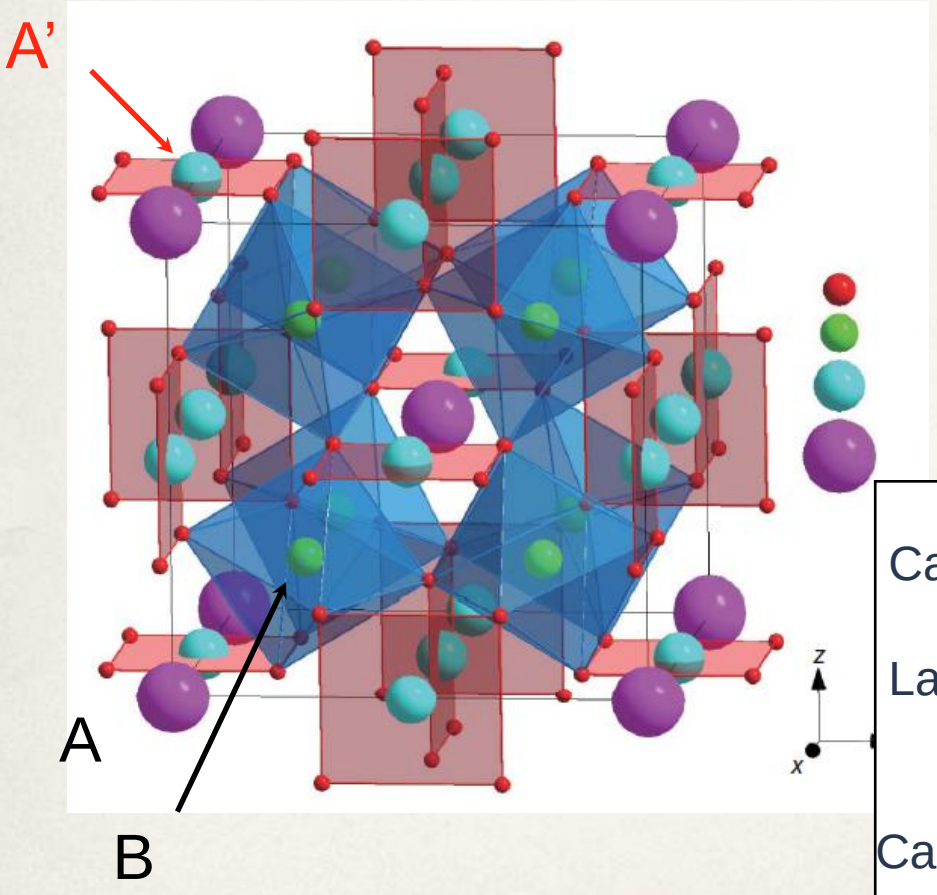
Aサイト秩序型ペロブスカイトの軟X線分光

JASRI/SPring-8　水牧 仁一朗

2011/09/13-14 @ PF研究会

A-site ordered Perovskite

$AA'_3B_4O_{12}$ $(ABO_3)_{x4}$



A:Na^+、Ca^{2+}、Ba^{2+}、La^{3+}…
A':Jahn-Tellerイオン(Cu^{2+}, Mn^{3+})
B:遷移金属イオン(Ti, Mn, Co…)

Aサイトに通常は入らない
遷移金属イオンが入る

→ 新奇な物性が期待

$CaCu_3Ru_4O_{12}$(W.Kobayashi et al., JPSJ, 2004)
　f電子を含まない重い電子系的振る舞い
$LaCu_3Fe_4O_{12}$(Y. Long et al., Nature, 2009)
　Cu-Feサイト間での電荷移動による負の熱膨張
　($Cu^{2+}+Fe^{3.75+} \rightarrow Cu^{3+}+Fe^{3+}$)
$CaCu_3Mn_4O_{12}$(Z. Zeng et al., PRL, 1999)
　低磁場での巨大磁気抵抗

$AMn'_3B_4O_{12}$の物性

Mnの形式価数　　MnはJahn-Teller ionのはず　　Mn^{3+}

- ✓ $RMn_3Al_4O_{12}$(R=Y,Dy,Yb)

  Mn^{3+}　　R^{3+} Al^{3+}

- ✓ $NaMn_3Ti_4O_{12}$

  $Mn^{2.33+}$　　Na^{+} Ti^{4+}

- ✓ $LaMn_3TM_4O_{12}$(TM=Ti,V,Cr)

