

強相関電子系の軌道状態とX線分光

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強相関遷移金属化合物

多彩な物性を示す

① 電気特性 金属 ReO_3 半導体 TiO_2 絶縁体 SrTiO_3

超伝導 $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{LaFeAsO}_{1-x}\text{F}_x$

金属絶縁体転移 VO_2 , V_2O_3 , NiS , CuIr_2S_4

② 磁性 強磁性体 CrO_2 , SrRuO_3 , YTiO_3

反強磁性体 FeO , CoO , NiO , La_2CuO_4

巨大磁気抵抗 $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$

③ 誘電性 強誘電体 BaTiO_3 常誘電体 SrTiO_3

マルチフェロイクス

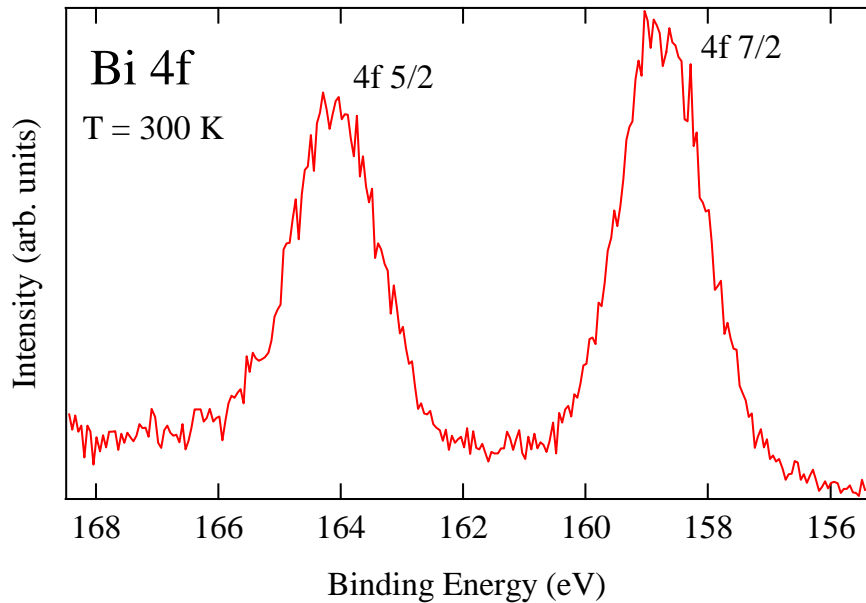
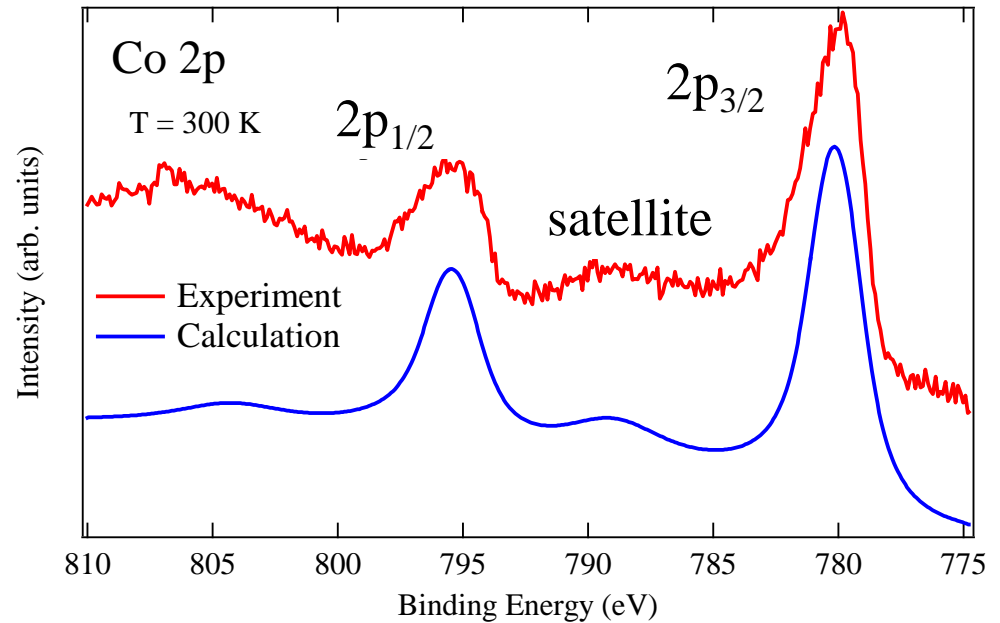
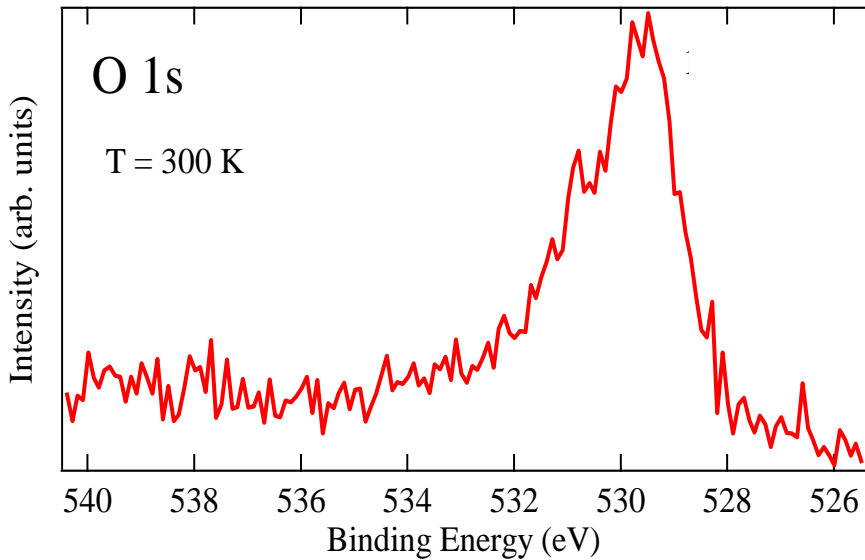
④ 熱電特性 Na_xCoO_2

