



PuCrO₃ compound synthesis, structural and thermodynamic studies

J. Léchelle, R. C. Belin, P. M. Martin, C. Martial, A. Pieragnoli, R. Thomas, G. Cecilia, P. Valenza, J. C. Richaud, M. Reynaud, et al.

► To cite this version:

J. Léchelle, R. C. Belin, P. M. Martin, C. Martial, A. Pieragnoli, et al.. PuCrO₃ compound synthesis, structural and thermodynamic studies. JdA2015 - 45èmes Journées des actinides, Apr 2015, Prague, Czech Republic. cea-02489490

HAL Id: cea-02489490

<https://cea.hal.science/cea-02489490>

Submitted on 19 Jun 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

FROM RESEARCH TO INDUSTRY



JDA2015 - Section: New compounds III

PuCrO₃ COMPOUND: SYNTHESIS, STRUCTURAL AND THERMODYNAMIC PROPERTIES

Journées des Actinides | J.Léchelle¹, R.C. Belin¹, P.M. Martin¹, C. Martial¹, A.Pieragnoli¹, R. Thomas¹, G. Cécilia¹, P.J. Valenza¹, J.C. Richaud¹, M. Reynaud¹, Y. Marc¹, A.C. Scheinost², J.M. Heintz³

¹ CEA, DEN, MAR, DTEC, SECA, LCC and CEA, DEN, CAD, DEC, SESC, LLCC , 13108 Saint-Paul-lez-Durance, France, e-mail: Jacques.lechelle@cea.fr

² Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, D-01314 Dresden, Germany

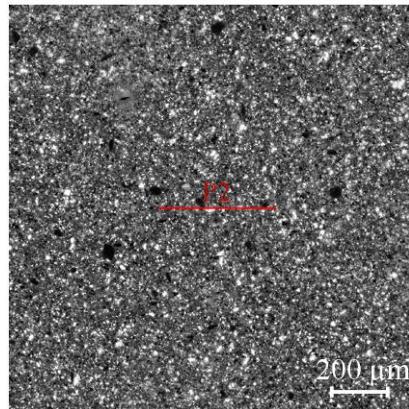
³ ICMCB – CNRS, UPR9048, 87 Avenue du Docteur Schweitzer, 33608 PESSAC cedex, France

APRIL 19th 2015

CONTEXT: FUEL HOMOGENIZATION DURING FABRICATION

($U_{0,89}Pu_{0,11}$) O_{2-x} doped with 3000 ppm Cr_2O_3 (sintered with $\mu(O_2)=-445\text{ kJ/mol}$)

Thomas R. PhD Thesis, University of Bordeaux I, 2013



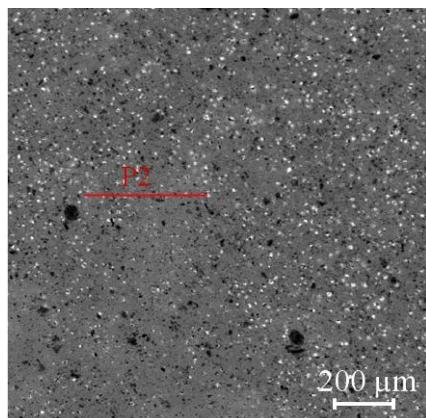
Without Cr_2O_3 addition

much

[Pu] varies

less

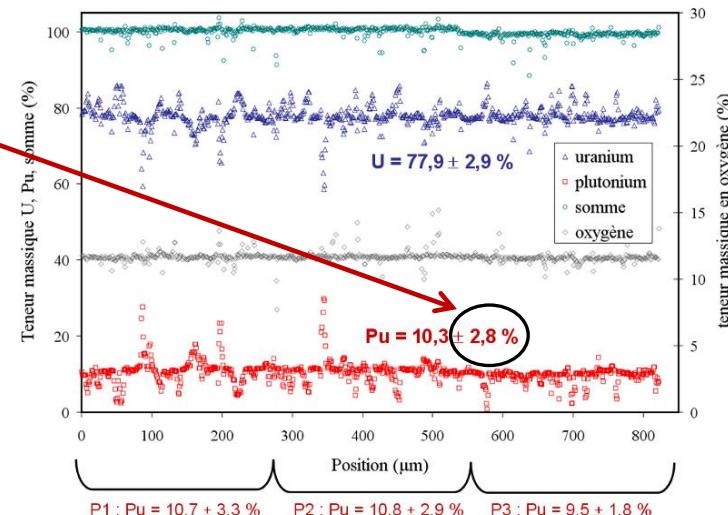
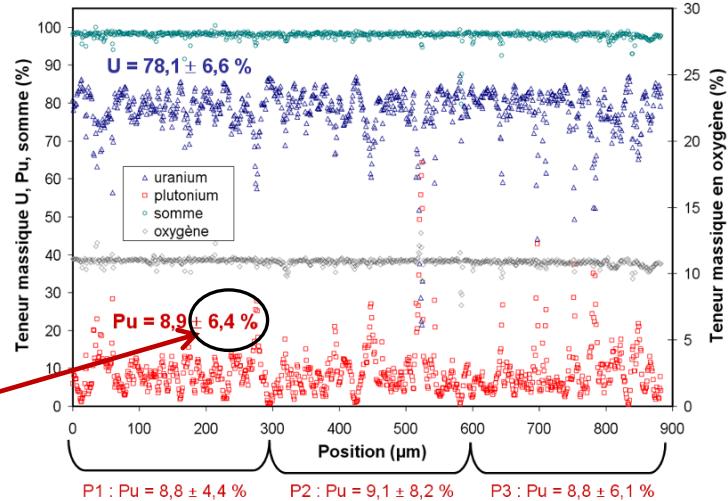
With Cr_2O_3 addition



