Coupled valence and spin state transitions resulting from an interplay between Pr and Co in oxides

F. Guillou, Q. Zhang, Z. Hu*, V. Hardy

► CRISMAT, CNRS, Caen, France

► *Max Planck Institute, Dresden, Germany

MAX-PLANCK-GESELLSCHAFT

► XAS experiments performed at NSRRC-TAIWAN

國家同步輻射研究中心
National Synchrotron Radiation Research Center

Fundings

CNRS Project « Magnetocaloric effects »

cnrs dépasser les frontières

Initial Training Network SOPRANO

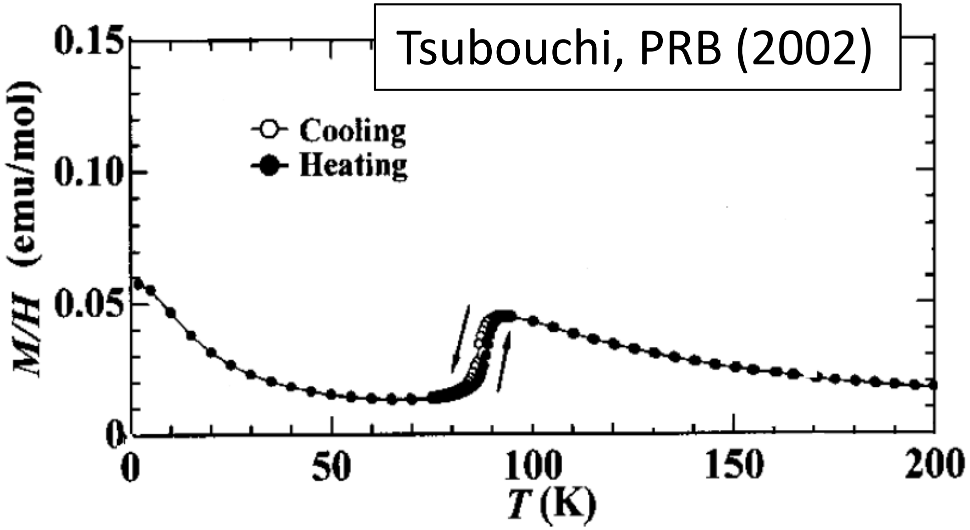
SEVENTH FRAMEWORK PROGRAMME

Spin State Transition

For some $3d^n$ in octahedral environment
(n = 4 , 5 , 6 , 7)
Competition between Δ_{CF} and J_H

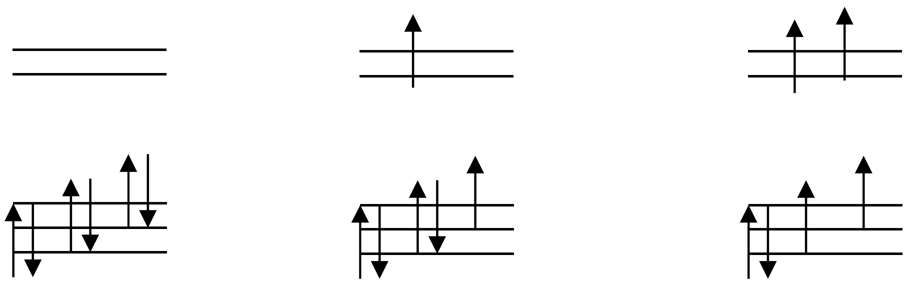
- Smooth transition : $LaCoO_3$
- Sharp transition : $Pr_{0.5}Ca_{0.5}CoO_3$
  (Co^{3+} / Co^{4+})

SST manifested by : ΔM / ΔS / ΔV / Δρ



Prototypical example : Co^{3+} ($3d^6$)

Low Spin	Intermediate Spin	High Spin



LS	IS	HS
S=0	S=1	S=2

Original picture of the SST

Co^{3+} LS / Co^{4+} LS → Co^{3+} IS / Co^{4+} LS → T

$T_{SST} \approx 90K$

It is not just a « simple » SST …

► Naito, JPSJ (2010) : SST extended to $(Pr_{1-y}RE_y)_{1-x}Ca_xCoO_3$ with RE=Nd, Sm, Gd and Y

but the **presence of Pr** seems to be always required …

► Baron-Gonzalez, PRB (2010) : Neutron Powder Diffraction

-At the transition, Co-O bonds are almost unaltered whereas **Pr-O changes a lot !**

-Possibility of a partial **charge transfer between Pr and Co**

► Knizek, PRB (2010) : DFT supports a **$(Pr^{4+}/Co^{3+}) \leftrightarrow (Pr^{3+}/Co^{4+})$** scenario

► Hejtmánek, PRB 82 (2010): C_p low-T $\Rightarrow$ Schottky anomaly $\Rightarrow$ **Pr^{4+} $(4f^1)$ …**

► Garcia-Munoz, PRB 84 (2011) : XAS $\Rightarrow$ **direct evidence of Pr^{4+} below T_{SST}**

Valence and Spin State Transition : VSST

Present picture

$\%Pr^{4+} \leftrightarrow \%Pr^{3+}$

$\%Co^{3+} \leftrightarrow \%Co^{4+}$

Co^{3+} LS $\leftrightarrow$ Co^{3+} IS

Co^{4+} LS = Co^{4+} LS

T

T*

Open questions

▶ Pr^{4+} fraction at T<T* ((Pr^{4+}/f.u. between 0.075 and 0.18)

