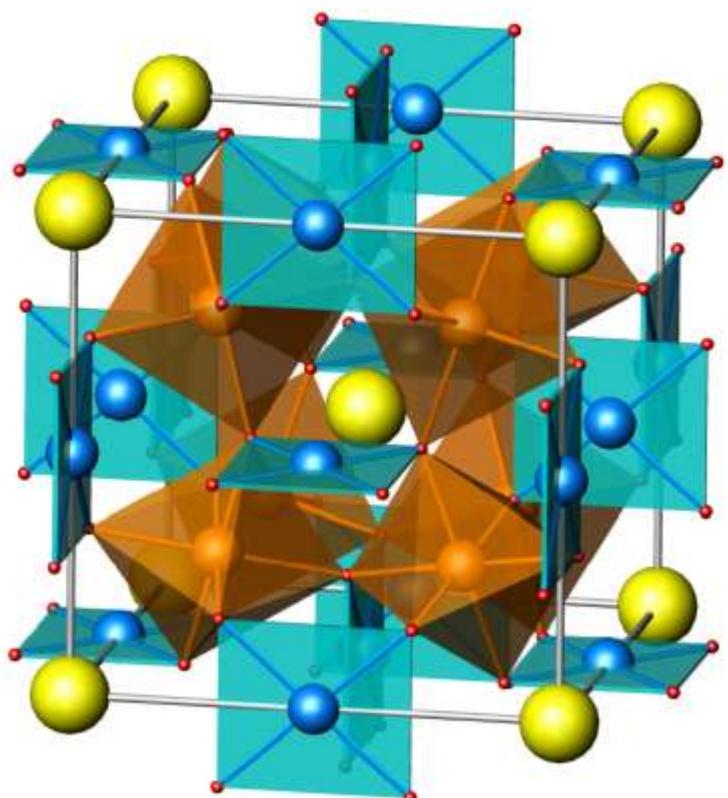


The electronic structure of A-site ordered perovskite $ACu_3Ru_4O_{12}$ ($A=La, Ca, Na$) by HAXPES



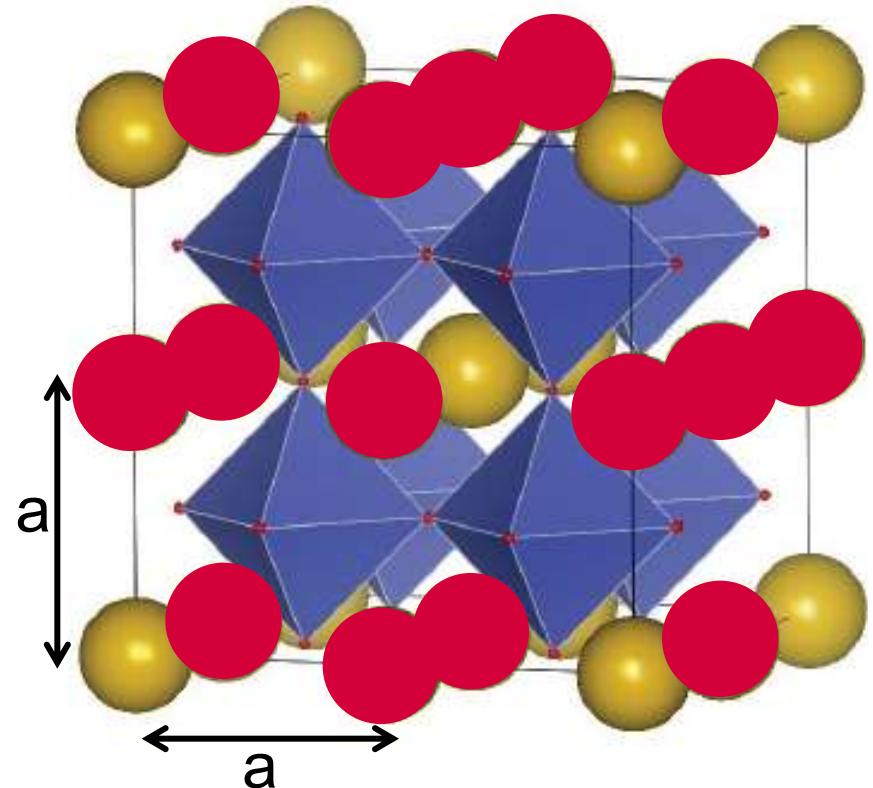
Munetaka TAGUCHI

RIKEN/SPring-8
Excited Order Research Team

2011 HAXPES
14-16/Sept/2011

- ✓ Introduction on A-site ordered perovskite
- ✓ Experiments
- ✓ Impurity model calculation
- ✓ Summary

Usual perovskite

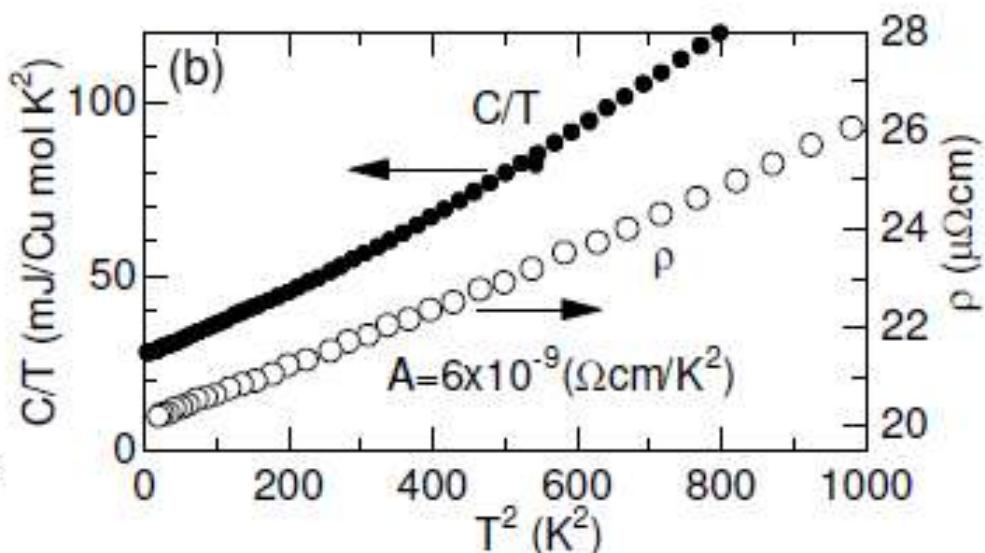
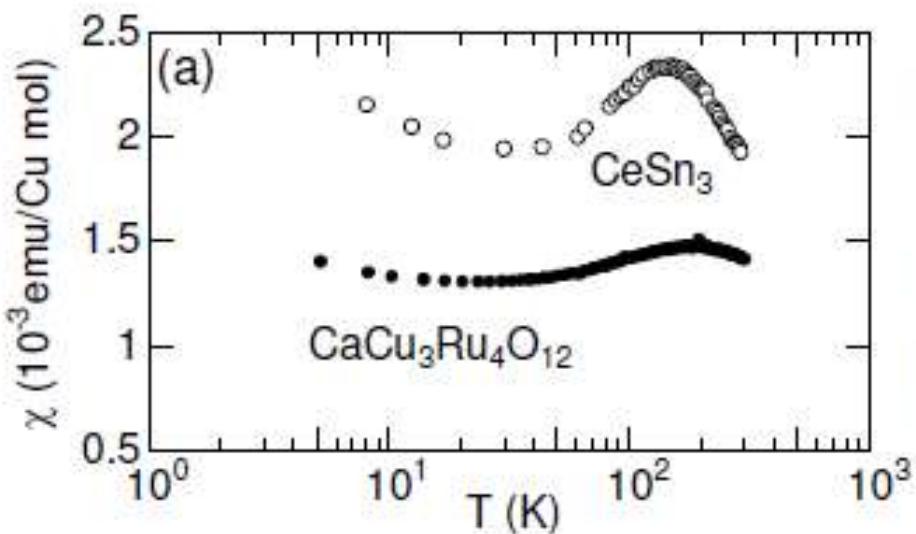


3 / 4 of the A sites are occupied by TM ions

Physical properties

Heavy-Mass behavior of $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$

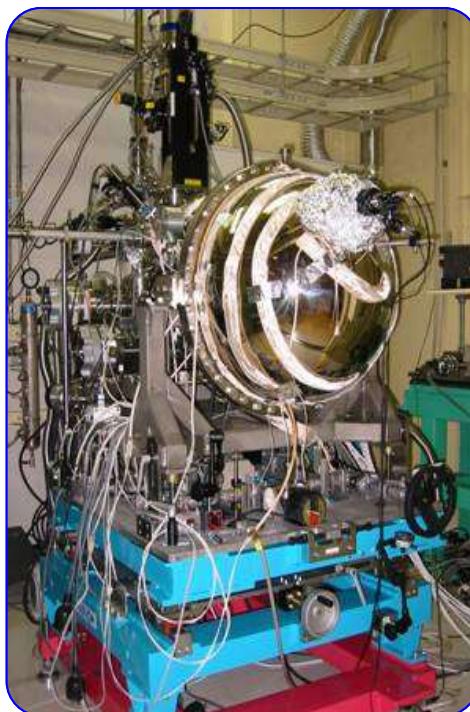
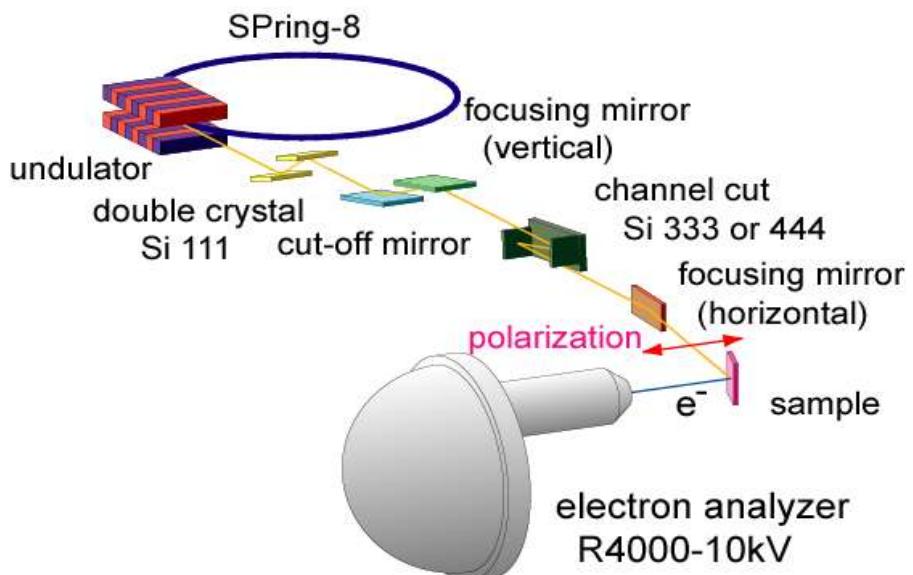
Kobayashi *et al.*, JPSJ **73** 2373 (2004)



1. Pauli paramagnetic susceptibility 1.4×10^{-3} emu/Cu mol
2. Magnetic susceptibility exhibits a broad peak at 200K
3. Specific heat coefficient $\gamma = 28\text{mJ}/(\text{Cu-mol K}^2)$
4. Satisfy the Kadowaki-Woods relation and the Wilson ratio