強相関遷移金属酸化物の軟X線吸収分光（1990年代）

Photon Factory BL-2B 10m斜入射分光器 遷移金属 2p, 酸素 1s 吸収端

- T. Mizokawa, A. Fujimori, T. Arima, Y. Tokura, N. Mori, and J. Akimitsu:
Electronic Structure of PrNiO₃ Studied by Photoemission and X-Ray
Absorption Spectroscopy: Band Gap and Orbital Ordering,
Phys. Rev. B **52** (1995) 13865--13873. Times Cited: 55 金属絶縁体転移
軌道秩序
- T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano:
Electronic Structure and Temperature-Induced Magnetism in LaCoO₃,
Phys. Rev. B **55** (1997) 4257--4266. Times Cited: 176 軌道状態
スピン転移
- J. Matsuno, T. Mizokawa, A. Fujimori, D. A. Zatsepin, V. R. Galakhov, E. Z. Kurmaev, Y. Kato, and S. Nagata:
Photoemission study of metal-insulator transition in CuIr₂S₄,
Phys. Rev. B **56** (1997) R15979--R15982. Times Cited: 72 軌道誘起パイエルス転移
- T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano:
Electronic Structure and Magnetic States in La_{1-x}Sr_xCoO₃ Studied by
Photoemission and X-Ray Absorption Spectroscopy,
Phys. Rev. B **56** (1997) 1290--1295. Times Cited: 96 軌道状態
スピン転移
- T. Tsujioka, T. Mizokawa, J. Okamoto, A. Fujimori, M. Nohara, H. Takagi, K. Yamaura, and M. Takano:
Hubbard splitting and electron correlation in the ferromagnetic metal CrO₂,
Phys. Rev. B **56** (1997) R15509--R15512. Times Cited: 51

Co 2p XPS of BiCoO₃



Cluster model calculation

Charge-transfer energy;