▶ Spin States of Co^{3+} and Co^{4+} at T<T* and at T>T*

Our contributions

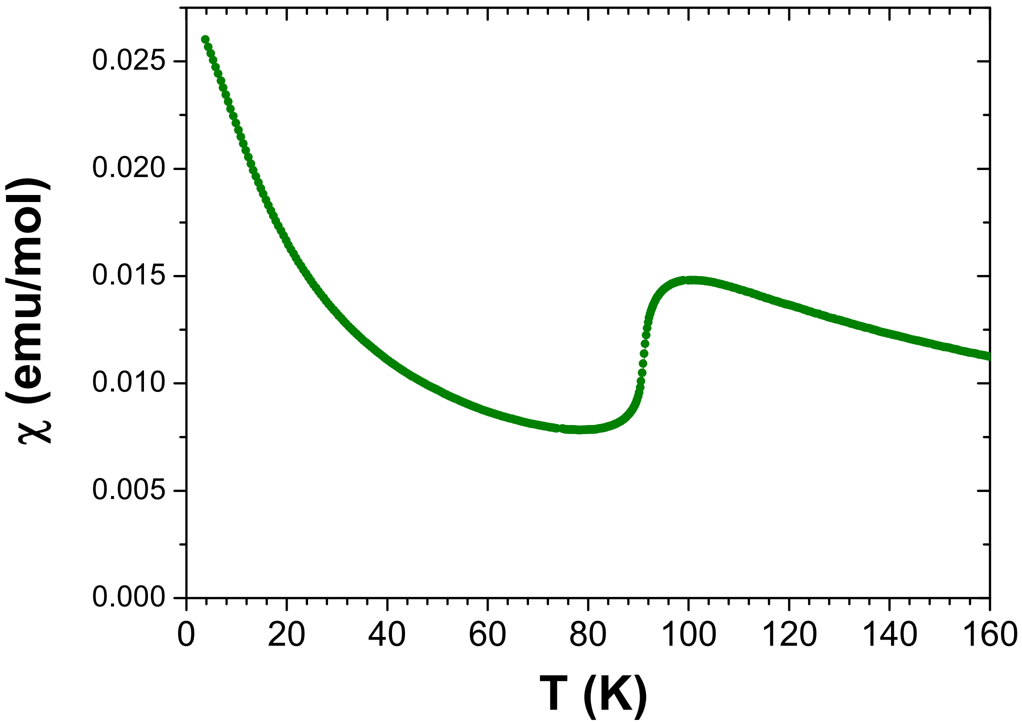
1/ Magnetocaloric effect

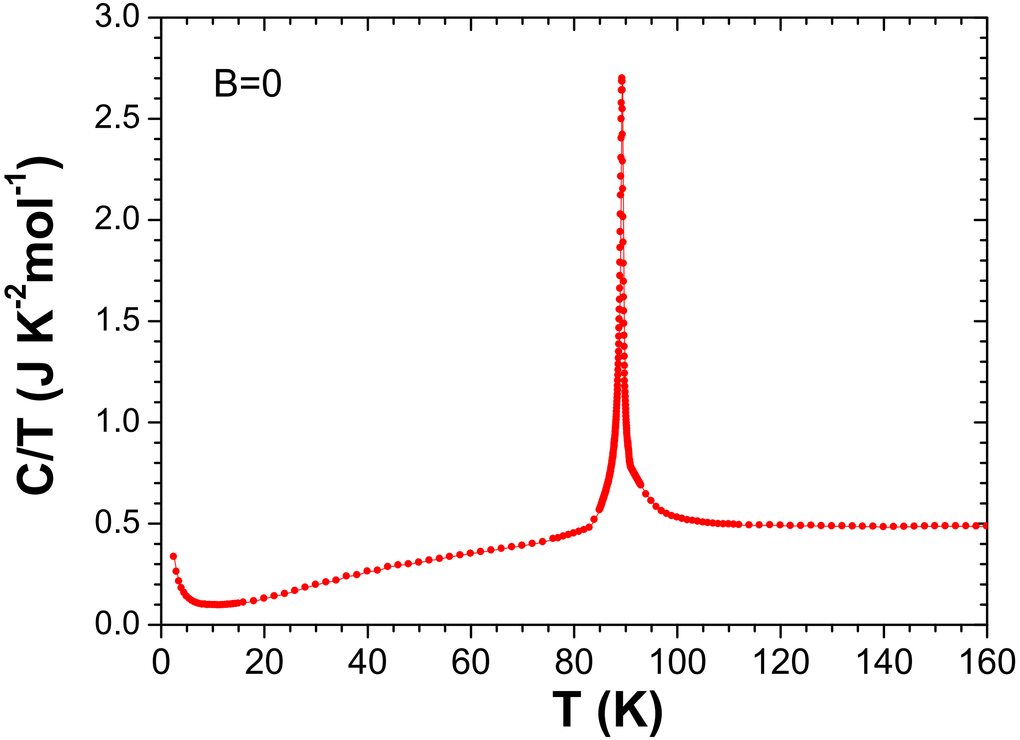
2/ X-ray Absorption Spectroscopy

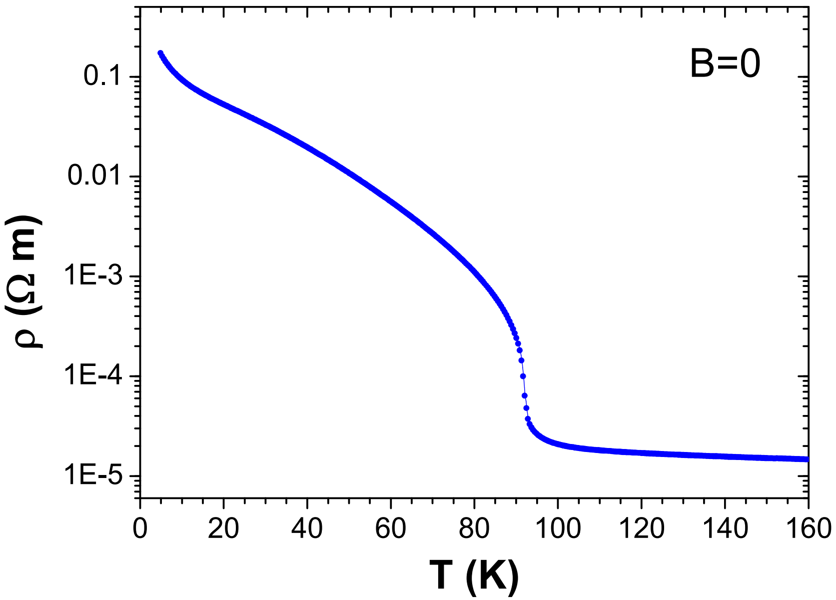
3/ Magnetic susceptibility

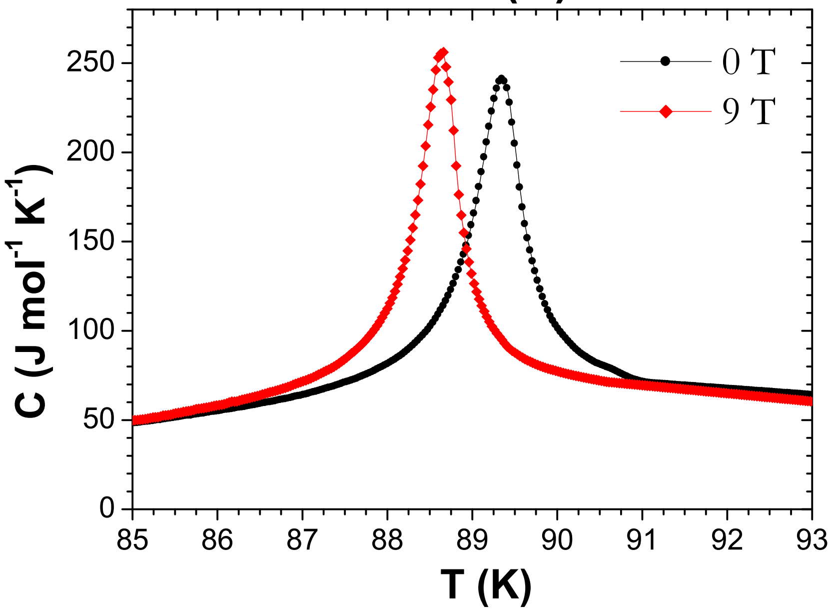
$(Pr_{0.7}Sm_{0.3})_{0.7}Ca_{0.3}CoO_3$

$Pr_{0.49}Sm_{0.21}Ca_{0.3}CoO_3$: First-order transition at T* ~ 90K