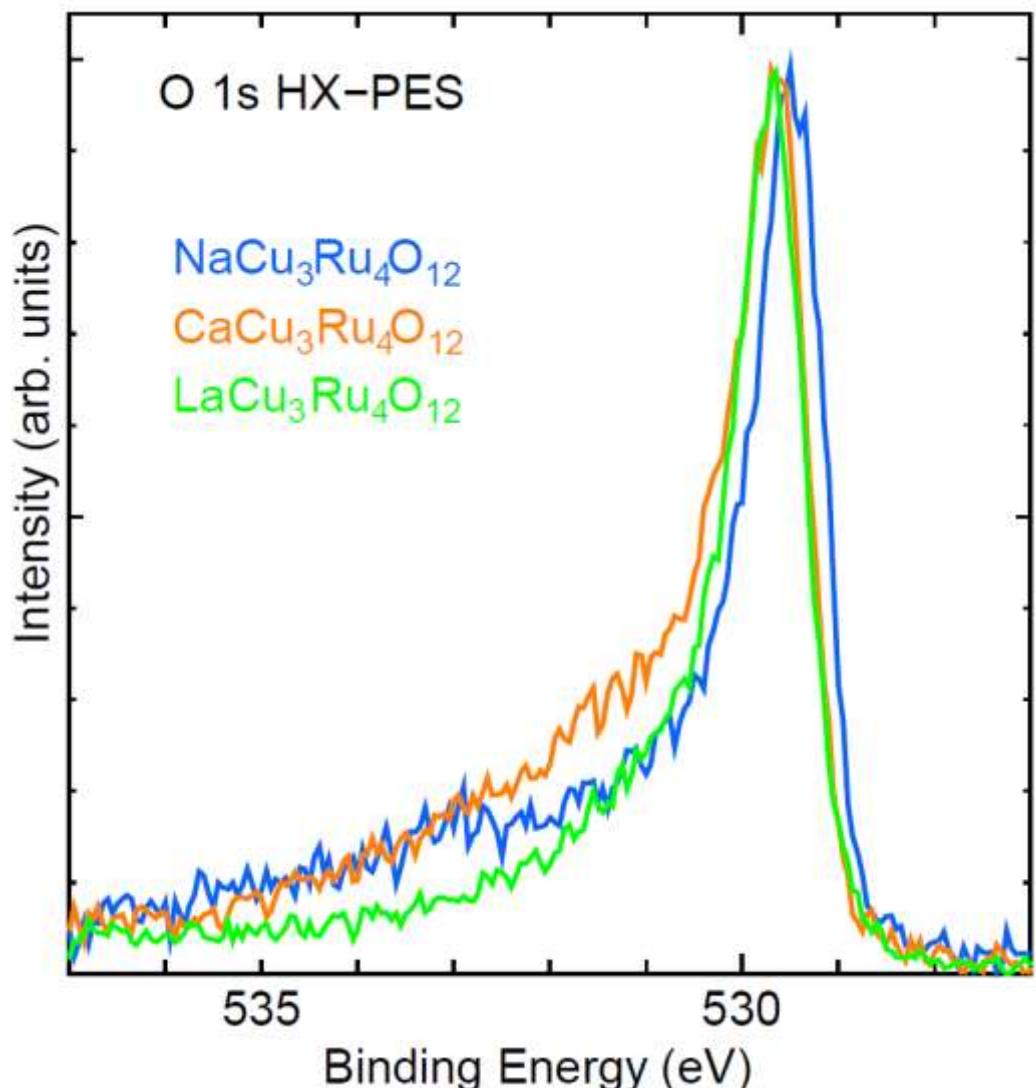
Experiment @BL29XU / SPring-8

Y. Takata *et al.*, Nuclear Instrum. and Methods A547, 50 (2005).
T. Ishikawa *et al.*, Nuclear Instrum. and Methods A547, 42 (2005).



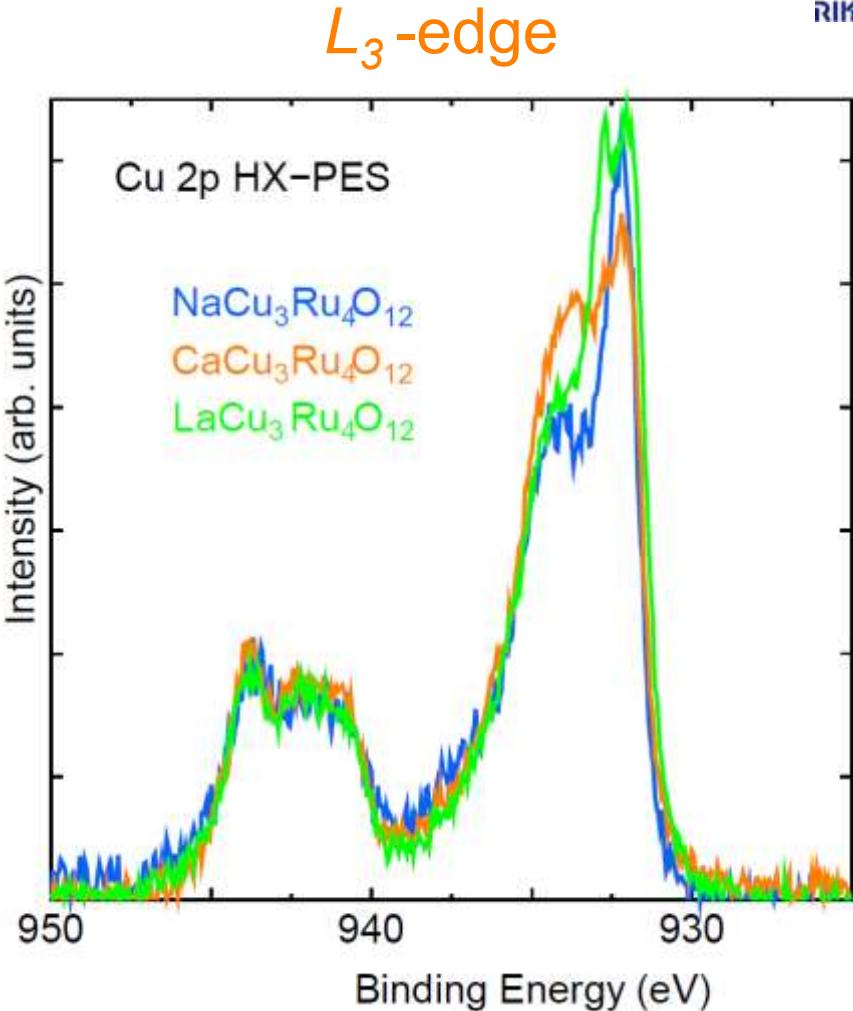
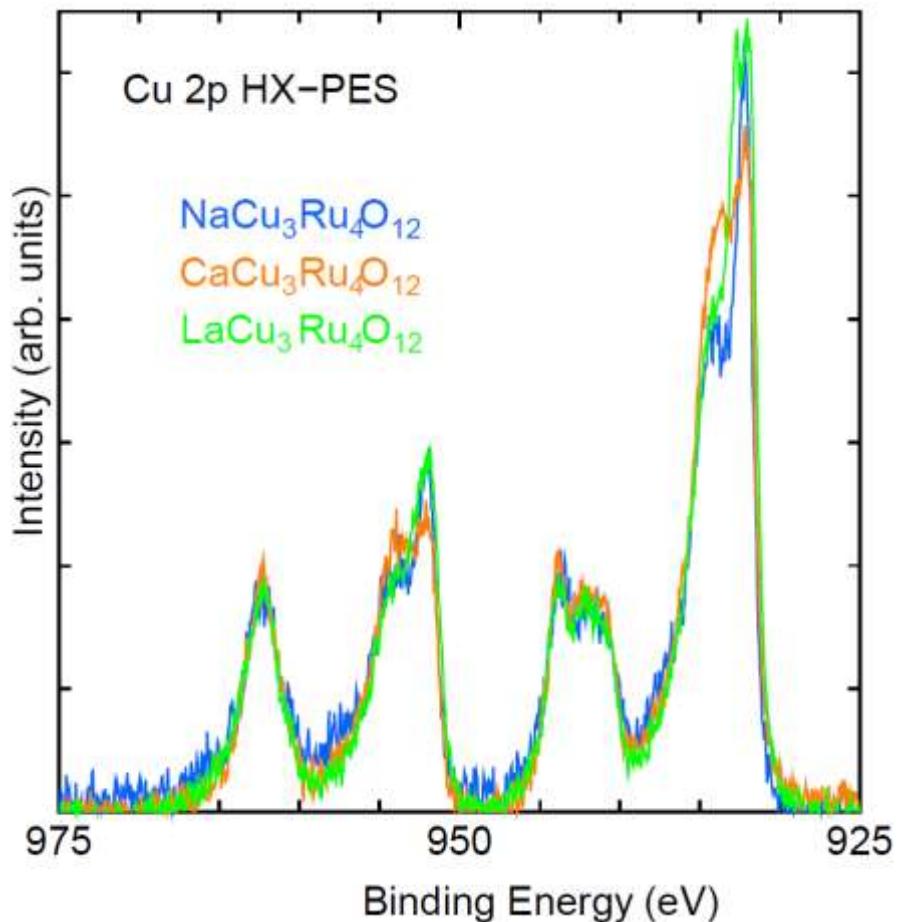
- ★ Photon Energy: 7.94keV, Resolution $\Delta E (hv)$: 150meV
- ★ photon flux: 10^{11} photons/sec @ 55(V)x 35(H) μm^2
- ★ Electron Analyzer: R4000-10kV (VG Scienta)
- ★ Base Pressure : $< 10^{-7}$ Pa

