Perovskite Oxides

CTM4XAS to simulate XAS and XMCD

$Pr_{0.5}Ca_{0.5}CoO_3$

$Pr_{0.5}Sr_{0.5}CoO_3$

$CaMnTi_2O_6$

Perovskite Oxides

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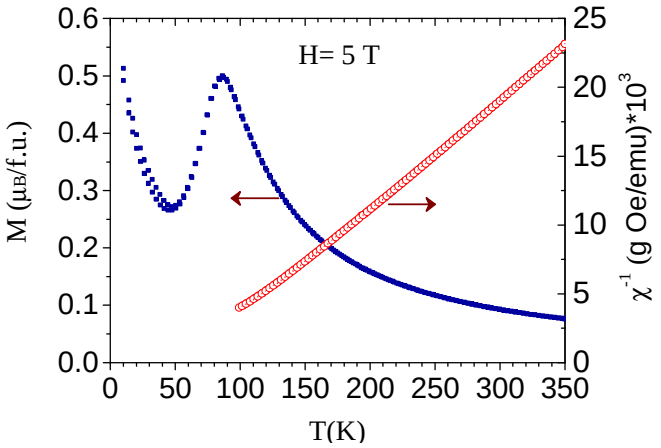
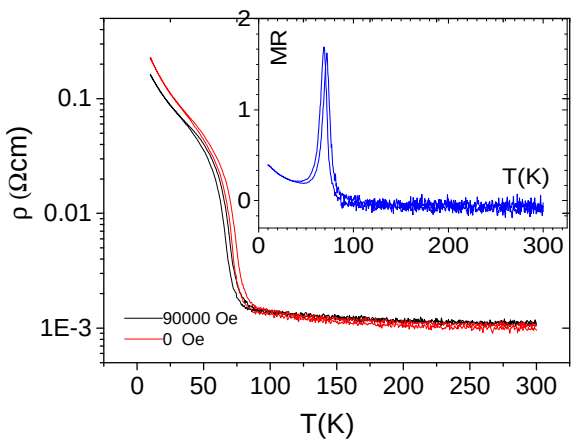
$CaMnTi_2O_6$

$Pr_{0.5}Ca_{0.5}CoO_3$ (PCCO)



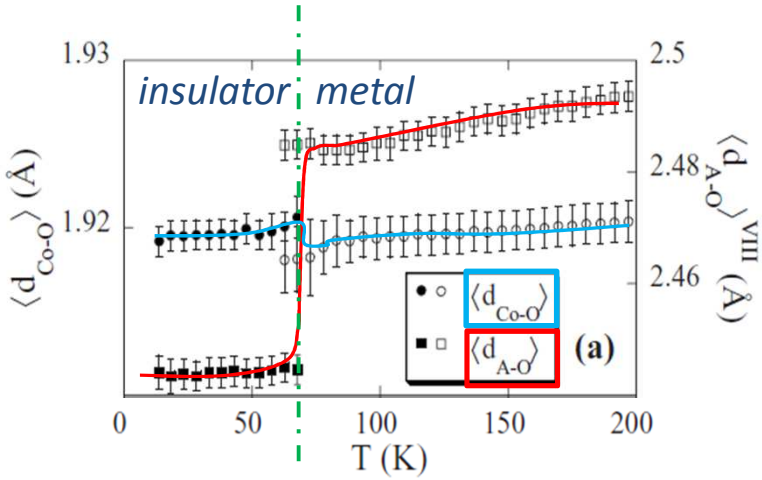


Interest and facts

- Co SS, CO and OO in half-doped oxides
- **MIT** at 75 K, **PM** in all T range
- MIT induceable by laser (photoresponse)
- Pr/Ca-O bondlength sharp contraction

Goal

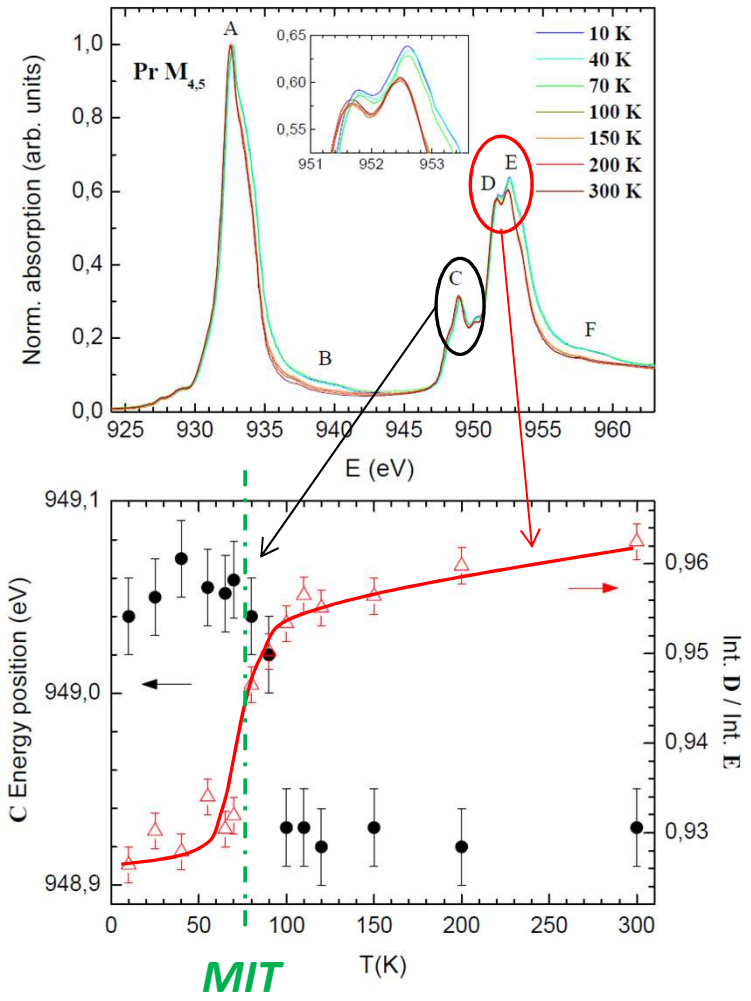
- Understand microscopic electronic configuration of Pr and Co atoms



MIT

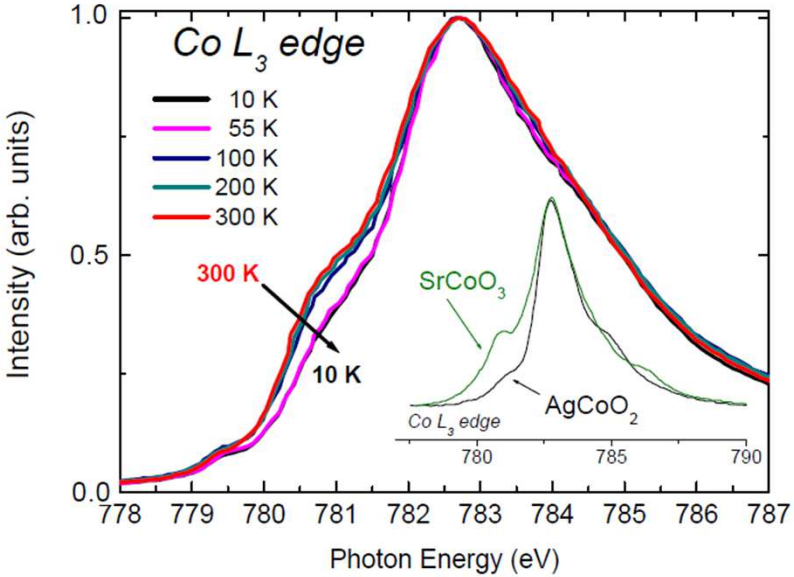
PCCO – experimental XAS

XAS @ Pr $M_{4,5}$ (3d → 4f)



- Pr and Co **valency changes** across MIT?

