An Overview of X-ray Compton Scattering: Basic and Applied Research

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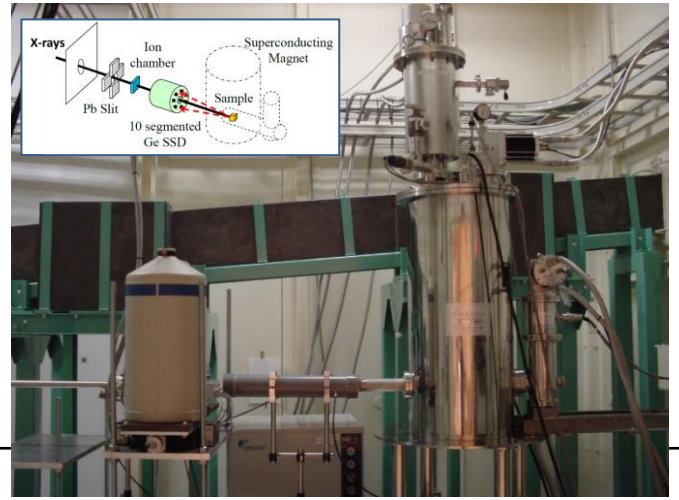
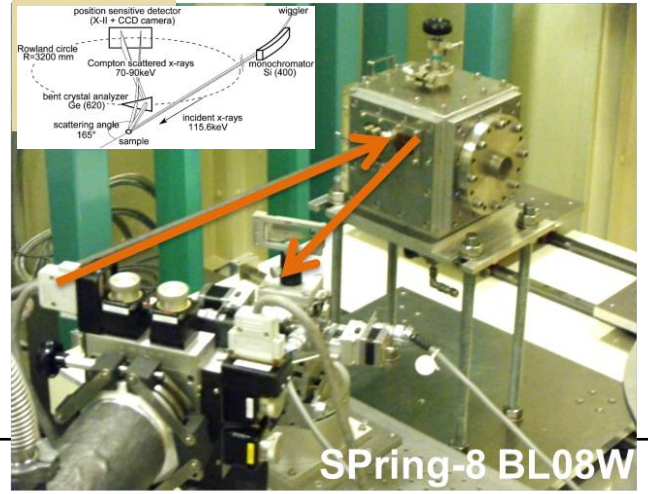
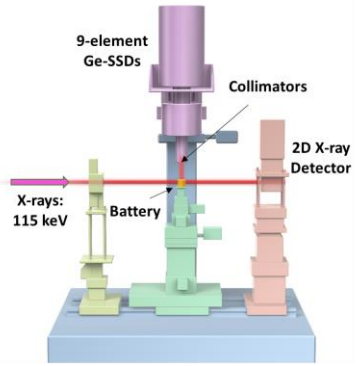
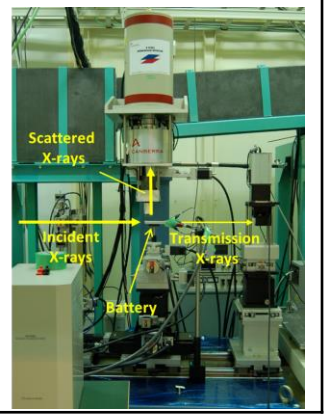
Spectrometers for X-ray Compton Scattering

	Magnetic Compton Scattering	Charge Compton Scattering	Compton-Scattering Imaging
Research Fields	• Magnetism	• Fermiology • Electronic Structures	• Electrochemical Engineering • Industrial Applications
Examples	• Magnetic Multilayers • Magnetic alloys and Compounds • LIB materials, etc.	• Cuprates, Cobaltites • f-electron systems • Metallic alloys, • LIB materials, etc.	• Li-ion batteries • Fuel cells • Combustion systems
Spectrom-eters			 

Plan of Talk

1. **Recent charge Compton scattering studies**
   - LIB cathode materials have been presented by B. Berbiellini.
   - This talk touches on other materials.

2. **Electron-doped T'- $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ (x = 0.10)**
   - Superconductivity appears after reduction annealing.
   - Influence of reduction annealing on the electronic state has been investigated.

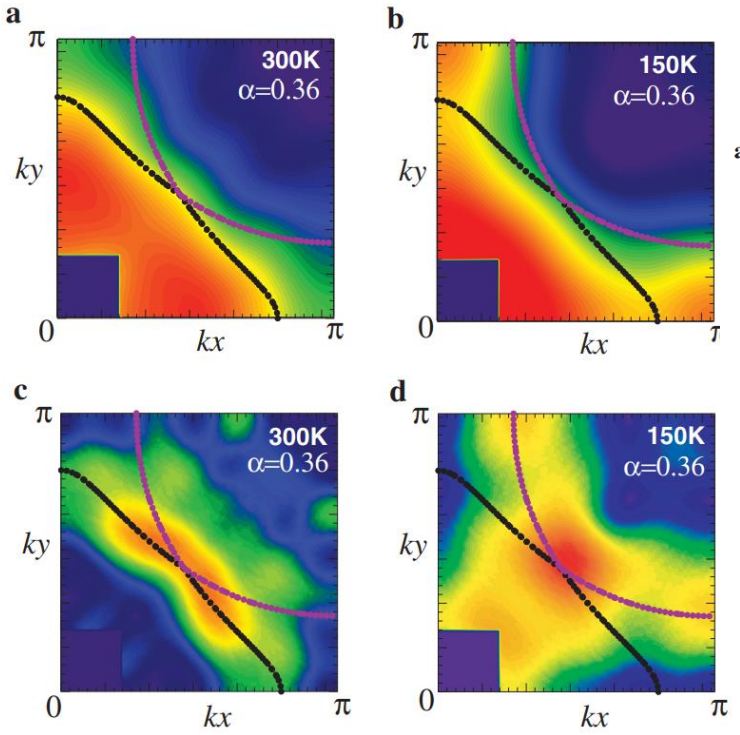
3. **Compton scattering imaging of electrochemical devices**
   - Li-ion batteries
   - Polymer electrolyte fuel cells

4. **Concluding Remarks and Perspectives**

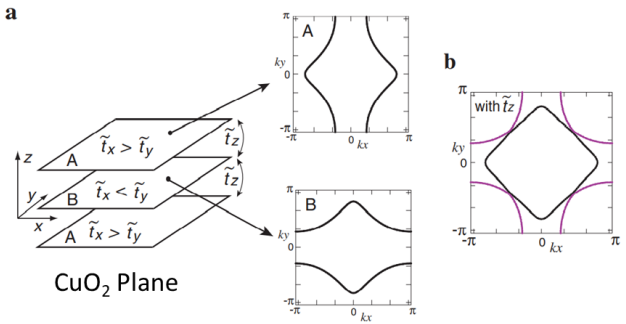
1. Charge Compton Scattering Studies

"Fermi surface in La-based cuprate superconductors (LSCO) from Compton scattering imaging,"
(H. Yamase *et al*., Nature Communications **12**, 2223 (2021))

- This study suggests that the FS is strongly deformed by the underlying nematicity in each CuO_2 plane, but the bulk FSs recover the fourfold symmetry.
- A theory based on nematicity can explain the experimental results: the derivatives of electron momentum density..



Electron momentum distributions and their derivatives.