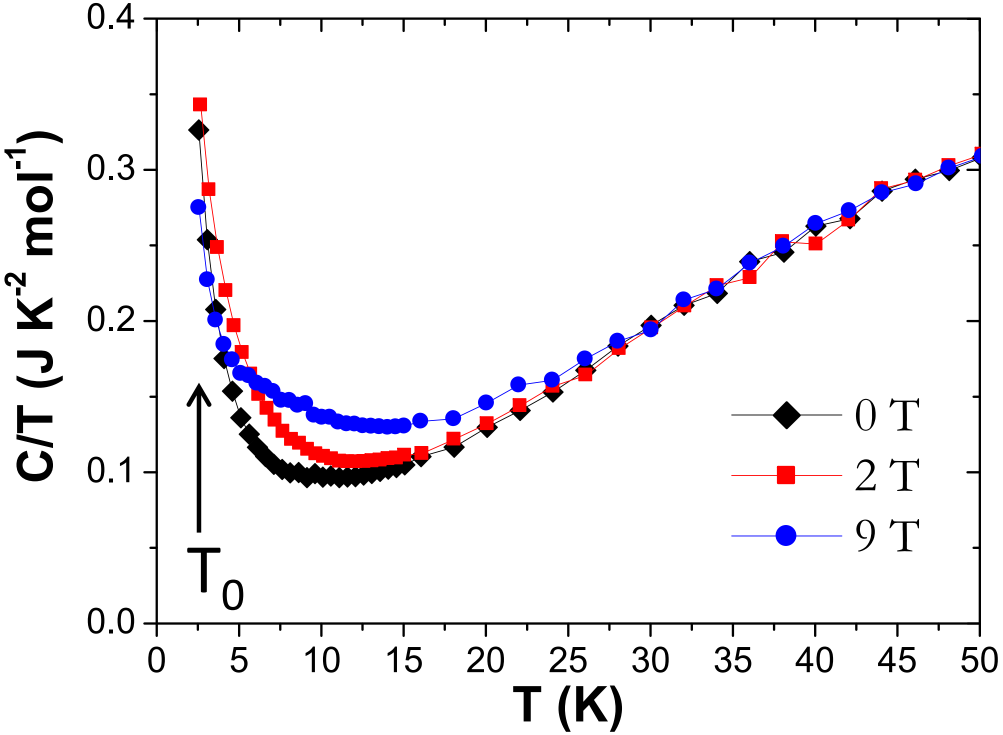




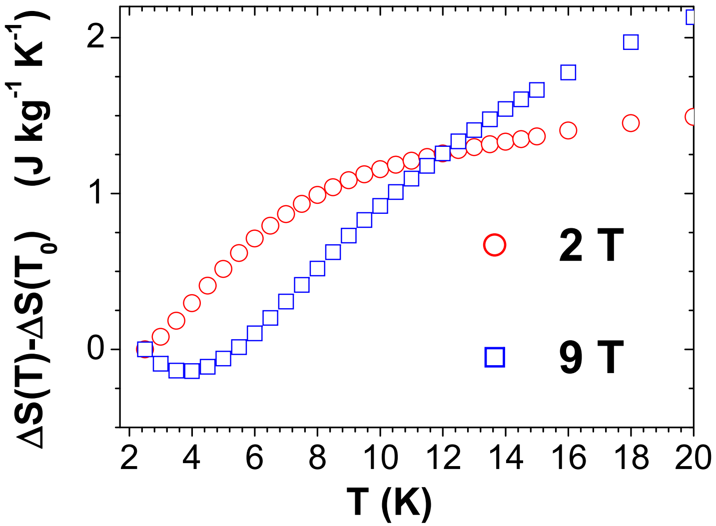




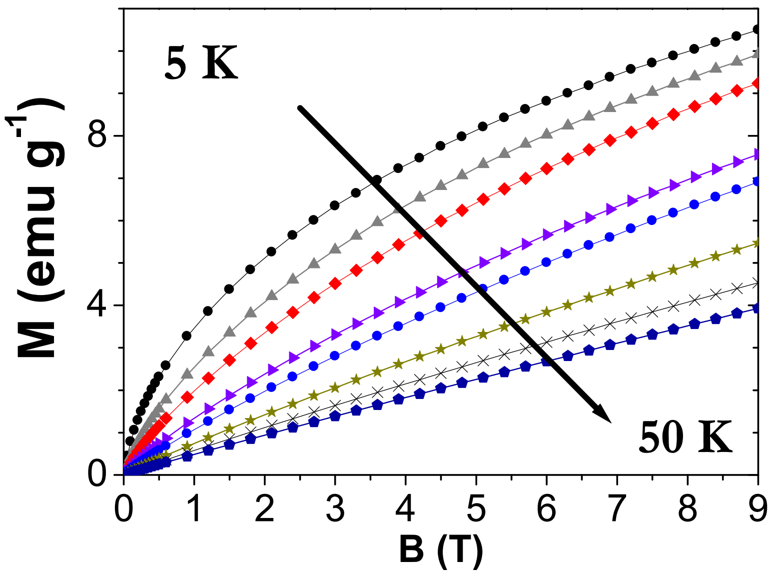
Magnetocaloric effect

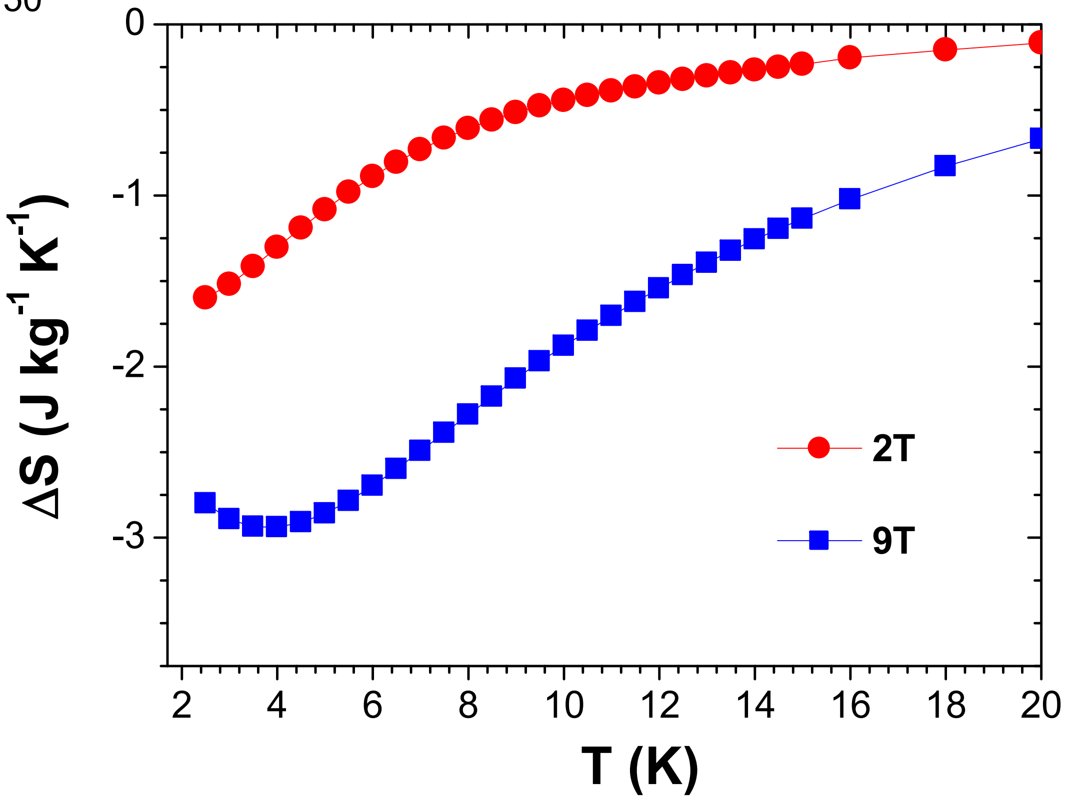


$$\Delta S(T;\Delta B) = \Delta S(T_0;\Delta B) + \int_{T_0}^{T} \frac{[C(T',B) - C(T',0)]}{T'} dT'$$



Maxwell equation : $\Delta S(T;\Delta B) = \int_{0}^{B} \frac{\partial M(T,B')}{\partial T} dB'$



