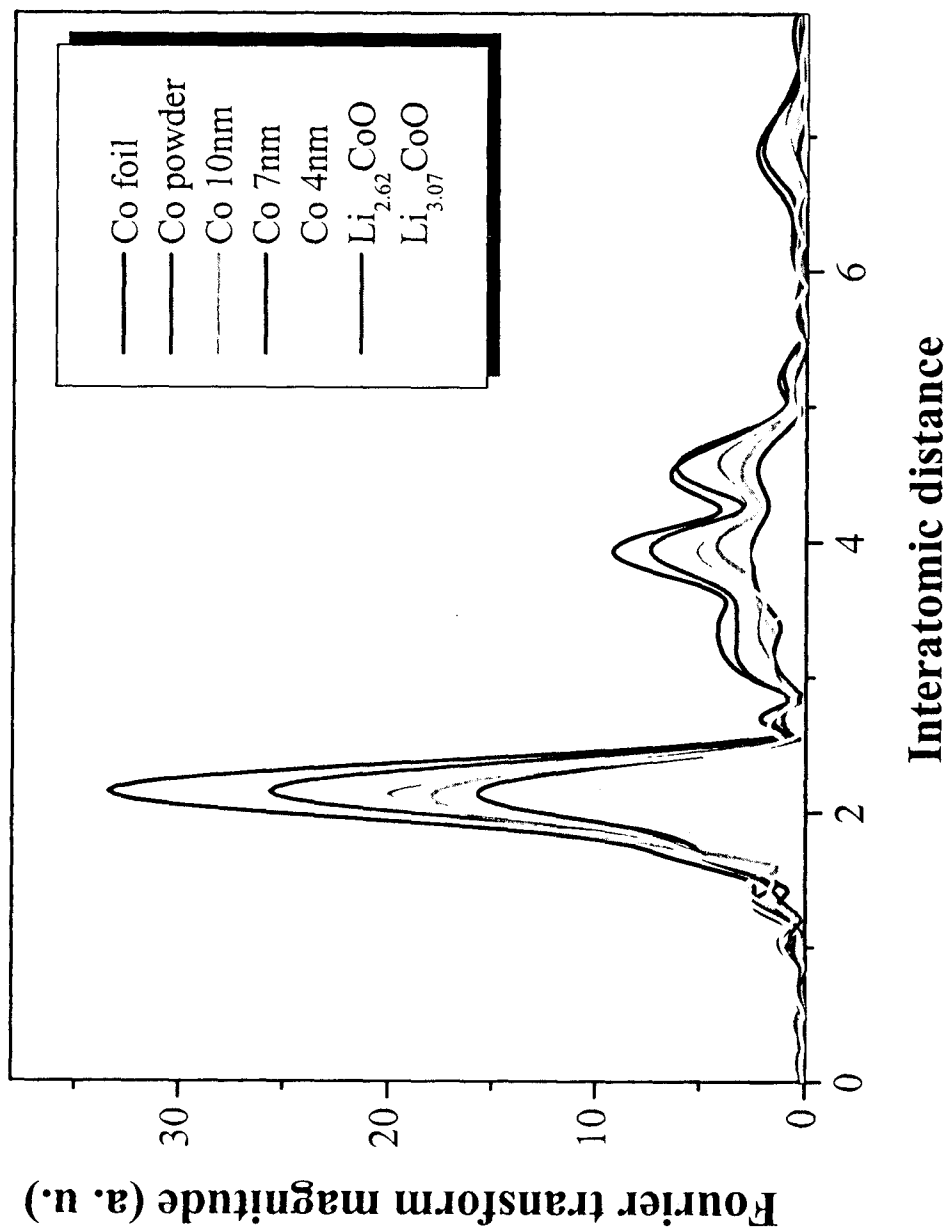


**Li<sub>y</sub>CoO System investigated by Co K-edge X-ray Absorption spectroscopy ~~FT-XAS~~**



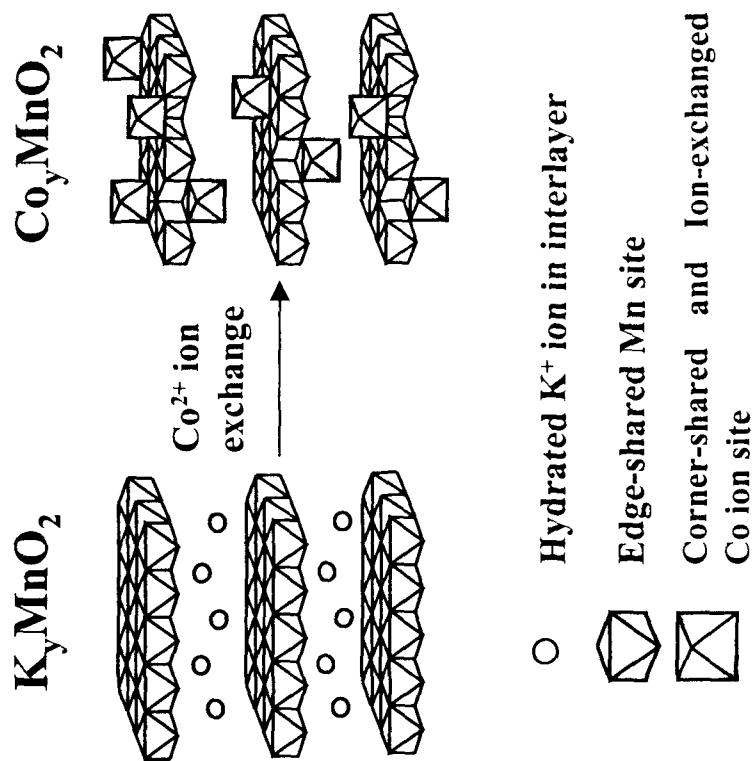