Experiments O 1s HX-PES



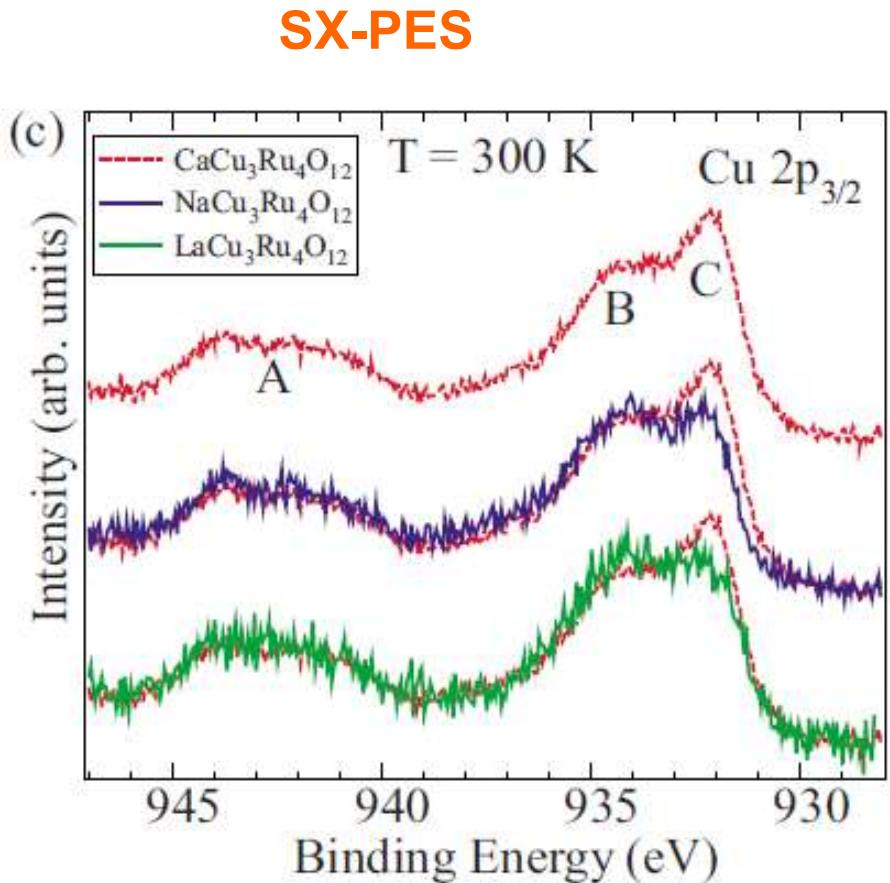
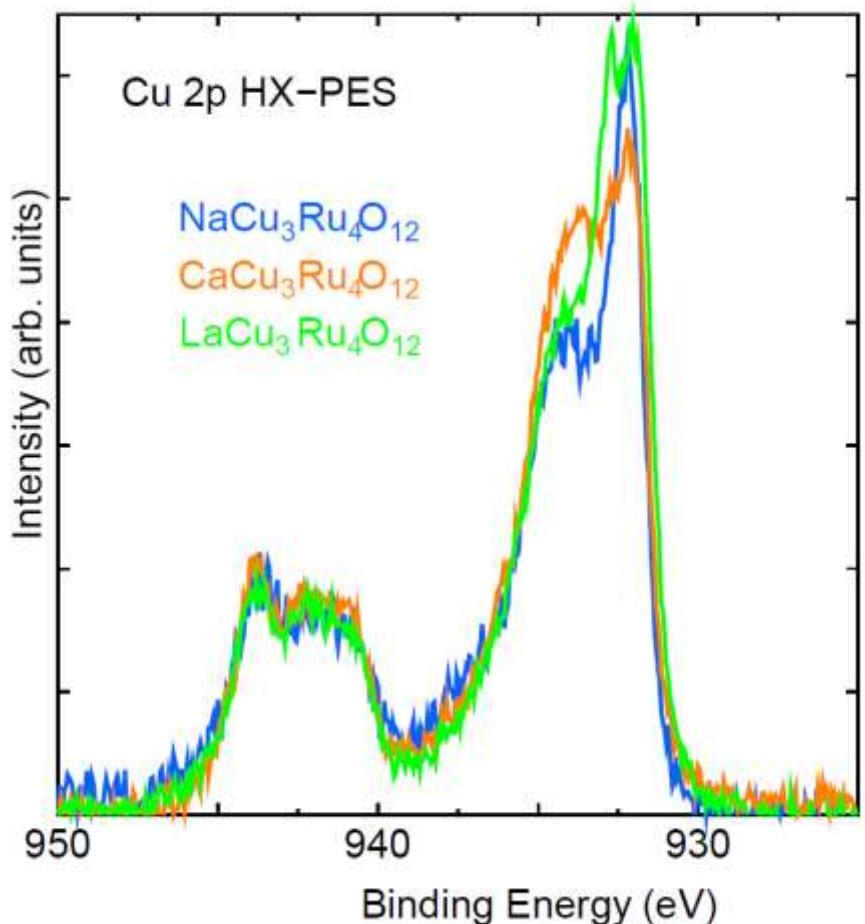
The main peak is shifted to the lower binding energy side in going from $\text{LaCu}_3\text{Ru}_4\text{O}_{12}$ to $\text{NaCu}_3\text{Ru}_4\text{O}_{12}$.

Experiments Cu 2p HX-PES



**Cu 2p spectra strongly depend on the replacement
of A-site Ca by Na and La !!.**

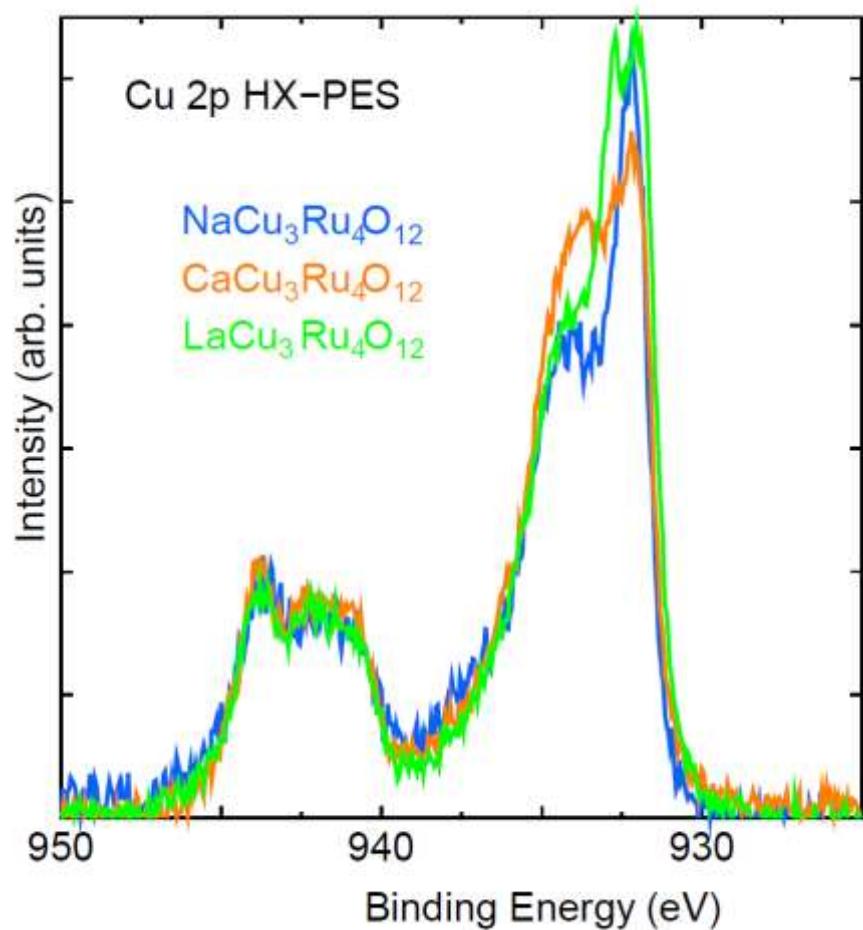
Experiments



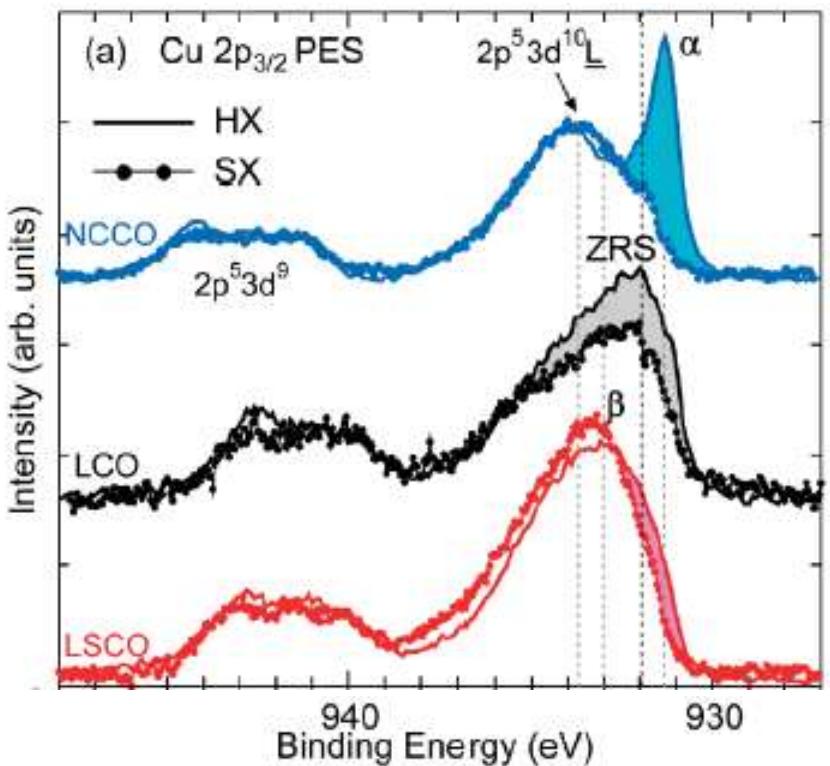
Sudayama *et al.*, PRB **80** 075113 (2009)

HX-PES spectra are drastically different from the previous results with soft x-ray.

Experiments

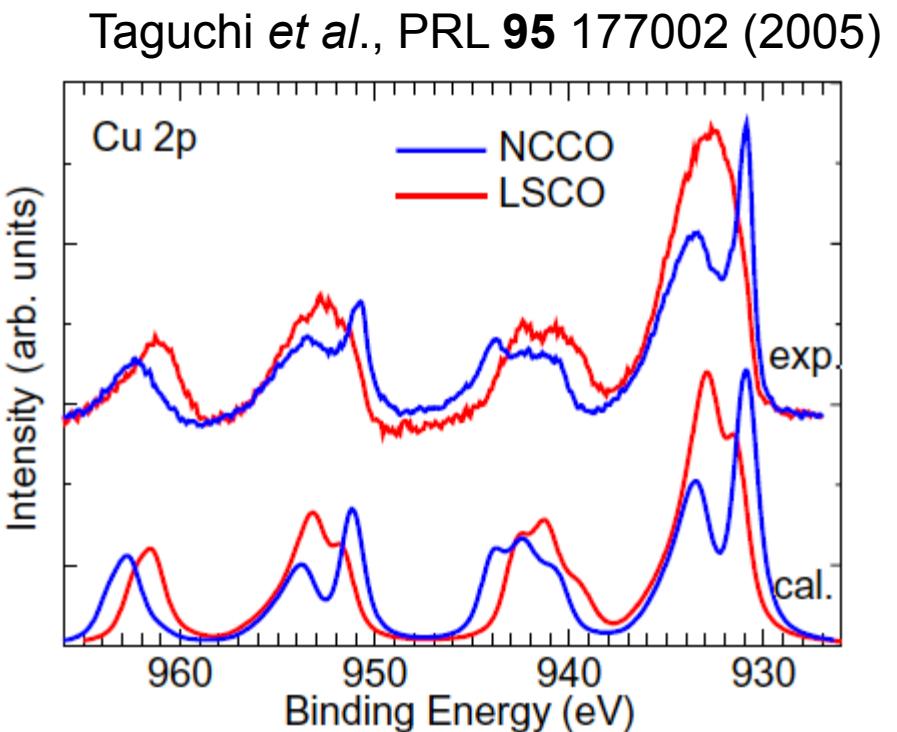
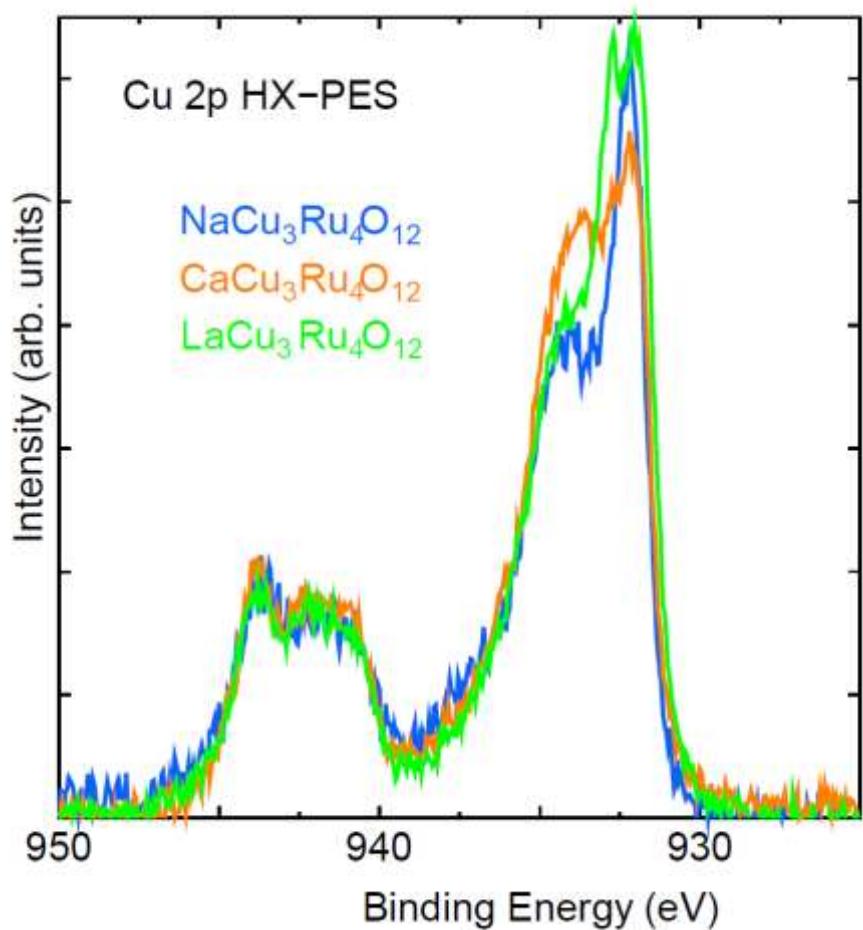