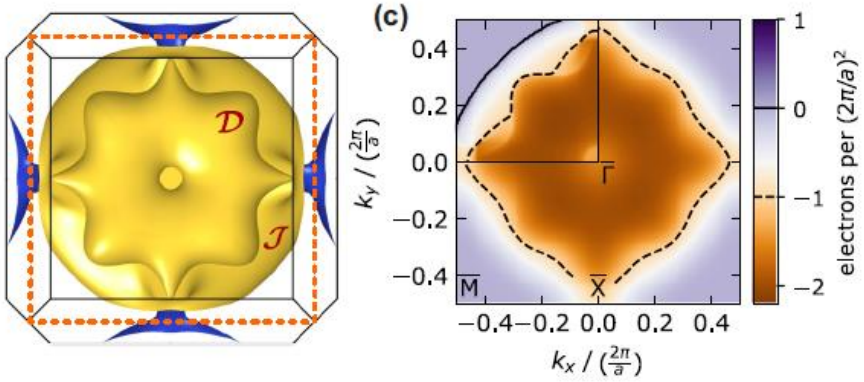
Fermi surface (FS) deformation in $La_{2-x}Sr_xCuO_4$.

1. Charge Compton Scattering Studies

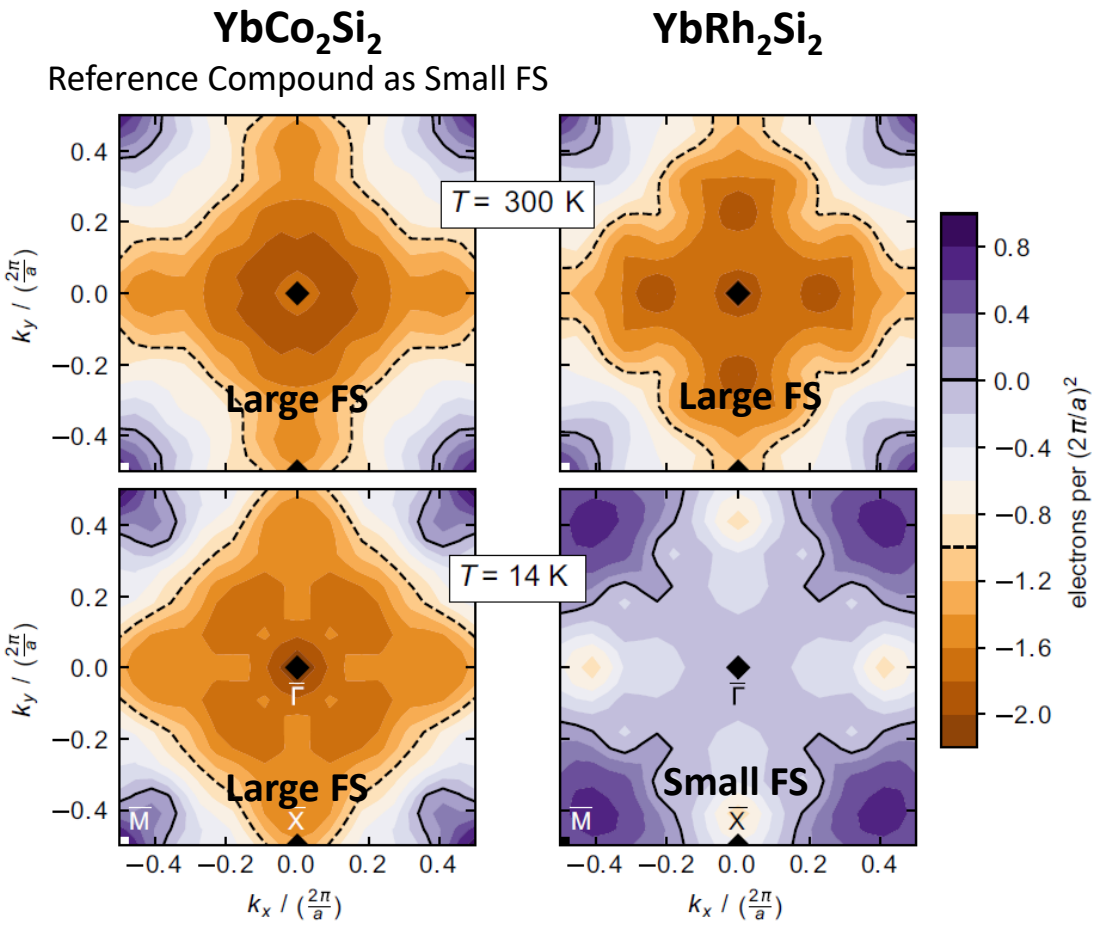
"Visualizing the Kondo lattice crossover in $YbRh_2Si_2$ with Compton scattering "

(M. Gütter *et al.*, Phys. Rev. B **103**, 115126 (2021)) (Editors' Suggestion)

- This study shows that the transition from large FS to small FS takes place with rising temperature in $YbRh_2Si_2$.
- This presents clear evidence for a largely restored small FS at RT.
- The temperature scale of Kondo crossover is about 100 - 300 K.



Calculated FS and 2D-EOND for $YbCo_2Si_2$

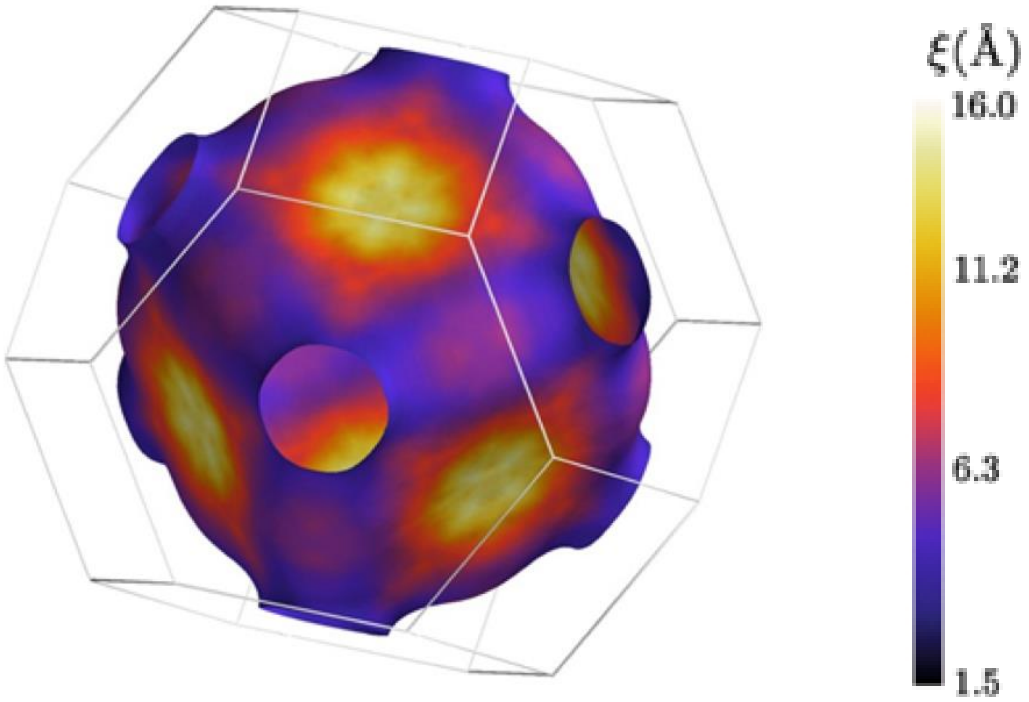


Projected experimental 2D Electron Occupation Number Density (EOND)

1. Charge Compton Scattering Studies

"Extreme Fermi Surface Smearing in a Maximally Disordered Concentrated Solid Solution, "
(H. C. Robarts *et al*., Phys. Rev. Lett. **124**, 046402 (2020))

- Equiatomic $Ni_{0.25}Fe_{0.25}Co_{0.25}Cr_{0.25}$ is a maximally disordered alloy.
- This study shows that the FS can survive the presence of extreme compositional disorder.
- Electron mean-free-path is as short as atomic distance on some parts of FS.



