Soft x-ray spectroscopies on strongly correlated Co oxides

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PF workshop "Current status and progress of condensed matter research by soft x ray spectroscopic and scattering measurements" (2011.09.13-14, presented on 14th)

Collaboration

Thank you all!

- **Group members including ex-grad students:**
  Mario Okawa
  Atsushi Hasegawa, Atsunori Hachimura, Junichi Nishimura

- **Crystal growing/structural, transport, magnetic measurements:**
  Yoshihiko Kobayashi (*Tokyo Medical University*)
  Kichizo Asai (*University of Electro-communications*)

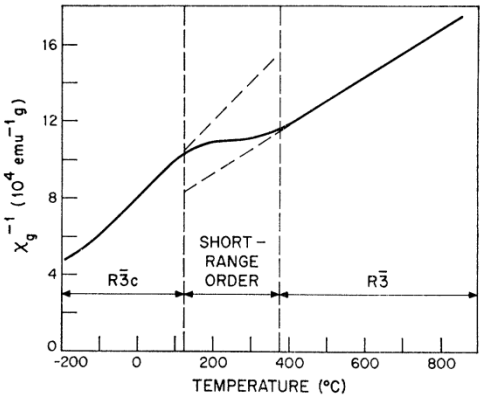
- **XAS/photoemission experiments**
  Takashi Mizokawa, Hiroki Wadati (*University of Tokyo*)
  Kou Takubo (*Waseda University*)
  Tom Regier (*Canadian Light Source*)

  Kenya Shimada, Masashi Nakatake (*HiSOR, Hiroshima Univ.*)
  Shigenori Ueda, Yoshiyuki Yamashita, Hideki Yoshikawa,
  Keisuke Kobayashi (*SPring-8/NIMS*)
  Eiji Ikenaga (SPring-8/JASRI)

- **Band structure calculations**
  Noriaki Hamada (*Tokyo University of Science*)

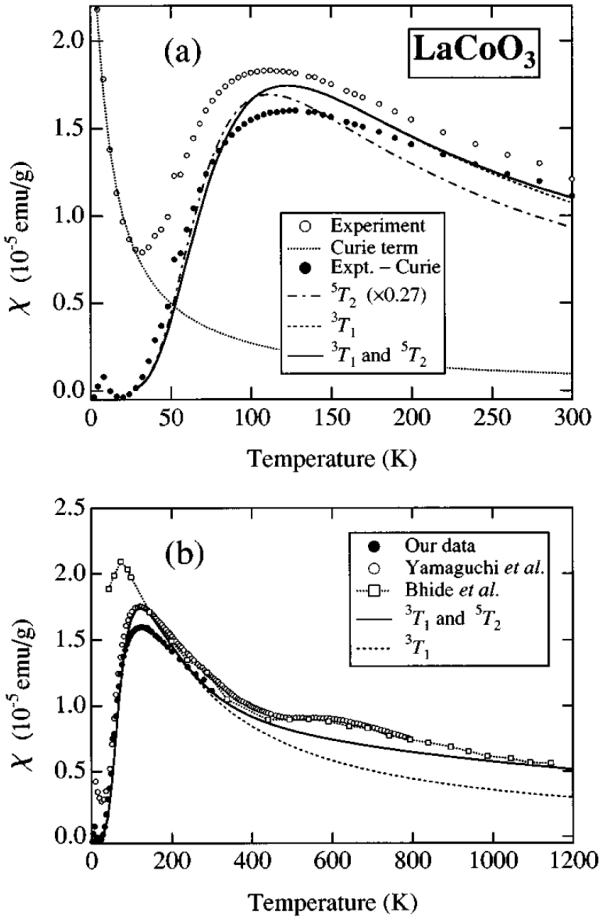
Spin crossover in $LaCoO_3$

χ of $LaCoO_3$

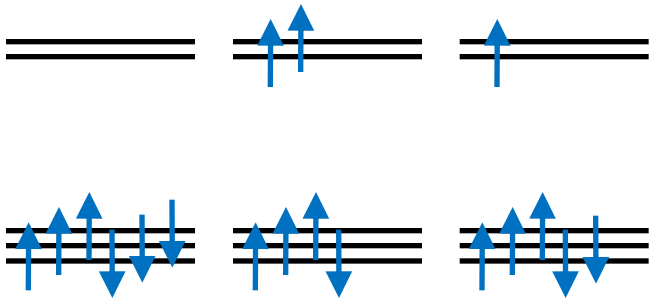


Raccah and Goodenough,
PR**155**, 932 (1967).