A necessary transient compound: $PuCrO_3$

(A. Pieragnoli PhD Thesis, University of Limoges, 2007)

Quantitative profiles (red line in the maps)



OUTLINE

1. Introduction

Synthesis conditions

2. Crystal chemistry

XRD and XAS studies

3. Thermodynamic and physical properties

Dilatometry, DSC studies

4. Conclusion

Phase change to be considered for thermodynamic databases

INTRODUCTION: SYNTHESIS CONDITIONS

Experimental Synthesis of PuCrO_3 from PuO_2 and Cr_2O_3

1. **L.E. Russell, J.D.L. Harrison, and N.H. Brett.** Perovskite-type compounds based on plutonium. *Journal of Nuclear Materials* 2, n°. 4 (1960), 310-320

2. **A. Pieragnoli,** Influence de l'adjvant de frittage Cr_2O_3 sur l'homogénéisation de la répartition en plutonium au sein d'une pastille MOX hétérogène. *Matériaux Céramiques et Traitements de Surface, Thèse de l'Université de Limoges*, 2007

3. **R. Thomas,** MOX dopé chrome : optimisation du dopage et de l'atmosphère de frittage, *Thèse de l'Université de Bordeaux 1*, 2013

	Formation Temperature of PuCrO_3 (°C)	Densification Temperature (°C) of the compact	
Ar*	1600-1700	1300	PuO ₂ sinters alone
Ar + 5 vol.% H ₂ + 850 vpm H ₂ O	1350 up to 1400	1520	PuCrO ₃ sinters
Ar* + 5 vol.%H ₂	1250-1300	1470	

(*: Ar is not pure but contains trace amounts of O₂ ~10vpm)

PHASE STABILITY JUSTIFICATION (1/2)

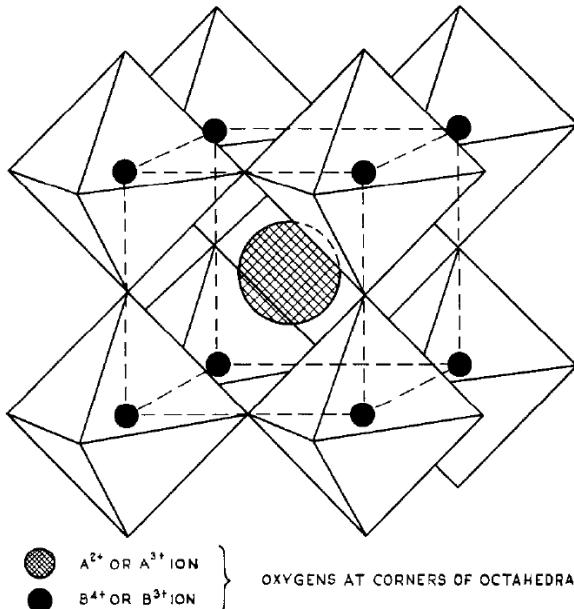
Simple way: hard spheres

$$r_{O^{2-}} = 1.40\text{\AA}$$

$$r_{Pu^{3+}} = 1.09\text{\AA} \text{ Coordination Number} = 12$$

$$r_{Cr^{3+}} = 0.64\text{\AA} \text{ Coordination Number} = 6$$

$$R_A + R_O = t \sqrt{2} (R_B + R_O)$$



Ideal lattice: $t=1$

Structure with these ions: $t=0.84$

PHASE STABILITY JUSTIFICATION (2/2)

Structure stability computations

M.L. Fullarton, Structure, properties and formation of PuCrO₃ and PuAlO₃ of relevance to doped nuclear fuels, J. Mater. Chem. A, 2013, 1, 14633-14640

- Context of the **assumption of in-pile PuCrO₃ formation** although :
 - In-pile conditions are oxidizing
 - In oxidizing conditions reactor temperature is not high enough for the formation of such a compound It would be more stable than $\frac{1}{2}$ Pu₂O₃ + $\frac{1}{2}$ Cr₂O₃ but Pu^{+III} is not stable in such conditions
- Among all possible space groups (R3c, Pnma, Pm-3m, R-3c, R-3m, C2/c) for the perovskite the most stable is **Pnma**, as observed in our study

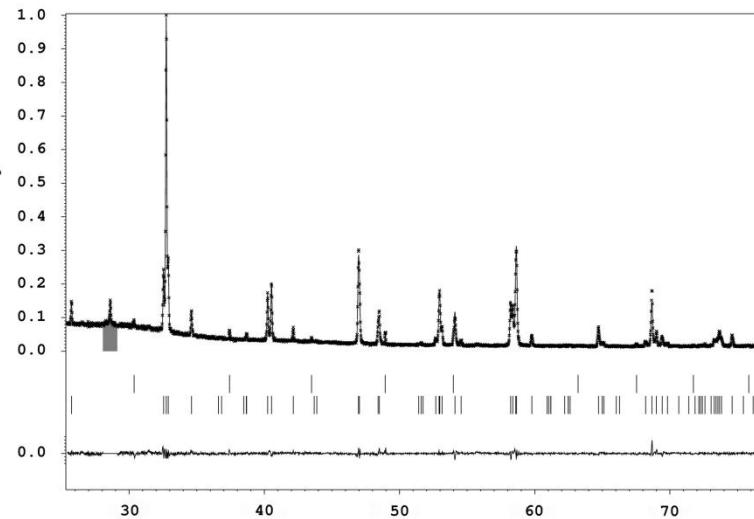
2 methods:

- DFT calculations with GGA-PBE exchange correlation and a Mott-Hubbard correction applied to Pu,
- Empirical potentials core-shell interaction for O²⁻ polarisability, Buckingham potential

- Possible **Cr and Pu point defects: interstitials**, no vacancy

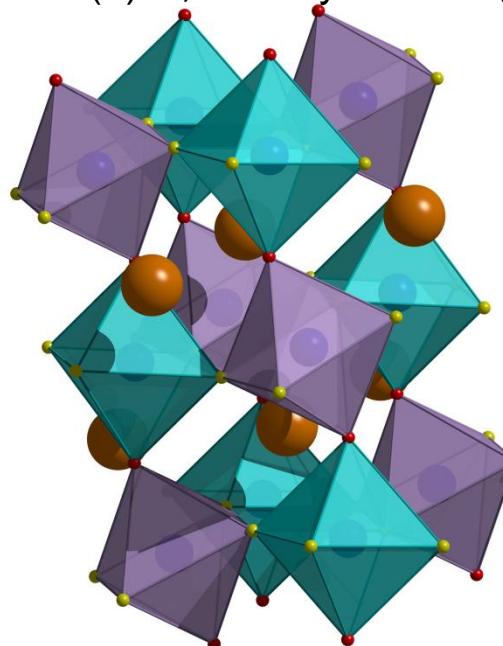
CRYSTAL CHEMISTRY (1/3)

XRD Rietveld refinement: Cu K_{α_1} radiation, $\lambda=1.5406\text{\AA}$



Space Group Pnma

$a=5.4958(1)\text{\AA}$, $b=7.7199(1)\text{\AA}$, $c=5.4397(1)\text{\AA}$
 $V=230.79(1)\text{\AA}^3$, density=9.8969(4) \AA^3



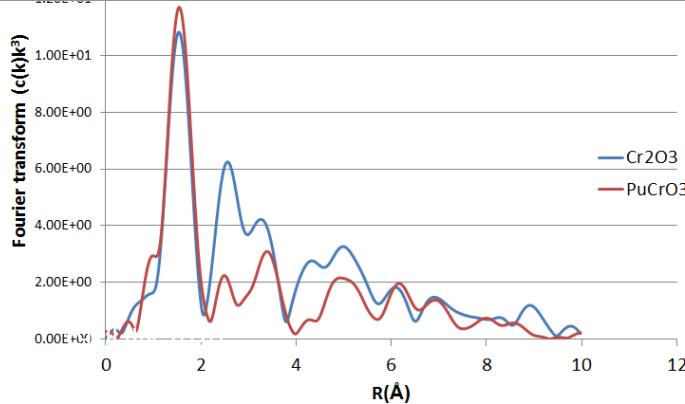
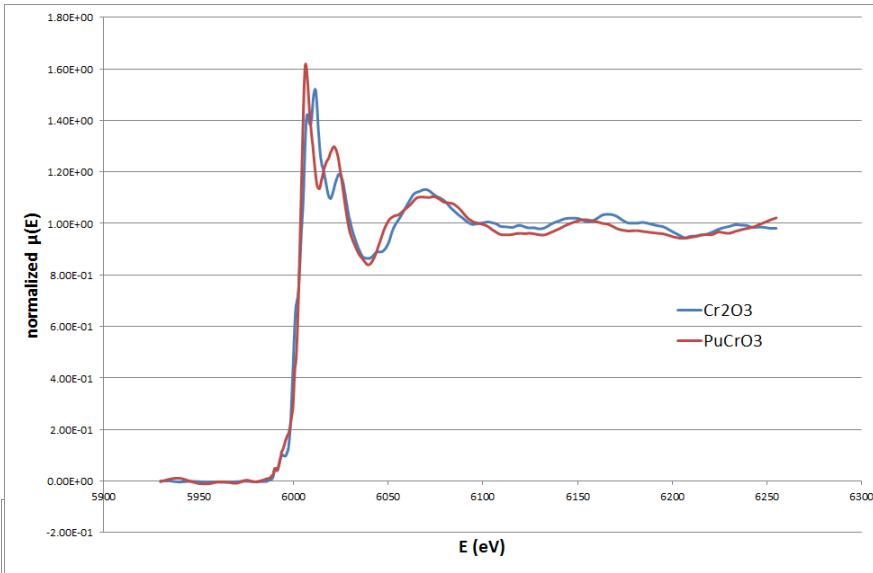
EPMA on precipitates :
 $(\text{Pu}_{0.98}\text{Am}_{0.02})\text{CrO}_3$
 Not any U in the compound
 (R. Thomas)

Atom	Site	x	y	z	SOF	$U_{iso}(\text{\AA}^2)$
Pu	4c	0.0414(2)	0.25	0.9927(5)	0.5	0.0149(7)
Cr	4a	0.5	0	0	0.5	0.010(2)
O1	4c	0.474(3)	0.25	0.061(5)	0.5	0.0192
O2	8d	0.704(4)	0.0474(3)	0.299(4)	1	0.0292