Fermi surface sheet and quasi-particle coherence length

1. Charge Compton Scattering Studies

"Symmetry change of Co 3d orbital associated with the 500 K spin crossover accompanied by insulator-to-metal transition in $LaCoO_3$, " (Y. Kobayashi *et al.*, Phys. Rev. B **98**, 115154 (2018))

- Perovskite cobaltite $LaCoO_3$ shows spin-crossover at around 100 and 500 K.
- Electron transfer between t_{2g} and e_g orbitals takes place, as shown in Fig. 3
- Hybridization between Co-e_g and O-*2p* largely increases at the 500 K spin-crossover, as shown in Fig. 4,
- Collective character of spin crossover is observed at 500K, while thermal-excitation-like spin crossover at around 100 K, as shown in Fig. 5.

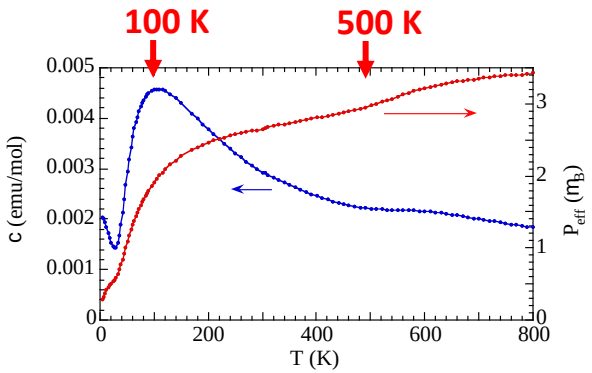


Fig. 1 : Temperature dependence of magnetic. susceptibility and effective magnetic moment of $LaCoO_3$.

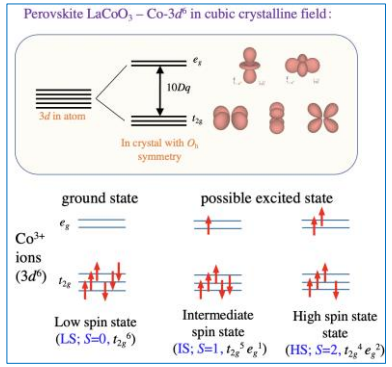


Fig. 2 : Orbital-spin state responsible for the spin-crossover in $LaCoO_3$.

t_{2g} - e_g transfer is experimentally confirmed

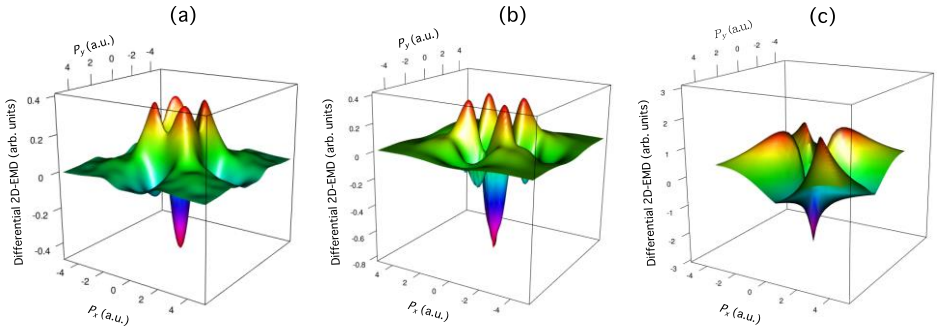


Fig. 3 : Aerial views of the difference two-dimensional electron momentum density (2d-EMD) of Co-3d in $LaCoO_3$ between 10 and 270 K for (a) measured and (b) calculated molecular orbitals (MO) and (c) calculated atomic orbitals (Atom).

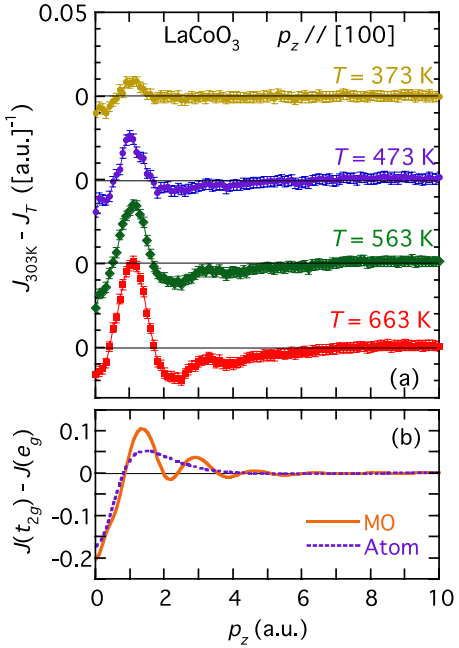


Fig. 4 : Temperature dependence of the difference Compton profiles.

Collective character at 500 K

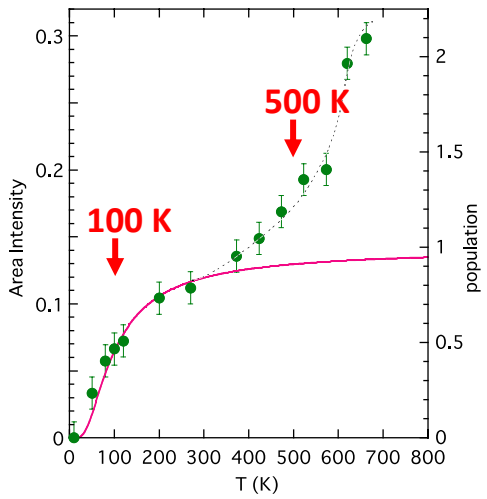


Fig. 5 : Temperature dependence of the area intensity of difference Compton profile.

2. Electron-doped T'- $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ (PLCCO)

"Electronic State in T'=$Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ (x=0.10) Studied by Compton Scattering"

T. Kawamata, S. Saito, N. Tsuji, T. Sumura, T. Adachi, M. Kato, Y. Sakurai and Y. Koike

To be published in J. Phys. Soc. Japan (2022).

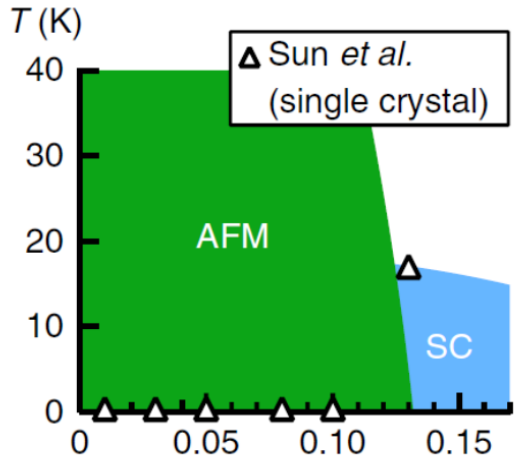
2. Electron-doped T'- $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ (PLCCO)

- As-grown samples are non-superconducting and AFM
- By protect annealing, AFM shrinks and SC appears

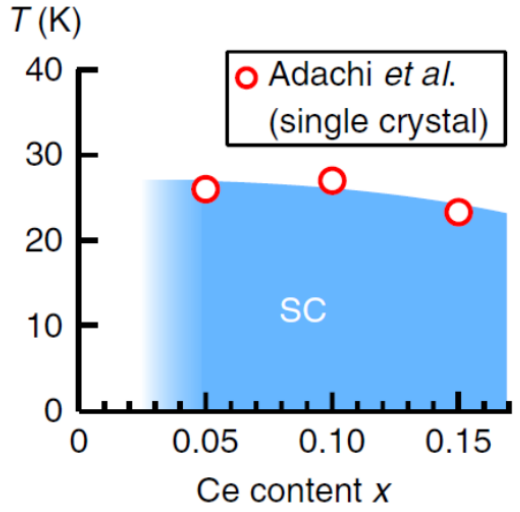
- The effect of annealing is not fully understood
- Apical oxygen, which stabilizes AFM, is possibly removed by annealing

- Protect annealing method can synthesize a bulk single-crystal with Tc=27K
- X-ray Compton scattering has been applied to investigate the annealing effects on the electronic states.
- The results are discussed with the molecular orbital calculations for LSCO.