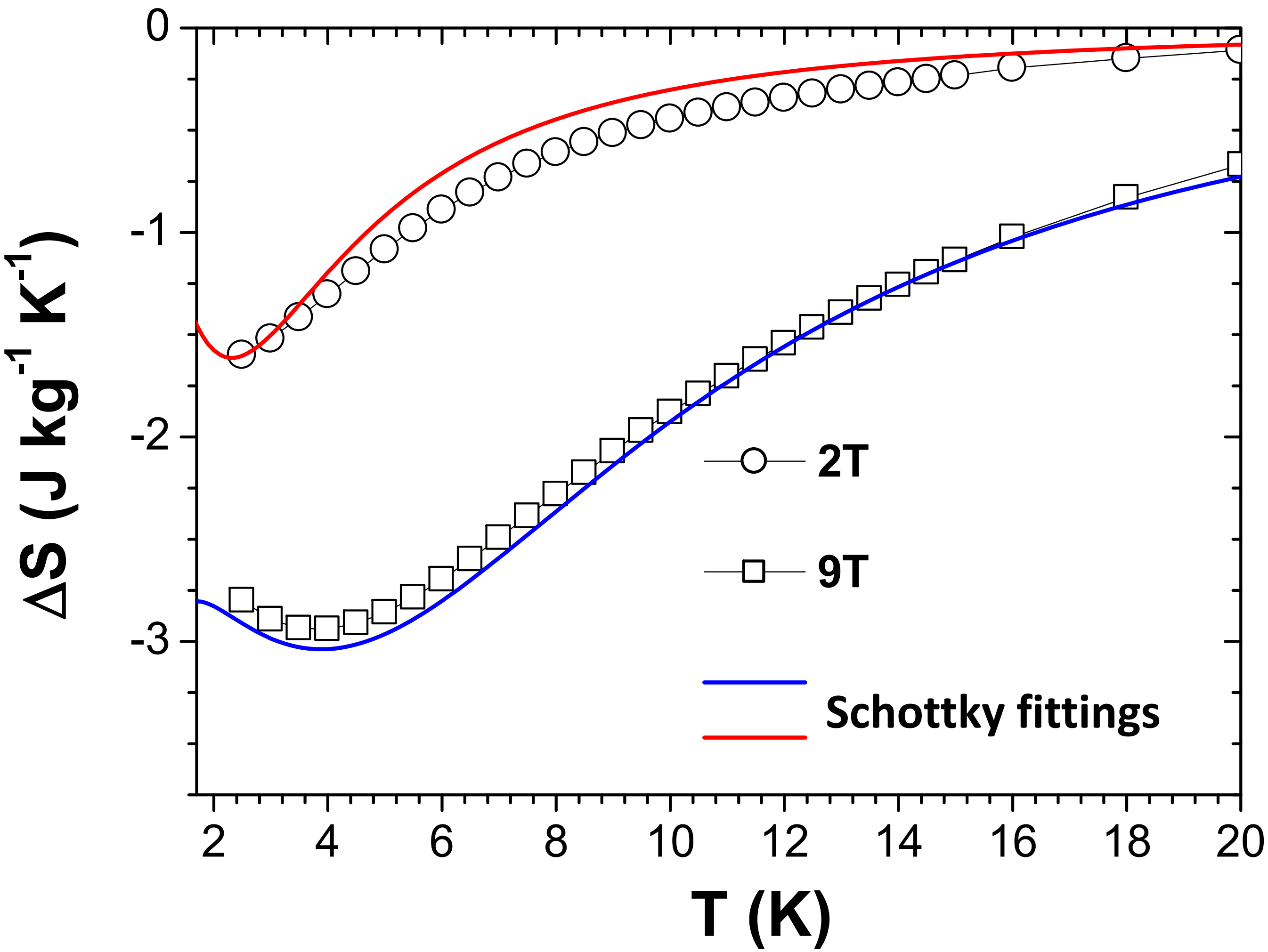


Pr^{4+} ($4f^1$) and Sm^{3+} ($4f^5$) ⇒ Schottky terms (doublets)

$$\frac{\Delta S_{ion}(T,\Delta B)}{R} = n\left[\ln(1+e^{-\frac{\varepsilon(B)}{kT}}) - \ln(1+e^{-\frac{\varepsilon(0)}{kT}}) + \frac{\varepsilon(B)}{kT(1+e^{\frac{\varepsilon(B)}{kT}})} - \frac{\varepsilon(0)}{kT(1+e^{\frac{\varepsilon(0)}{kT}})}\right]$$

n : amount per formula unit

$$\varepsilon(B) = \tilde{g}\ \mu_B(B_{mol} + B)$$



$Pr_{0.49}Sm_{0.21}Ca_{0.3}CoO_3$

$\tilde{g}\ (Sm^{3+}) = 0.3$

$\tilde{g}\ (Pr^{4+}) = 3.35$

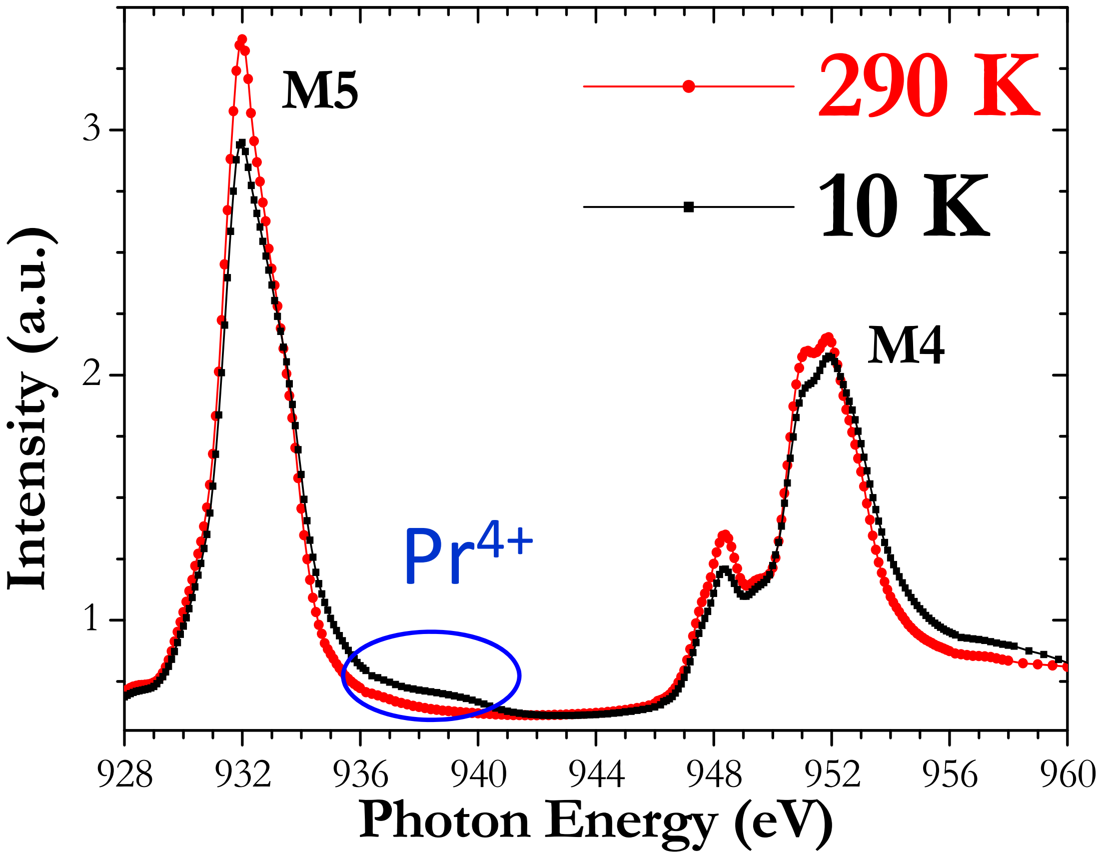
$B_{mol} = 1.7\ T$

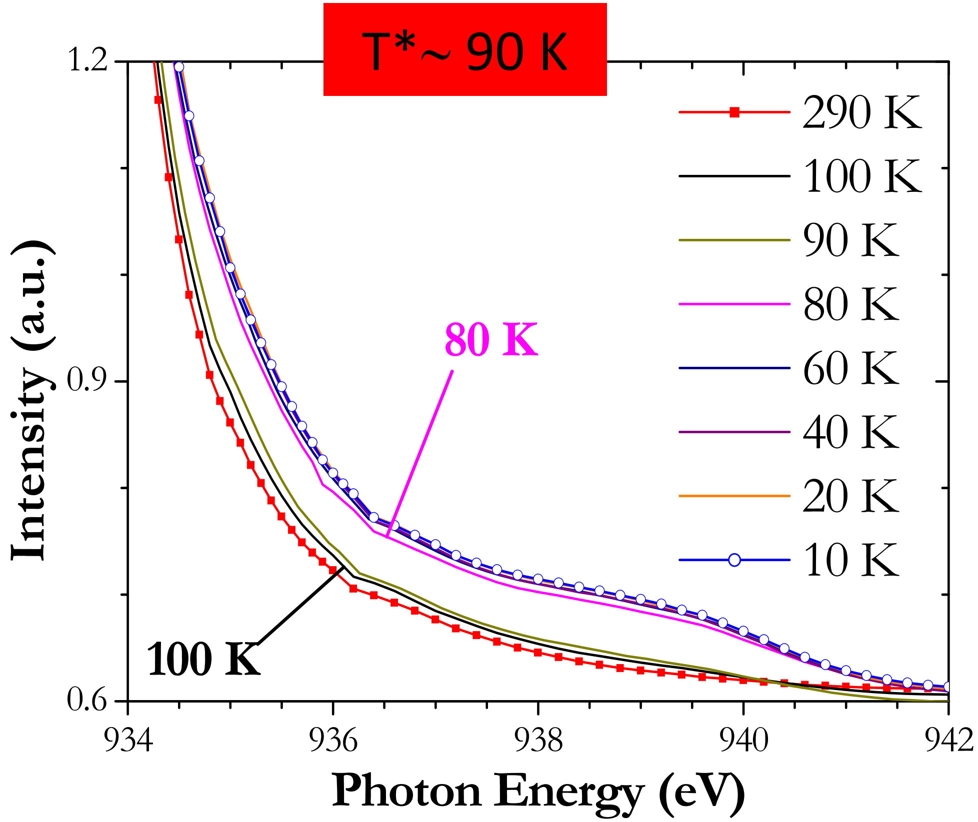
$n(Sm^{3+}) = 0.21$

$n(Pr^{4+}) = 0.13$

⇒ T<<T* : 0.13 Pr^{4+} /f.u. (Hejmanek : 0.12-0.18 Pr^{4+} /f.u.)