$$\Delta = 0 \text{ eV}$$

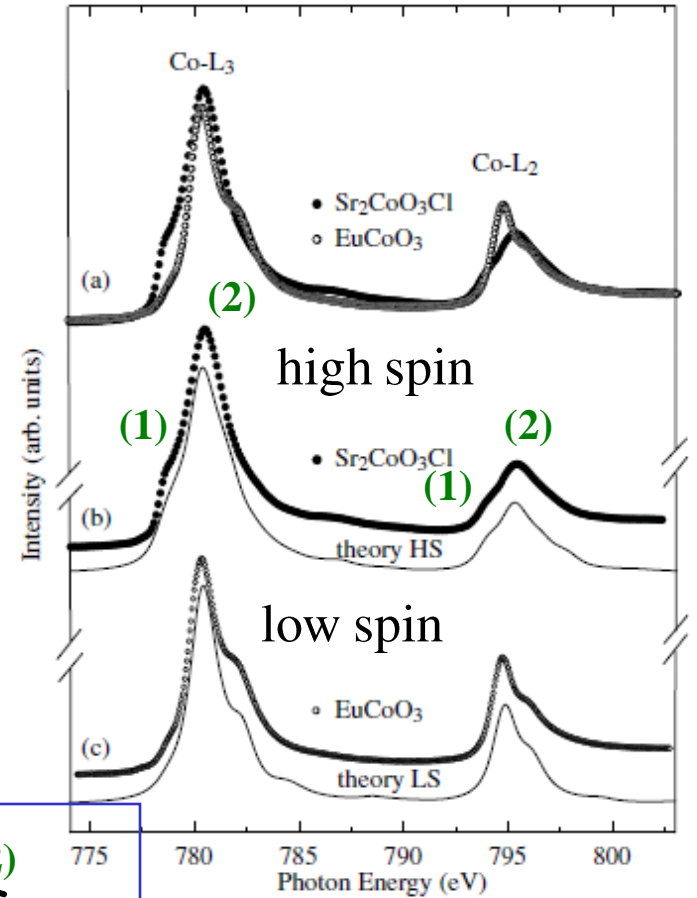
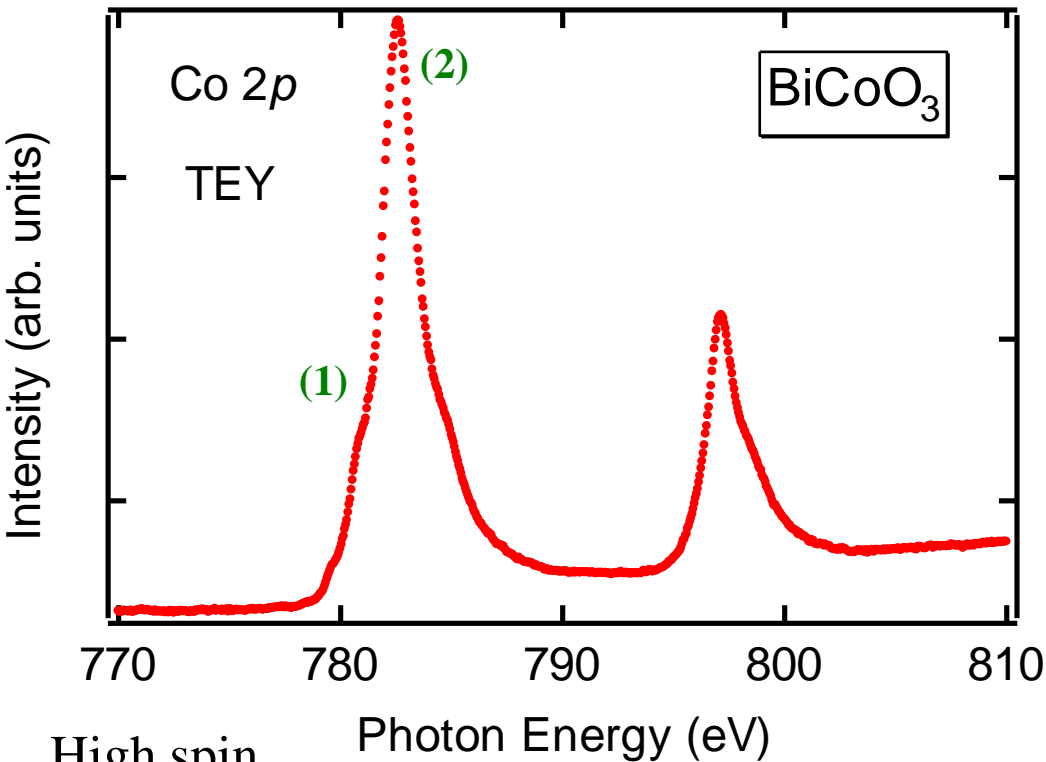
d-d Coulomb interaction energy;

$$U = 6.5 \text{ eV}$$

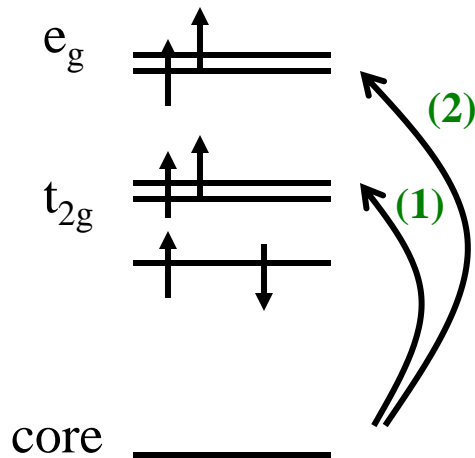
Slater-Koster parameters;