  $Mn^{1.67+}$　　La^{3+} $Ti(V)^{4+}$

  Mn^{3+}　　La^{3+} Cr^{3+}

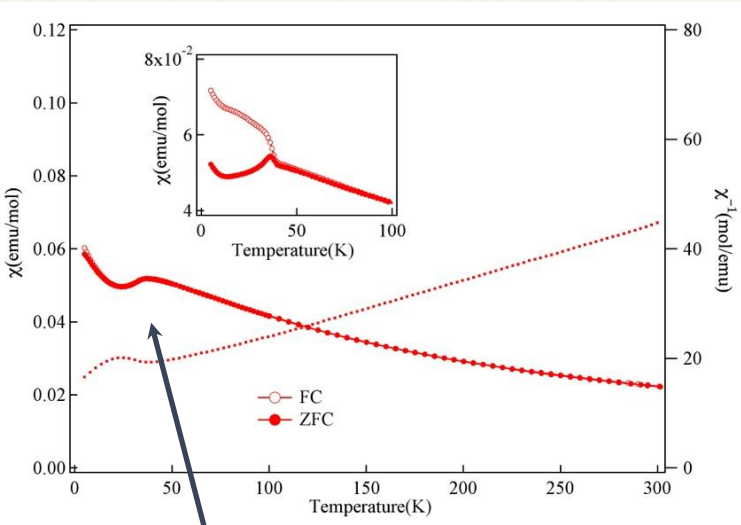
Mnに着目

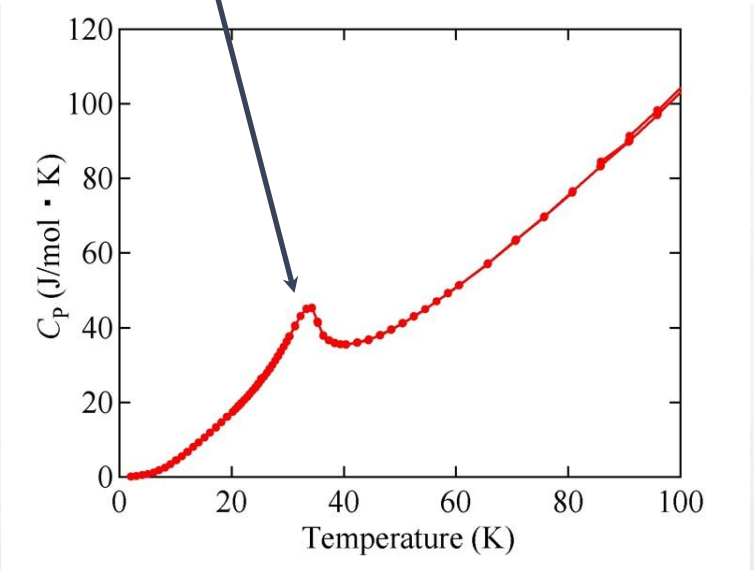
BVSによっては支持

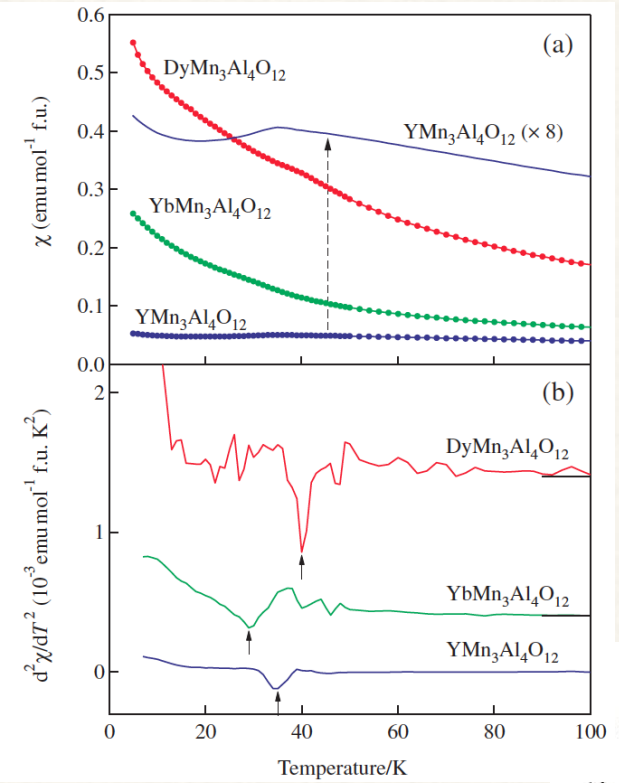
$RMn'_3Al_4O_{12}$(R=Y,Dy,Yb)

磁性

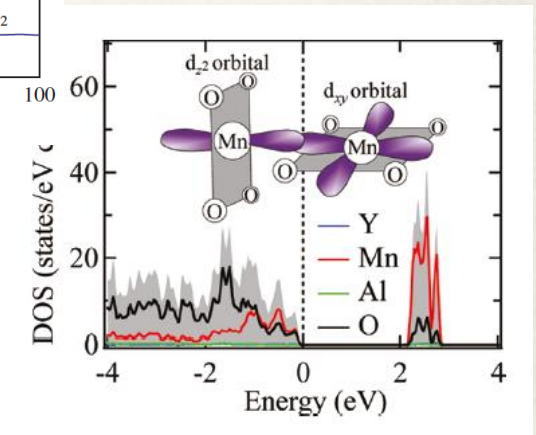
比熱







絶縁体

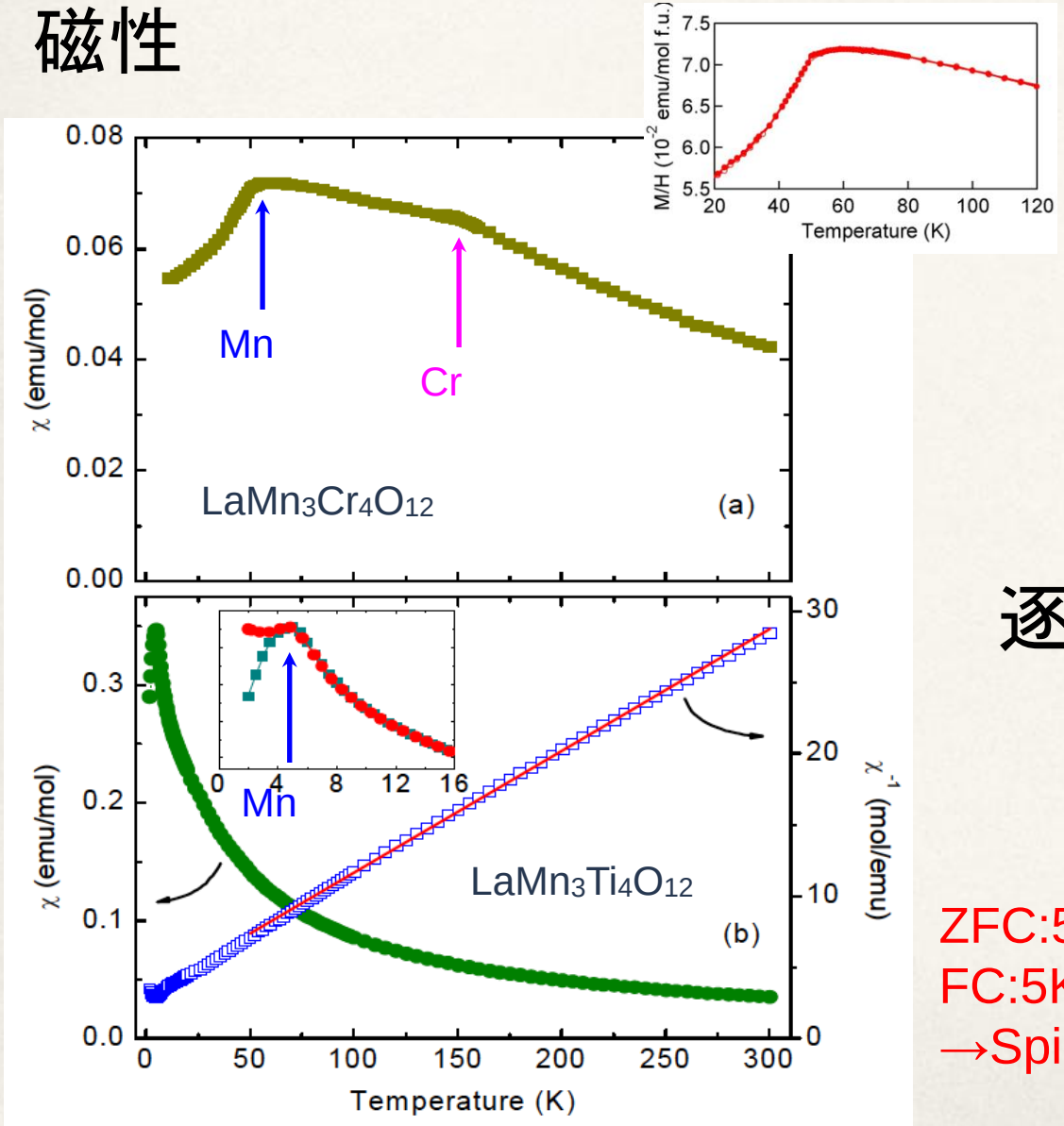


T.Tohyama, Inorg. Chem. (2010) T. Saito, Bull. Chem. Soc. Jpn.(2011)