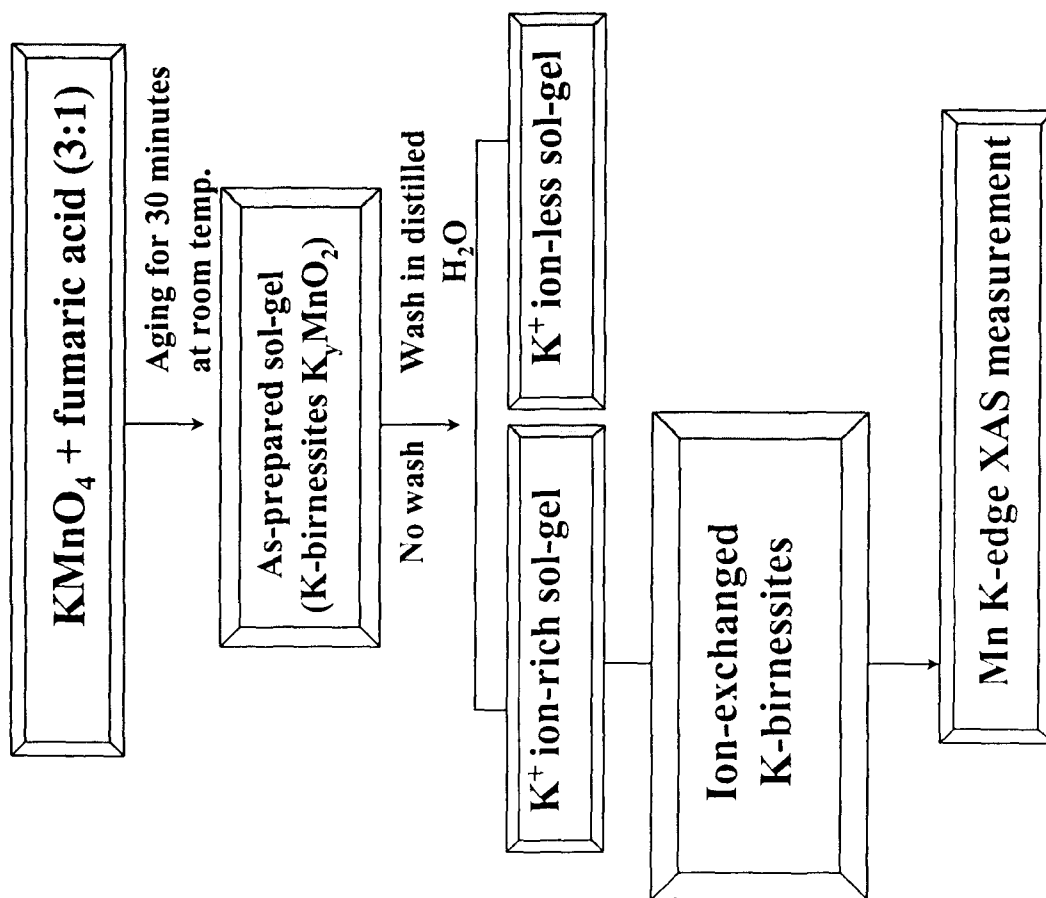
**$k^3$ -weighted Co K-edge EXAFS spectra and corresponding FT for CoO anode (Li<sub>y</sub>CoO) in the charge process**