Taguchi *et al.*, PRL **95** 177002 (2005)



There are three structures in the main line.

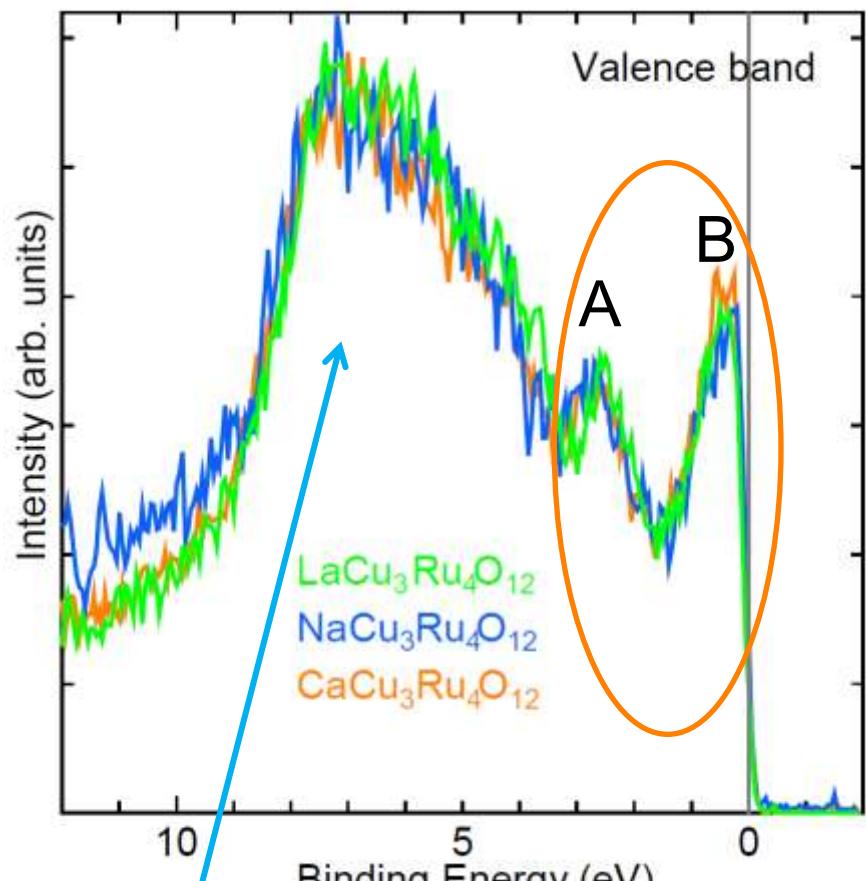
Experiments



$3d^9$, $3d^{10}\underline{\text{L}}$, $3d^{10}\underline{\text{Z}}$

There are three structures in the main line.

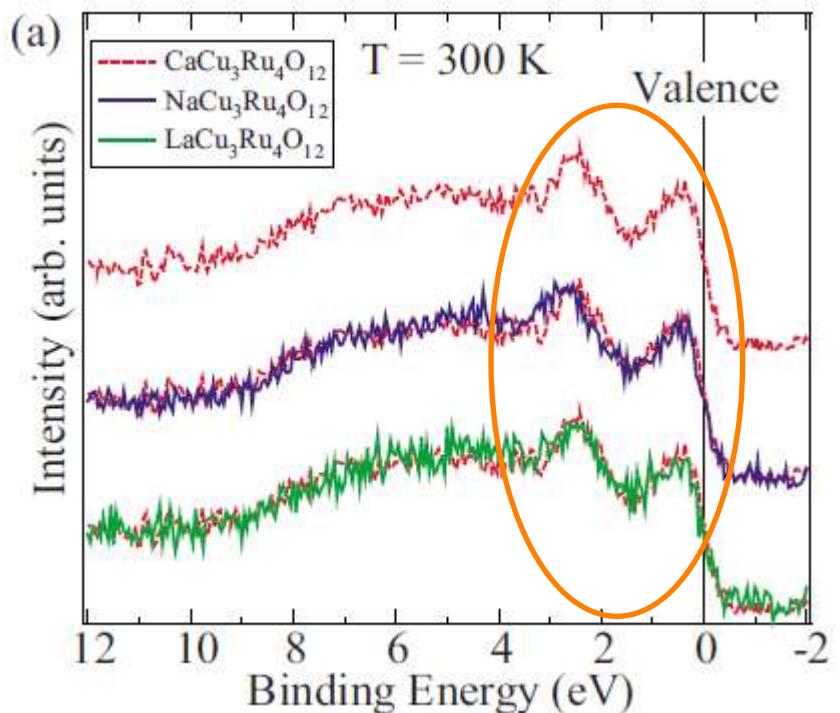
HX-PES



4s states

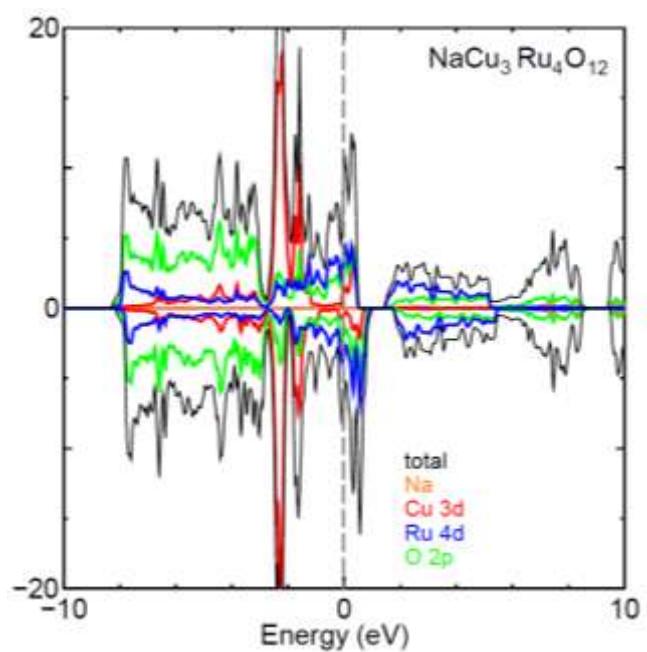
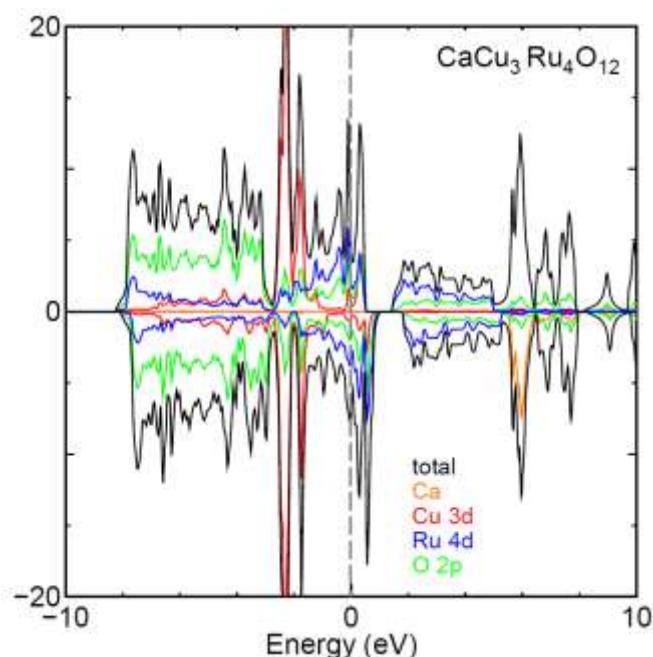
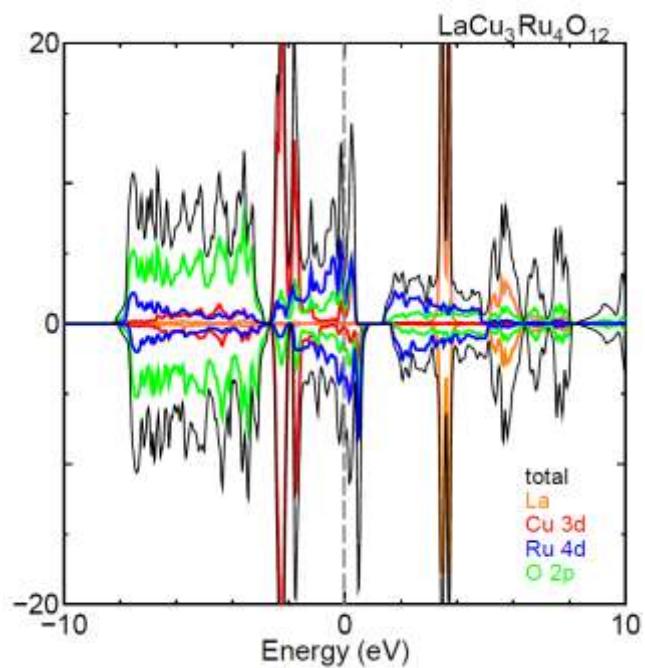
The intensity ratio between first
two peaks are changed in HX-PES.