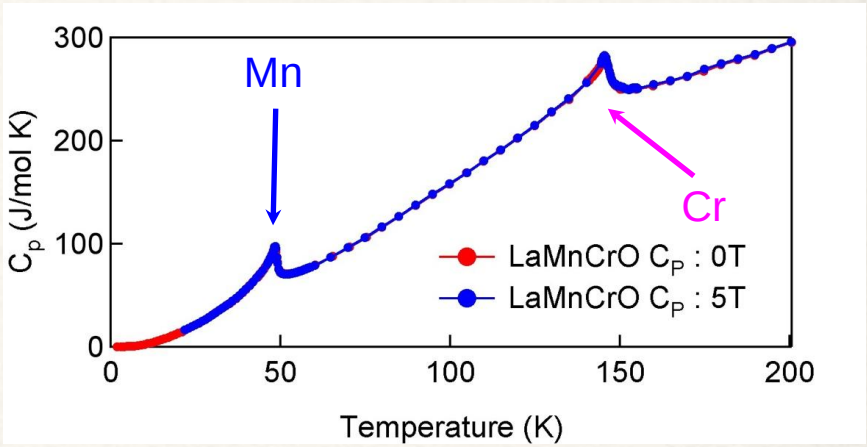
$LaMn_3B_4O_{12}$

Y. Long, J. Am. Chem. Soc. (2009)

磁性



比熱



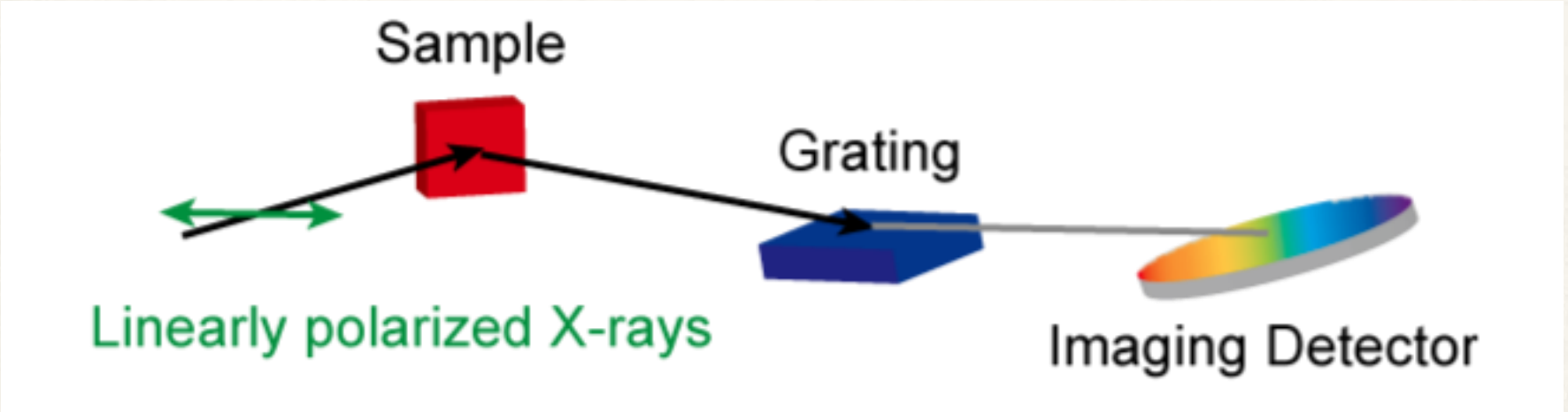
逐次磁気秩序(Cr→Mn)