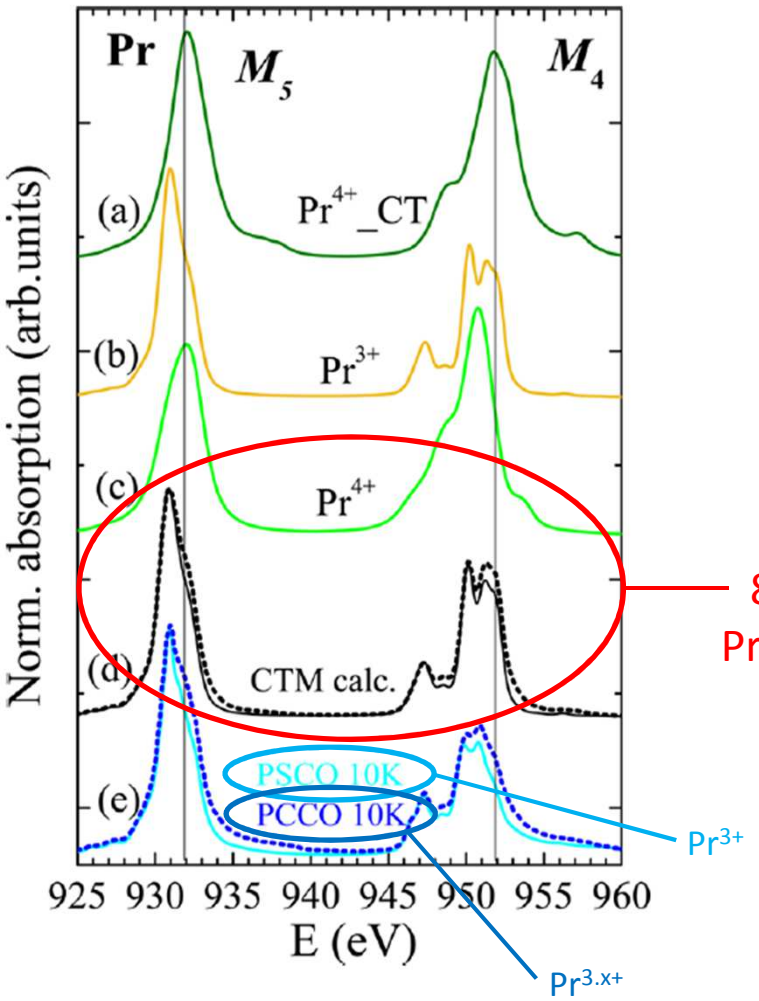
XAS @ Co L_3 (2p → 3d)



PRB 84, 045104 (2011)

PRB 84, 115131 (2011)

PCCO – calculated XAS (CTM4XAS) – Pr $M_{4,5}$

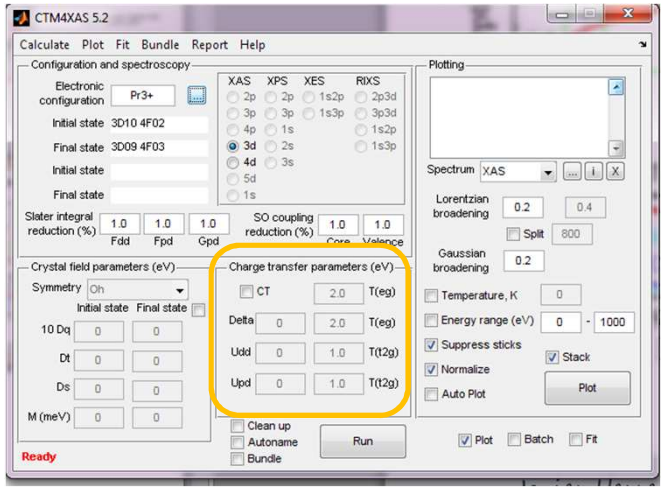


85:15 of Pr^{3+}:Pr^{4+} CT

- Pr^{3+} and Pr^{4+} calculated with CTM4XAS

- Pr^{4+} CT calculated with Cowan code; unable (freezing process) with CTM4XAS

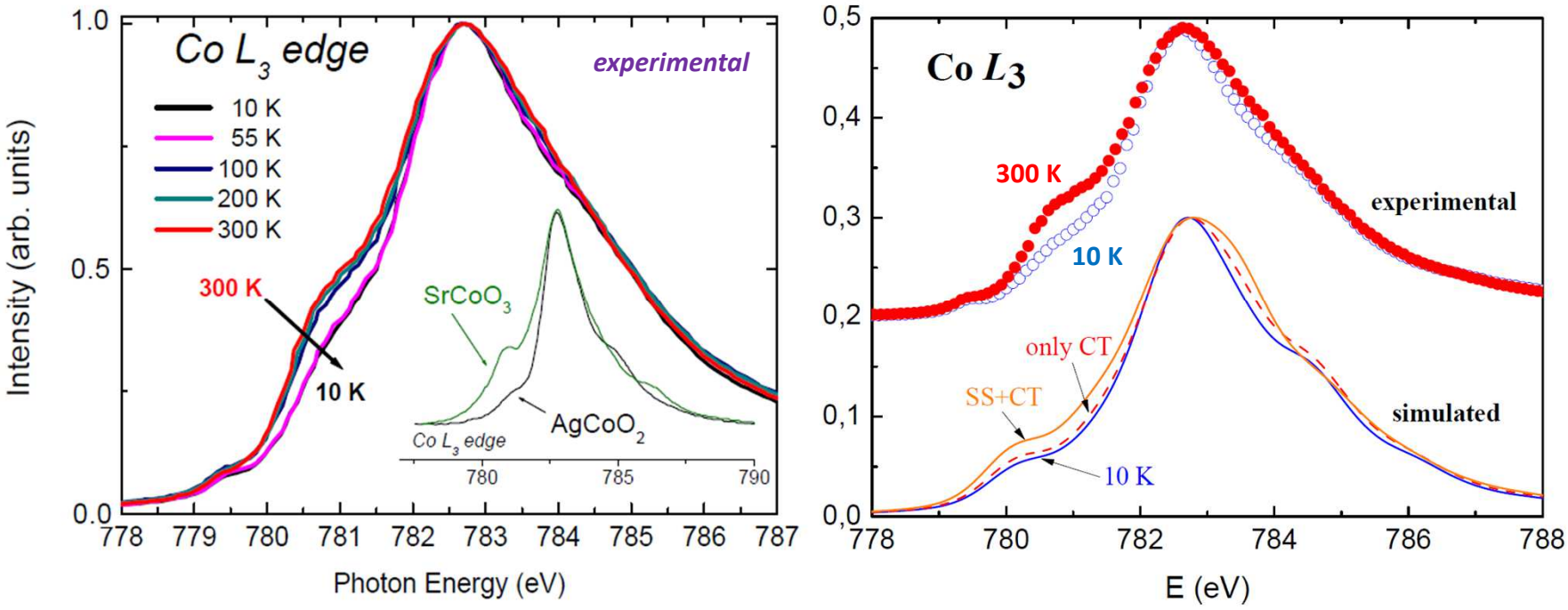
- Local symmetry option not available for REs in CTM4XAS… probably not critical



- Calculations allow to understand and quantify the PCCO XAS changes vs T across the Pr $M_{4,5}$ edges

PCCO – calculated XAS (CTM4XAS) – Co $L_{2,3}$

- Electrons leaving Pr **(-0.15 e-**/atom) must go to Co **(+0.075 e-**/at, i.e. $Co^{3.5+}$ → $Co^{3.42+}$). Calculations permit us correcting previous interpretation of XAS changes at Co L_3 edge: **Co SS** plays a **leading** (spectral) **role**



[25] Parameters employed (eV), $Co^{3+}O_6$: $10Dq = 1.6$ (LS), 1.3 (IS), 0.9 (HS), $\Delta = 3.0$, $U_{pd} - U_{dd} = 1.3$; $Co^{4+}O_6$: $10Dq = 2.4$, $\Delta = -3.5$, $U_{pd} - U_{dd} = 2.3$.