CRYSTAL CHEMISTRY (2/3)

XANES and EXAFS : ESRF ROBL beamline

- Cr K-edge (5989 eV) and plutonium L₂ (22256 eV) edges collected in fluorescence mode, comparison with Cr₂O₃



Edge position: **Cr oxidation state +III**
 pre-peaks @ ~5992 eV and ~5994 eV:
 transitions of Cr 1s → unoccupied 3d valence with
 octahedral symmetry (Oh), signature of
octahedral coordinated Cr(+III) materials

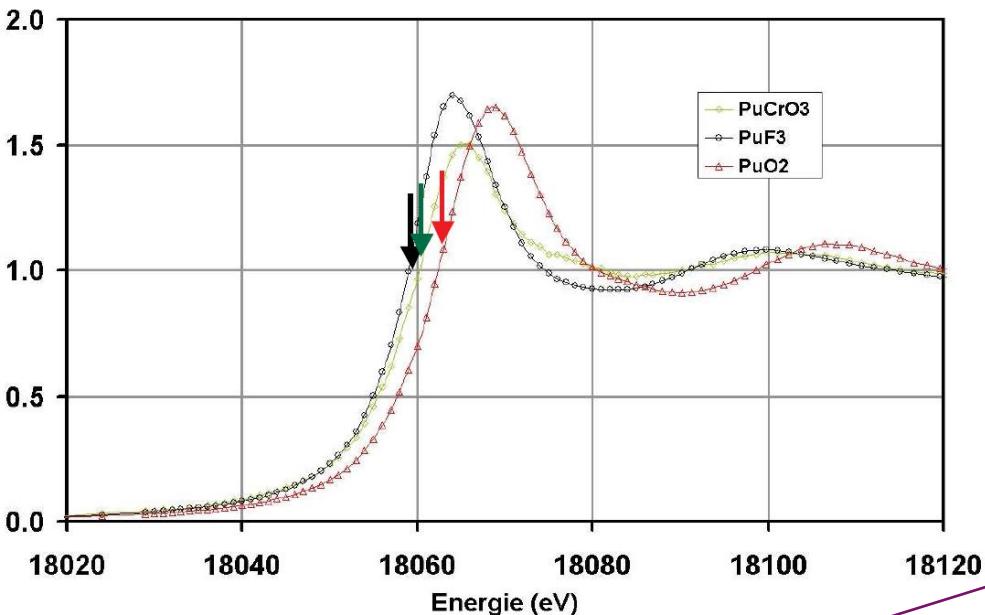
In the range [1 Å - 4 Å]:
 6 O²⁻ @ 1.98 Å as for Cr in Cr₂O₃

**Chromium oxidation state +III at B sites
 of the perovskite structure**

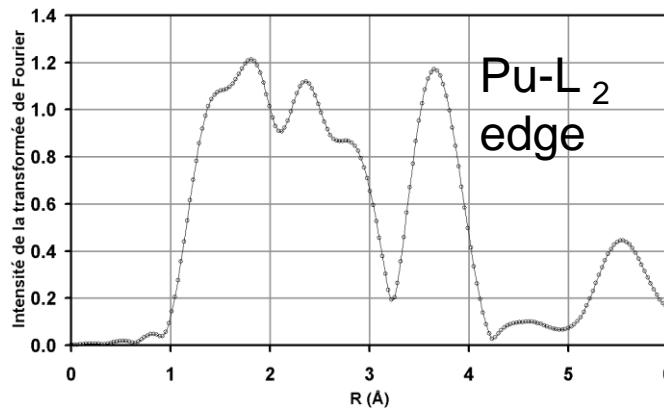
CRYSTAL CHEMISTRY (3/3)

XANES and EXAFS: ESRF ROBL beamline

- Pu L₃-edge (18057 eV) and Pu L₂-edge (22226 eV) transmission mode.



**Plutonium peak position:
oxidation state +III**

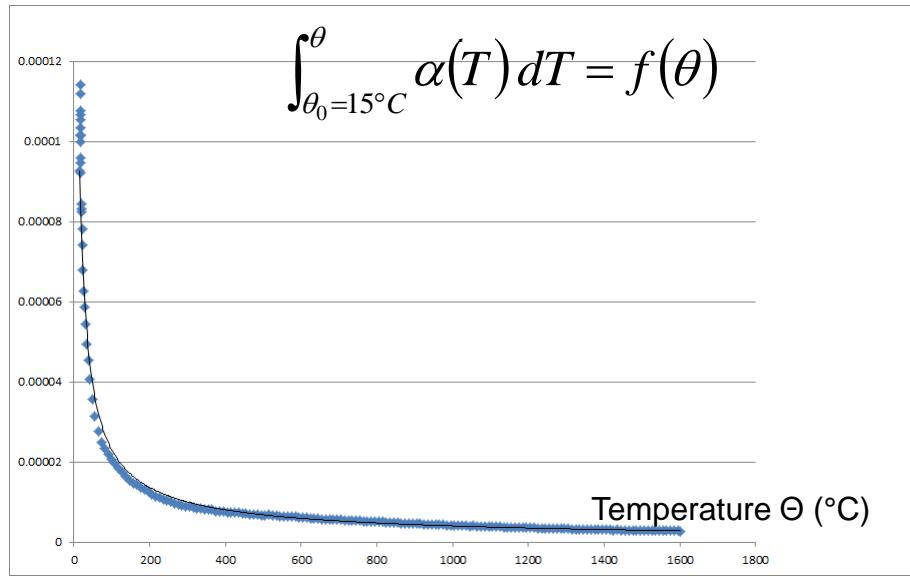


Pu-L₂: O²⁻ lying in [1 Å; 4 Å] :
distorted cubic environment
(A sites of the perovskite
structure)