絶縁体

ZFC:5Kにピーク
FC:5K以下で一定
→Spin Glass 的

測定方法・条件

吸収および発光分光測定@BL27SU



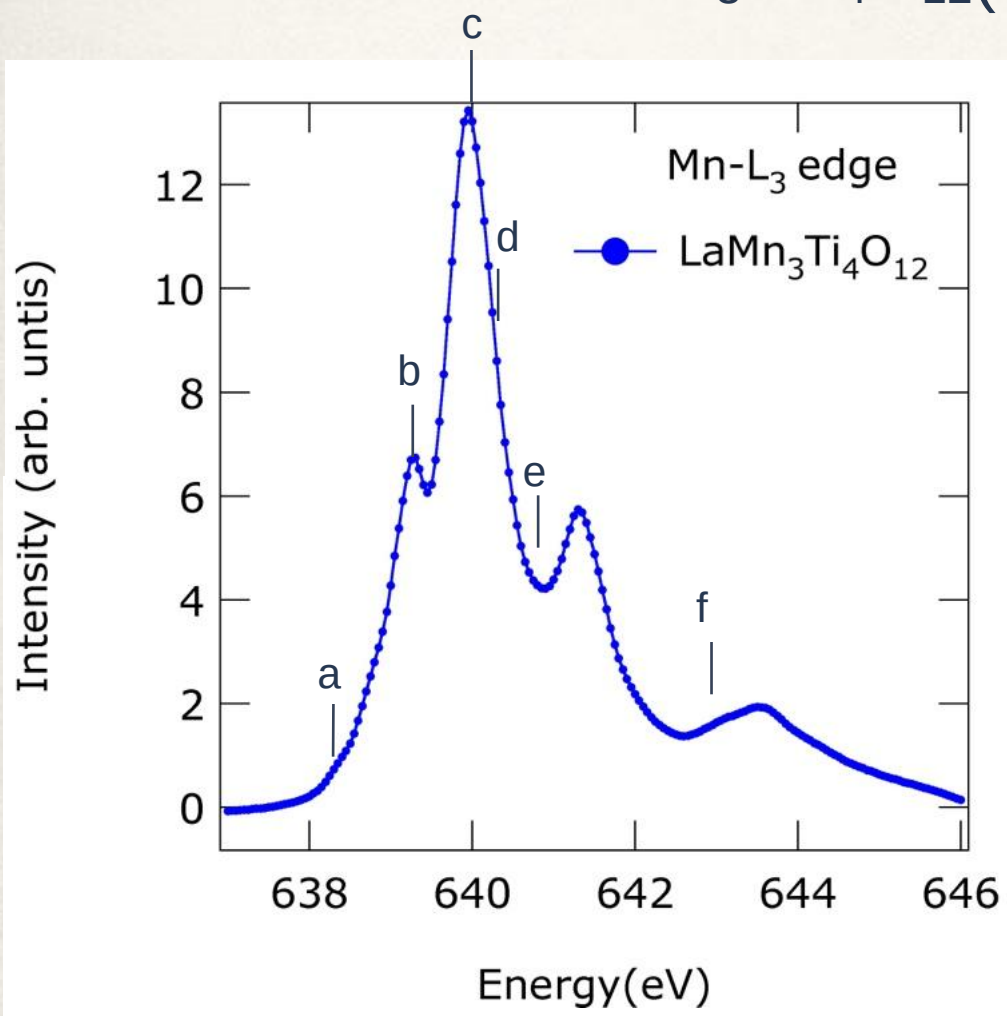
Mn-L 吸収端　　偏光非保存配置

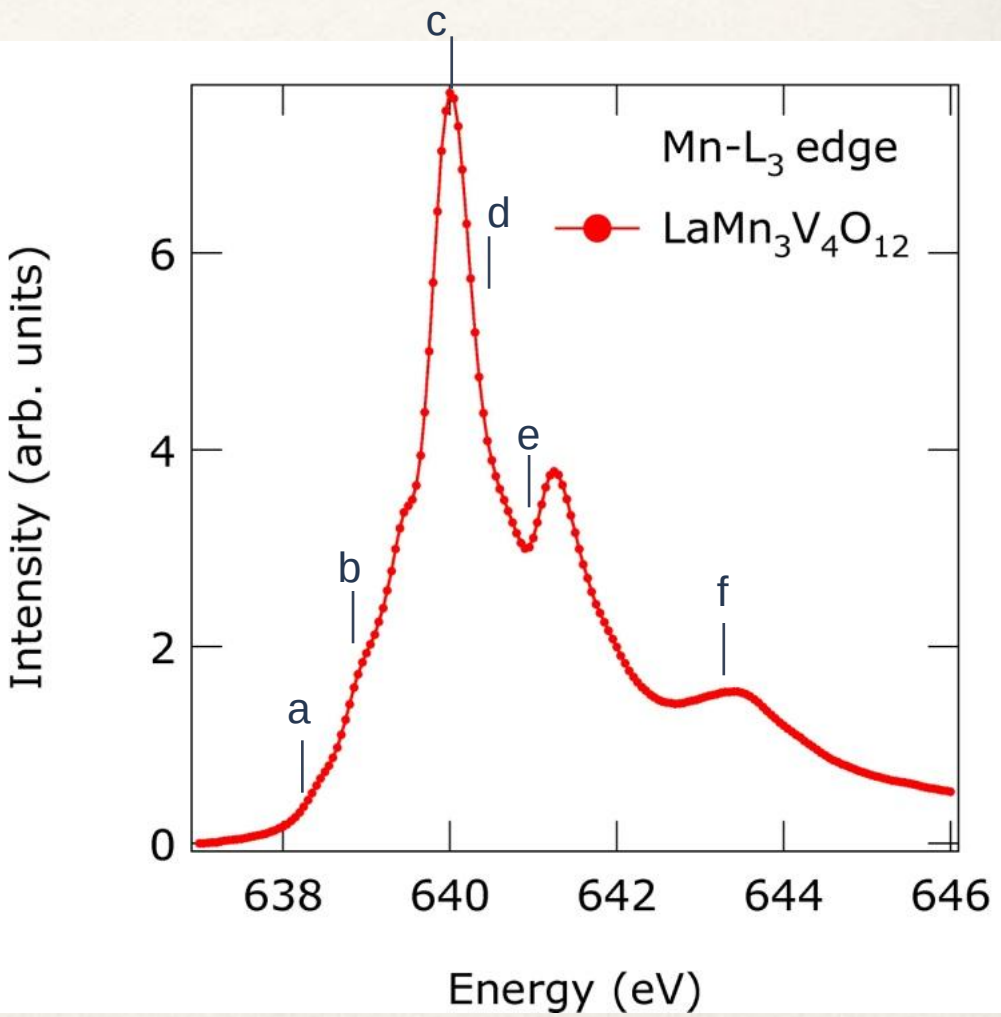
全電子収量法　　室温

Mn-2pXAS (実験)