Bhide et al.,
PRB**6**, 1021 (1972).
Yamaguchi et al.,
PRB**54**, R11022 (1996).
Saitoh et al.,
PRB**55**, 4257 (1997).



Possible lowest magnetic states in $LaCoO_3$

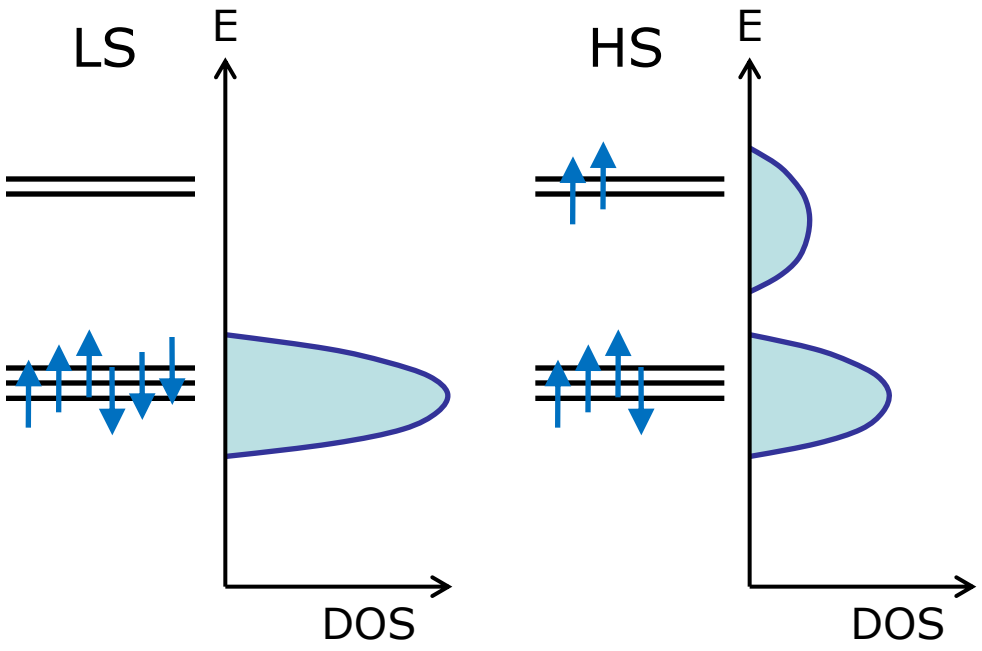


S: 0 2 1

$^1A_1$ $^5T_2$ $^3T_1$
Symmetry of local electronic structure

Simple $^1A_1$-$^5T_2$ model cannot reproduce χ, while $^1A_1$-$^3T_1$-$^5T_2$ 3-state model describes χ well in a wide temperature regime.

Why electronic-structure study?

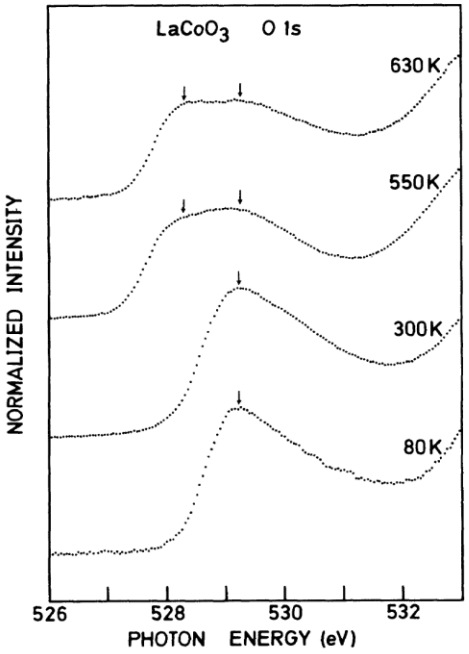


(Very simplified figure)