**Plutonium: oxidation state +III at A sites of
the perovskite structure**

THERMODYNAMIC AND PHYSICAL PROPERTIES (1/4)

Dilatometry: Synthesis of a pure PuCrO_3 from PuO_2 and Cr_2O_3 followed by dilatometry → interpretation of the cooling behavior



Then, internal energy reads:

$$U(\theta) = U(\theta_0) + \frac{3V_m}{K\gamma} \left\{ \frac{A}{a} \left(\frac{T_c}{1-a} \left(\frac{T-T_c}{T_c} \right)^{1-a} - T \right) + BT + \frac{\alpha_p^2 V_m}{2K} T^2 + CT^3 + 3.5.R.T \int_0^{\frac{\theta_D}{T}} x \left(\frac{1}{2} + \frac{1}{e^x - 1} \right) \frac{x^2}{x_D^3} dx + Fe^{-\frac{E_D}{RT}} \right\}$$

Fit results:

- Signature of a critical phenomenon @ $T_c=272.7\text{K}$
- Critical exponent $a=0.244$

Unusual shape of the curve at low temperature: critical phenomenon

Fit of $\int_{\theta_0=15^\circ C}^{\theta} \alpha(T) dT = \frac{K\gamma}{3V_m} (U(\theta) - U(\theta_0))$ vs. θ with
U the internal energy

If $\alpha = \alpha_{magnetic} + \alpha_{paramagnetic}$
with $\alpha_{m.} = \frac{A}{a} \left(\left(\frac{T-T_c}{T_c} \right)^{-a} - 1 \right)$

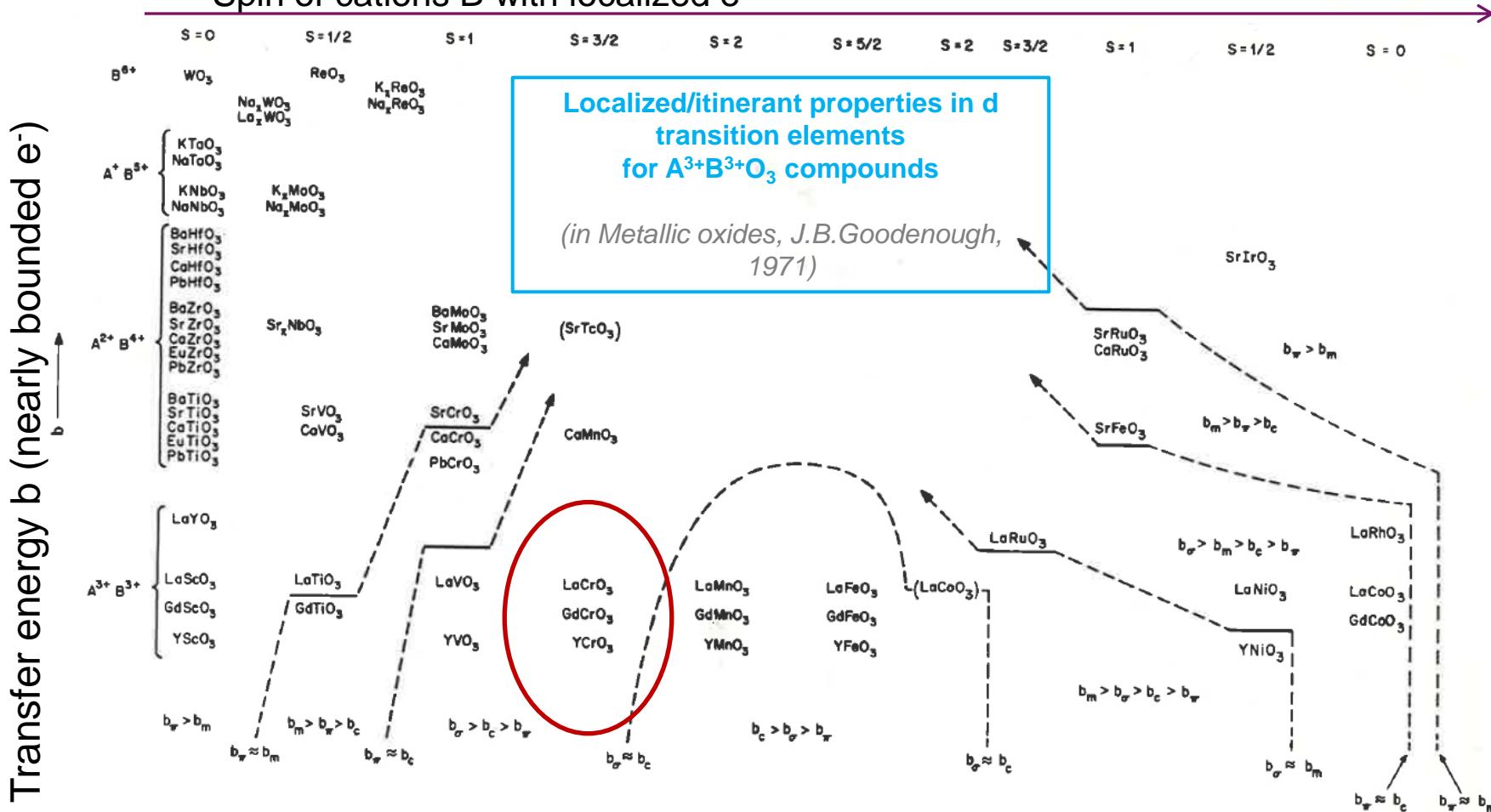
Close to:
 $(\text{La}_{1-x}\text{Ca}_x)_{1-y}\text{Mn}_{1-y}\text{O}_3$
Zhao PRL 78,5, 1997
with $T_c= 270\text{K}$

THERMODYNAMIC AND PHYSICAL PROPERTIES (2/4)

A ferro/para magnetic transition?