SX-PES



Sudayama *et al.*, PRB **80** 075113 (2009)

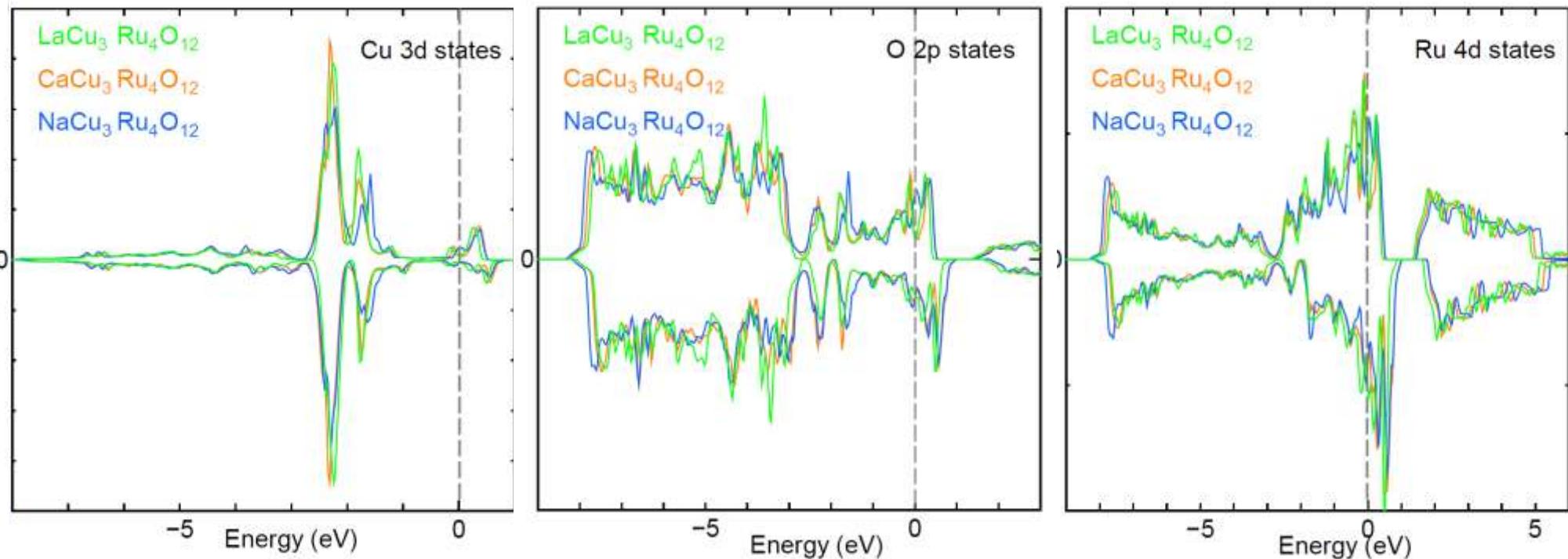
Full-potential linearized augmented plane-wave calculations with GGA
(Wien2k code)



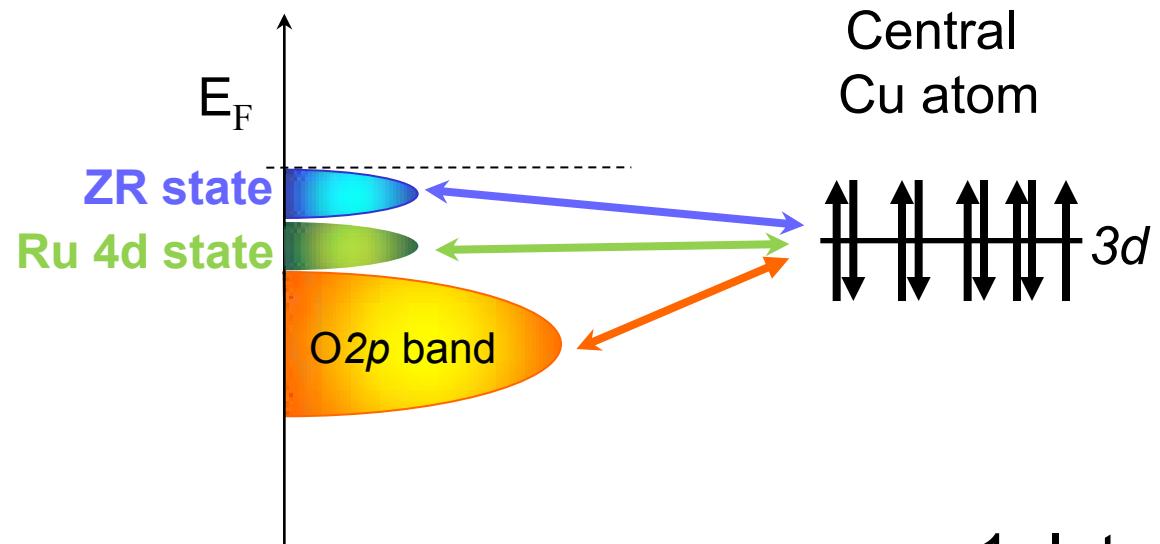
almost the same band structure

Band structure calculation

Partial density of states (PDOS)



Impurity model with full multiplet (D_{4h})



1. Intra atomic multiplet
- 2 . Hybridization between
O 2p and Cu 3d
- 3 . Screening from ZR state
4. Screening from Ru 4d state

Hamiltonian

$$H = \sum_{\Gamma\sigma} \varepsilon_{3d}(\Gamma) a_{3d,\Gamma\sigma}^\dagger a_{3d,\Gamma\sigma} + \sum_{m\sigma} \varepsilon_{2p} a_{2p,m\sigma}^\dagger a_{2p,m\sigma} + H_{\text{mult.}}$$

Cu 3d **Cu 2p** **multiplet**

$$+ U_{dd} \sum_{(\Gamma\sigma) \neq (\Gamma'\sigma')} a_{3d,\Gamma\sigma}^\dagger a_{3d,\Gamma\sigma} a_{3d,\Gamma'\sigma'}^\dagger a_{3d,\Gamma'\sigma'}$$

Cu 3d Coulomb interaction

$$- U_{dc} \sum_{\Gamma m\sigma\sigma'} a_{3d,\Gamma\sigma}^\dagger a_{3d,\Gamma\sigma} (1 - a_{2p,m\sigma'}^\dagger a_{2p,m\sigma'})$$

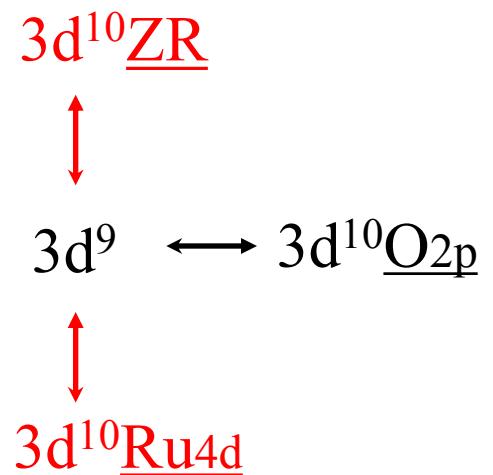
Cu 2p-3d core-hole potential

$$+ \sum_{X,k,\Gamma\sigma} \varepsilon_X(k) a_{X,k\Gamma\sigma}^\dagger a_{X,k\Gamma\sigma} + \sum_{X,k,\Gamma\sigma} \frac{t_X(\Gamma)}{\sqrt{N}} (a_{3d,\Gamma\sigma}^\dagger a_{X,k\Gamma\sigma} + a_{X,k\Gamma\sigma}^\dagger a_{3d,\Gamma\sigma})$$

X band states
(X=O 2p, Ru 4d, and Zhan-Rice)

Screening from X band to Cu 3d state

Ground state :
linear combination of 4 configurations



Slater Integrals (Racah parameter) are calculated by Hartree-Fock method and are rescaled by 85%

Parameters

$t_x (\Gamma)$: Hybridization

U_{dd} : On-site Coulomb interaction

U_{dc} : Core-hole potential

Δ_x : Charge transfer energy

$X = 2p$: O 2p band
 $X = 4d$: Ru 4d t_{2g} band
 $X = ZR$: Zhang-Rice band

$$\Delta_X = \varepsilon_{3d} - \varepsilon_X + 9U_{dd}$$

$W(X)$: band width

$$\varepsilon_X(k) = \varepsilon_X + \frac{W(X)}{N} \left(k - \frac{N+1}{2} \right)$$

$$k = 1, \dots, N$$

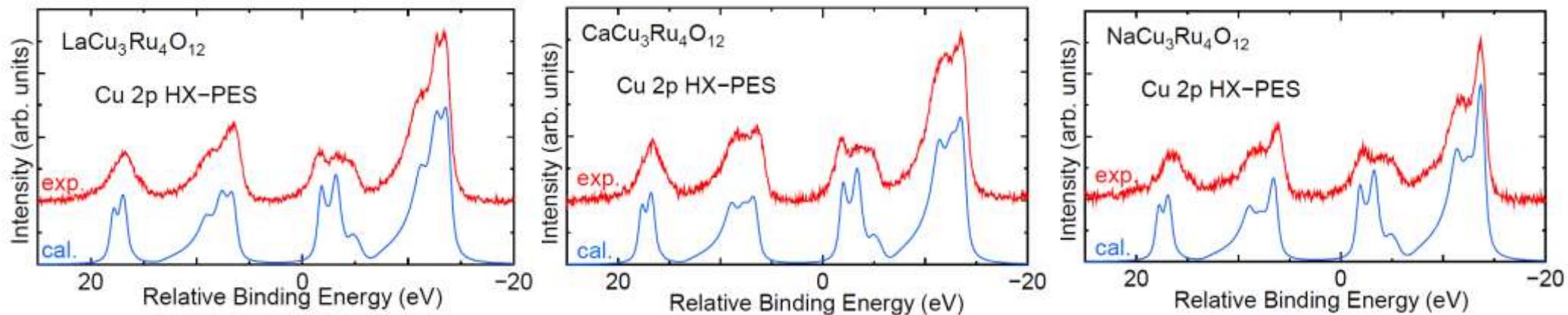
Rectangular band
(N discrete levels)