Mn^{2+} d^5

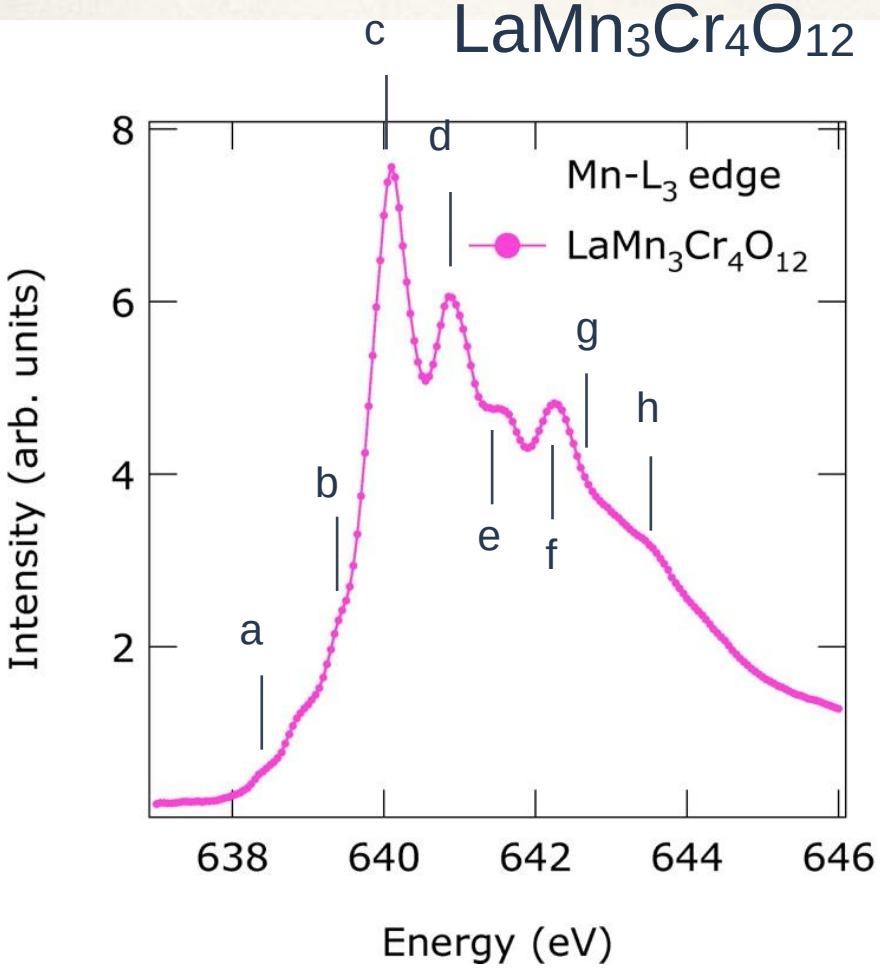
$LaMn_3TM_4O_{12}(TM=Ti,V)$

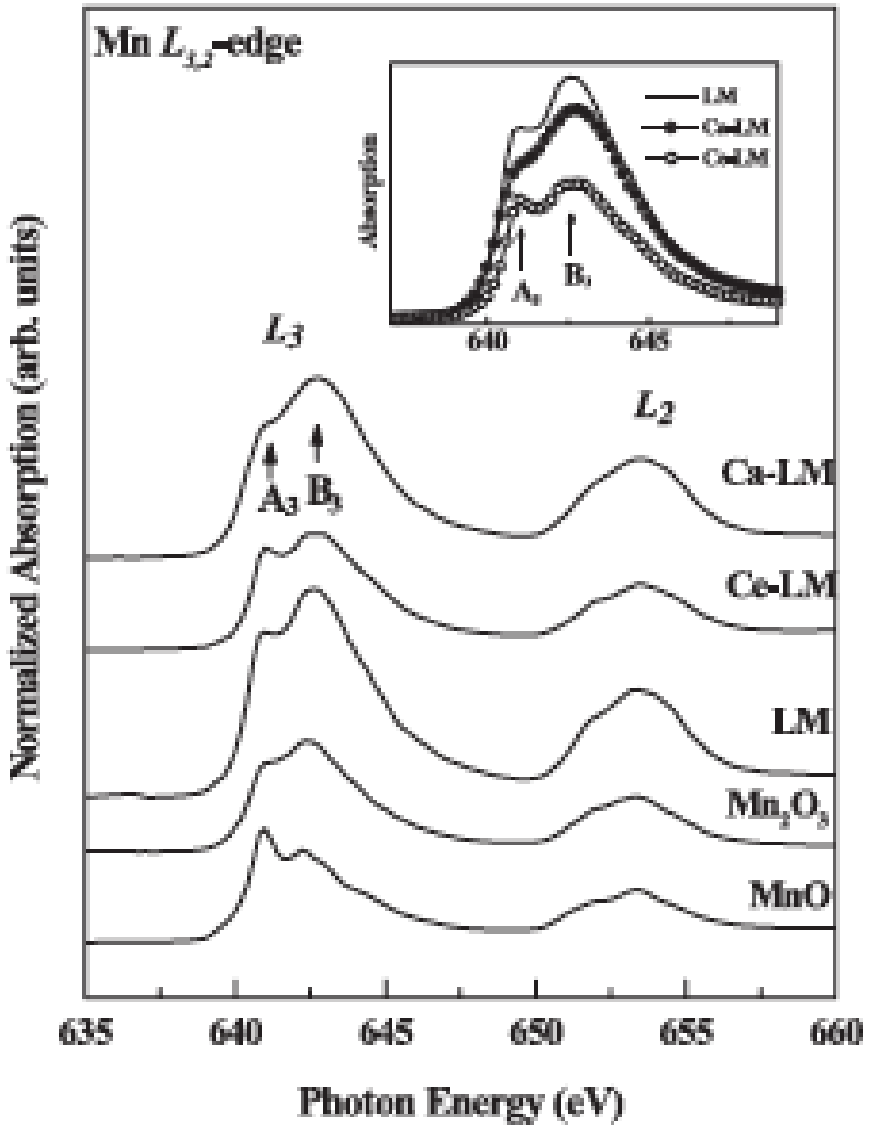




Mn-2pXAS (実験)