# Li<sub>y</sub>CoO System investigated by Co K-edge X-ray Absorption spectroscopy ] XAFS

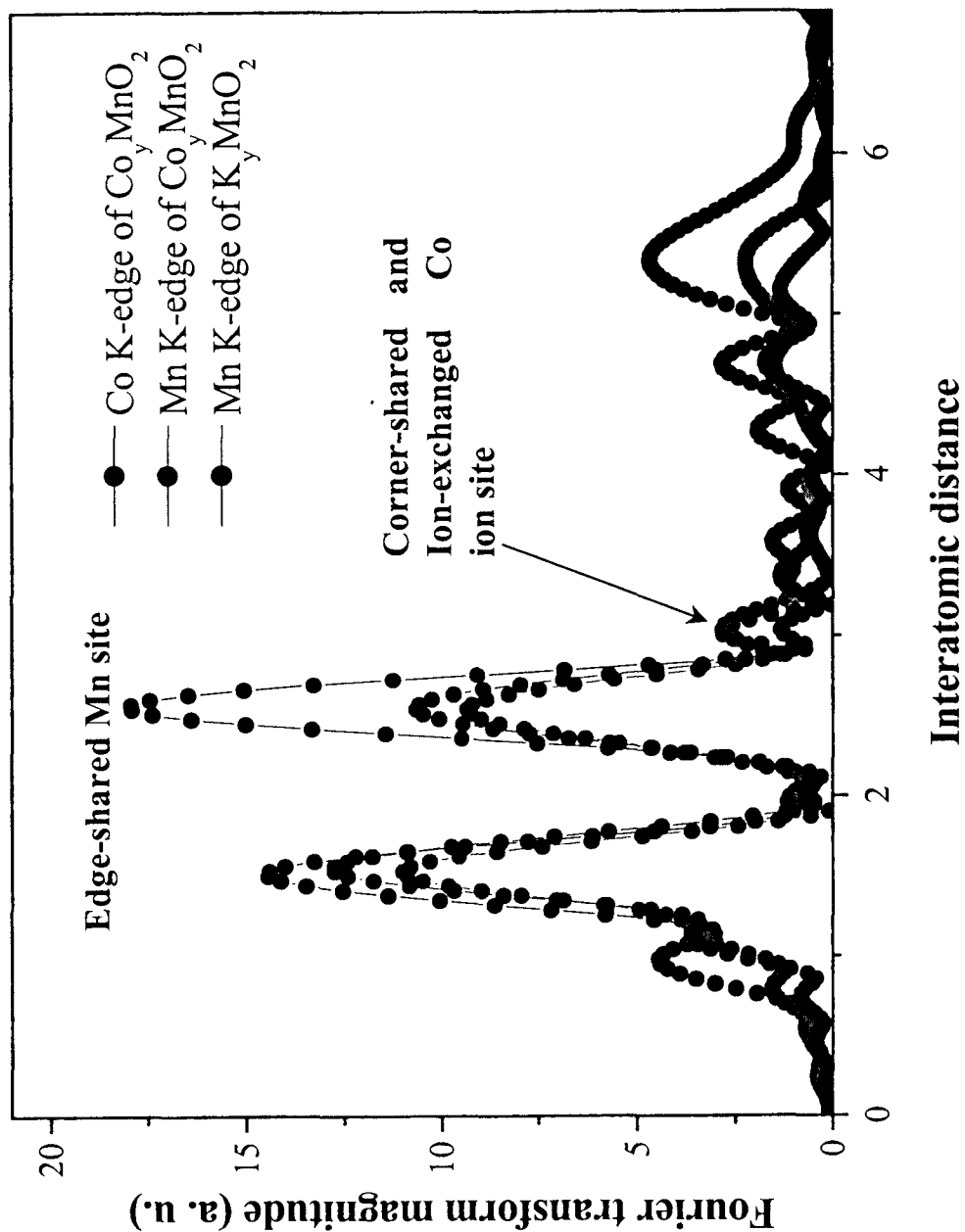


FT peaks of  $k^3$ -weighted Co K-edge EXAFS spectra for Li<sub>y</sub>CoO and Co