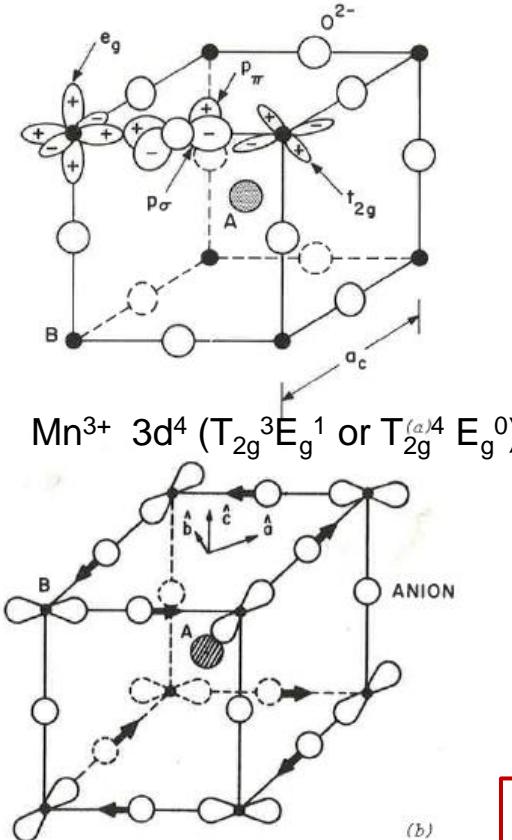
Cr^{3+} $3d^3$ ($T_{2g}^3 E_g^0$)

Spin of cations B with localized e^-



THERMODYNAMIC AND PHYSICAL PROPERTIES (3/4)

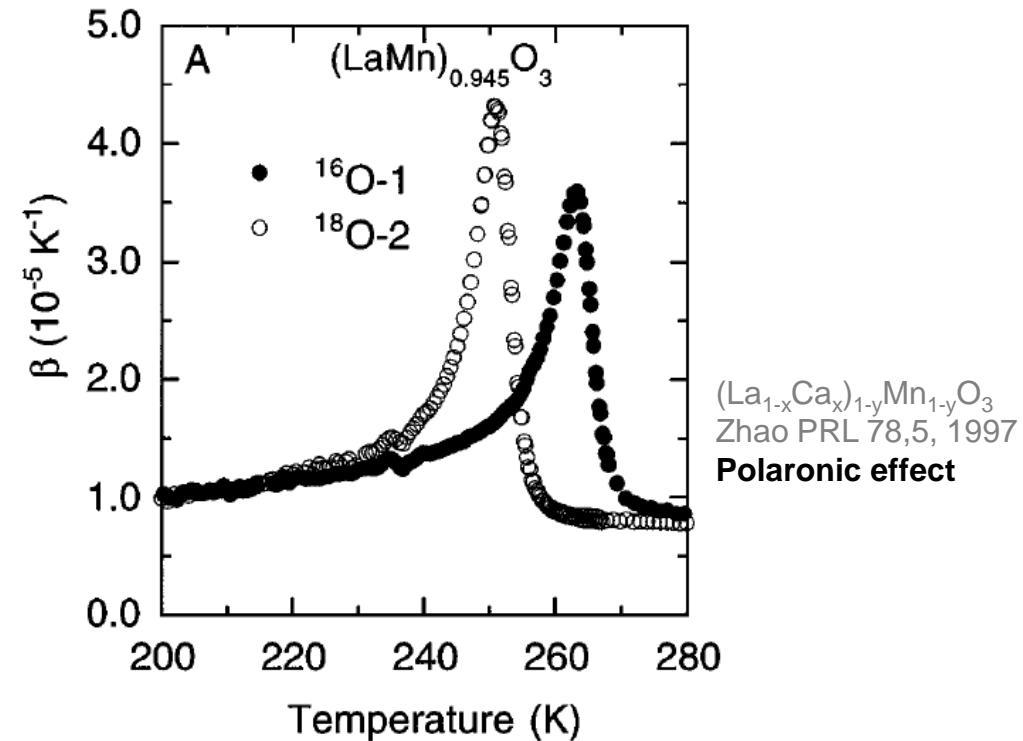
A ferro/para magnetic transition? comparison with LaMnO₃



(in Metallic oxides,
Goodenough, 1971)