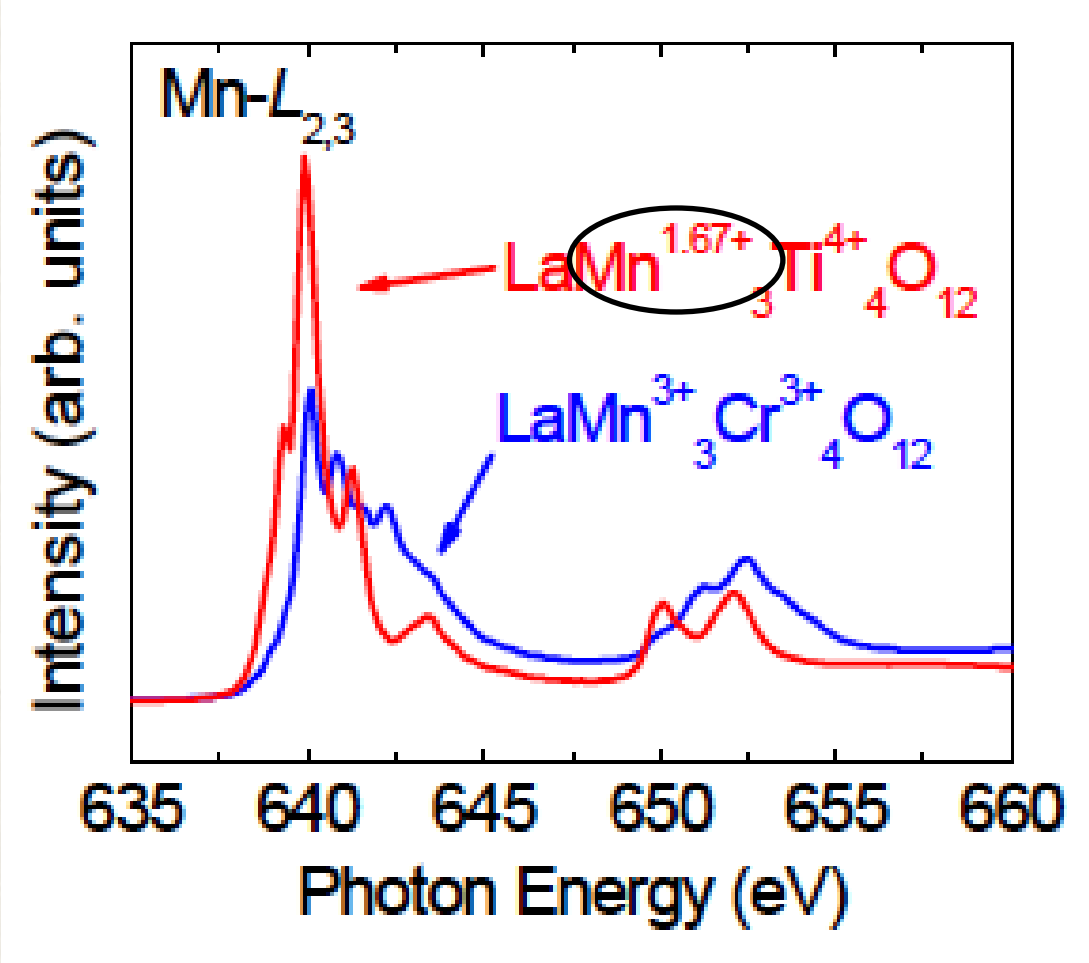
Mn^{3+} d^4

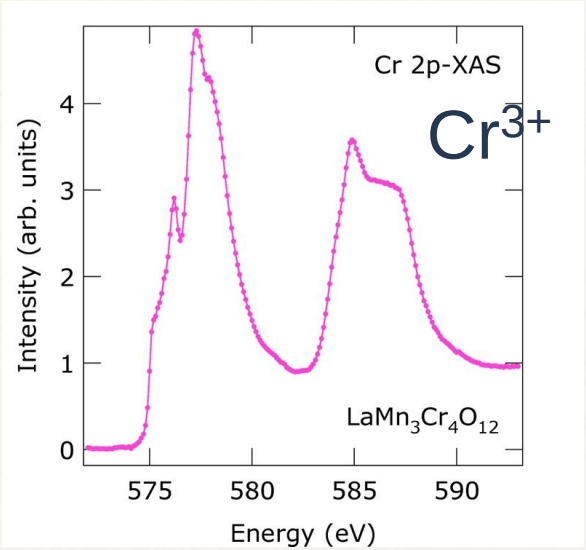


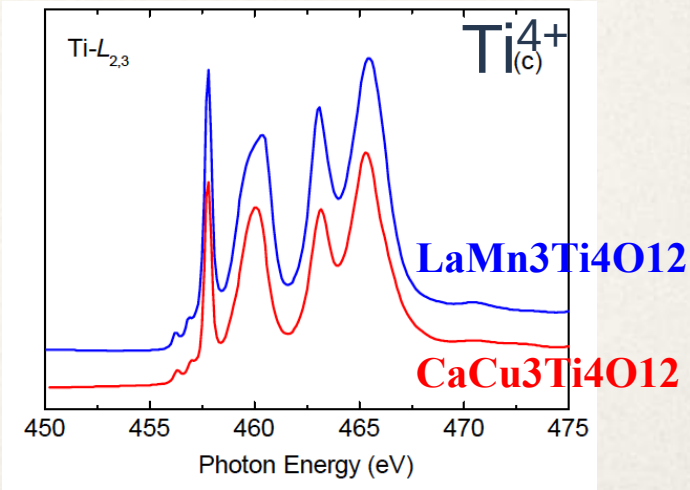


$LaMn_3B_4O_{12}$

Y. Long, J. Am. Chem. Soc. (2009)







Mnは様々な価数をとる！

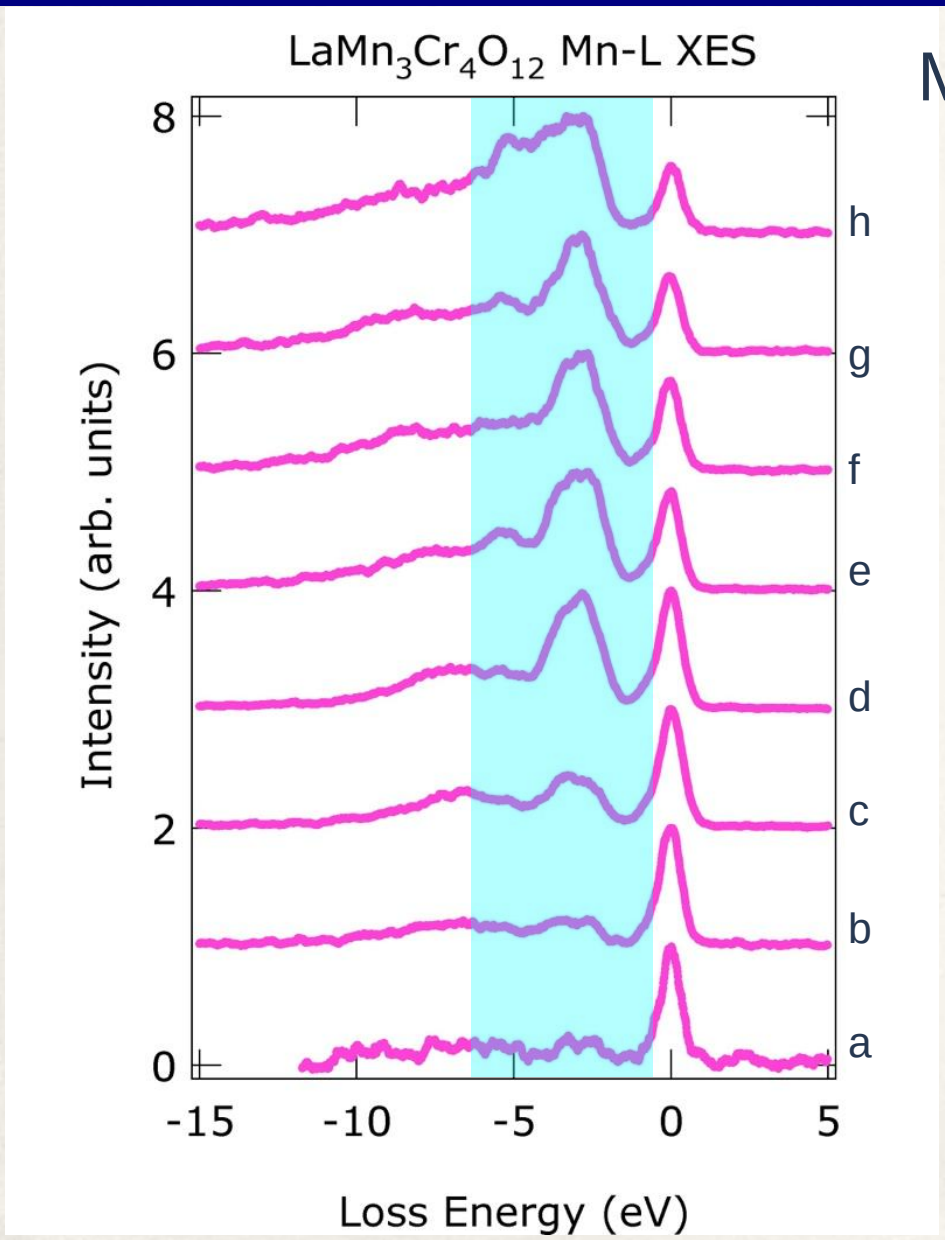
Mnの価数

	$YMn_3Al_4O_{12}$	$NaMn_3Ti_4O_{12}$	$LaMn_3Ti_4O_{12}$	$LaMn_3Cr_4O_{12}$