$$(pd\sigma) = -2.2 \text{ eV}$$

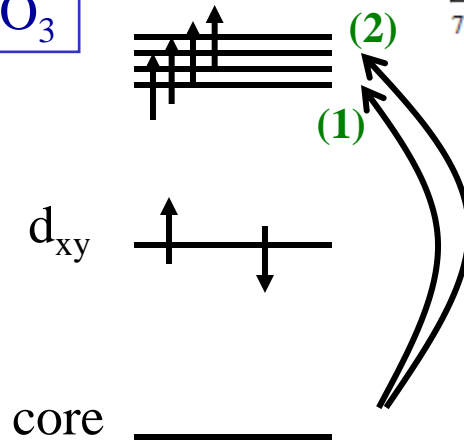
Co 2p XAS of BiCoO₃



High spin



BiCoO₃



• High spin state

• Small 10Dq

UHF calculation for BiCoO₃

	Total energy per Co (meV)	Magnetic moment (μ_B)	Gap size (eV)
C-type	0	3.32	3.31
G-type	0.967	3.32	3.30
A-type	91.4	3.37	2.47
FM	177	3.37	2.24
Low spin	2290	0	1.71

C-type antiferromagnetic structure is stable.

Calculation for magnetic moment (C-type) : 3.32 μ_B Experiment : 3.24 μ_B

Co-O-O-Co superexchange pathway in BiCoO₃

$$(pp\sigma) = (pp\pi) = 0$$

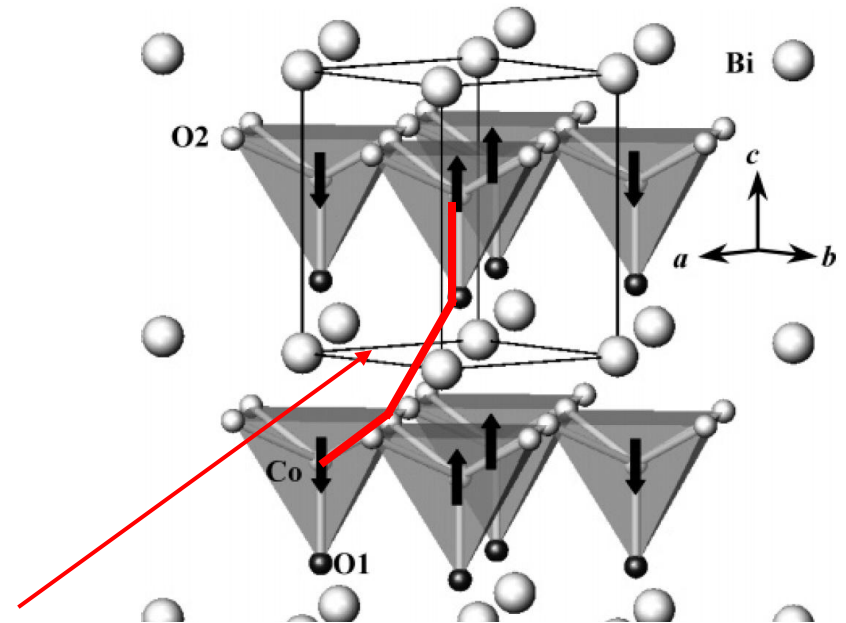
$(pp\sigma)$ and $(pp\pi)$; Transfer integrals between O 2p and O 2p

	Total energy (per Co) (meV)	Magnetic moment (μ_B)	Gap size (eV)
C-type	0	3.36	3.65
G-type	-0.475	3.36	3.74

With $(pp\sigma) = (pp\pi) = 0$,
G-type structure becomes stable.



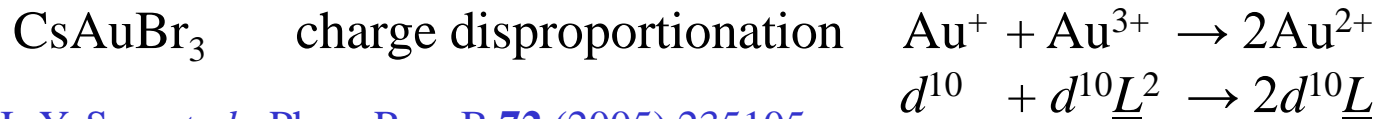
C-type structure is stabilized due
to $(pp\sigma)$ and $(pp\pi)$.



The path of Co - O - O - Co is important.

Small (or negative) Δ transition-metal compounds

Perovskite-based materials **corner sharing** structure



J.-Y. Son *et al.*, Phys. Rev. B **72** (2005) 235105.