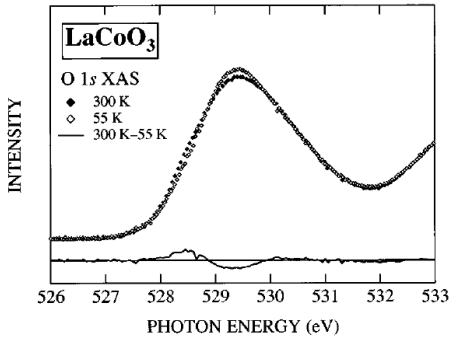
Electron density of states (DOS) should be sensitive to the spin configurations.

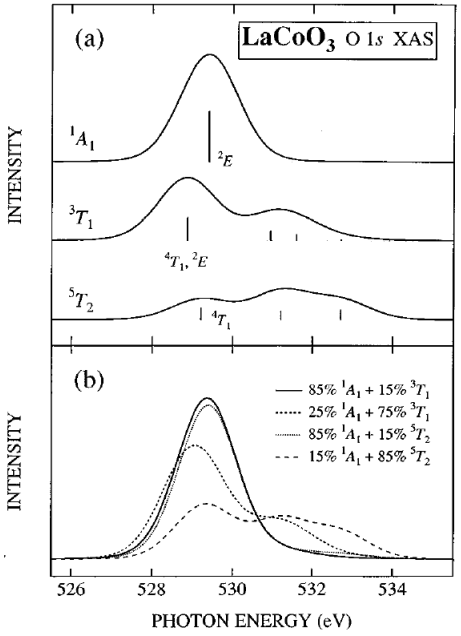
Experiment: Photoemission (Occupied states)
Soft x-ray absorption
(Unoccupied states, multiplet structure)
Theory: Band structure calc., cluster model calc.

$LaCoO_3$: O K edge x-ray absorption spectra

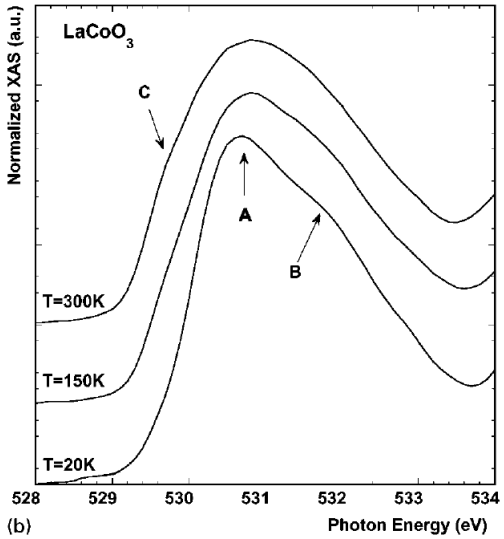


Abbate et al., PRB**47**, 16124 (1993). [TEY]





Saitoh et al., PRB**55**, 4257 (1997). [TEY]



Toulemonde et al., J. Solid State Chem. **158**, 208 (2001). **[TFY]**

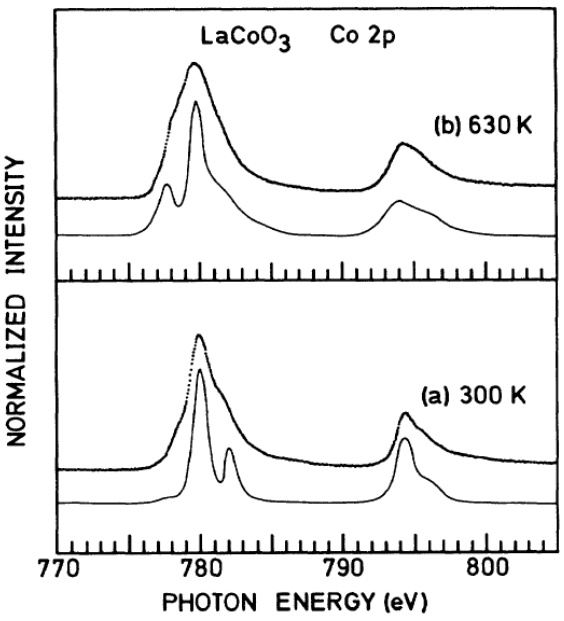
TEY mode is not as sensitive to T-dep changes as TFY mode.