Annealed by Conventional Method



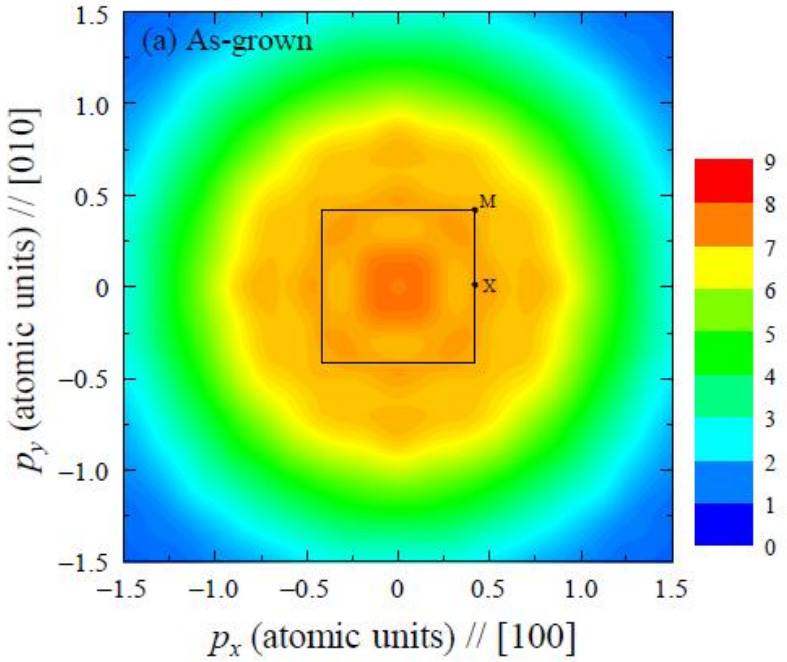
Protect-Annealed



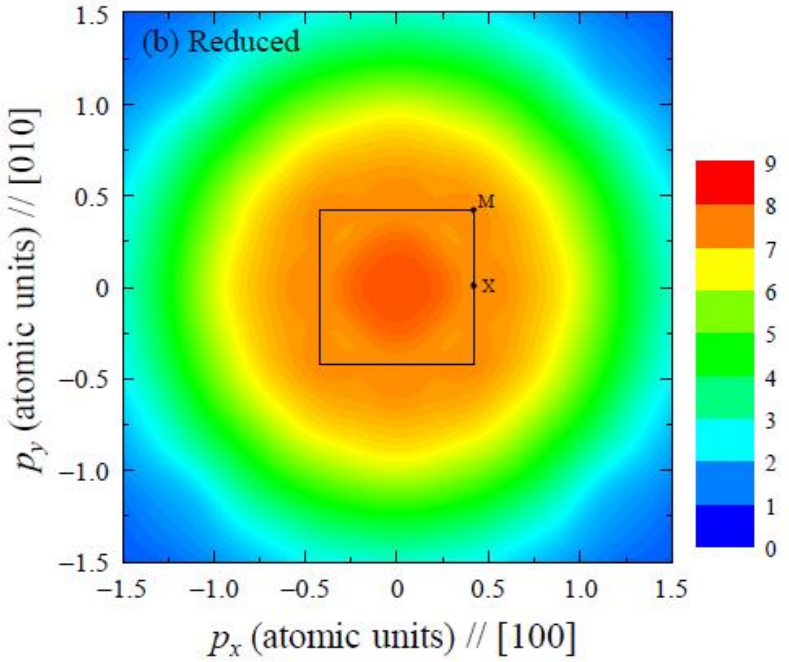
2. Electron-doped T'- $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ (PLCCO)

- Single crystal of T'-PLCCO with x=0.10 were grown by the traveling-solvent floating-zone method.
- The reduced single-crystal was obtained by the protect annealing, showing superconductivity at Tc=27K.
- The Compton scattering measurements were carried out for as-grown and reduced single crystals at RT.
- Ten Compton profiles were measured at even intervals between [100] and [110], to obtain two-dimensional electron momentum density (2D-EMD).

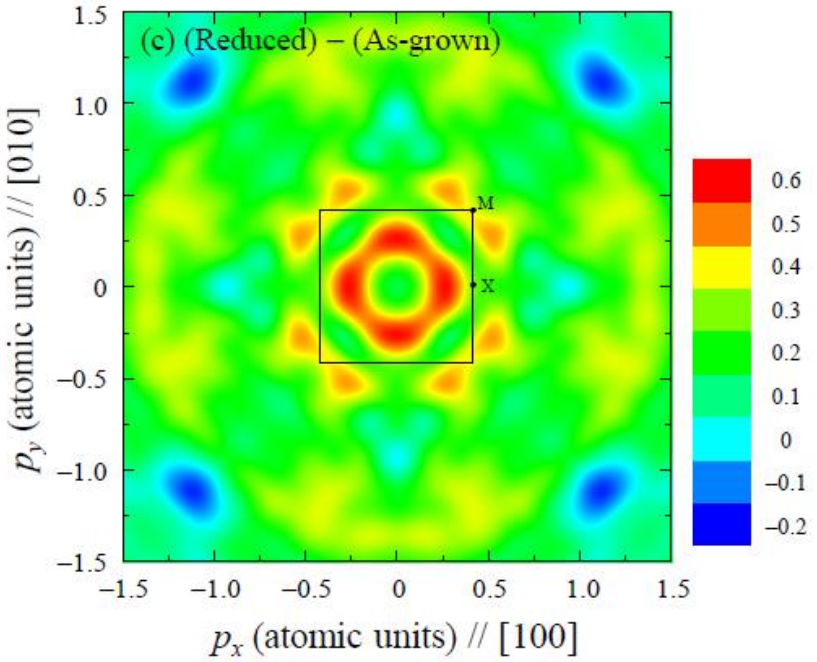
As-grown



Reduced
(by Protect Annealing)



Difference
(Reduced – As-grown)