T. Mizokawa *et al.*, Phys. Rev. B **80** (2009) 125105.

BiCoO₃ Co-O-O-Co superexchange pathways

Triangular lattice materials **edge sharing** structure

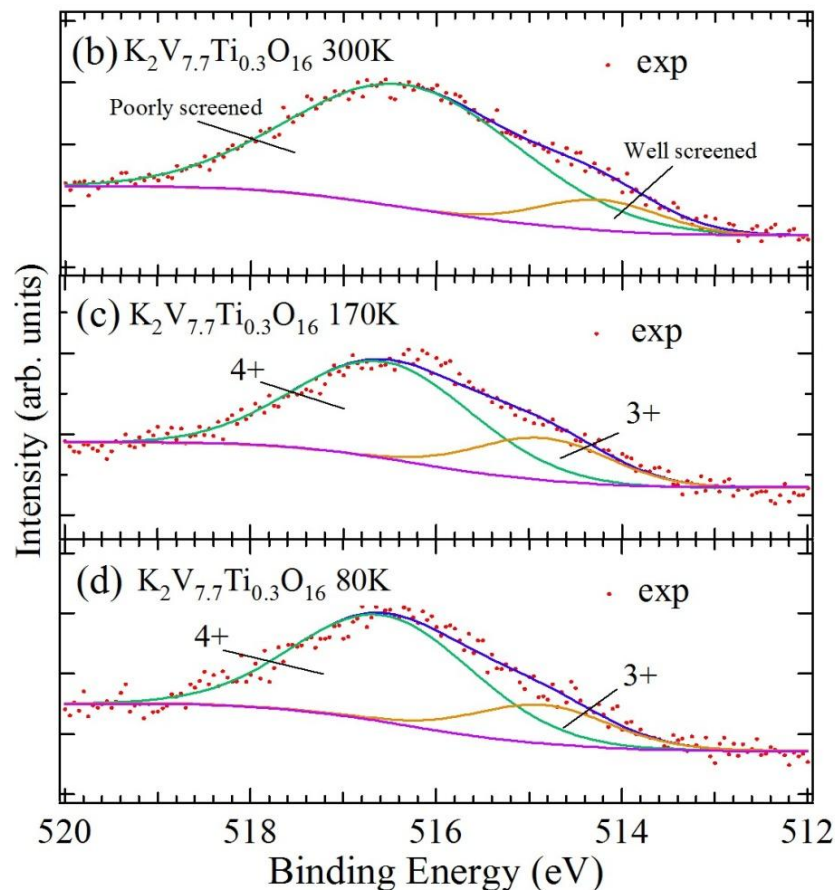
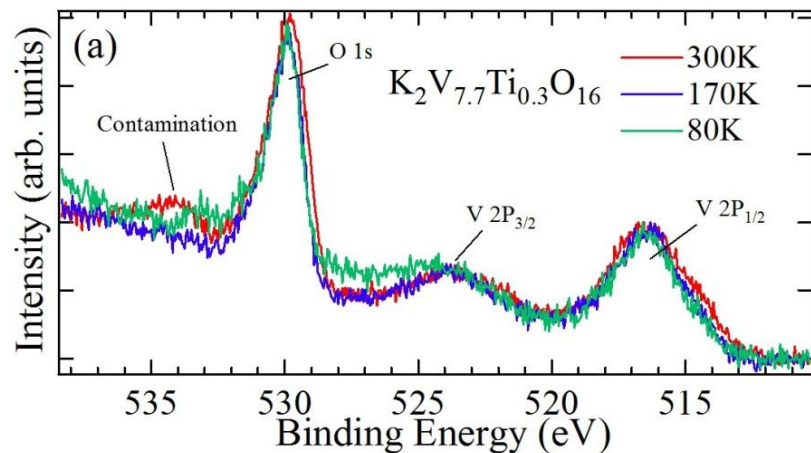
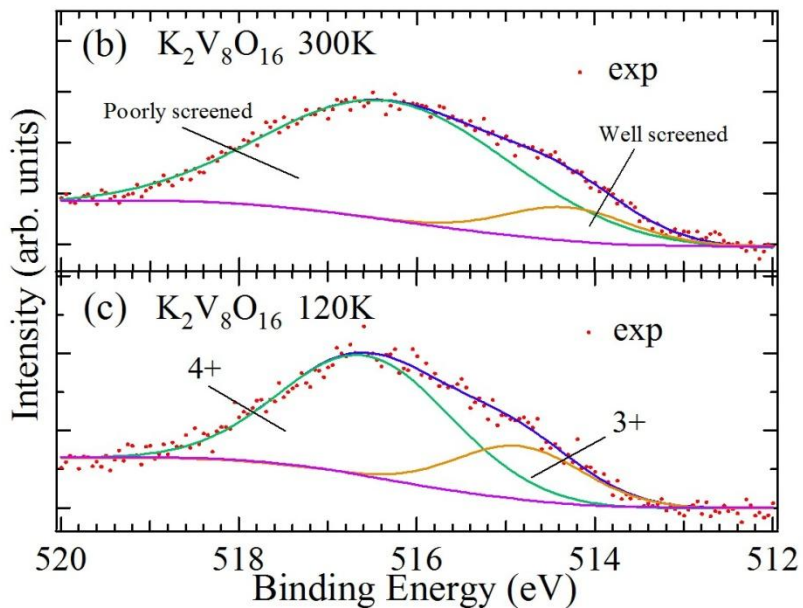
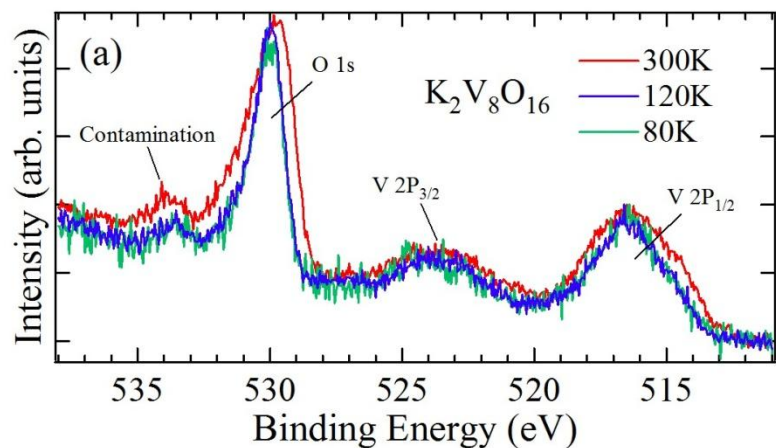