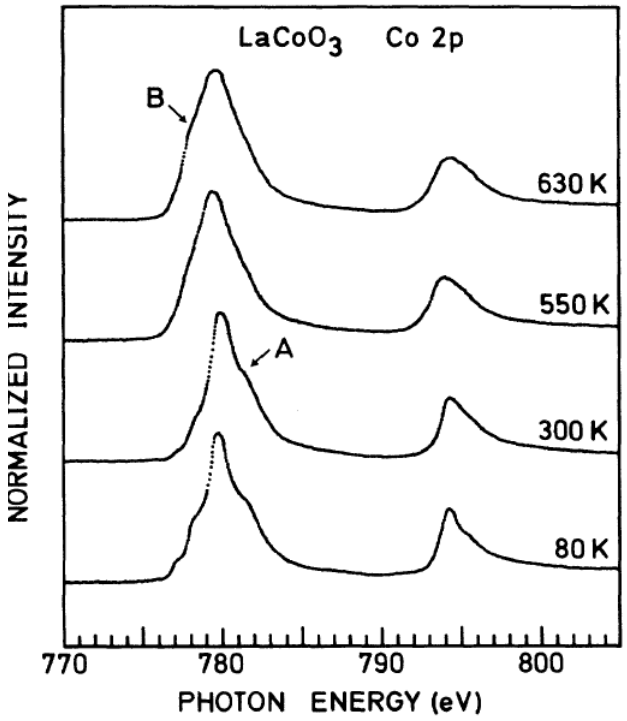
Small changes at low temperatures, which may be consistent with the LS-IS-HS model.

$LaCoO_3$: Co L edge x-ray absorption spectra

LS and HS calcs. without Spin-orbit interaction (SOI) compared with exp.

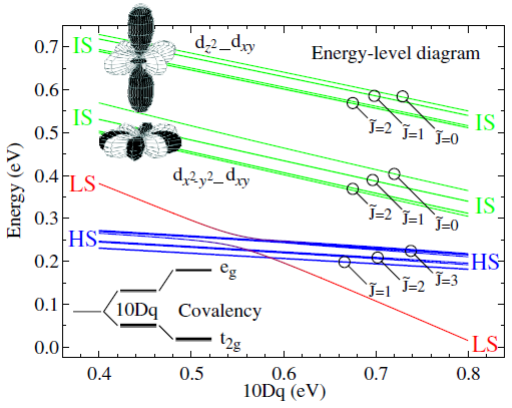
Abbate et al., PRB**47**, 16124 (1993).

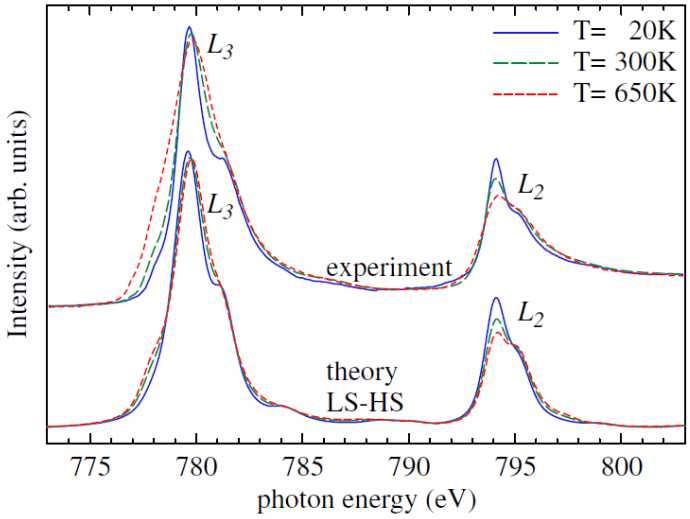




LS-HS model with SOI compared with exp.