XAS : Pr $M_{4,5}$ absorption edges

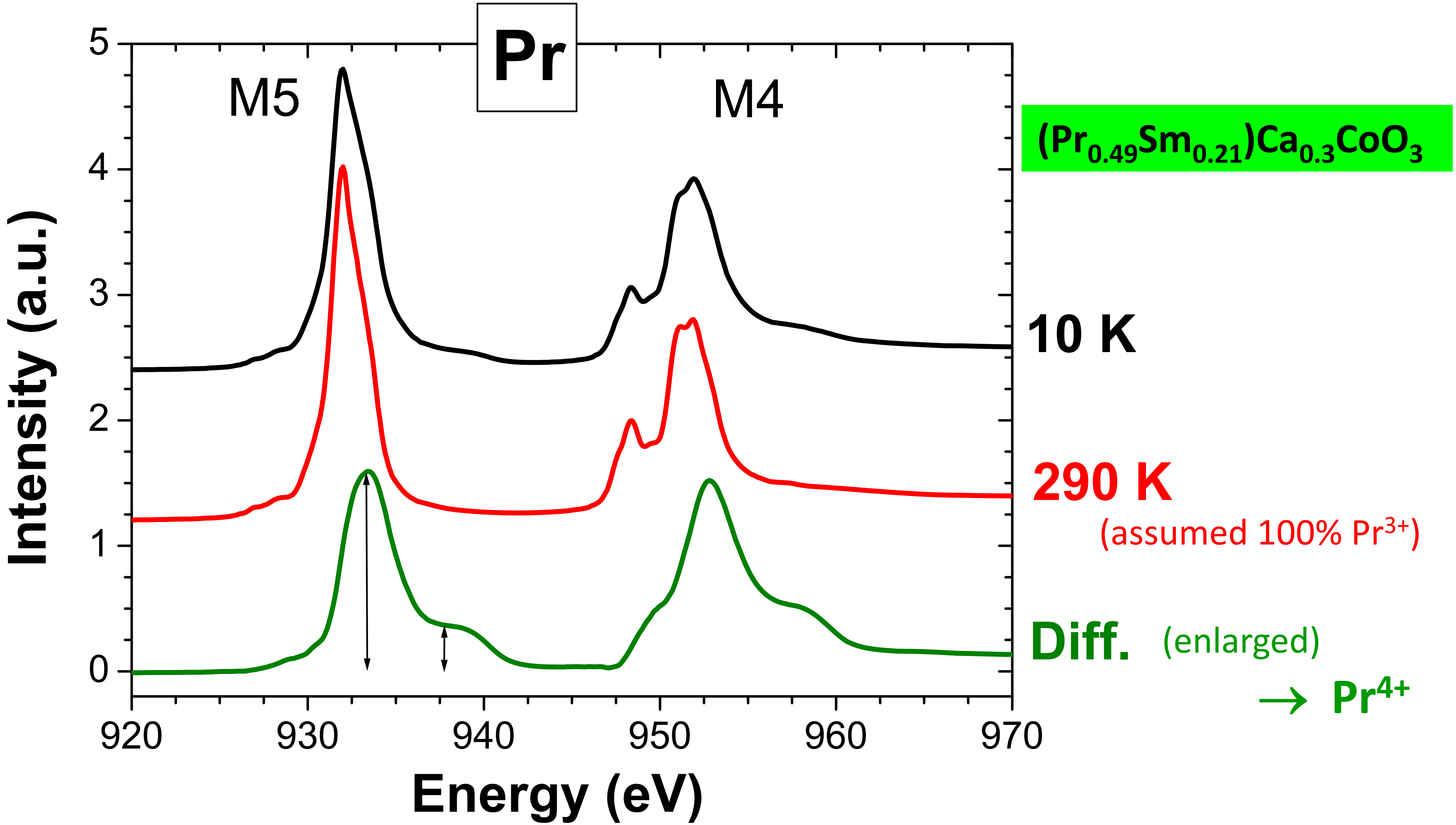




Direct evidence of Pr^{4+} appearance below T*

in agreement with Garcia-Munoz, PRB (2010) and Herrero-Martin, PRB (2011)

Quantitative analysis of Pr^{4+} at 10 K



⇒ T=10K : 0.13 Pr^{4+} /f.u. (= result from ΔS !)

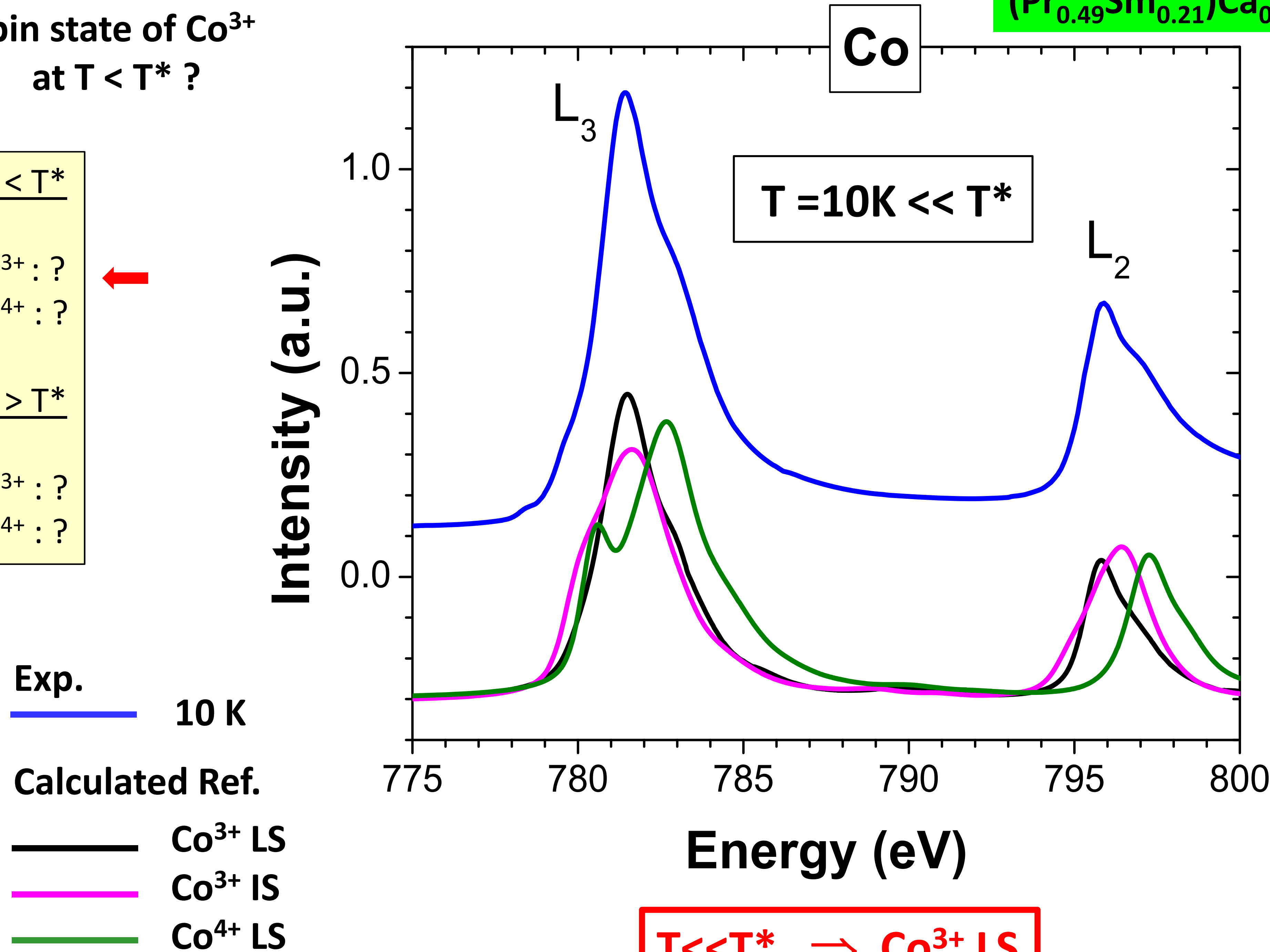
(OK Hejmanek / OK Garcia-Munoz / but larger than Herrero-Martin : 0.075 Pr^{4+}/f.u.)