K. Takubo *et al.*, Phys. Rev. Lett. **99** (2007) 037203; **104** (2010) 226404

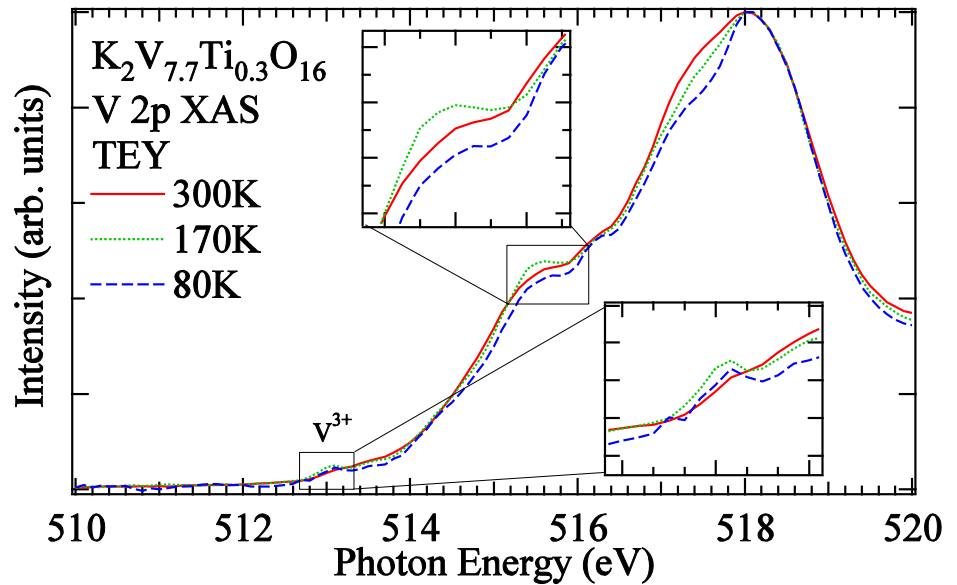