nanoparticles in the discharge process

# Mn K-edge X-ray Absorption Spectroscopic Study for Ion-exchanged $K_yMnO_2 \cdot xH_2O$ Birnessites

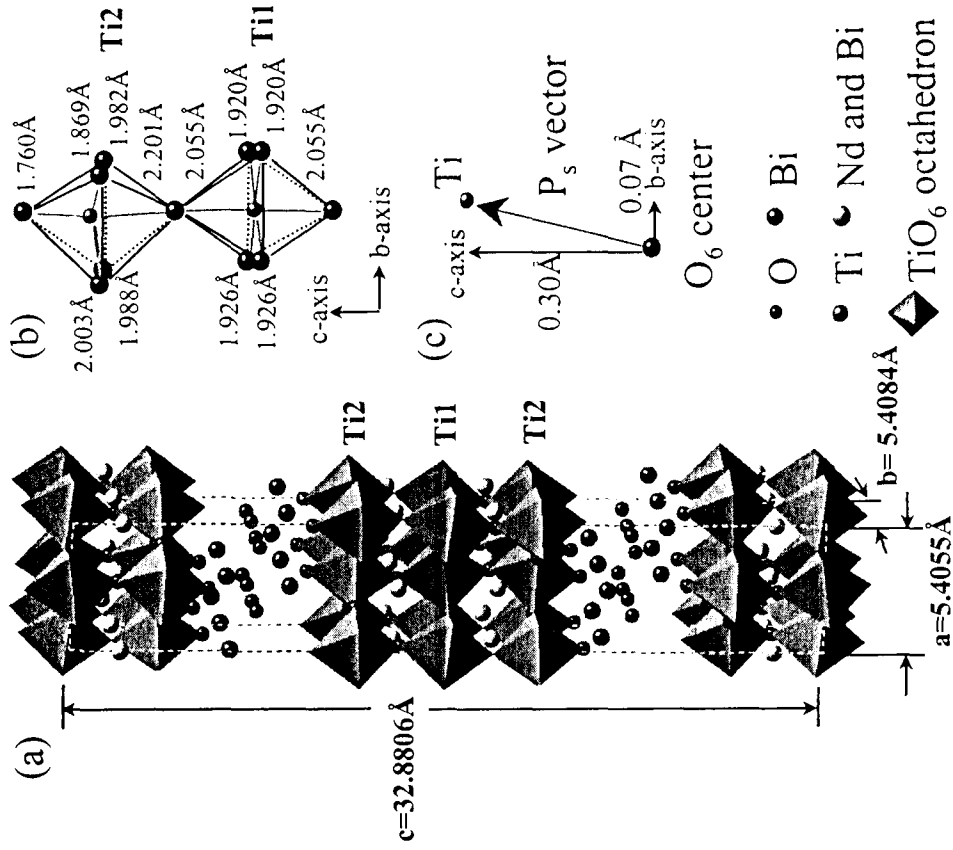
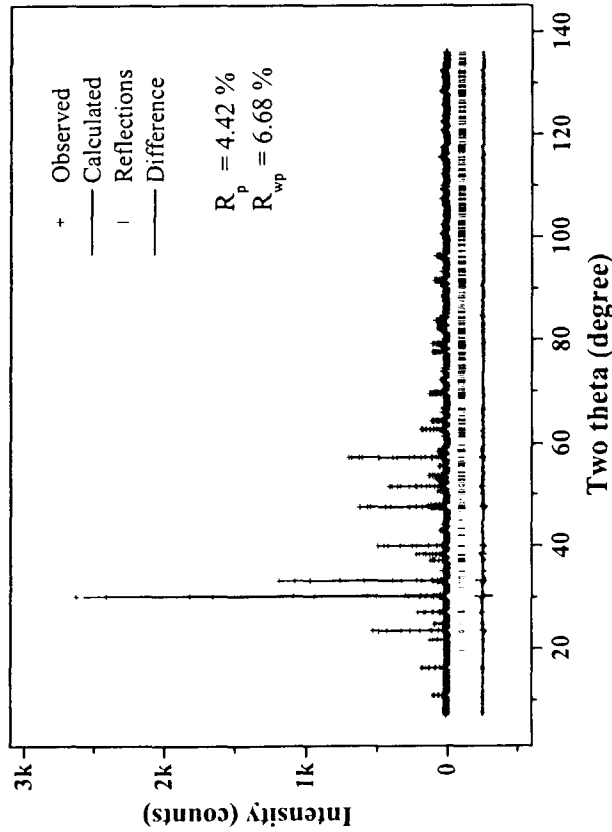