PRB 86, 125106 (2012)

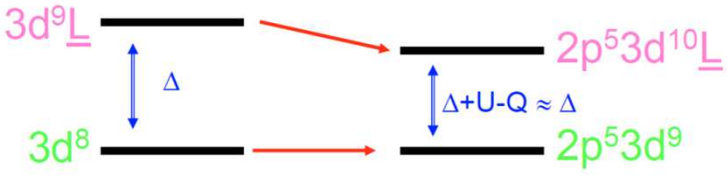
…about CT parameters…

[25] Parameters employed (eV), $Co^{3+}O_6$: $10Dq = 1.6$ (LS), 1.3 (IS), 0.9 (HS), $\Delta = 3.0$, $U_{pd} - U_{dd} = 1.3$; $Co^{4+}O_6$: $10Dq = 2.4$, $\Delta = -3.5$, $U_{pd} - U_{dd} = 2.3$.

Charge Transfer in XAS

NiO: Ground state: $3d^8$ + $3d^9\underline{L}$

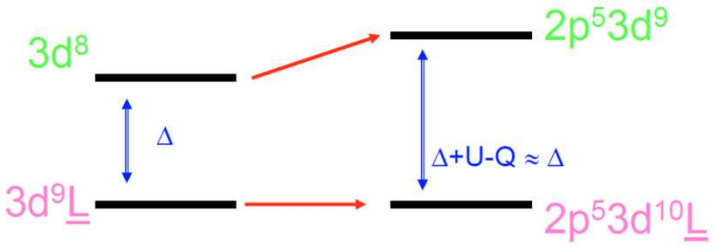
Energy of $3d^9\underline{L}$: Charge transfer energy Δ



Charge Transfer in XAS

Cu^{III}: Ground state: $3d^8$ + $3d^9\underline{L}$

Energy of $3d^9\underline{L}$: Charge transfer energy Δ<0

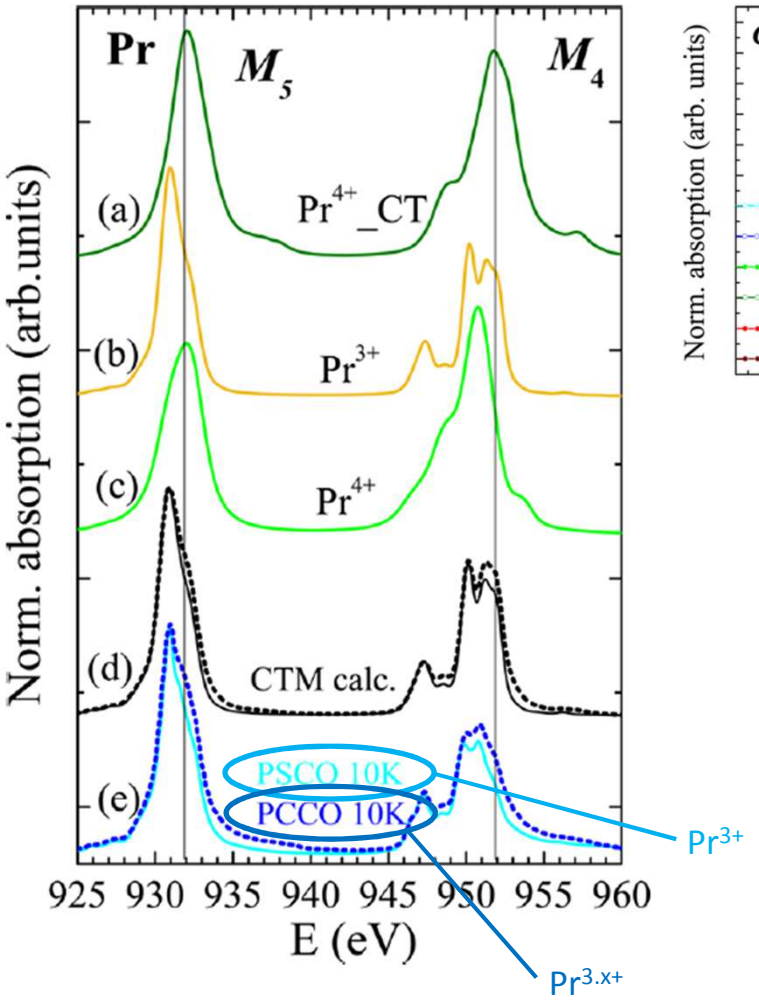


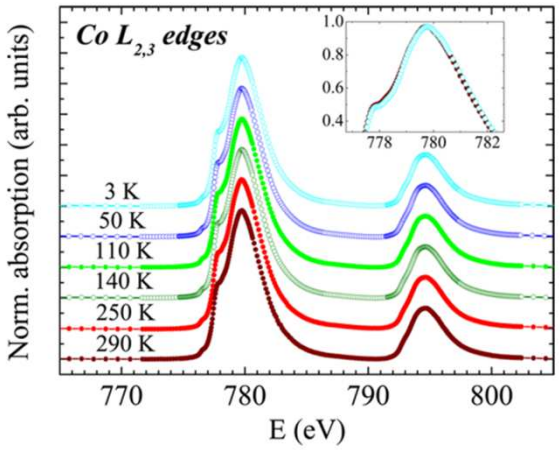
"stolen" from F.M.F de Groot slides…

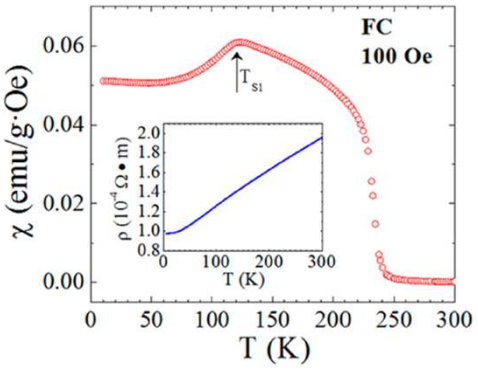
Q-U ~ 1-2 eV (i.e. U-Q <0)

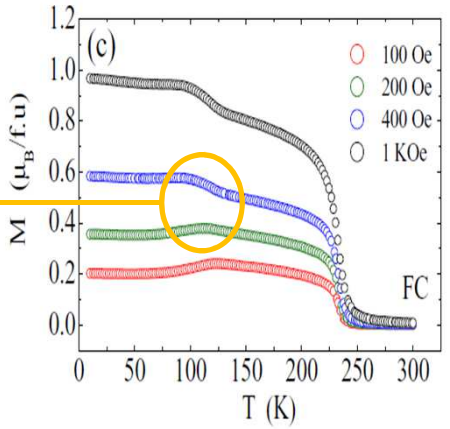
Alternative notation…: **$Q=U_{pd}$ or U_{cd}; $U=U_{dd}$**