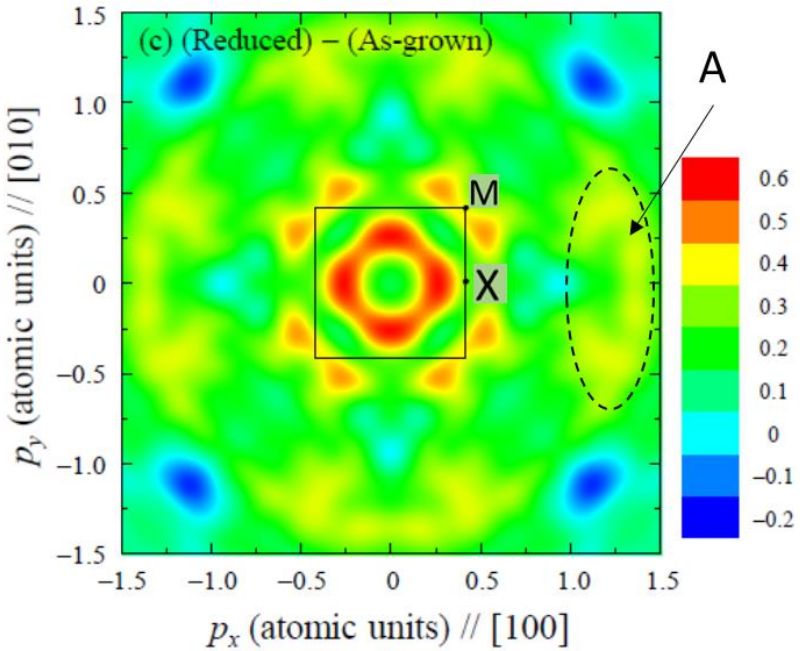


2. Electron-doped T'- $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ (PLCCO)

Comparison with the molecular orbital calculations shows that…

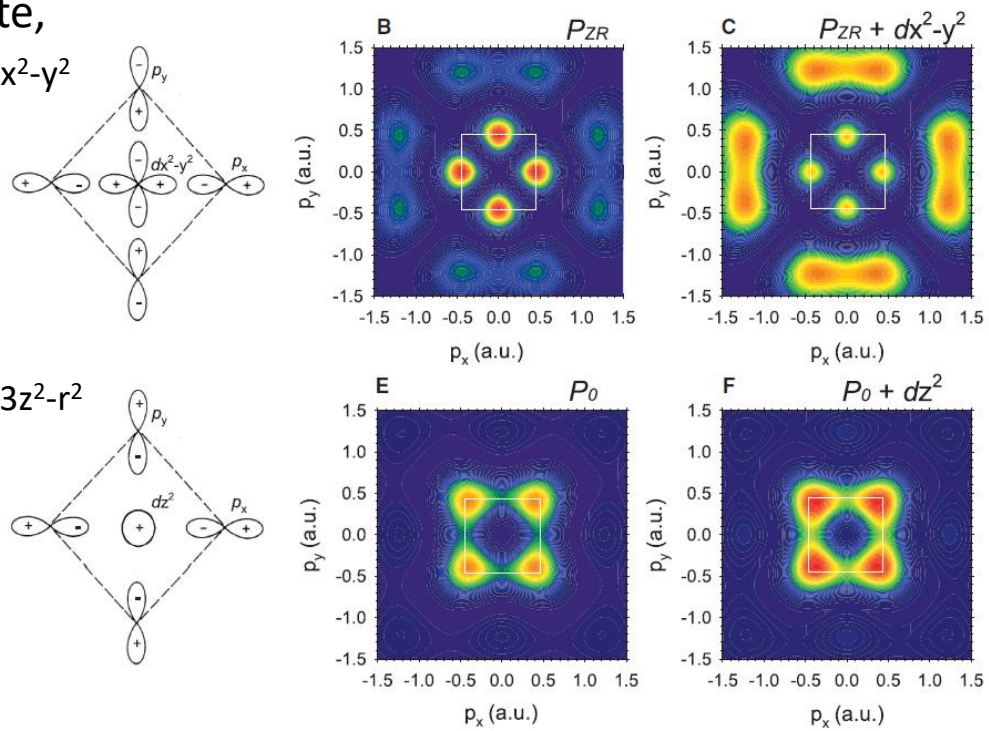
- Feature around X shows the number of electron increase in the Zhang-Rice singlet band,
- Feature A indicates that the hybridization between ZR and Cu $d_{x^2-y^2}$ increases,
- Feature around M shows the number of electron increases in the Cu $d_{3z^2-r^2}$ state, by annealing.

Difference
(Reduced – As-grown)



Zhang-Rice Singlet State,
hybridized with Cu $3d_{x^2-y^2}$

O $2p_{x/y}$ MO State.
hybridized with Cu$3d_{3z^2-r^2}$

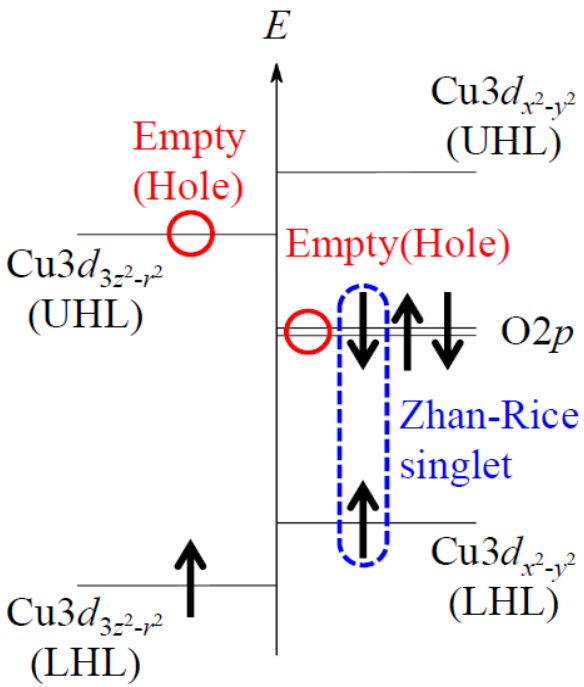


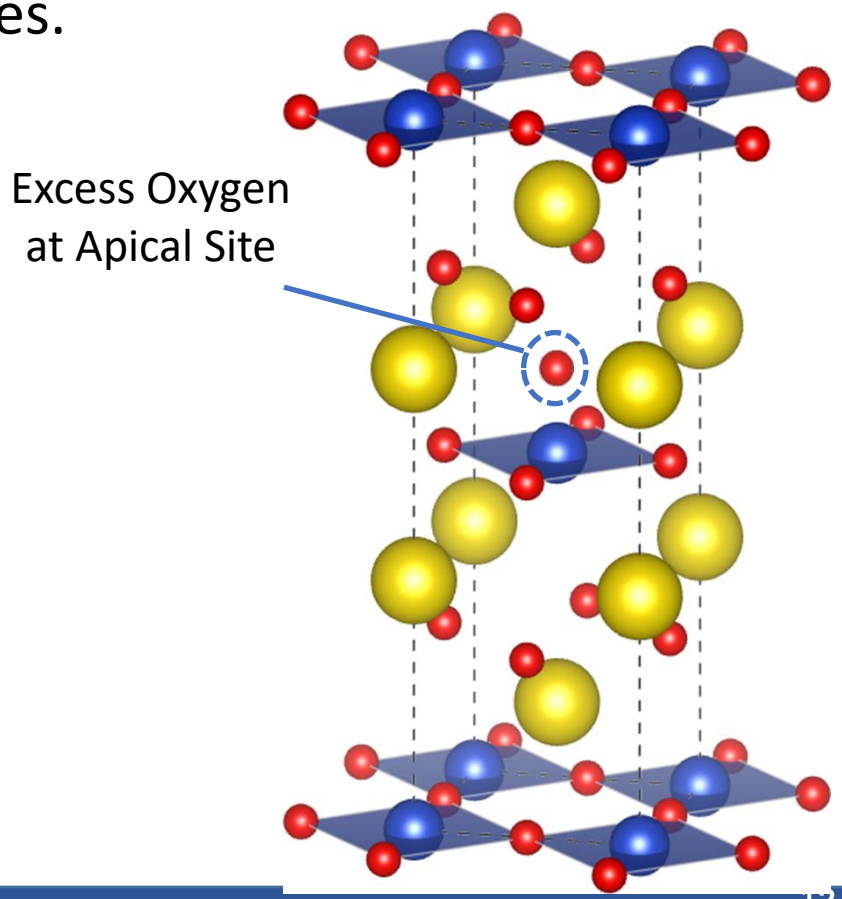
Molecular Orbital (MO) Calculations: Science 332, 698 (2011)

Proposed Electron-doping Scenario for T'- PLCCO

- Excess oxygen is placed at the apical site in as-grown samples.
- Excess oxygen is ionized, and thus two holes (red circles) are generated.
- With annealing, excess oxygen is removed, which leads to electron doping.
- These results provide information on the electronic states of the undoped superconductivity in the mother compound of T'-cuprates.