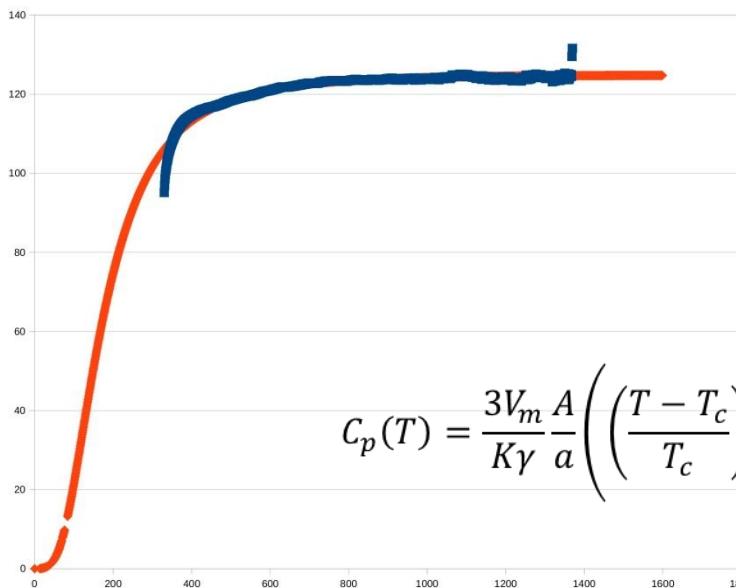
Results:

- Possibility of Cr^{3+} spin coupling along a and b directions
- Role of Pu^{3+} which is $5f^5$?



THERMODYNAMIC AND PHYSICAL PROPERTIES (4/4)

DSC: Heat capacity measurement of a 95 w% of PuCrO₃ and 5 w% of PuO₂ sample



Heat capacity corrected from the heat produced by the sample itself

$$\text{Corr. } C_p = \text{raw } C_p + P/v$$

$$P=5.74\text{W/g}_{\text{Pu}} - v(\text{heating rate})=20^\circ\text{C}.\text{min}^{-1}$$

$$C_p(T) = \frac{3V_m}{K\gamma} \frac{A}{a} \left(\left(\frac{T - T_c}{T_c} \right)^{-a} - 1 \right) + 5 * 3 * R \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx + \frac{\alpha_p^2 V_m}{K} T + \frac{F E_D}{R T^2} e^{-E_D/RT}$$

Fit results:

- Debye Temperature $\theta_D=562.7 \text{ K}$
- Energy of creation of defects at high temperature $E_D=3987.5 \text{ J}$

CONCLUSIONS

Possibility of porosity formation around PuCrO_3 (always located at grains boundaries of $(\text{U}, \text{Pu})\text{O}_2$) during cooling down after fabrication, i.e. loosening of PuCrO_3 from its matrix

→ due to the abnormal thermal coefficient behaviour at room temperature

→ it is necessary to control $\mu(\text{O}_2)$, T, the material for addition of Cr_2O_3 (master blend or matrix), and Cr_2O_3 amount to avoid residual PuCrO_3 precipitates

Integration of PuCrO_3 data into the TAF-ID database

→ Needs to take into account this phase transition in order to make Cr-O and Pu-Cr-O data consistent

Thank you for your attention

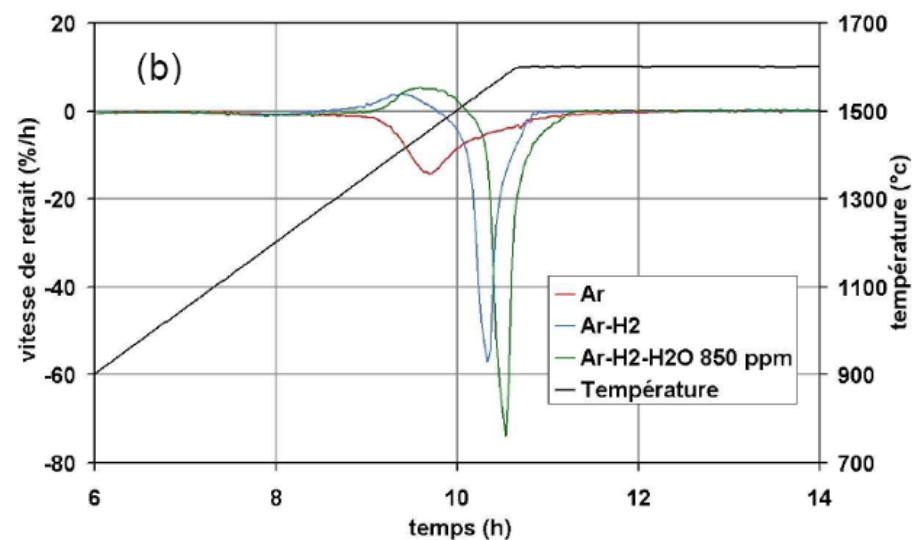
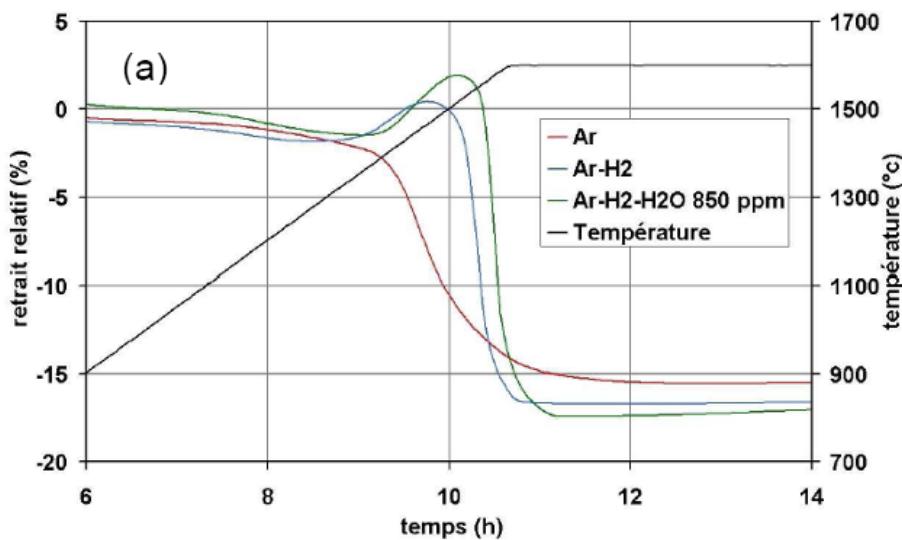
Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Cadarache | 13108 Saint-Paul-Lez-Durance
T. +33 (0)4 42 25 70 00