Calculated Results

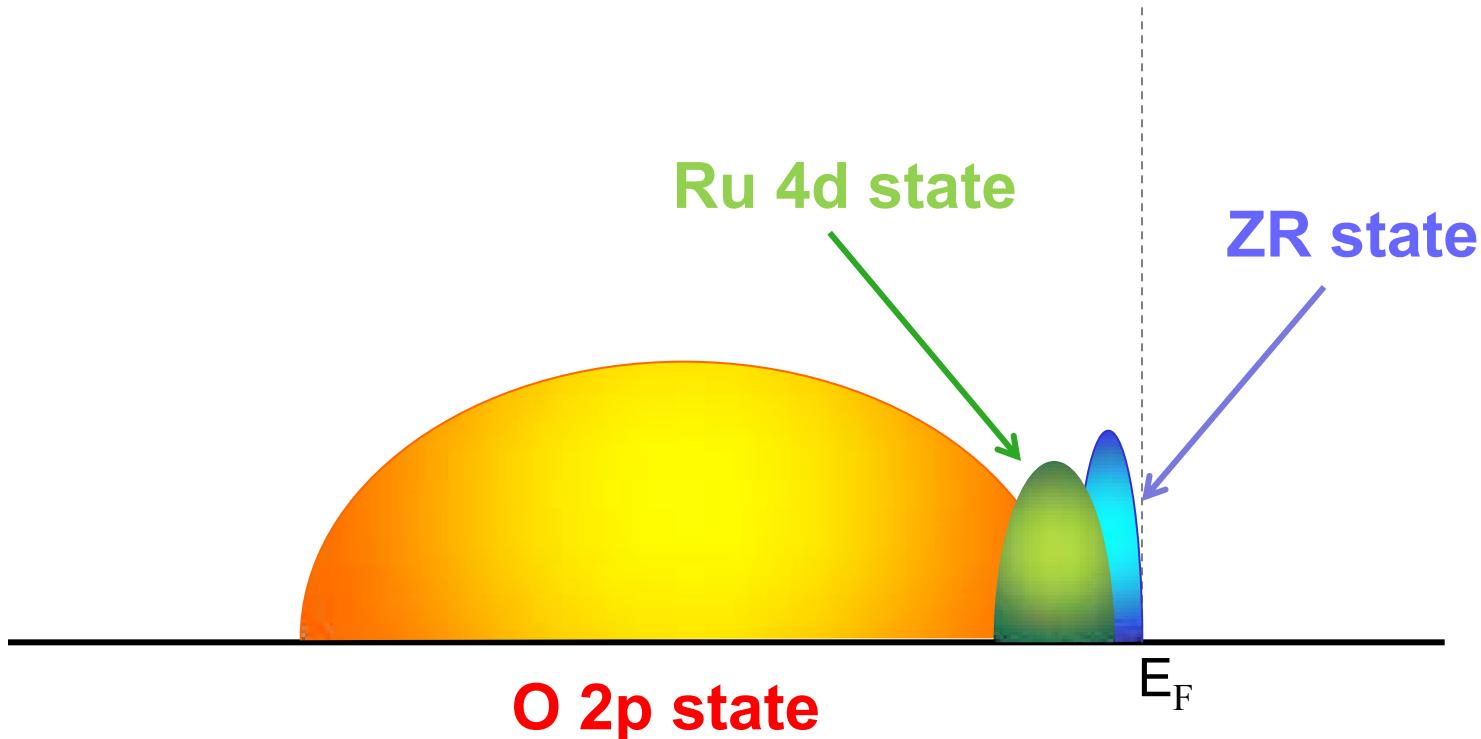
Table

System independent parameters							
U_{dd}	U_{dc}	Δ_{2p}	$t_{2p}(b_{1g})$	$W(2p)$	$W(4d)$	$W(ZR)$	N
7.0	10.0	4.8	3.73	4.5	1.5	1.0	13

System dependent parameters				
System	Δ_{4d}	$t_{4d}(b_{1g})$	Δ_{ZR}	$t_{ZR}(b_{1g})$
$\text{NaCu}_3\text{Ru}_4\text{O}_{12}$	2.85	0.94	1.6	1.49
$\text{CaCu}_3\text{Ru}_4\text{O}_{12}$	2.95	0.971	1.78	1.19
$\text{LaCu}_3\text{Ru}_4\text{O}_{12}$	2.85	1.170	1.55	1.22



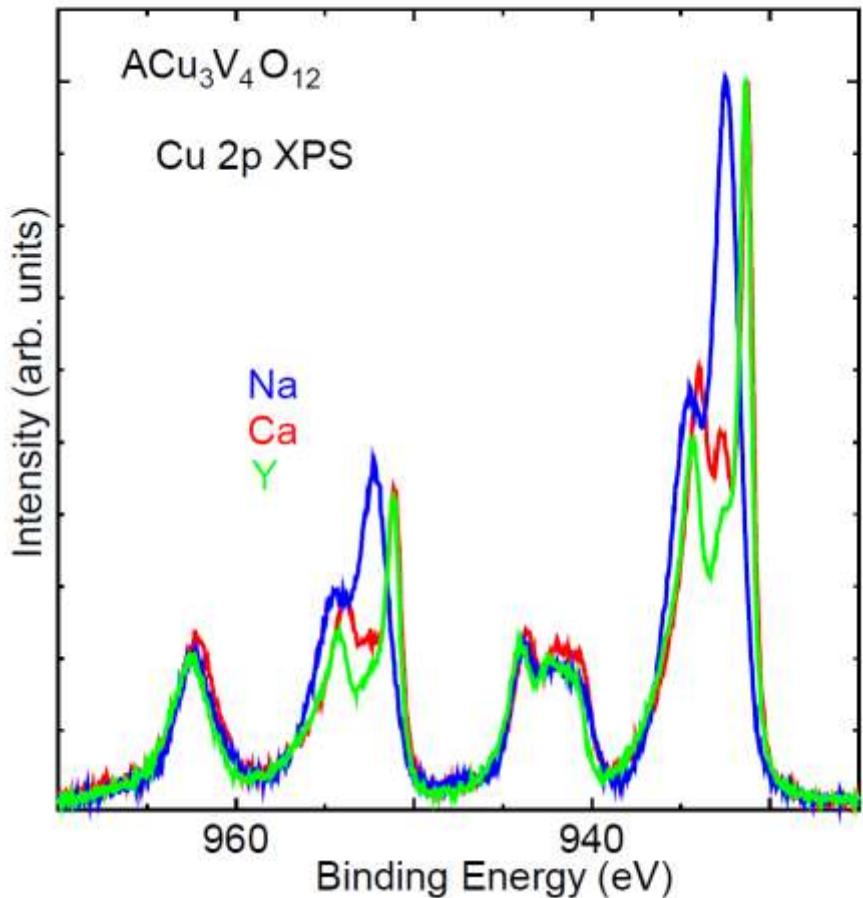
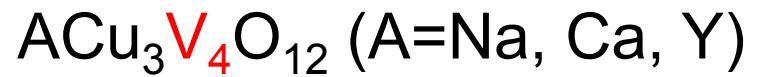
Energy Diagram



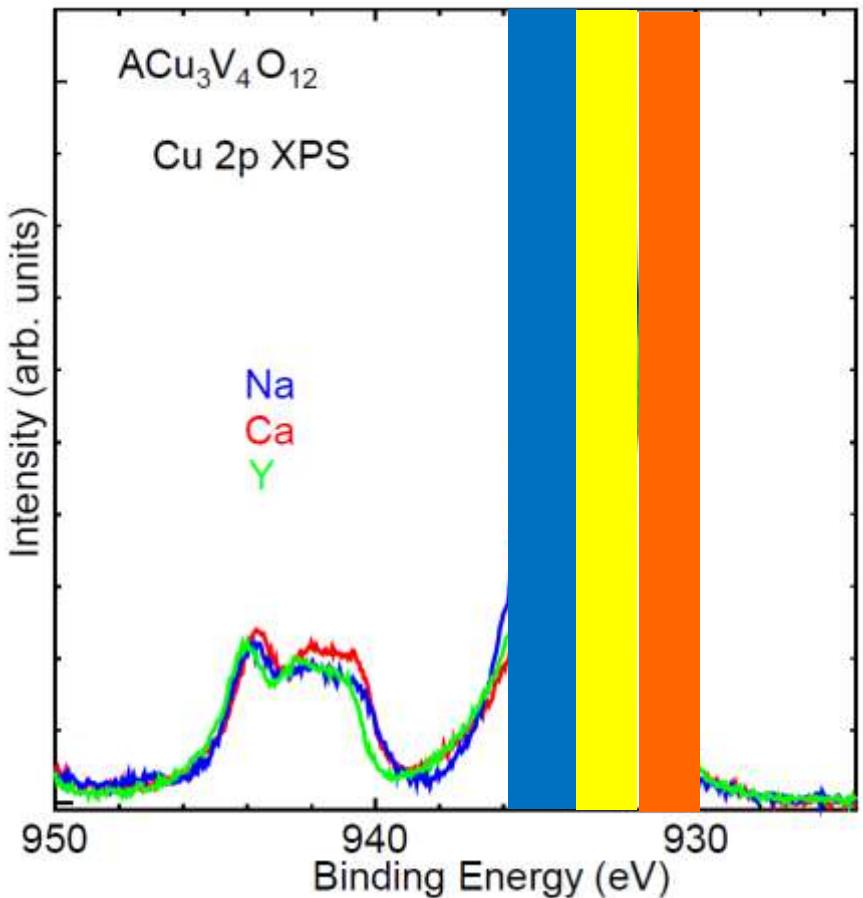
Negligible shift in O 2p and Ru 4d states
from $\text{LaCu}_3\text{Ru}_4\text{O}_{12}$ to $\text{NaCu}_3\text{Ru}_4\text{O}_{12}$.

Systematic change in the intensity of Ru 4d
states from $\text{LaCu}_3\text{Ru}_4\text{O}_{12}$ to $\text{NaCu}_3\text{Ru}_4\text{O}_{12}$.

Other A-site ordered perovskite



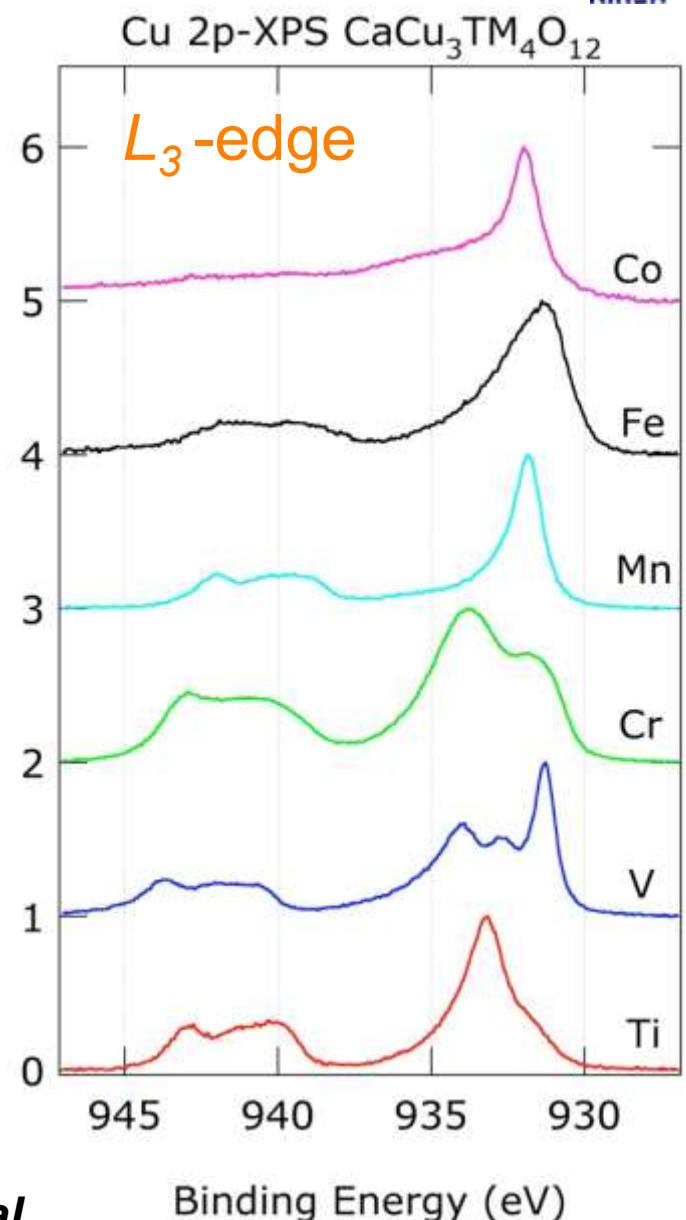
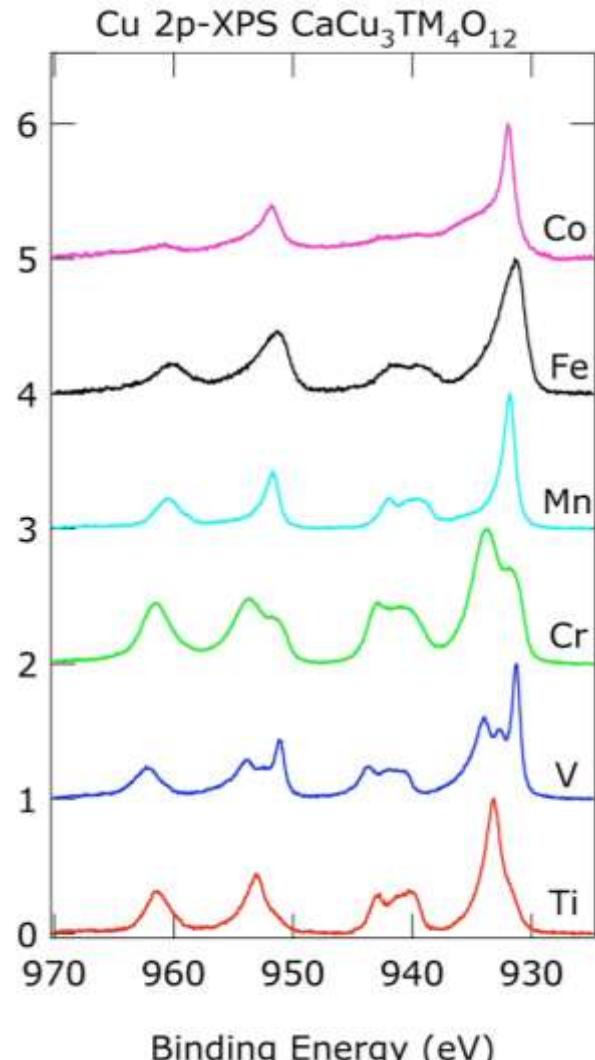
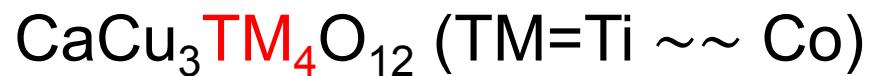
L_3 -edge