As-grown, around excess oxygen

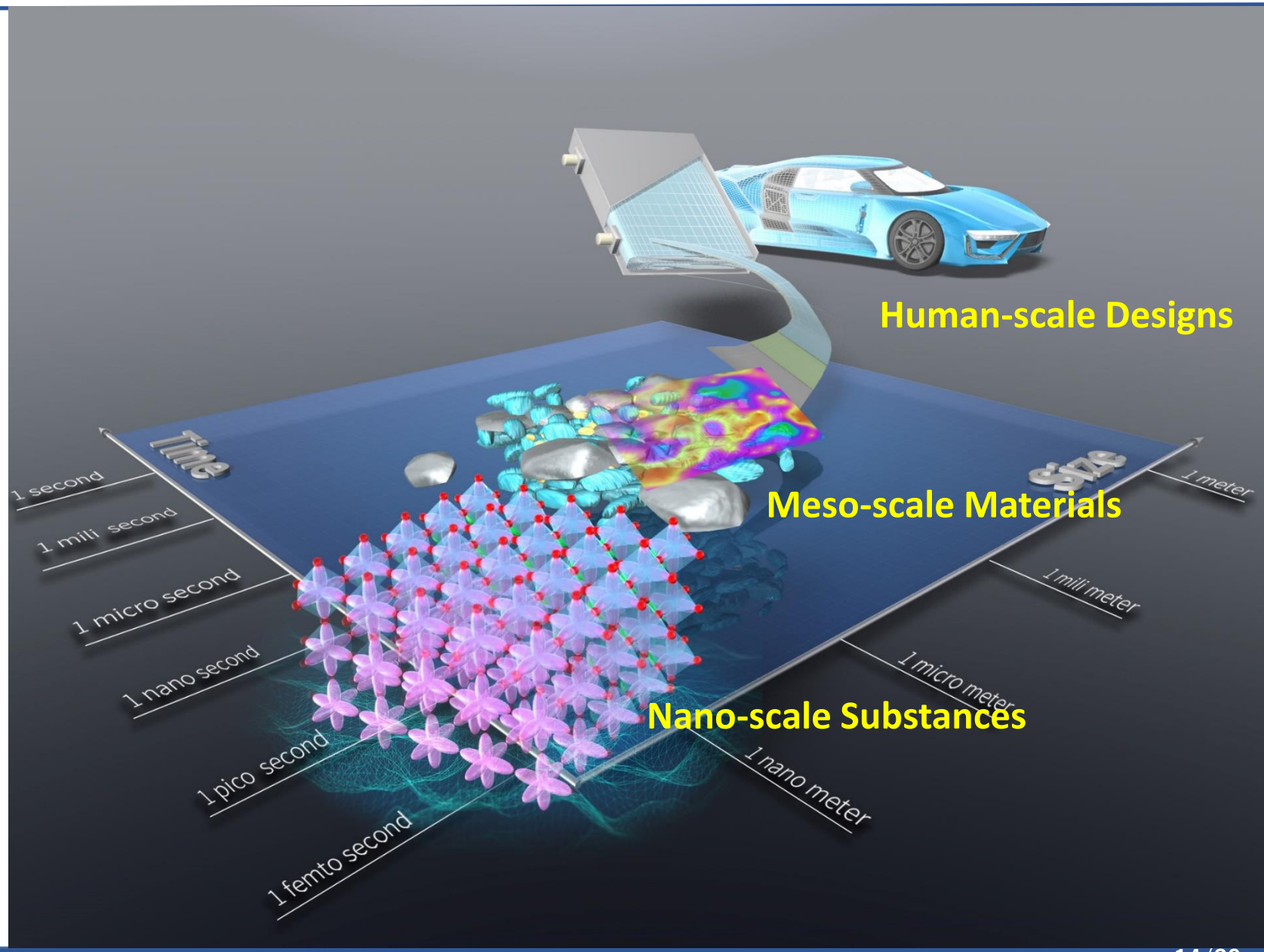




3. Compton scattering imaging (CSI) of electrochemical devices

Electrochemical Energy Storage Devices

- The operation principles are well known.
- The performance of manufactured devices, however, depends on the hierarchical details.
- The details are complicated, and interplayed among nano-scale substances, meso-scale materials, and human-scale device designs.
- Electrochemical Energy Storage Devices are mysterious as much as Strongly Correlated Electron Systems.



First Demonstration of SR-based CSI on Battery

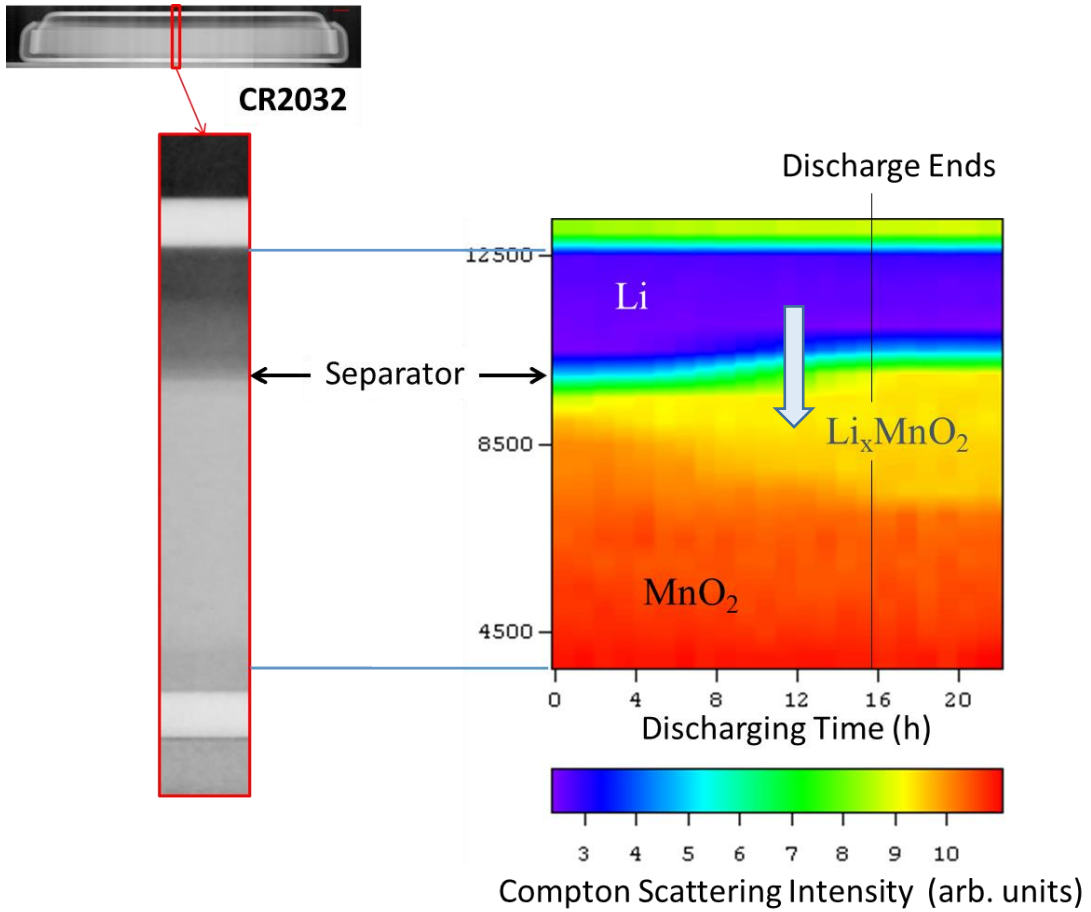
"Compton scattering imaging of a working battery using synchrotron high-energy X-rays,"
M. Itou *et al*., J. Synchrotron Rad. (2015). 22, 161–164

Advantages of Compton Scattering Imagine over X-rat CT Techniques :

① High-sensitivity to light-element materials and chemical states

② Applicable to a manufactured device, because of the use of high-energy X-rays.