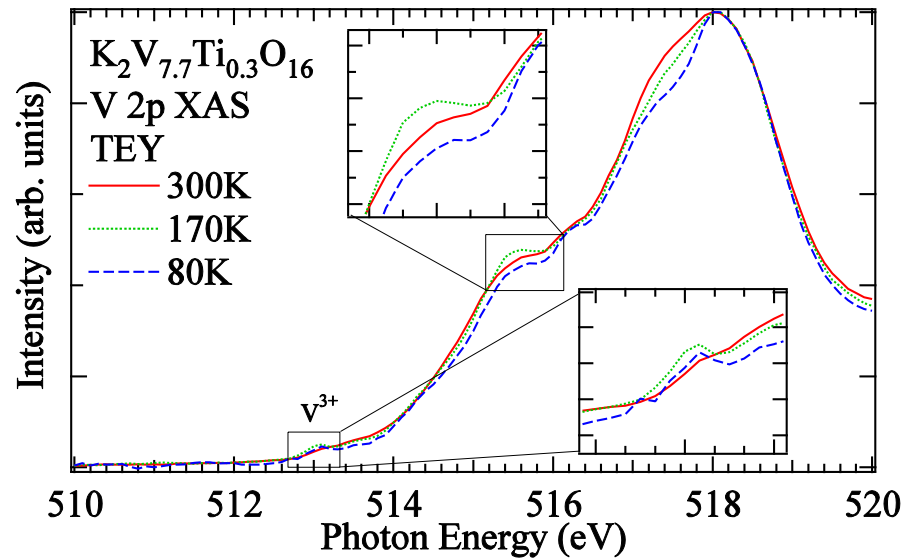
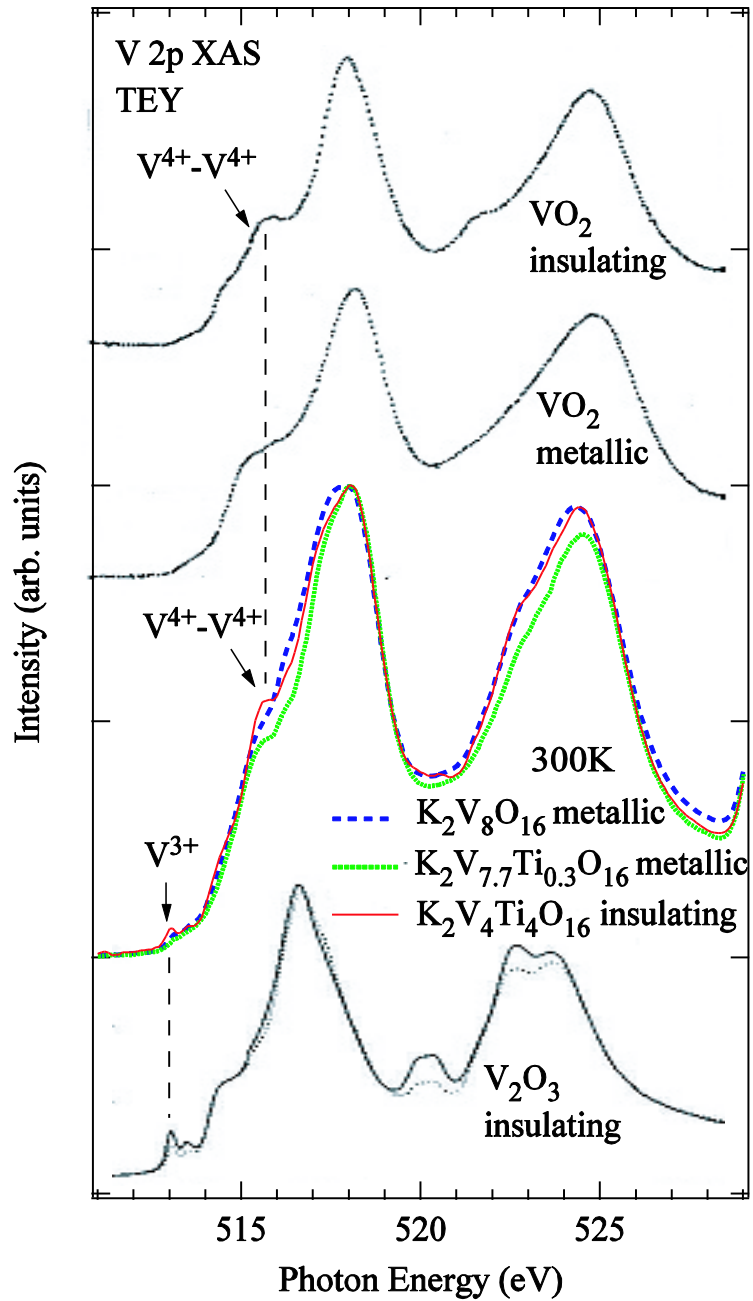