Mizumaki & Mizokawa *et al.*

Experiments: BL47XU @ SPring-8

Other A-site ordered perovskite



Mizumaki & Mizokawa et al.
Experiments: BL47XU @ SPring-8

Summary

- ✓ New structures in Cu 2p spectra
- ✓ Those peaks strongly depend on the A-site atom
- ✓ impurity calculation with D_{4h} local symmetry
- ✓ Resonant photoemission is needed for the assignment of the valence band character.

Acknowledgements

RIKEN/SPring-8
Excited Order
Research Team.

S. Shin
Y. Takata
A. Chainani
E. Eguchi
M. Matsunami

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T. Ishikawa
M. Yabashi
K. Tamasaku
Y. Nishino

Univ. of Tokyo

T. Mizokawa
T. Sudayama

JASRI/SPring-8

M. Mizumaki

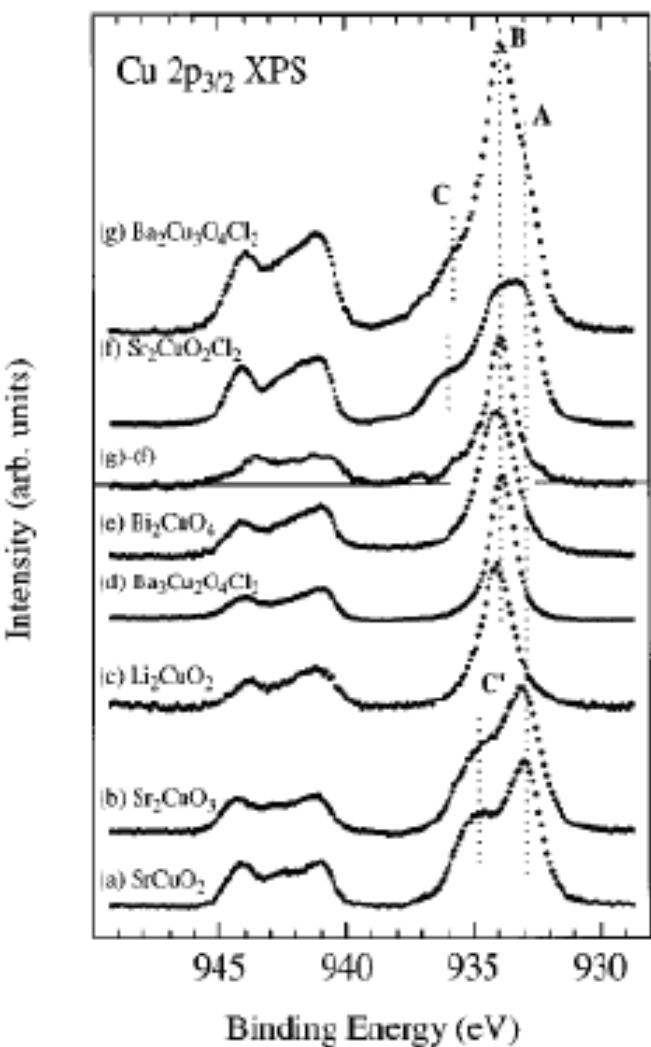
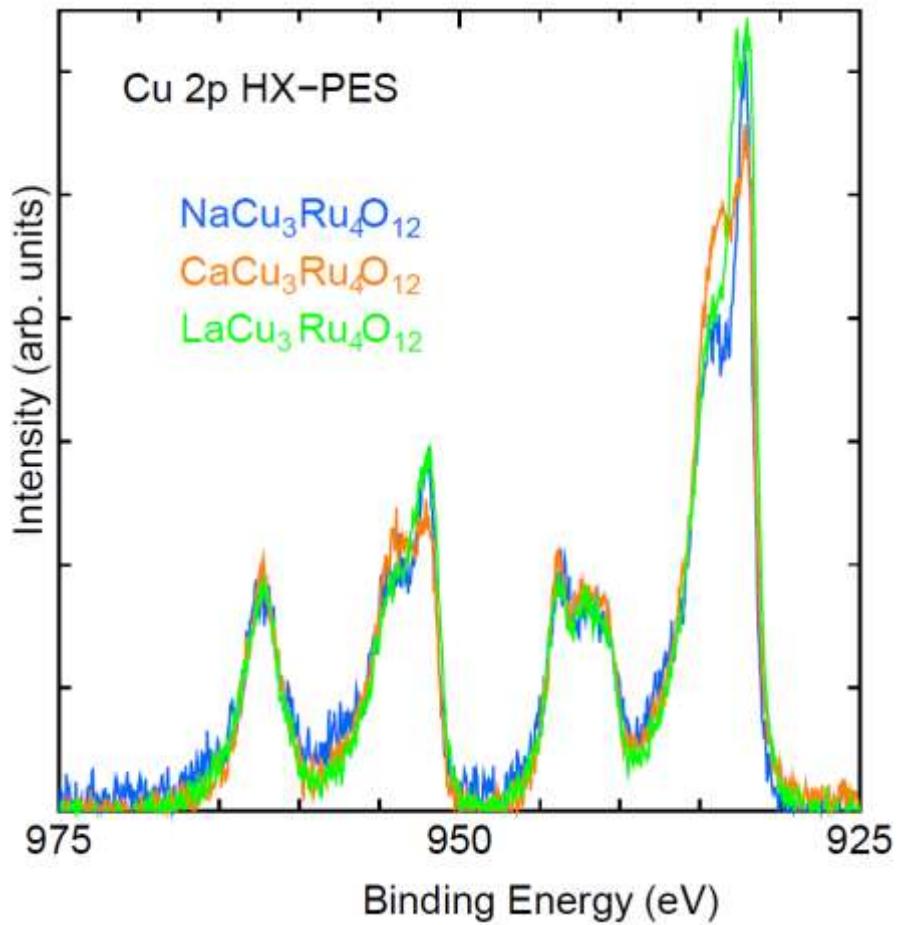
Kyoto Univ.

Y. Maeno
S. Yonezawa
H. Takatsu
S. Tanaka

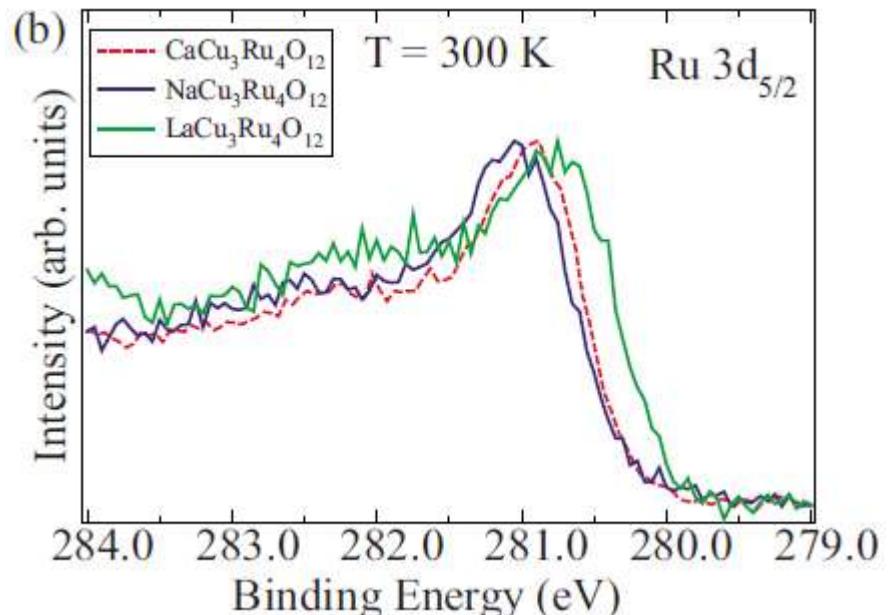
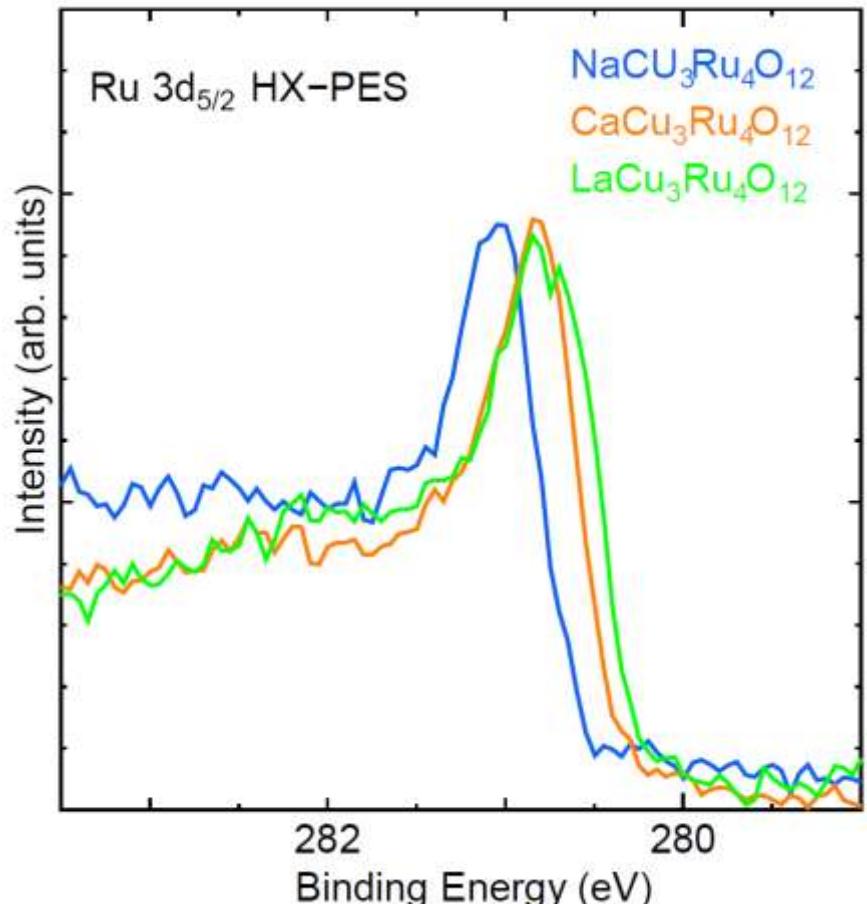
Thank You very much for your attention