③ No need of sample rotation



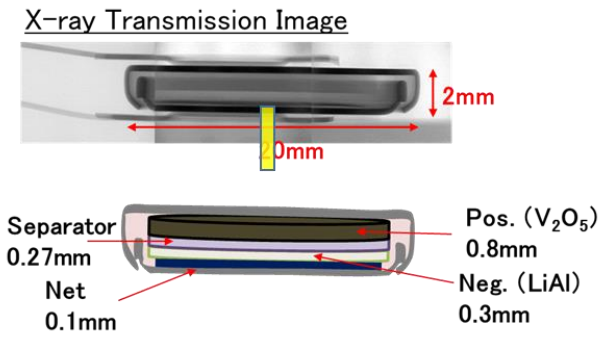
S-parameter Analysis of CSI on Battery

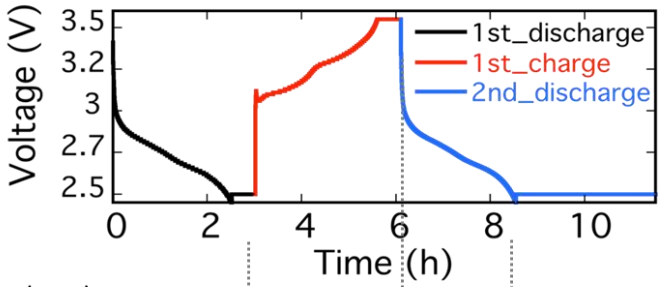
"In operando quantitation of Li concentration for a commercial Li-ion rechargeable battery using high-energy X-ray Compton scattering"

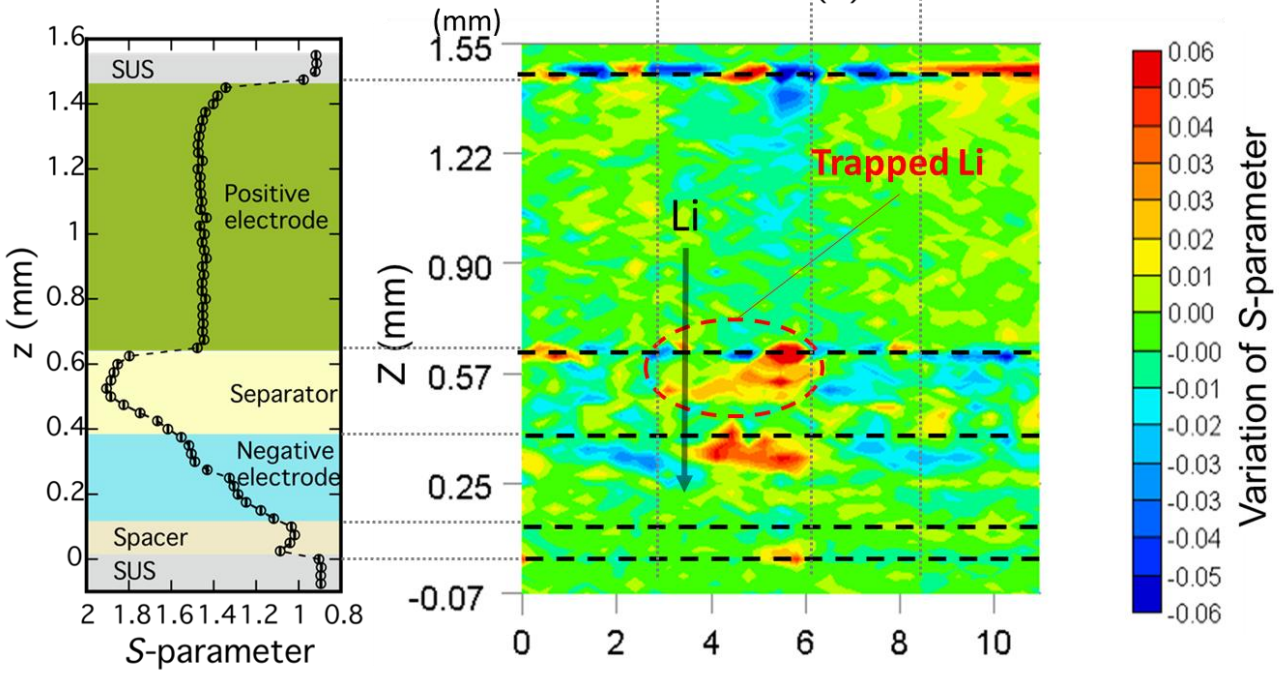
K. Suzuki *et al*., J. Synchrotron Rad. **24**, 1006–1011 (2017)

- Trapped Li in separator is the cause of degradation.

VL2020	
Positive Electrode	V_2O_5
Negative Electrode	LiAl
Electrolyte	1,2-dimethoxyethane
Capacity (mAh)	20
Voltage (V)	3