PSCO – invariant Pr $M_{4,5}$ & Co $L_{2,3}$ XAS







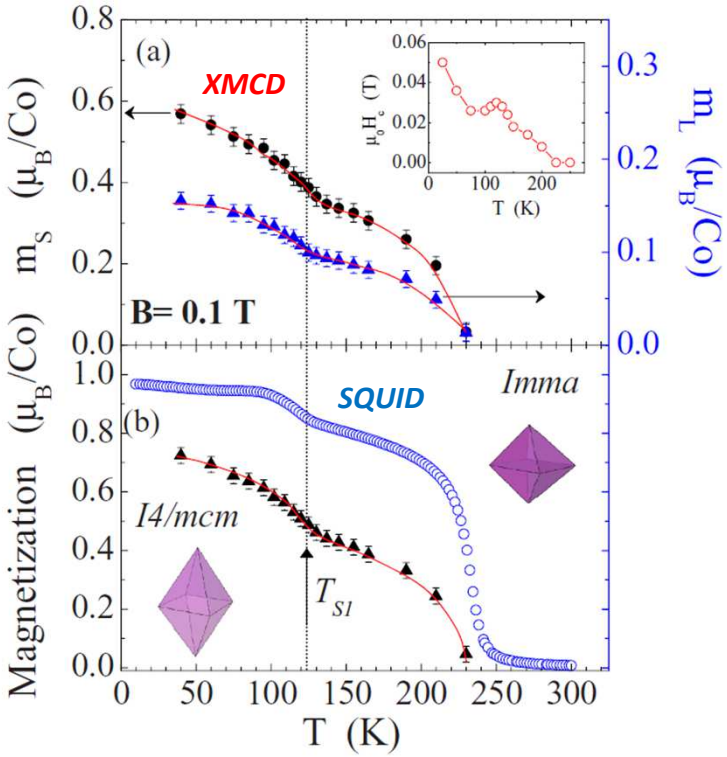


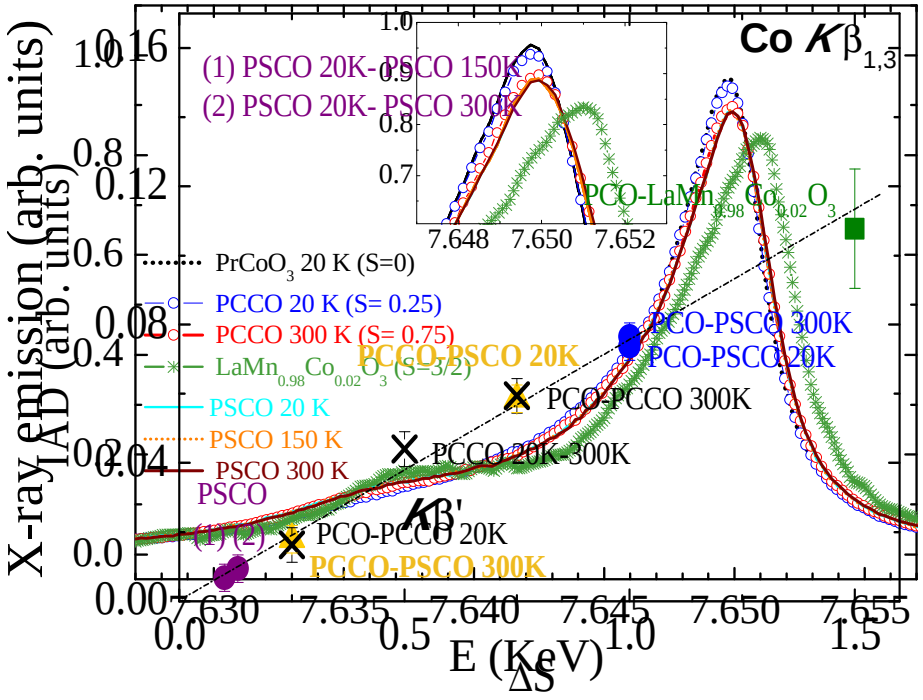
Crossover ~30 mT

- PSCO shows **stable** Pr^{3+} and $Co^{3.5+}$ (regardless of T)
- No MIT, always **metallic** and **FM** below 230 K
- Unexpected **FM-FM** transition at 120 K

Inorg.Chem. 53, 8854 (2014)

PSCO – calculated XMCD (CTM4XAS) – Co $L_{2,3}$





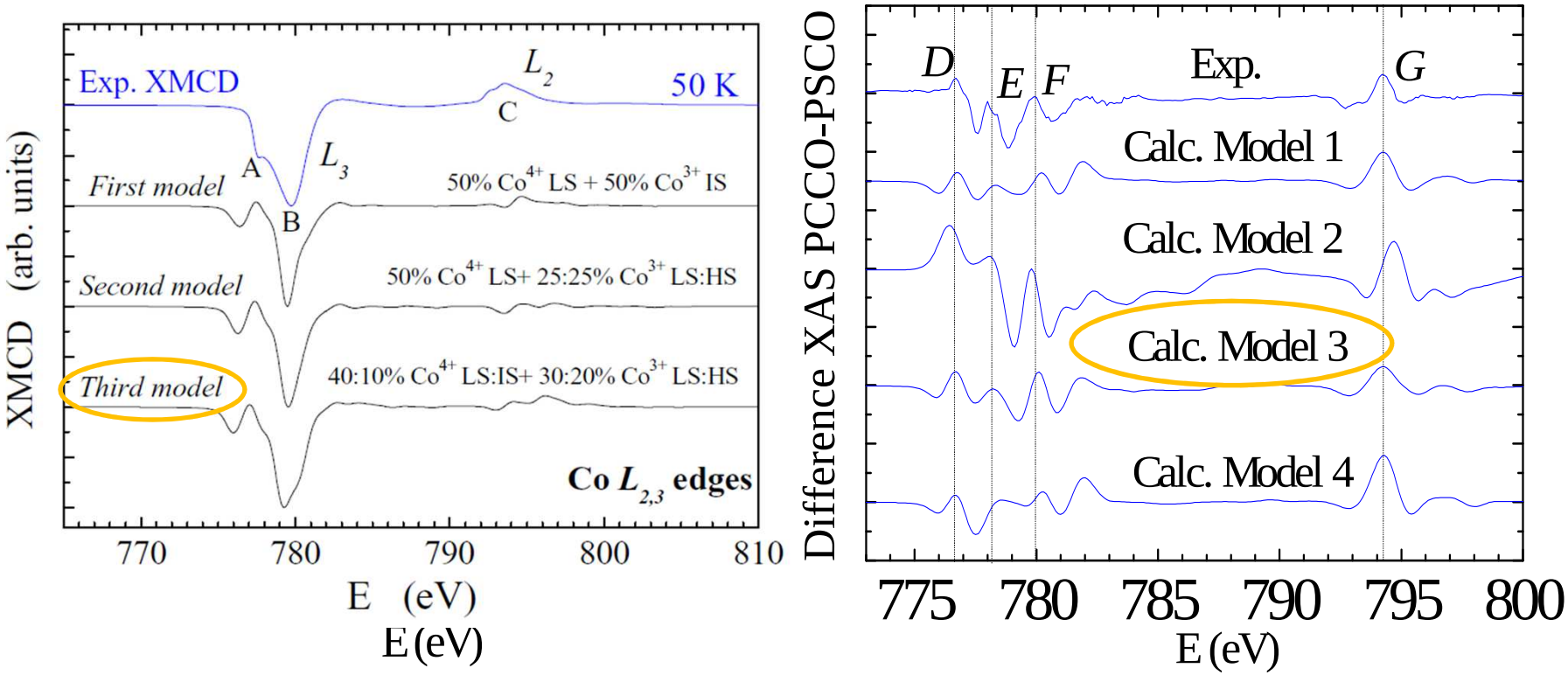
- *PSCO → **S ~1.0***

*[PCCO → **S ~0.25 (10 K), ~0.75 (300 K)**]*

- Sizeable orbital moment **m_L ~ 1/3 m_S**
- Same evolution m_S and m_L ⇨ **large SPIN-ORBIT** coupling