XAS : Co $L_{2,3}$ absorption edges

$(Pr_{0.49}Sm_{0.21})Ca_{0.3}CoO_3$

Spin state of Co^{3+} at T < T* ?

T < T*
Co^{3+} : ?
Co^{4+} : ?
T > T*
Co^{3+} : ?
Co^{4+} : ?



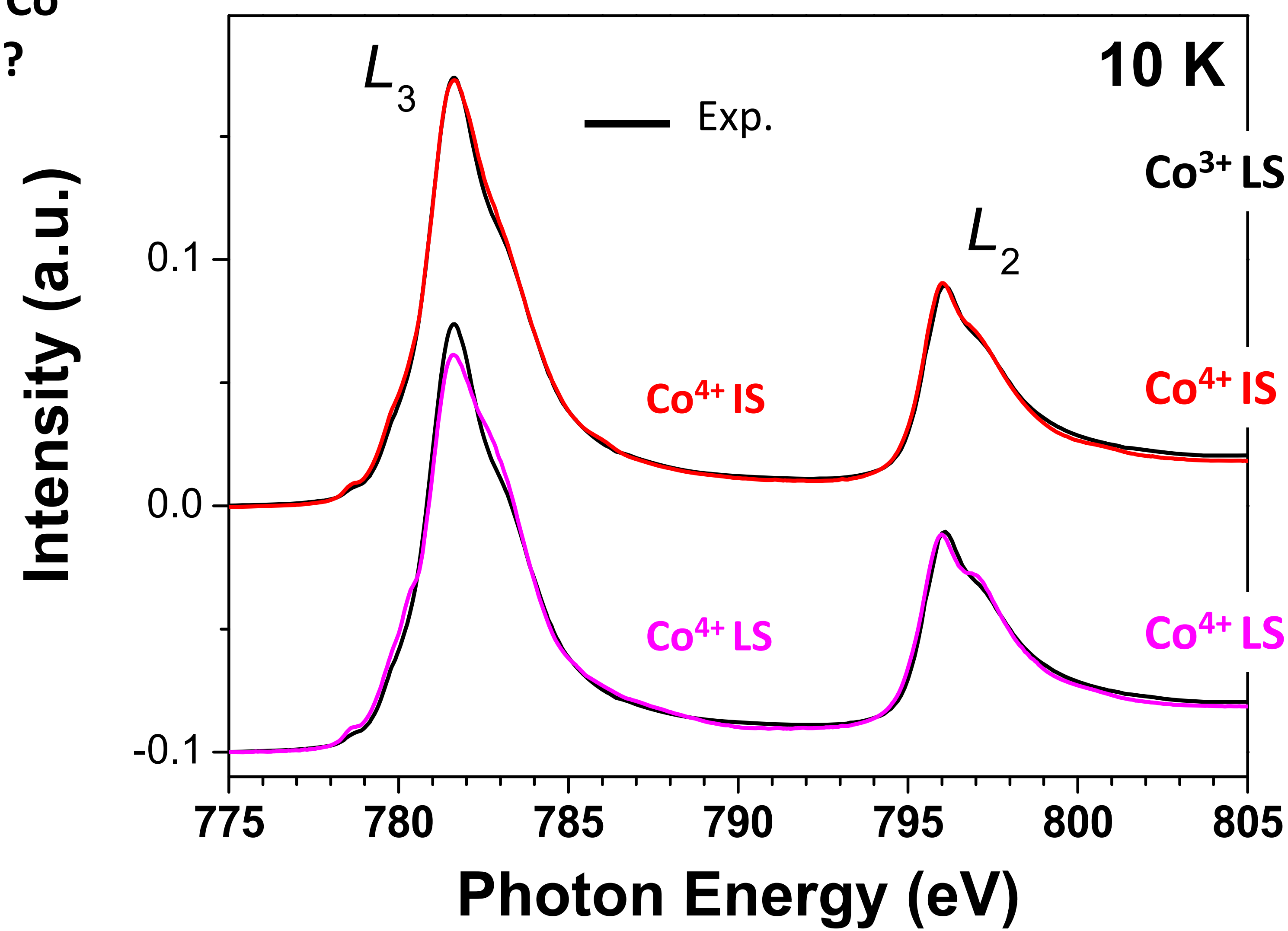
T<<T* ⇒ Co^{3+} LS

XAS : Co $L_{2,3}$ absorption edges

$(Pr_{0.49}Sm_{0.21})Ca_{0.3}CoO_3$

Spin state of Co^{4+} at T < T* ?

T < T*
Co^{3+} : LS
Co^{4+} : ?
T > T*
Co^{3+} : ?
Co^{4+} : ?



Co^{4+} IS fitting $\Rightarrow$ n (Co^{4+}) = 0.16 /f.u. (~ 0.17=0.3 – 0.13)

T<<T* $\Rightarrow$ Co^{4+} IS (→ up to RT)