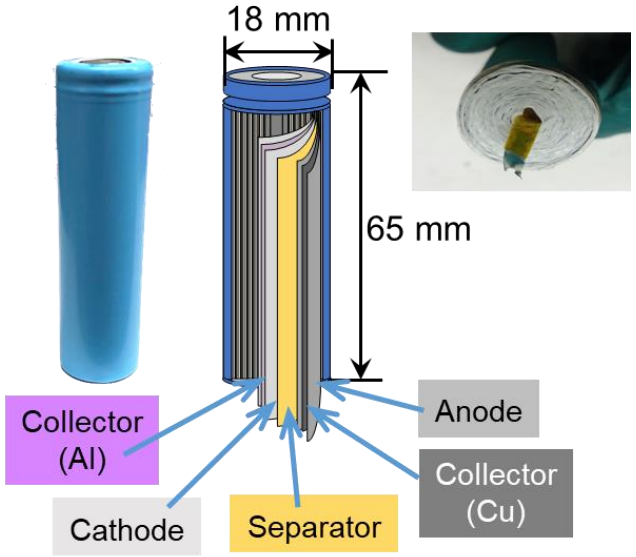


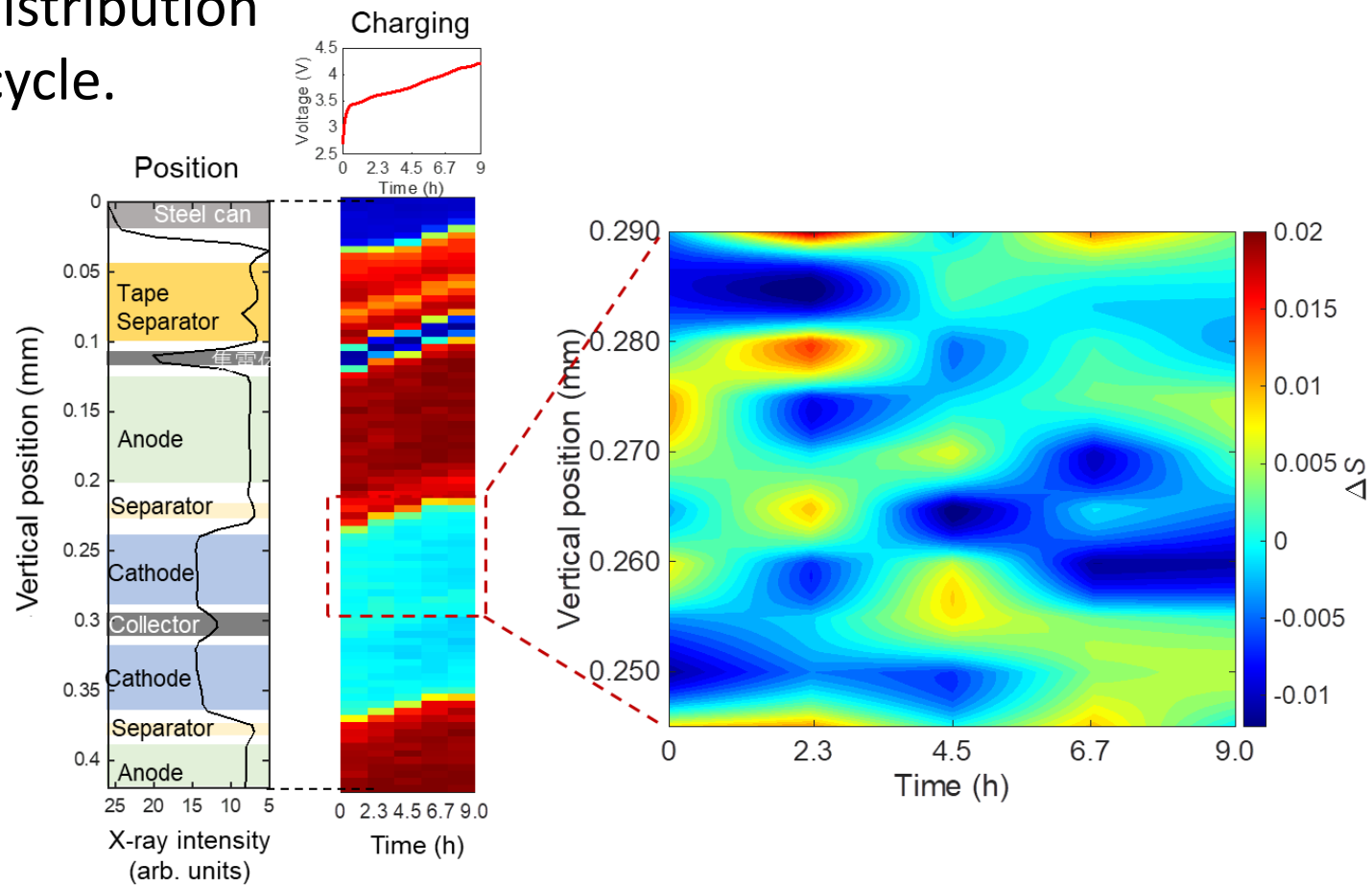


S-parameter Analysis of CSI on Battery

"Redox oscillations in 18650-type lithium-ion cell revealed by in operando Compton scattering imaging," K. Suzuki *et al*., Appl. Phys. Lett. **118**, 161902 (2021).

- This study reveals inhomogeneous Li distribution patterns during the charge-discharge cycle.



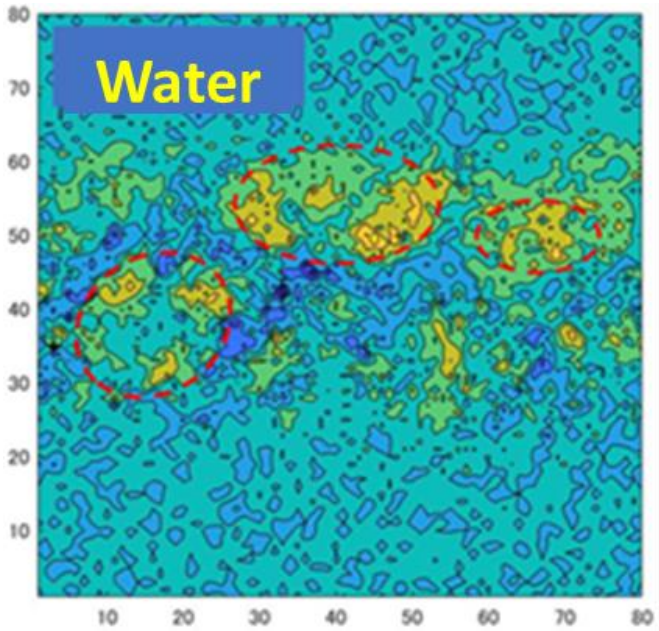


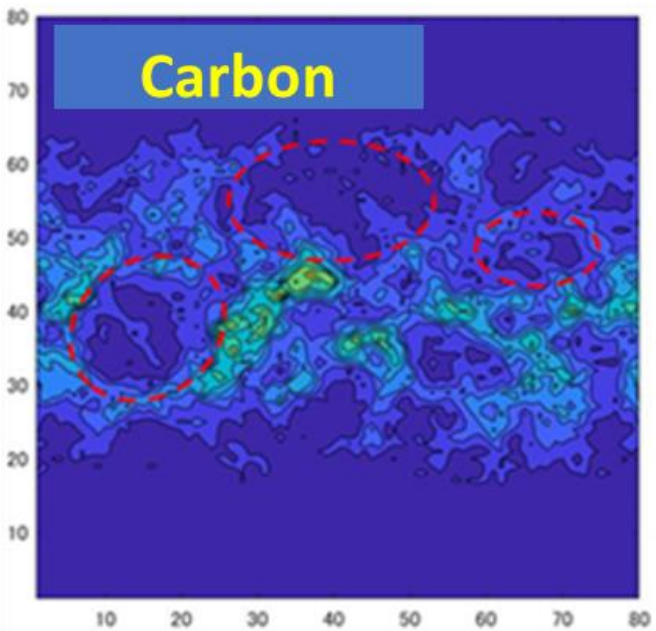
Visualizing Water in GDL Materials

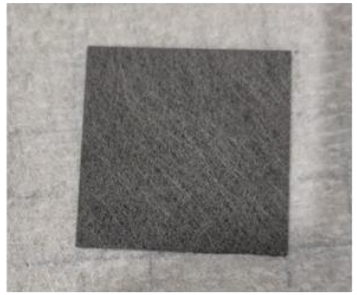
"Compton Scattering Imaging of Liquid Water in Porous Carbon-Based Materials"

N. Tsuji *et al*., Appl. Sci. **11**, 3851 (2021)

- This study successfully shows the cross-sectional distribution of liquid water, as well as the depth dependency of the water content

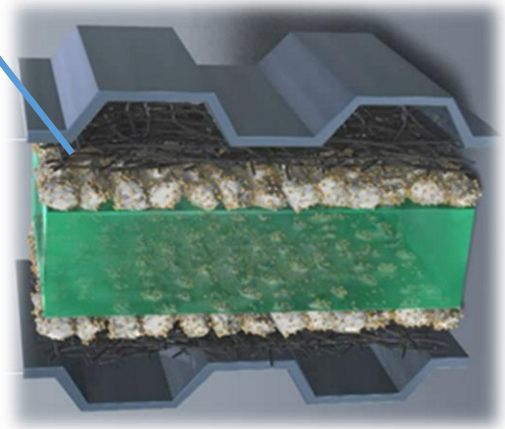






SAMPLE : TGP-H-030 (TORAY)	
SIZE	30 mm x 30 mm
THICKNESS	110 μm
POROSITY	80 %
BULK DENSITY	0.4 g/cm^3
MATERIALS	Carbon Fiber/ Carbon Composite

GDL: Gas Diffusion Layer



Concluding Remarks and Perspectives

- Synchrotron-based X-ray Compton scattering has a long history of about 40 years.
- The mainstream has been condensed matter physics, based on the electron momentum density studies.
- For the last decade, Compton scattering imaging has emerged for applied research and engineering under close collaboration with industries.
- The future of X-ray Compton scattering at high-energy synchrotrons is a hub that brides basic research, applied research and engineering.