BVS(Mn)	3.02	2.22	1.76	2.74
BVS(B)	2.80	4.03	3.94	2.89
$P_{eff}(\mu_B)$ exp.	5.06	5.42	5.58	------
$P_{eff}(\mu_B)$ theo.	4.90(Mn^{3+})	5.58($Mn^{2.33+}$)	5.58($Mn^{1.67+}$)	------

Mnは様々な価数をとり、
Jahn-Teller イオンでなくともよい

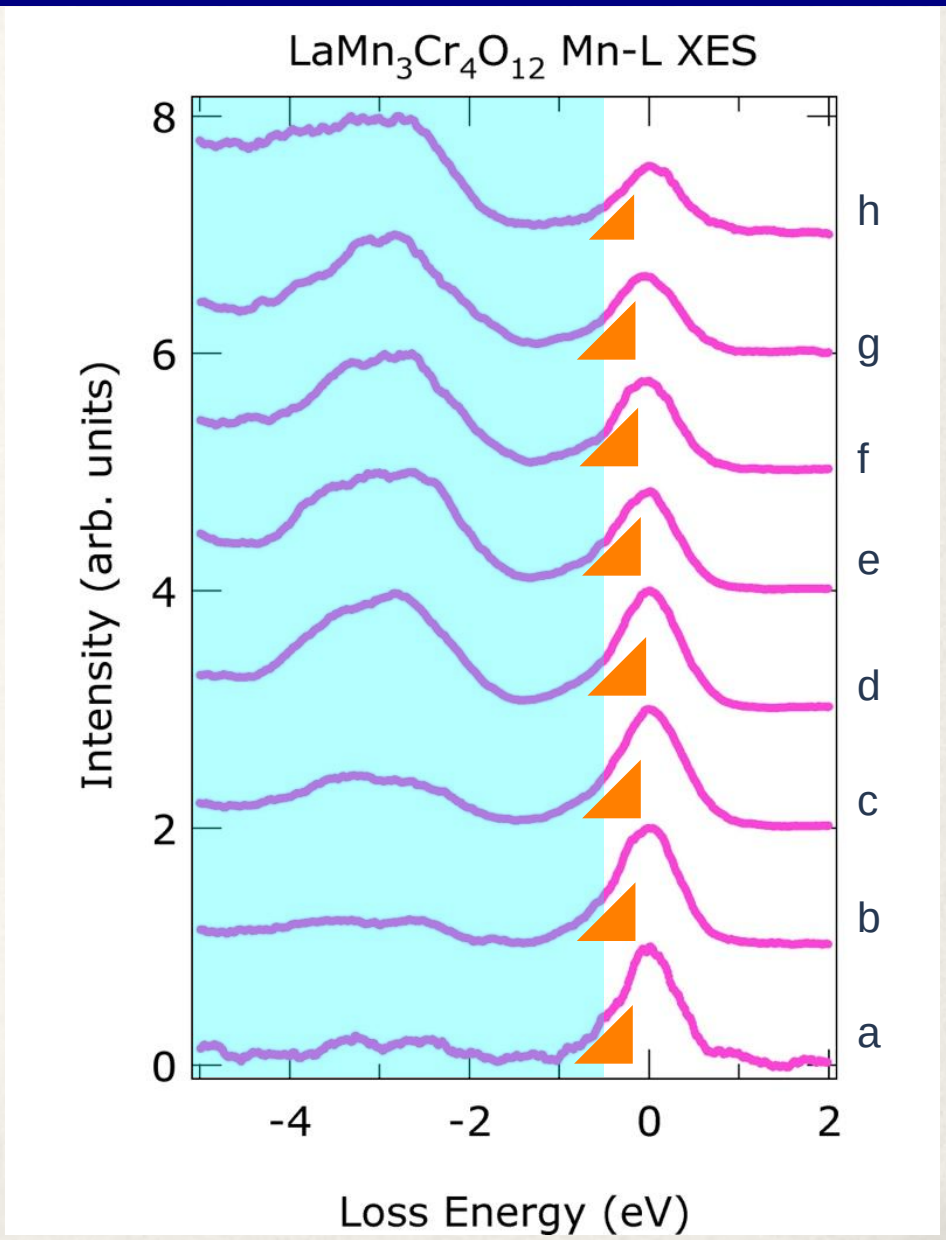
Mn-2pXAS (実験)