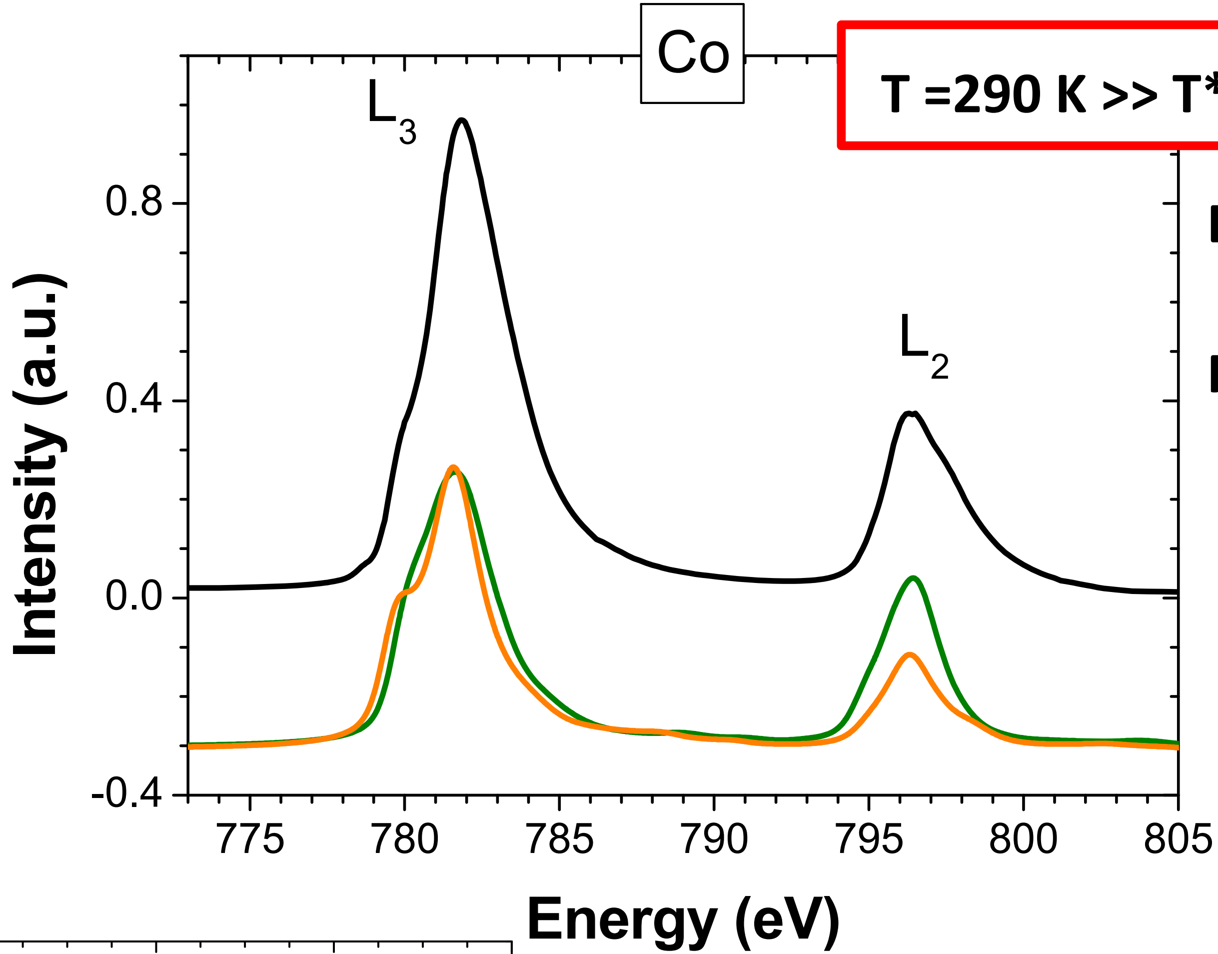
<u>T < T*</u>

Co^{3+} : LS
Co^{4+} : IS

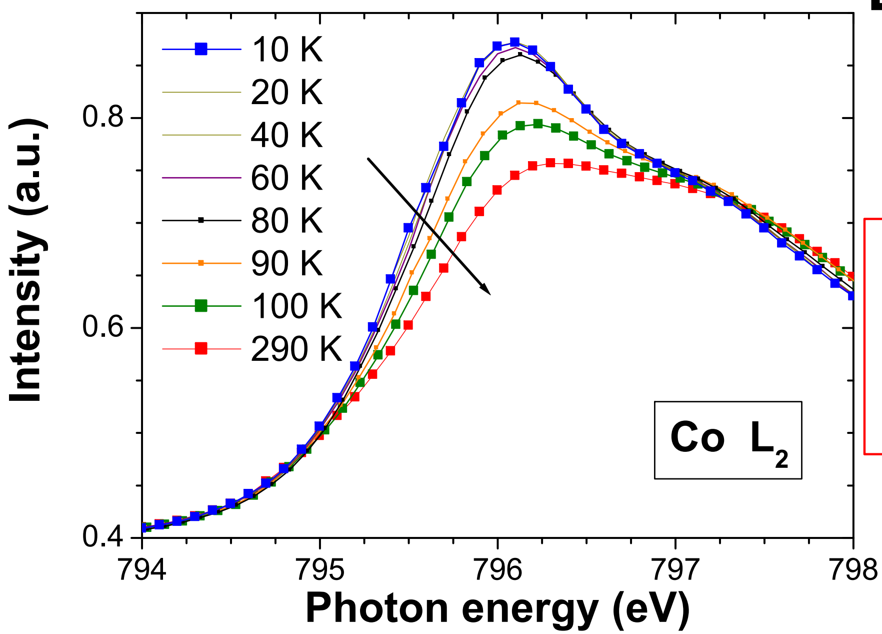
<u>T > T*</u>

Co^{3+} : ?
Co^{4+} : IS

T =290 K >> T*



Shoulder at the low-E side of L_3
⇓
Supports Co^{3+} HS rather than Co^{3+} IS

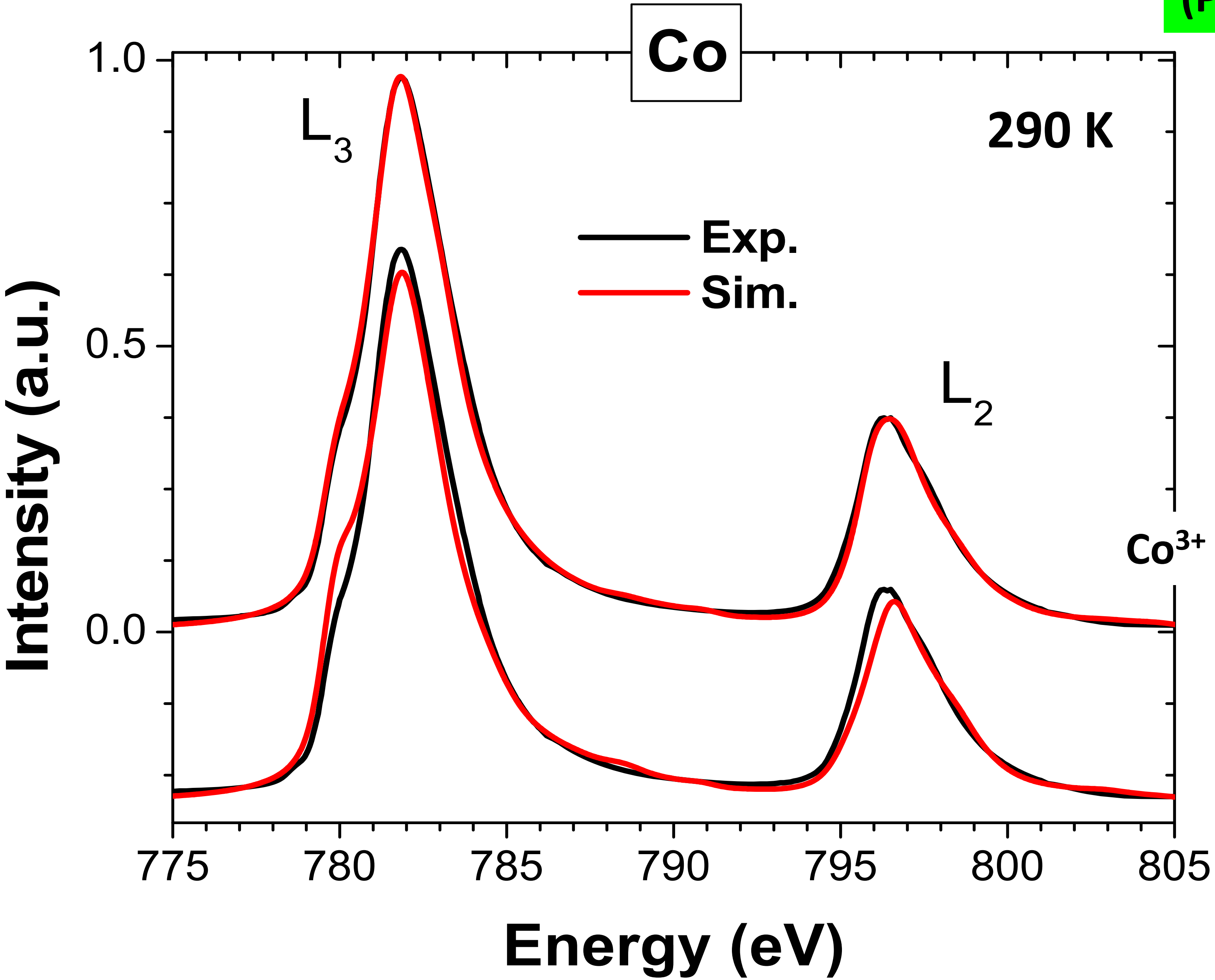


The transition still develops between 100 and 290K …

⇒ Mixed state Co^{3+} (HS,LS) for T>T* ?