Haverkort et al., PRL**97**, 176405 (2006).





Effects by SOI seem to be small.

Motivations

Which model is appropriate to describe the spin crossover in $LaCoO_3$? LS-HS, LS-IS-HS, or others?

Three strategies

(1) Temperature-dependent measurements to change the LS/IS/HS populations.

$LaCoO_3$: T. Saitoh et al., PRB**55**, 4257 (1997) / many other studies

(2) Changing rare earths to change the LS/IS/HS populations at a fixed temperature.

$LaCoO_3$, $PrCoO_3$, $NdCoO_3$: T. Saitoh et al., JMMM **310**, 981 (2007).

(3) Experimental determination of the LS, IS, and HS electronic structure by non-crossover compounds

$Pr_{0.5}Ca_{0.5}CoO_3$: Spin/MIT simultaneous transitions

: T. Saitoh et al., JESRP **144-147**, 893 (2005).

Sr_2CoSbO_6 & related oxides: HS Co oxide with O_h symmetry

Experiment

Samples: Poly-crystals of
Sr_2CoMO_6 (M=Sb, Nb, Ta), Ba_2CoMO_6 (M=Nb, Ta)

Light source: XAS: Canadian Light Source SGM beamline
PES: HiSOR BL-1, BL-7
SPring-8 BL-15XU
Lab XPS

XAS mode: TEY, TFY, PFY

Photoemission Analyzer: VG-Scienta SES series, JEOL-XPS system

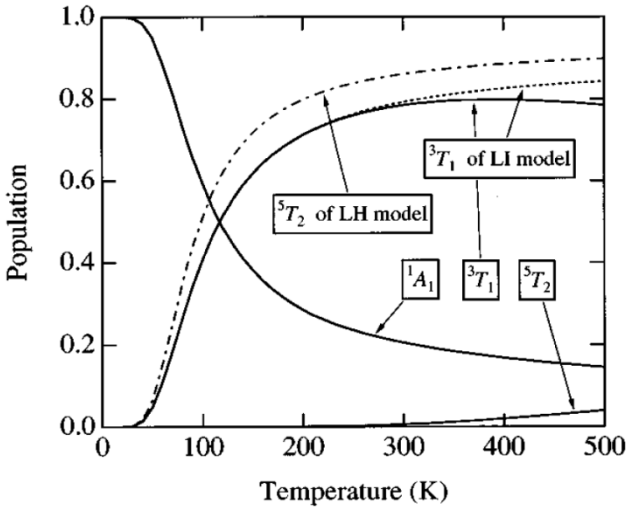
$h\nu$: From about 100 eV to 5 KeV

Surface treatment: Cleaved *in situ*

Seeking HS spectrum: Background

HS cannot be the ground state in $RECoO_3$. Besides, the HS population may not be large even at high temperatures.

High-temperature photoemission measurement is difficult due to its high surface sensitivity.

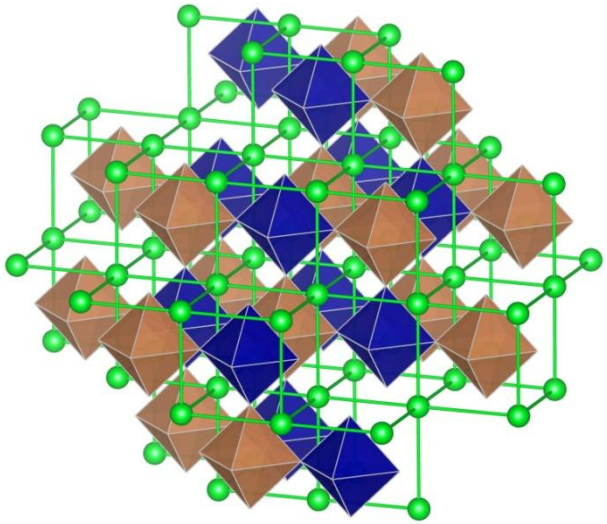


Saitoh et al., PRB**55**, 4257 (1997).