PRB 92, 245136 (2015)

PCCO vs PSCO – Co $L_{2,3}$ XAS



- Complex mixture of Co^{3+}, Co^{4+} configurations: **little Co^{3+} LS** and **lifted Co^{4+} spin state**

PCCO & PSCO – summary

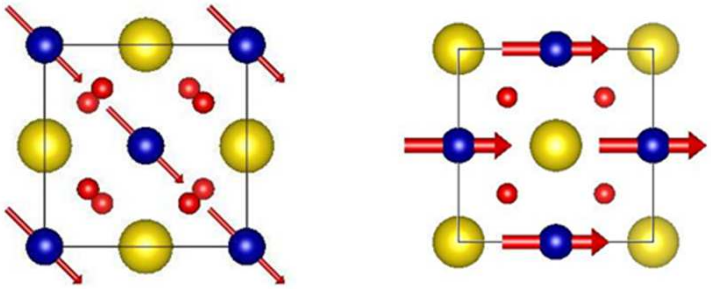
*" $Pr_{0.5}A_{0.5}CoO_3$ (**A=Sr, Ca**) show very different electrical and magnetic properties, but both display **singular low T phase transitions** "*

$Pr_{0.5}Ca_{0.5}CoO_3$

- *$Pr_{0.5}Ca_{0.5}CoO_3$ shows Pr → Co charge transfer and Co^{3+} SS change at MIT (CTM4XAS)*

$Pr_{0.5}Sr_{0.5}CoO_3$

- *Across T_{S1} (FM1-FM2) the **oxidation** & **spin** state of **Co** & **Pr ions** remains **stable***
- *We have modelled the Co 3d configuration: **lifted SS** at low T (CTM4XAS)*
- *At T_{S1} (FM1-FM2) the **orbital moment** (~ 1/3 m_S) drives a 45º rotation of Co spins triggered by the orth. → tetr. transition (large magnetostructural coupling)*



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$Pr_{0.5}Ca_{0.5}CoO_3$

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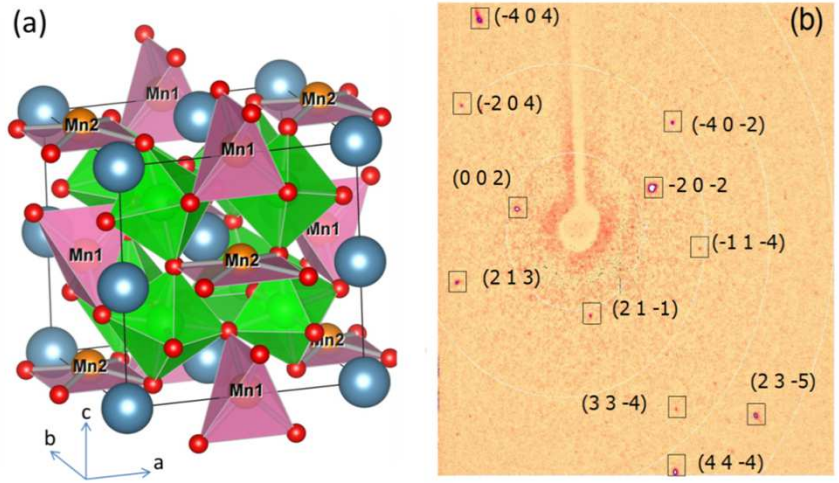
$CaMnTi_2O_6$

$CaMnTi_2O_6$ (CMTO)



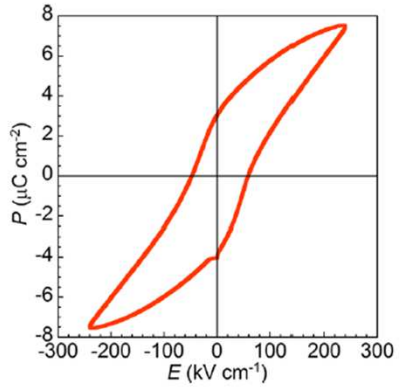


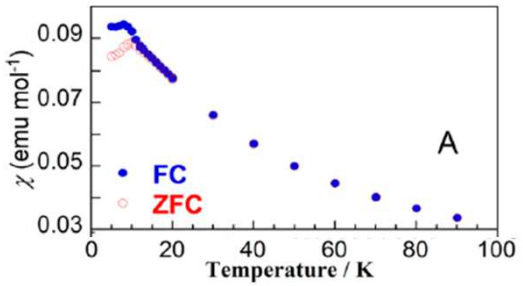
Figure 3. *P-E* hysteresis loop for $CaMnTi_2O_6$ at room temperature. A sample thickness is 0.18 mm and measurement frequency is 200 Hz.

Interest and facts

- **FE at RT**, based on accessible elements
- **A-ordered** DP (rare)
- PM; **AFM** order only at T< 10 K
- **2 Mn sites**; 1 Ti site
- FE of ion (Mn, Ti) **displacive type**