Experiments

Boske *et al.*, PRB (1998)

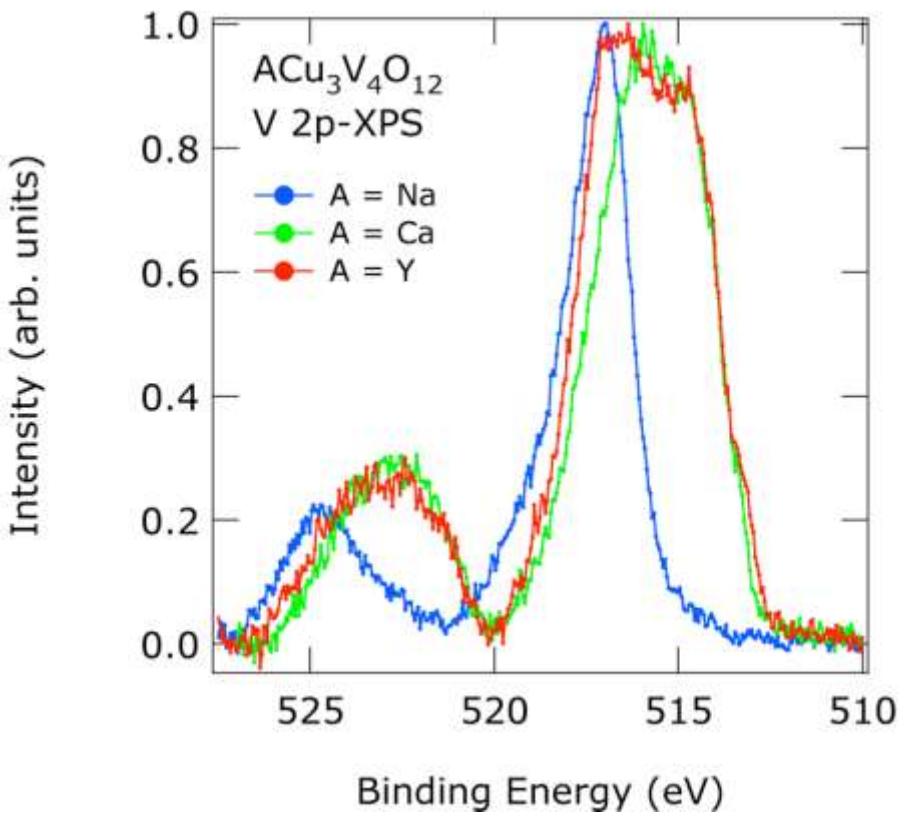
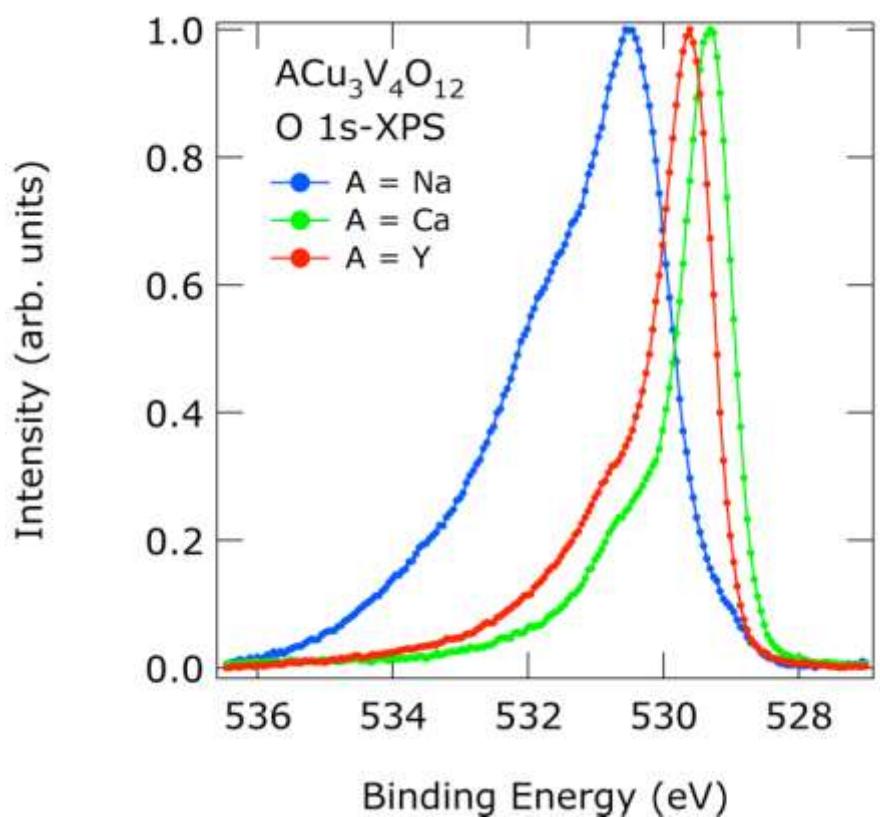


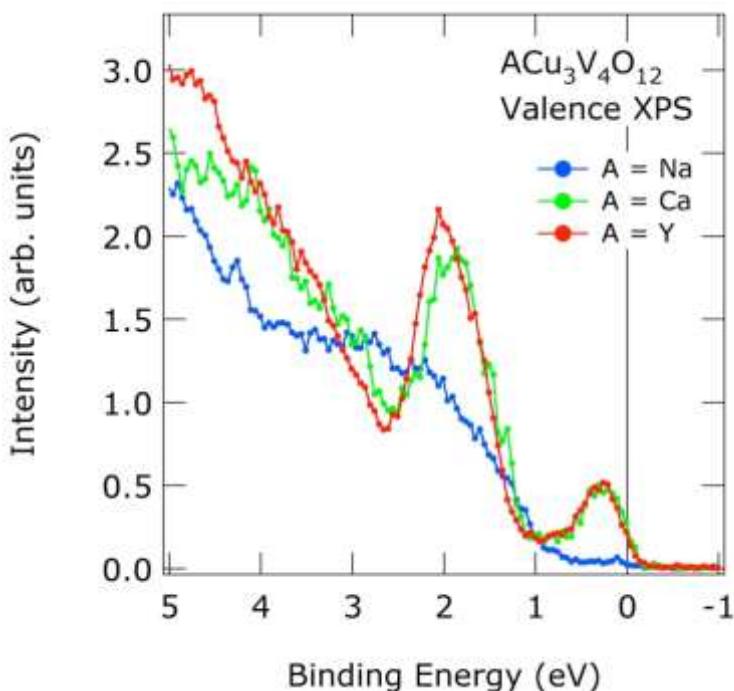
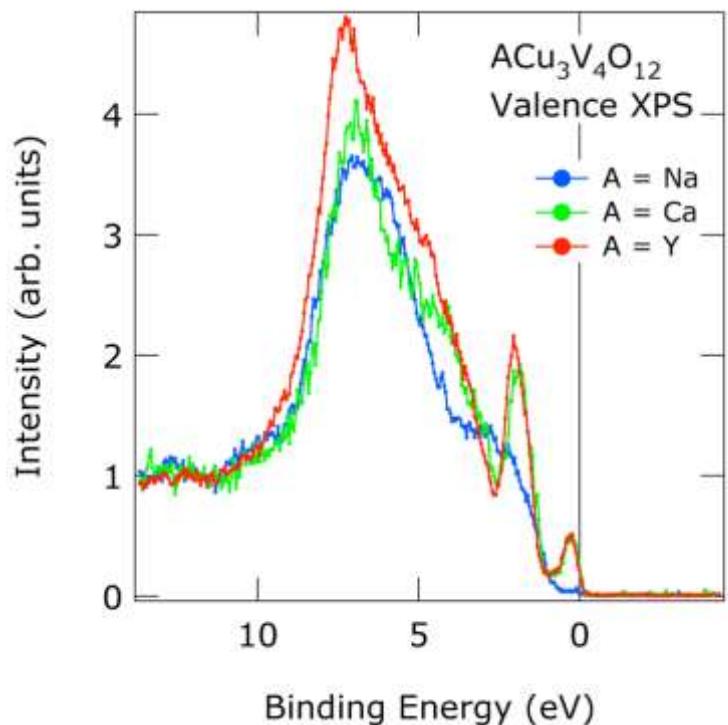
Ru $3d_{5/2}$ HX-PES

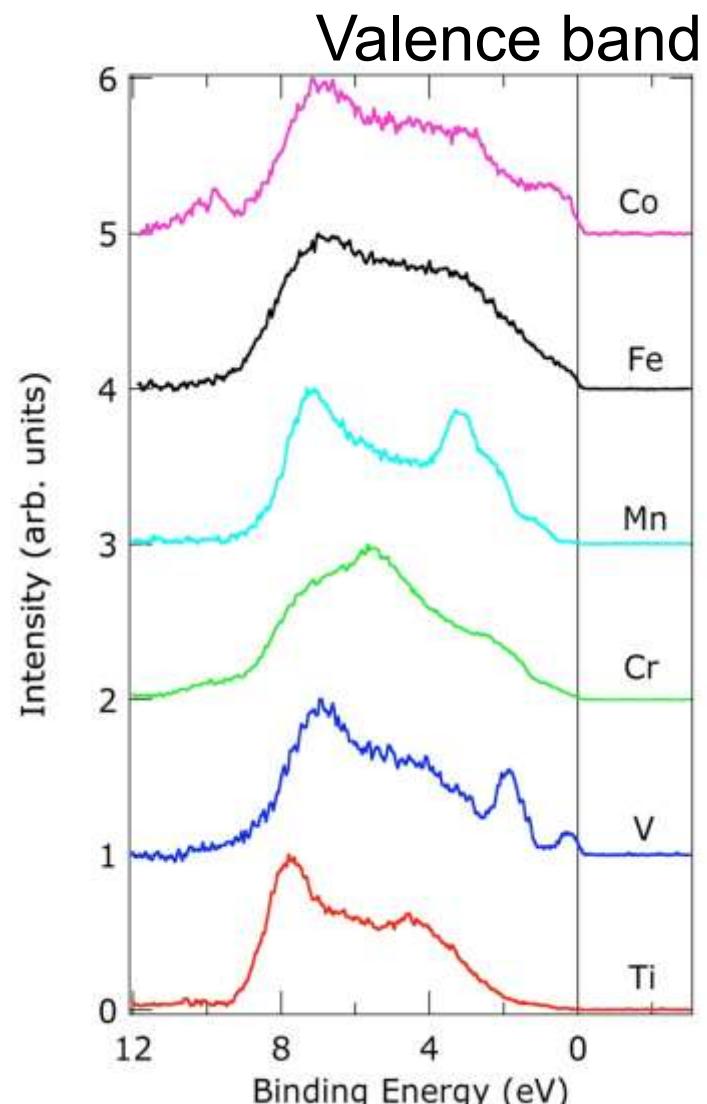


Sudayama *et al.*, PRB **80** 075113 (2009)

HX-PES spectra of Ru $3d_{5/2}$ core-level are also very similar to the previous results with soft x-ray.







metallic
metallic
Semi-conductor
metallic
metallic
insulator