Observing the pure HS state in $RECoO_3$ is difficult.

The answer is Co double perovskite

(Ordered) Double perovskite type Co oxides have or may have the HS ground state.



Drawn with VESTA by Fujio Izumi at NIMS

$A^{2+}_2\ Co^{3+}\ B'^{5+}\ O^{2-}_6$

B'= Sb^{5+} ($[Kr]4d^{10}$), Nb^{5+} ($[Kr]$), Ta^{5+} ($[Xe]4f^{14}$)

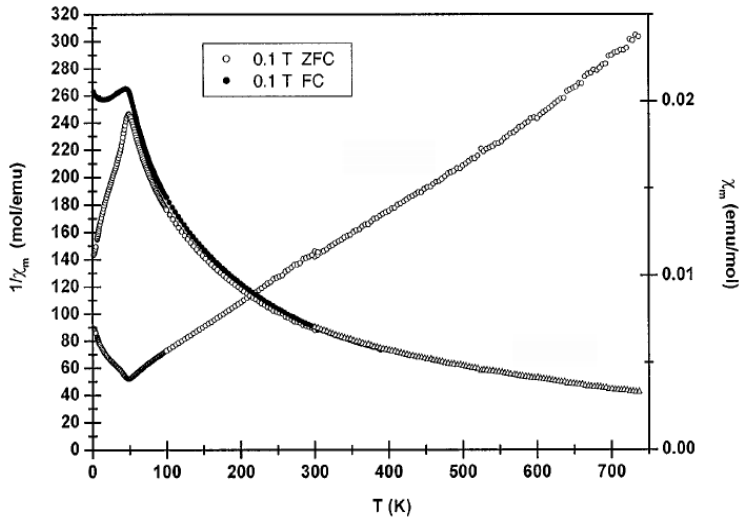
Sr_2CoSbO_6	Co^{3+} HS	Order
Sr_2CoNbO_6	Co^{3+} HS ?	Disorder
Sr_2CoTaO_6	Co^{3+} IS ?	Disorder ?
Ba_2CoNbO_6	Co^{3+} HS ?,IS ?	Disorder
Ba_2CoTaO_6	Co^{3+} HS ?,IS ?	Disorder

V. Primo-Martin *et al.*, J. Solid State Chem. **157**, 76 (2001).
K. Yoshii, J. Solid State Chem. **151**, 294 (2000).
K. Yoshii, J. Alloys Compounds **307**, 119 (2000).
G. Blasse, J. Inorg. Nucl. Chem. **27**, 993 (1965).
鴨川他、日本物理学会秋季大会講演概要 **62**, 540 (2005).

Typical HS Co oxide Sr_2CoSbO_6

$$P_{eff} = 2\sqrt{S(S+1)}\mu_B$$

Co 3*d* (HS : S=2) : P_{eff}=4.90μ_B



Vicent Primo-Martin *et al.*, J. Solid State Chem. **157**, 76 (2001).

G. Blasse : P_{eff}=5.2μ_B

V.Primo-Martin et al. : P_{eff} = 3.83μ_B
With oxygen defects : P_{eff} = 4.85μ_B

Co^{3+} in Sr_2CoSbO_6 is HS.

G. Blasse, J. Appl. Phys. **36**, 879 (1965).
V. Primo-Martin *et al.*, J. Solid State Chem. **157**, 76 (2001).

Conclusions

First observation of Co $L_{2,3}$ and O K edge spectra from HS Co^{3+} oxides with O_h symmetry.

XAS and PES are powerful to probe the spin states of solids. Nevertheless, there is still controversy about which model is appropriate for the $LaCoO_3$ problem.

Spin crossover occurs.
= Energy levels are nearly degenerated.
= low-energy couplings may not be ignored.
SOI
reconsideration on χ_0 (van-Vleck term)

- SOI should be seriously considered in calcs. and exps.
- Other mechanisms should also be examined.