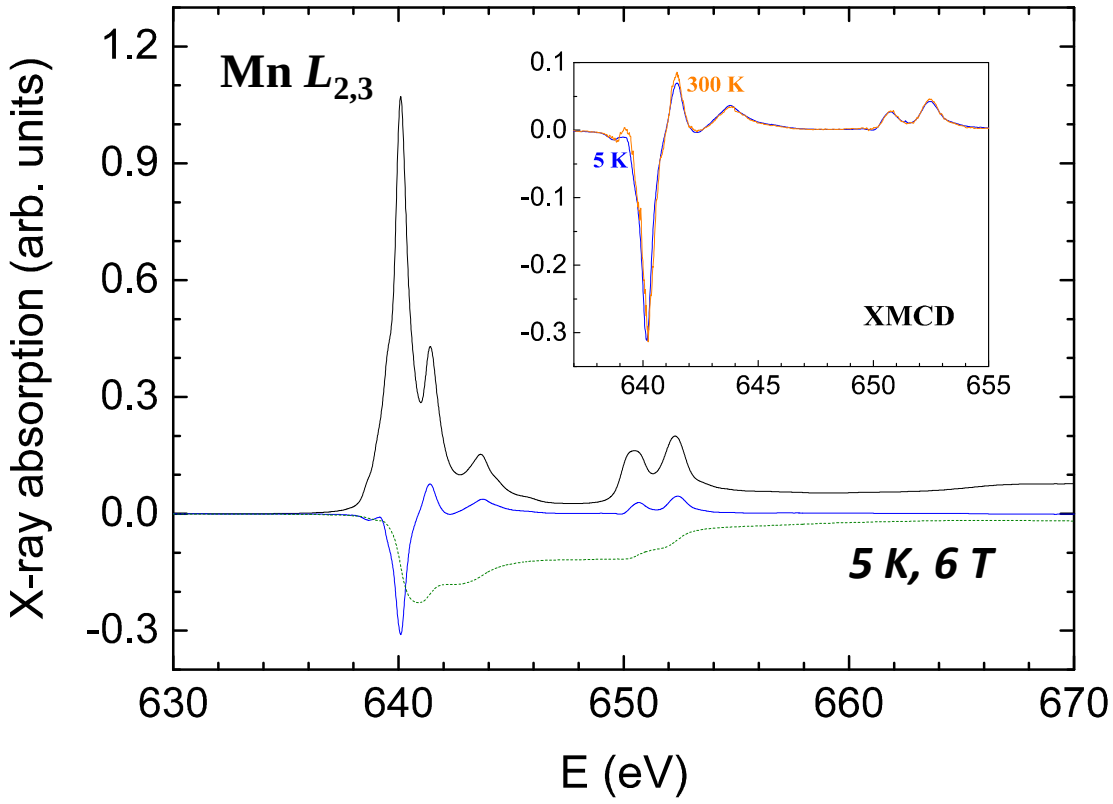
Goal

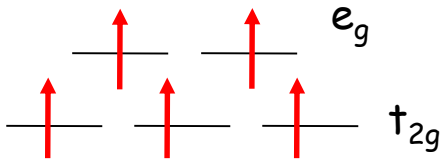
- electronic state of Mn1, Mn2 and Ti
- Type of AFM (?) order at low T



Chem.Mater.26, 2601 (2014)

CMTO – experimental XAS



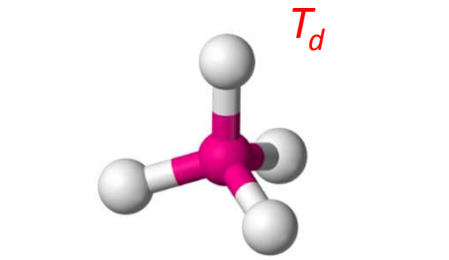


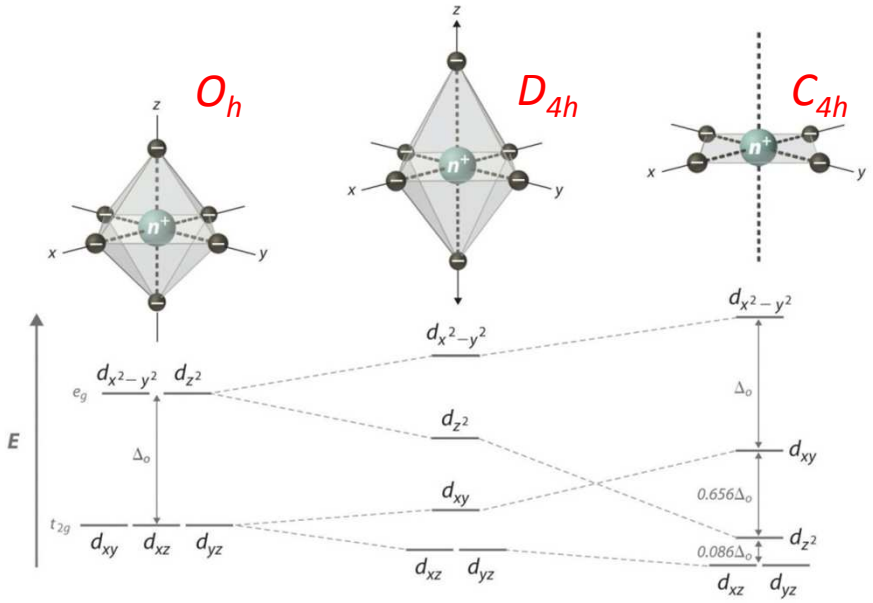
d^5 HS (cubic)

- For (ideally atomic) Mn^{2+}: S=5/2 (m_S=5.81 μB/at, m_L=0)
- Experimentally (XMCD sum rules): **m_S=0.73 μB**, **m_L=0.03 μB** (at 5 K) → PM or AFM (not FM)
- ~ no changes of XAS and XMCD vs T (PM vs AFM? phase)