# Local Structure Refinement of Ion-exchanged Layered $\text{Co}_y\text{MnO}_2$ Birnessite



FT magnitude of Co and Mn K-edge  $k^3$ -weighted EXAFS spectra for Ion-exchanged Layered  $\text{Co}_y\text{MnO}_2$  Birnessite

# Ferroelectric supercapacitors based on layered perovskite $\text{Bi}_{3.15}\text{Nd}_{0.85}\text{Ti}_3\text{O}_{10}$ XRD



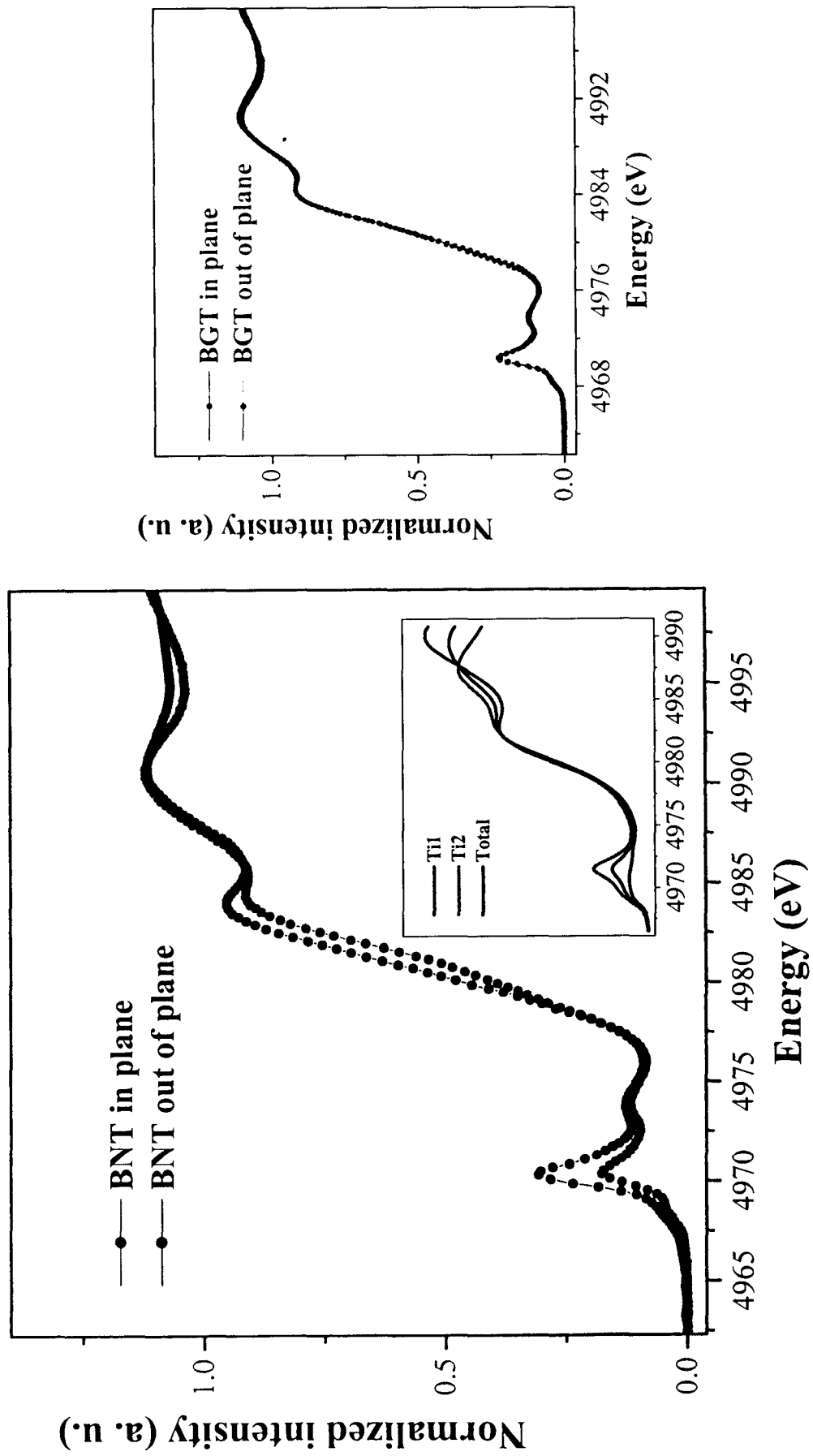