Y. Wakisaka *et al.*, Phys. Rev. Lett. **103** (2009) 026402

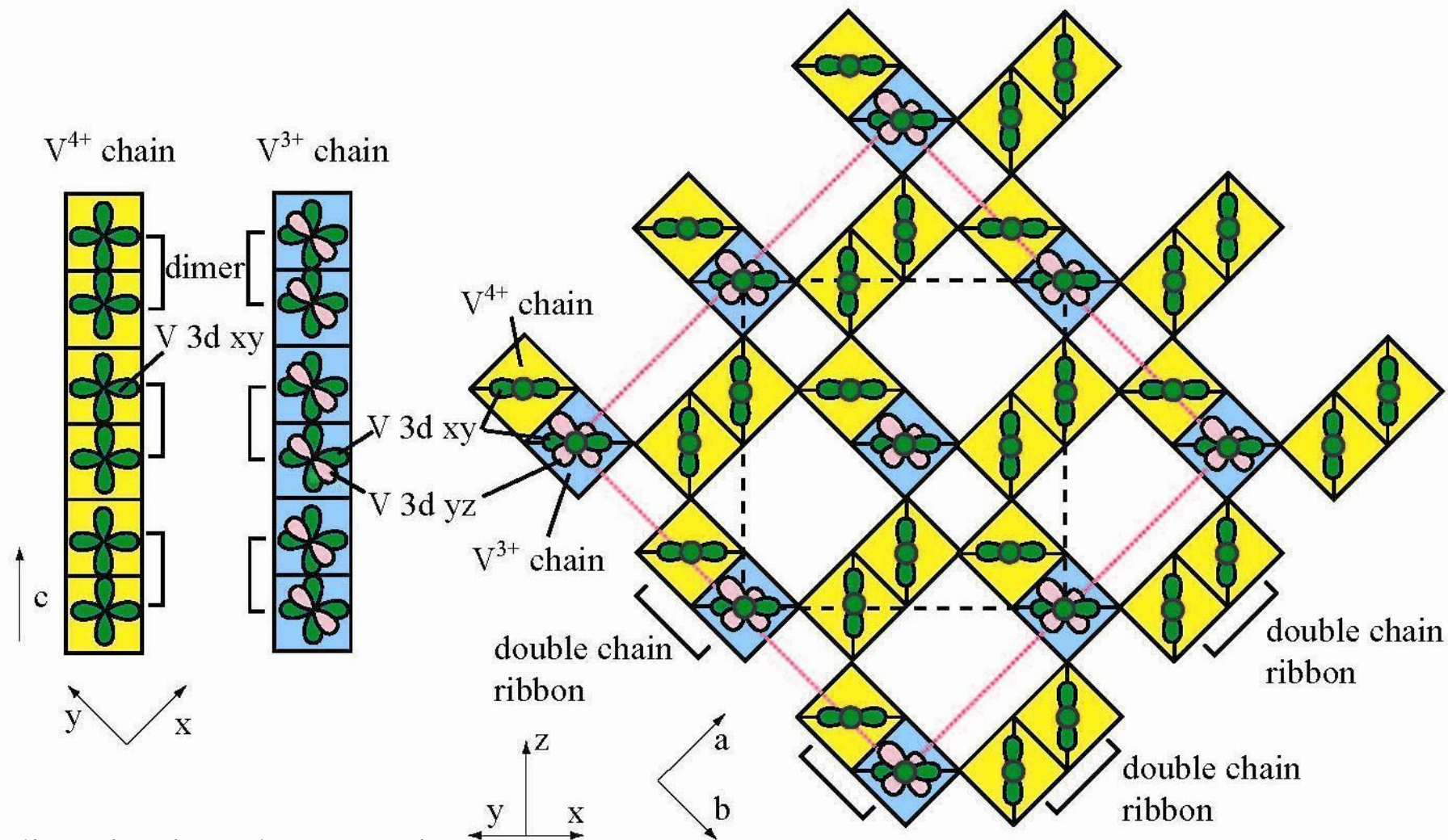
O 1s and V 2p XPS spectra of $K_2V_{8-y}Ti_yO_{16}$



V2p XAS spectra of $K_2V_{8-y}Ti_yO_{16}$



Charge and orbital model for $K_2V_8O_{16}$



dimerization along c -axis
very similar to VO_2

There is no inversion symmetry. Multiferroic?

今後の展望

新物質

Fe系超伝導体、Aサイト秩序型ペロブスカイト、...

遷移金属酸化物薄膜、ヘテロ界面

$\text{LaTiO}_3/\text{SrTiO}_3$, $\text{SrVO}_3/\text{SrTiO}_3$, ...

内殻光電子分光による
界面の原子価制御

外場誘起相転移、相制御

$(\text{Pr,Ca,Sr})\text{MnO}_3$, Ca_2RuO_4 , $(\text{Ti,Co})\text{O}_2$, LaCoO_3 , ...

元素選択的ポンププローブ分光

トポロジカルな励起の秩序化

MnSi , $\text{Dy}_2\text{Ti}_2\text{O}_7$, ...

軟X線散乱、顕微分光