CMTO – Mn^{2+} local symmetries

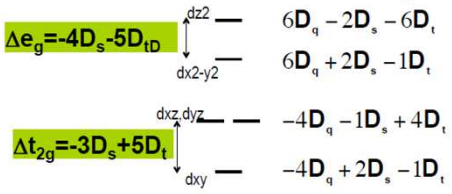
Local symmetry around transition metals



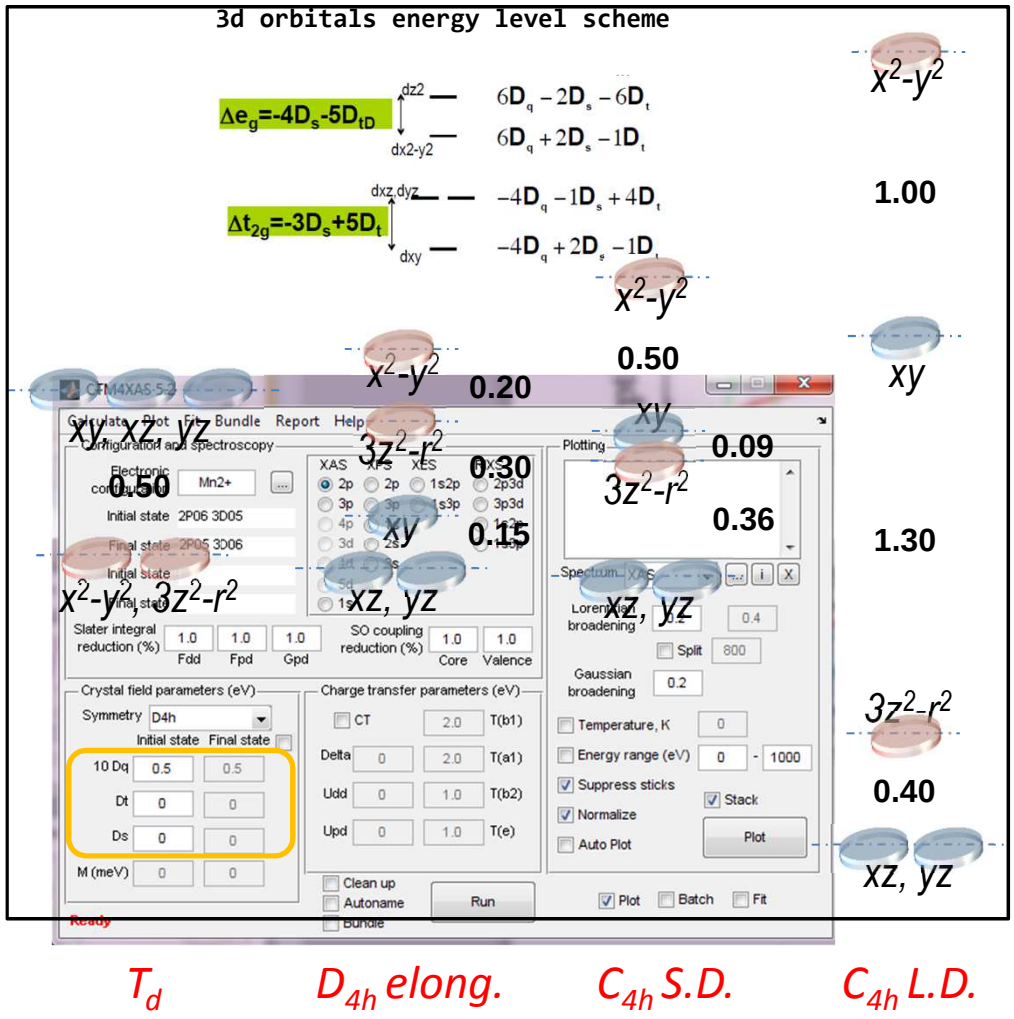


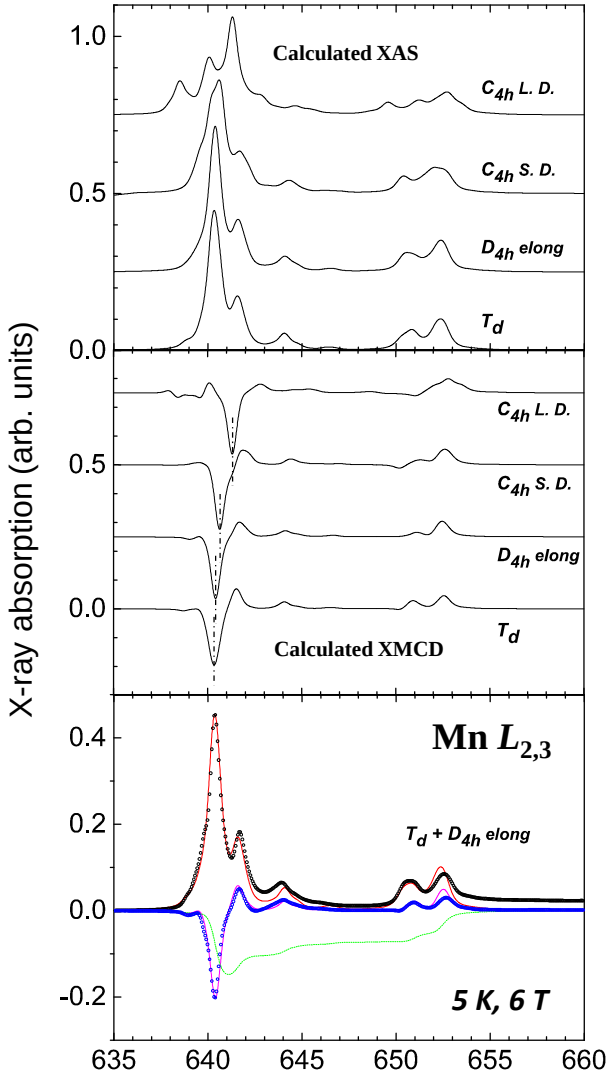
Mn1 **Mn2?**

3d orbitals energy level scheme

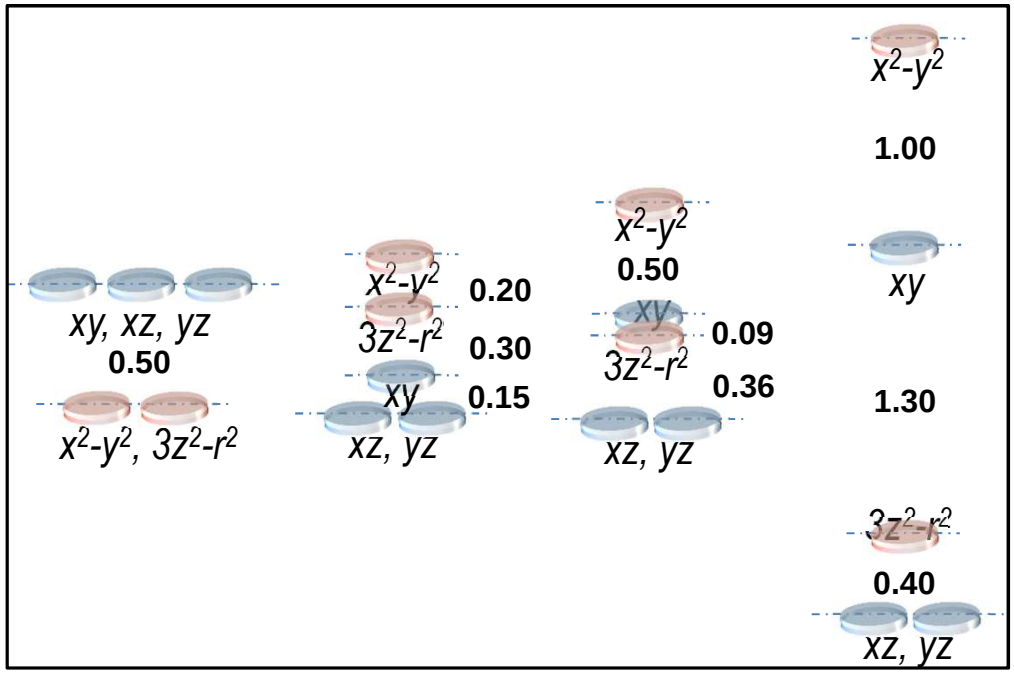


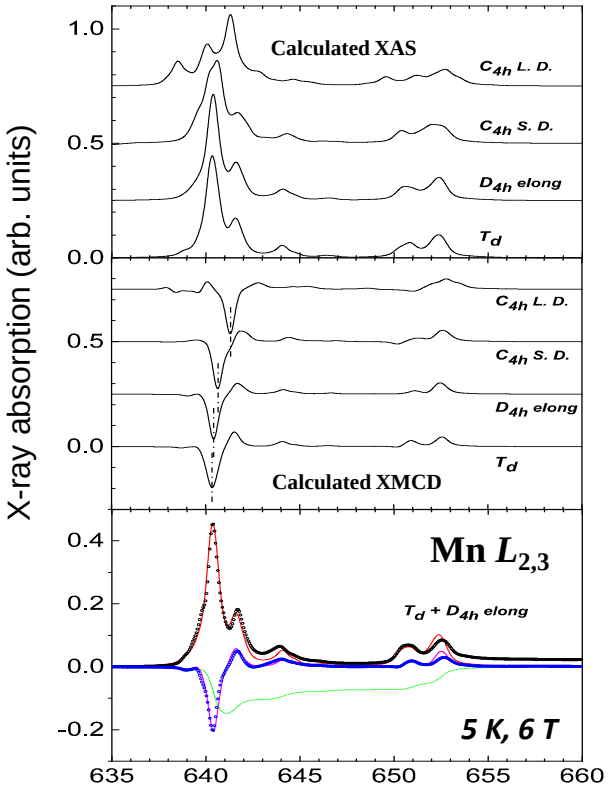
CMTO – XAS calculations – Mn $L_{2,3}$





CMTO – XAS calculations – Mn $L_{2,3}$

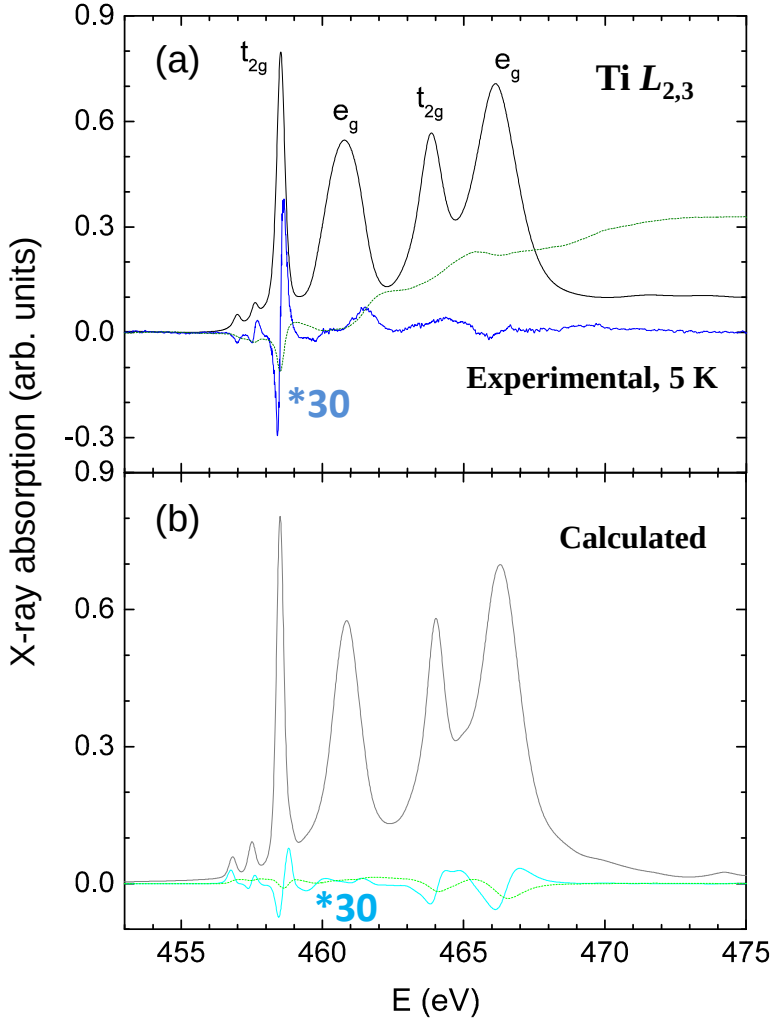




- Mn2 sites **not** really **square planar** (contrarily to as claimed) ($E_{3z2-r2}>E_{xy}$)
- **Mn1 and Mn2** moments [projection over applied B field (6 T)] add up in a **parallel** way in the AFM phase (~ PM phase)

Parameters (eV) for Mn1: T_d symmetry, 10Dq = -0.5, Ds=Dt=0; for Mn2: C_4 symm., 10Dq = 0.5, Ds=0.05, Dt=0. In all cases M=1 meV

CMTO – XAS calculations – Ti $L_{2,3}$

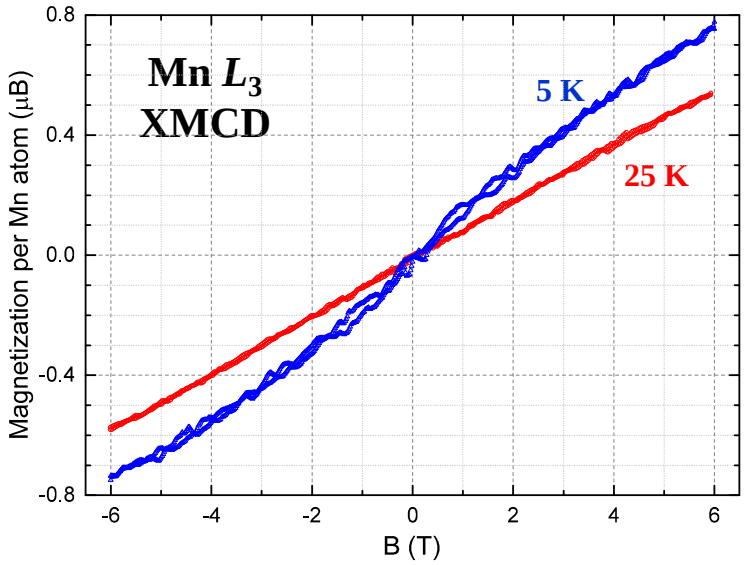


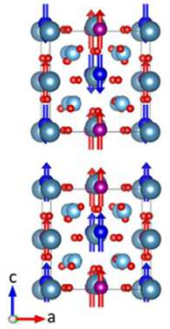
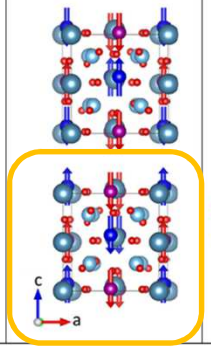
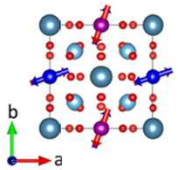
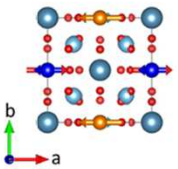
- Ti^{4+}, as expected (no Ti^{3+} traces)
- Relatively large XMCD signal
- m_S=0.018, m_L=-0.013 → m_{TOT}=0.004

- CT from O needed: $0.7 \cdot 3d^0 + 0.3 \cdot 3d^1\underline{L}$ as GS
- calc. XMCD not that good; mL=0 in calcs.
- actual C_1 symm. (Ti^{4+} off center) unavailable using CTM4XAS

Parameters employed (eV) for Ti: C_4 symm., 10Dq = 2.2, Ds=0.1, Dt=0.06, Δ(C – T) =3.0, $U_{cd} - U_{dd}$ = 2.0. In all cases M=1 meV

CMTO – magnetic order



Magnetic Space Group	*P4₂m'c'* (No. 105.215)	*P42'm'c* (No. 105.213)	*Cc'c2'* (No. 37.182)	*Pm'm2'* (No. 25.59)
Transformation to standard setting	(a, b, c; 0, 0, 0)	(a, b, c; 0, 0, 0)	(a+b, -a+b, c ; 0, 0, 0)]	(-b, a, c ; 0, 0, 0)