Space group  $B 2 C B$

Atomic coordinates

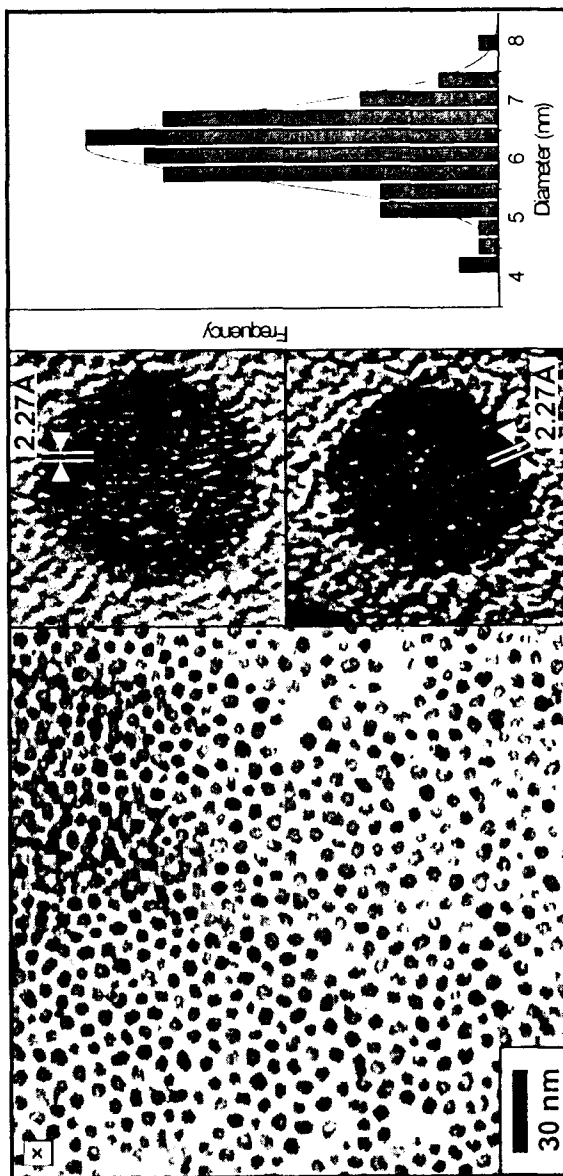
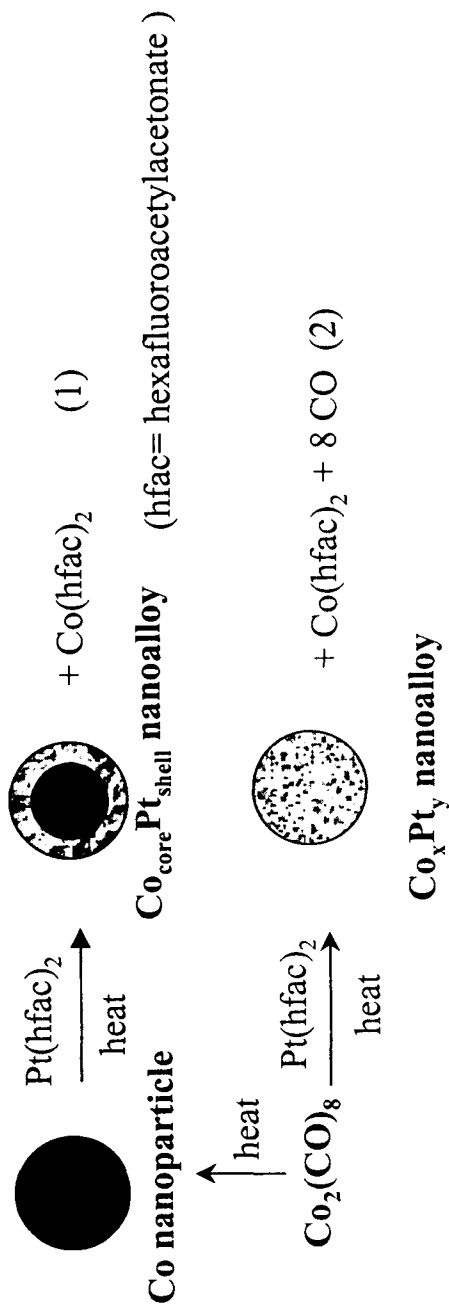
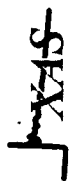
	x	y	z
Ti1	0.03862	0.01768	0.37000
Ti2	0.01861	0.00000	0.50000
Bi	0.01716	0.02104	0.21084
Bi	0.00000	-0.00180	0.06639
Nd	0.00000	-0.00180	0.06639
O1	0.29427	0.26500	0.00690
O2	0.26500	0.26300	0.24850
O3	0.05281	0.05117	0.43773
O4	0.05200	0.94530	0.31930
O5	0.28400	0.25300	0.11090
O6	0.21700	0.20100	0.87560

Highly c-axis oriented BNdT film

Ti K-edge X-ray absorption spectra for layered perovskite  $\text{Bi}_{3.15}\text{Nd}_{0.85}\text{Ti}_3\text{O}_{10}$  