Etablissement public à caractère industriel et commercial | RCS Paris B 775 685 019

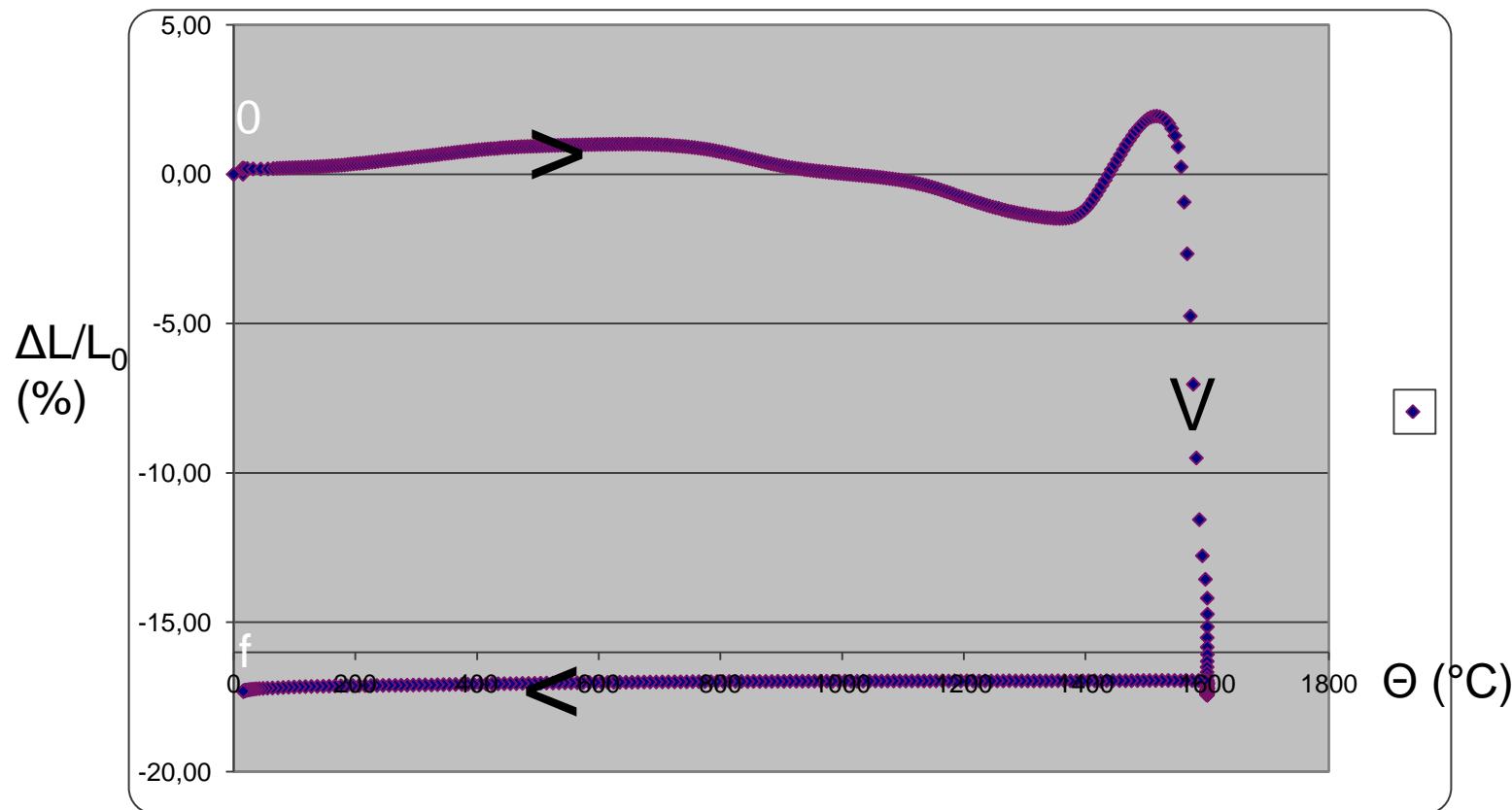
DEN
DEC
SESC
LLCC

APPENDIX 1

(R. Thomas PhD Thesis, Bordeaux 1 University, 2013)



APPENDIX 2



$$\int_{\theta_f}^{\theta} \alpha(t) dt = \frac{L - L_f}{L_f} = \frac{L - L_0}{L_f} + \frac{L_0 - L_f}{L_f} = \left[\left(\frac{L - L_0}{L_0} \right) - \left(\frac{L_f - L_0}{L_0} \right) \right] \frac{L_0}{L_f}$$