Magnetic Point Group	4m'm' (#13.4.47)	4'm'm (#13.3.46)	m'm2' (#7.3.22)	m'm2' (#7.3.22)
Independent magnetic Wyckoff positions (expressed in parent Tet. setting)	Mn1 (0,1/2,z | 0,0,m_z) Mn2 (0,1/2,z | 0,0,m_z)	Mn1 (0,1/2,z | 0,0,m_z) Mn2 (0,1/2,z | 0,0,m_z)	Mn1 (0,1/2,z | m_x,m_y,0) Mn2 (0,1/2,z | m_x,m_y,0)	Mn11 (0,1/2,z | m_x,0,0) Mn12 (1/2,0,z+1/2 | m_x,0,0) Mn21 (0,1/2,z | m_x,0,0) Mn22 (1/2,0,z+1/2 | m_x,0,0)
Magnetic structure				

- (weak) **FM** interactions (along *c*) **within** the **AFM** (interchain) **phase** below T_N=10 K

- All (**FM** and **AFM**) interactions are **weak** (AFM due to SSE coupling) which explains: i) low ordering T and ii) Mn^{2+} XMCD: Mn1 and Mn2 parallel to B applied field

Not possible without…

- ***Dr. Jessica Padilla-Pantoja*** *(ICN2)*
- ***Prof. José Luis García-Muñoz****, C. Frontera (ICMAB), J. Blasco (ICMA)*
- *Dr. Javier Ruiz-Fuertes (UNICAN)*
- *Dr. Manuel Valvidares, Dr. Pierluigi Gargiani, Dr. Hari-Babu Vasili… (BL29-BOREAS)*
- *Prof. F. M. F. De Groot (CTM4XAS)*

To finish… my personal experience with CTM4XAS

- ***User friendly**, easy to choose oxidation states and some local symmetries*
- *Crystal field energy **easy** to work with to simulate different **spin states***
- *Be **careful** with (default) **energy shifts** between different oxidation states…*
- ***Limited** when **symmetry** gets lowered… for instance loss of inversion symmetry center*
- *XMCD calculations do not provide **freedom** to play with **magnetic anisotropy** axis*
- ***Molecular field** energy [M(meV)] seems to comprehend applied+internal field and values behave as **quantized**..?*
- ***One misses** the possibility to provide 1st coord. shell **bondlengths** as an input to calculate some of the electronic parameters (that otherwise one has to guess)…*