Quantitative analysis of a mixed (LS,HS) Co^{3+} at T>T*

$(Pr_{0.49}Sm_{0.21})Ca_{0.3}CoO_3$

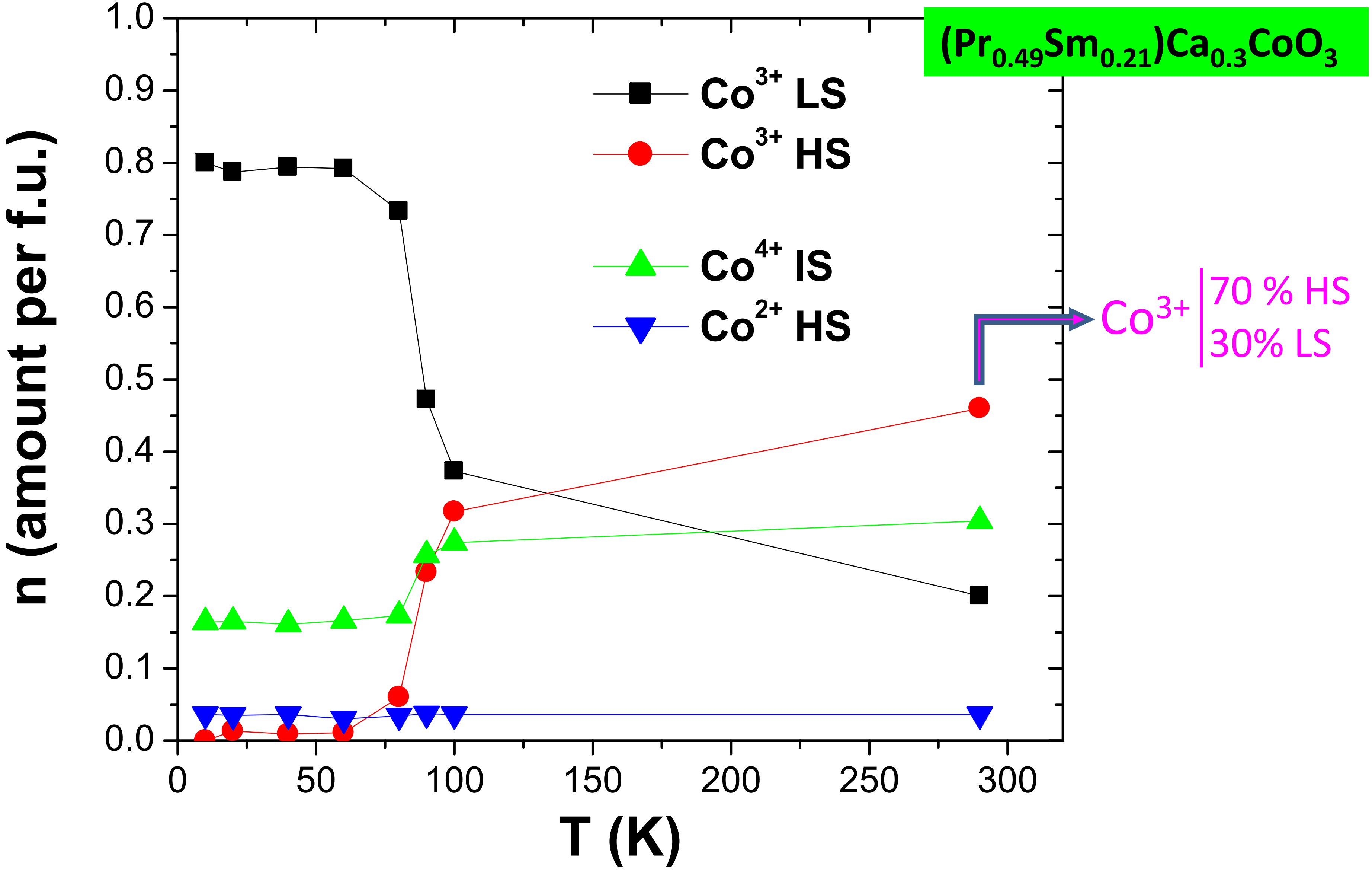


Co^{4+} : IS (100%)

Co^{3+} : HS (70%) + LS (30%)

Co^{3+} : HS (100%)

From all XAS spectra vs. T

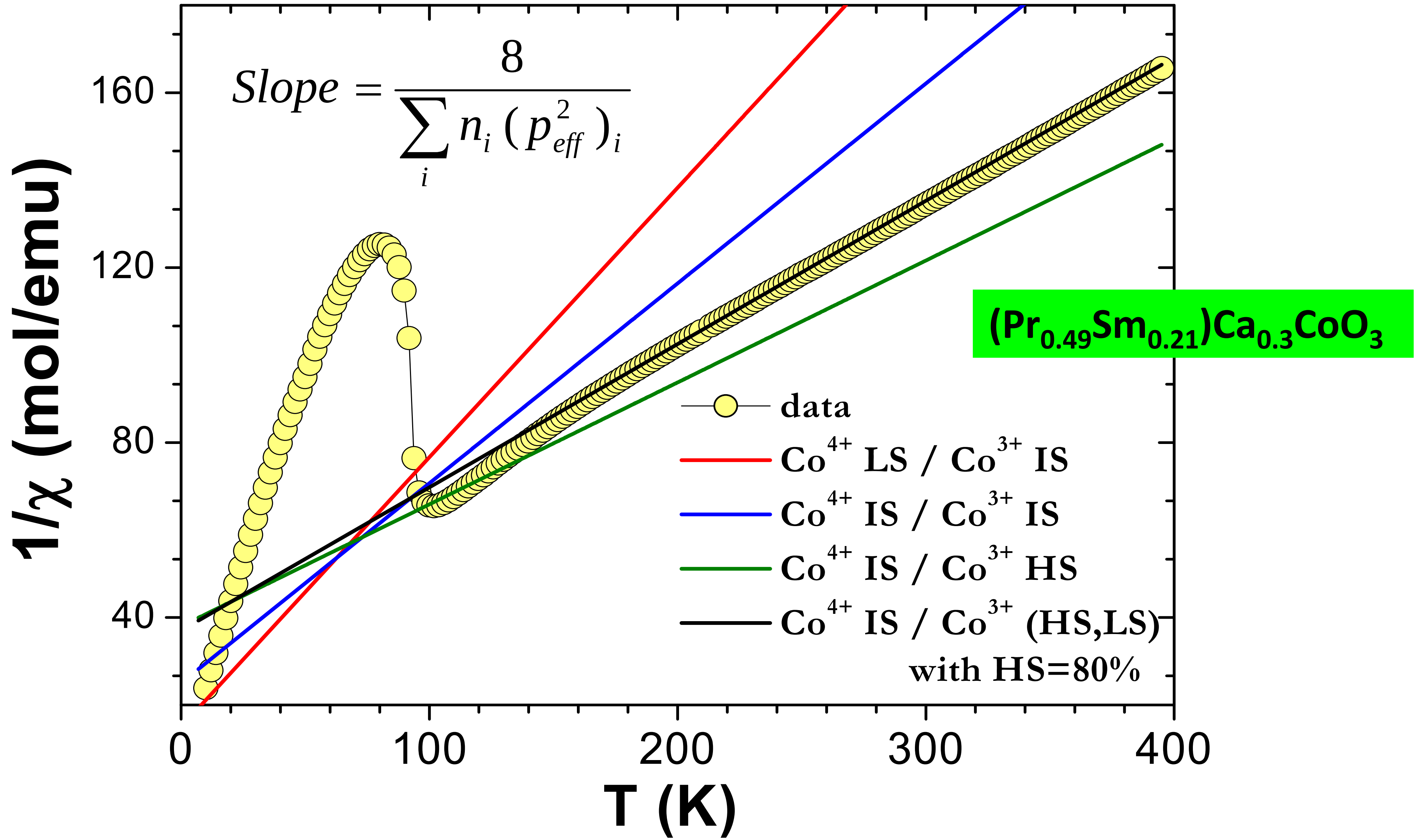


Sharp but only partial spin state transition at T*

(superimposed on a smoother evolution ?...)

Magnetic susceptibility T>>T*

All schemes with a « pure » Co $^{3+}$ Spin State fail to account for the data ,



, whereas mixed Co^{3+} (HS,LS) can do it !

→ reasonable consistency with XAS result at 300 K (80% instead of 70% …)

Conclusion

$(Pr_{0.49}Sm_{0.21})Ca_{0.3}CoO_3$: Valence & Spin State Transition at T* ~ 90 K

- **Suggestion of a new scenario for the VSST in cobaltites**

Valence
- **0.13 Pr^{4+}** + 0.36 Pr^{3+} ↔ 0.49 Pr^{3+}
- 0.13 Co^{3+} + 0.17 Co^{4+} ↔ 0.30 Co^{4+}

Spin
- 0.17 **Co^{4+} IS** ↔ 0.30 **Co^{4+} IS**
- 0.83 **Co^{3+} LS** ↔ 0.70 **Co^{3+} (LS+HS)**

T*

- **To do list:**

  # Use a Co^{3+} IS experimental reference !

  # Reinvestigate the temperature dependence above T*

Thank you for your attention