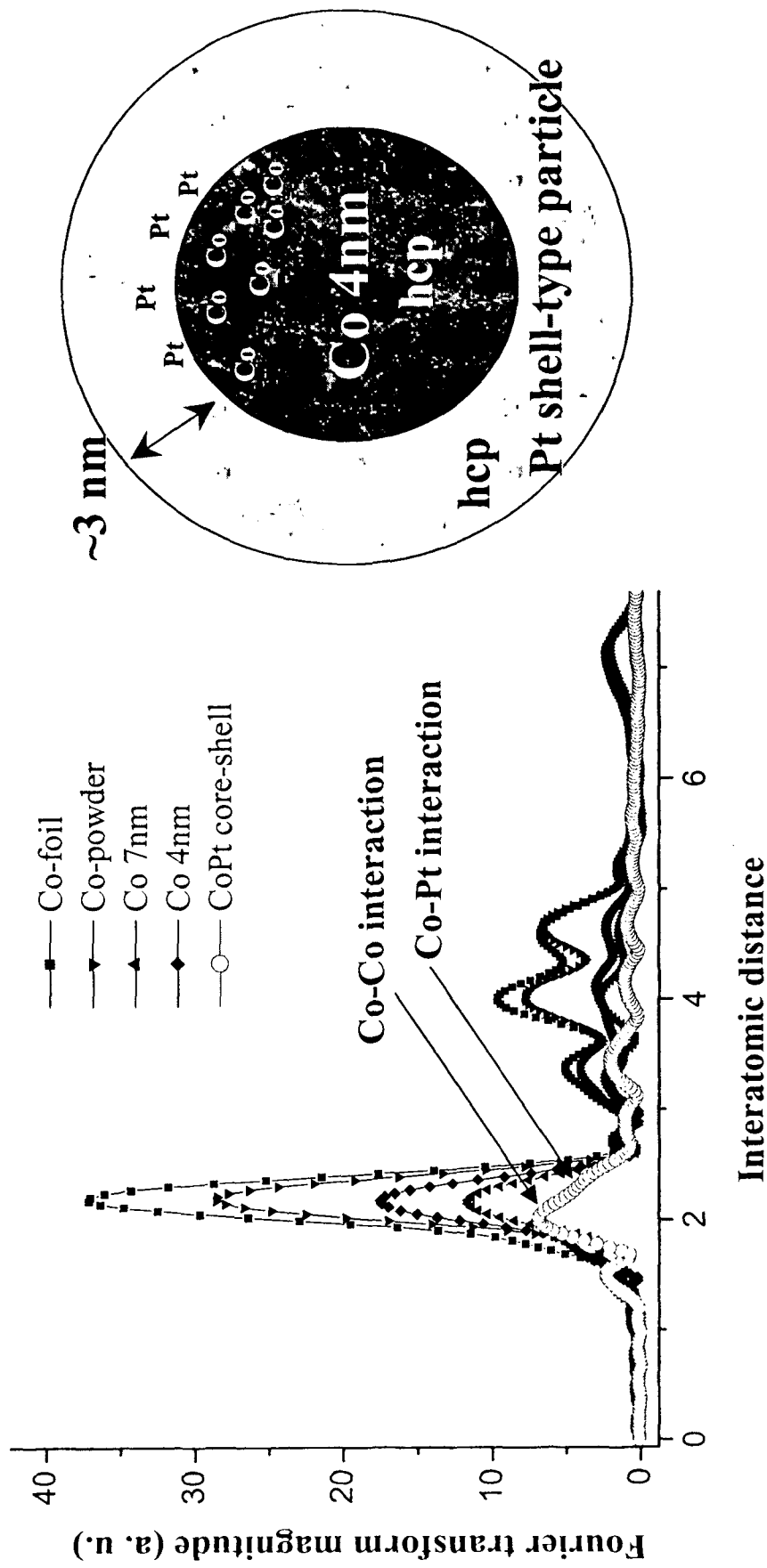
# Core-Shell type CoPt nanoparticle



TEM, HRTEM images and histogram of  $\sim 6.27$  nm  $\text{Co}_{\text{core}}\text{Pt}_{\text{shell}}$  nanoalloys

# EXAFS refinement of Core-Shell Type CoPt nanoparticle

EXAFS



FT magnitude of Co K-edge  $k^3$ -weighted EXAFS spectra for core-shell type CoPt nanoparticle and pure Co nanoparticles



## Conclusion



### **Amorphous or Polycrystalline Powder or Film**

**under chemical, physical perturbations**

#### **XANES (X-ray absorption near edge structure)**

- Electronic structure, bond covalency, site symmetry such as tetrahedral and octahedral, spin state (low spin or high spin)

#### **EXAFS (Extended X-ray absorption fine structure)**

- Interatomic distance, Coordination number, Debye-Waller factor