$LaMn_3Cr_4O_{12}$



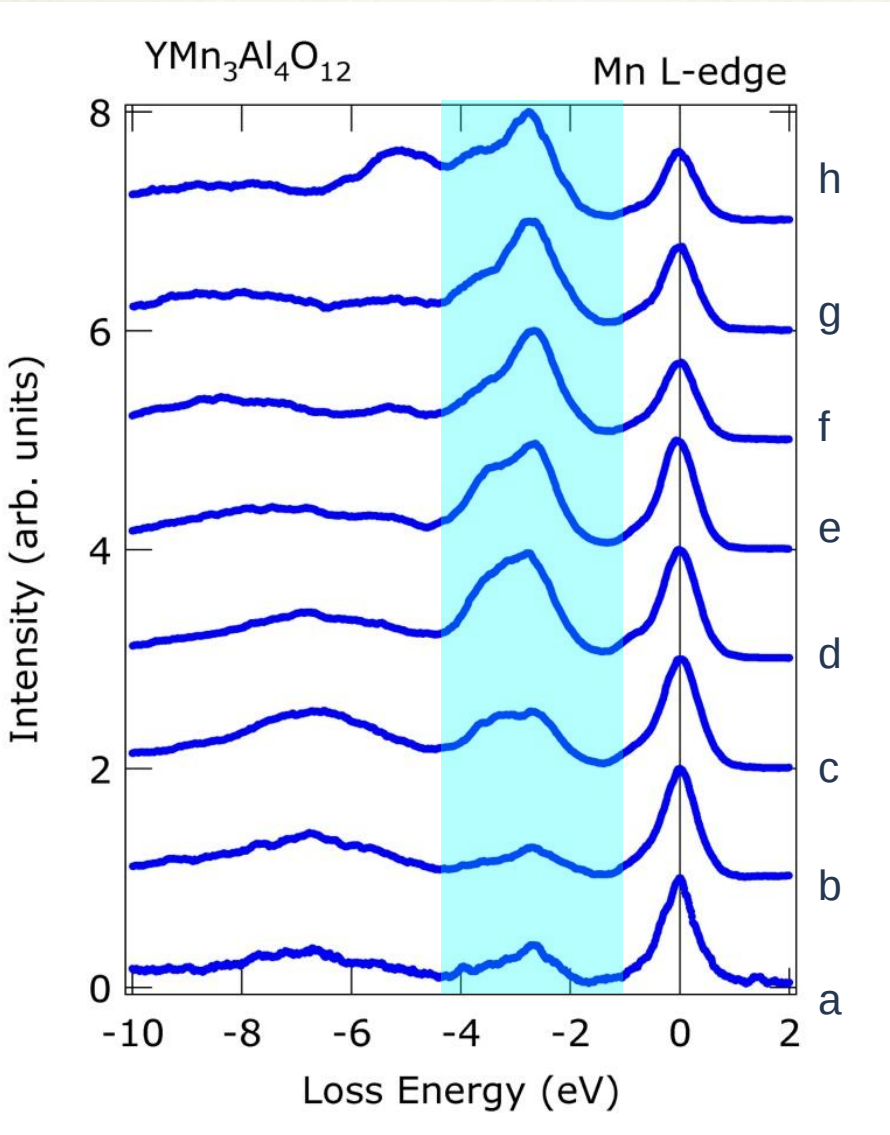
Mn^{3+}

d^4



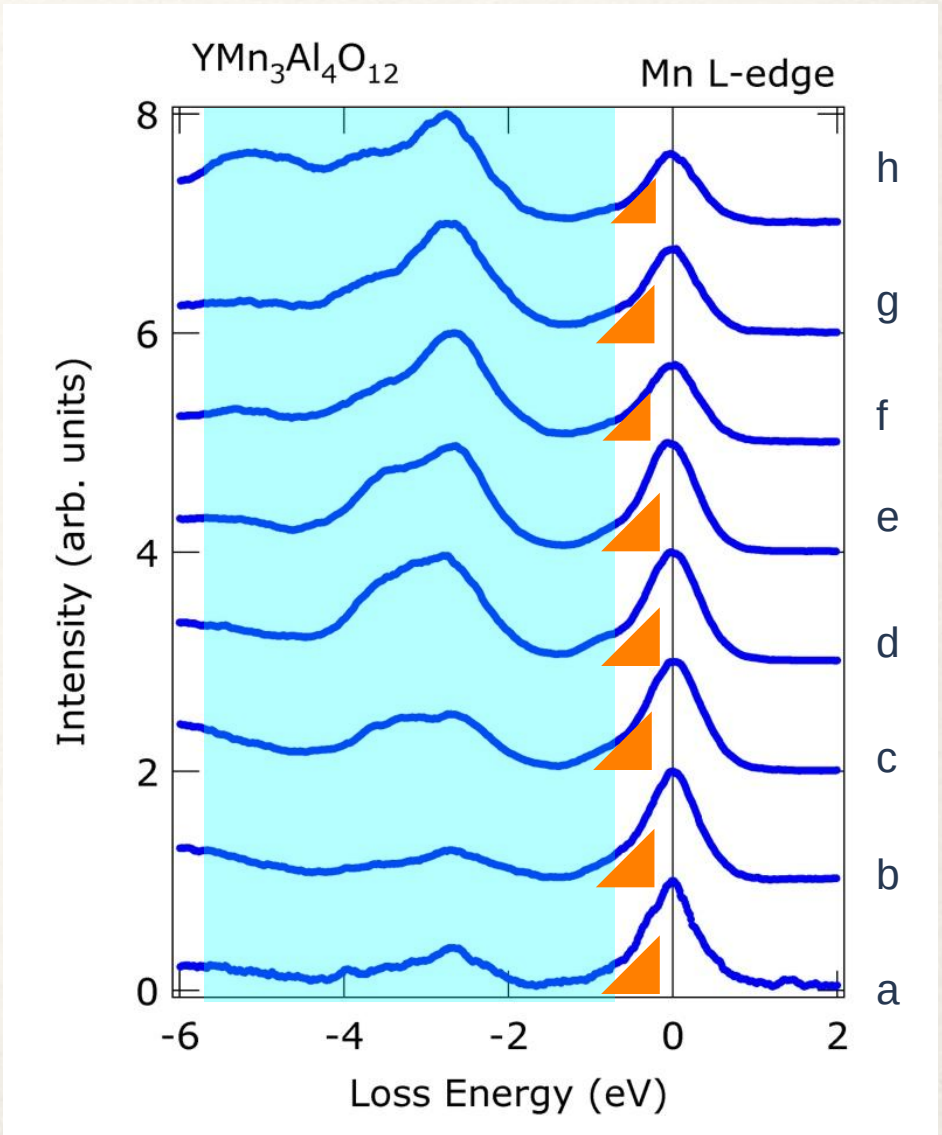
Mn-2pXAS (実験)

$YMn_3Al_4O_{12}$



Mn^{3+}

d^4



Cluster模型

TM-3d　　TM-2p　　O-2p

$$H = \sum_{\Gamma,\sigma} \epsilon_{3d}(\Gamma) d^+_{\Gamma,\sigma} d_{\Gamma,\sigma} + \sum_{m,\sigma} \epsilon_{2p} p^+_{m,\sigma} p_{m,\sigma} + \sum_{\Gamma,\sigma} \epsilon_p(\Gamma) a^+_{\Gamma,\sigma} a_{\Gamma,\sigma}$$

$$+ \sum_{\Gamma,\sigma} \frac{V(\Gamma)}{\sqrt{N}} (d^+_{\Gamma,\sigma} a_{\Gamma,\sigma} + a^+_{\Gamma,\sigma} d_{\Gamma,\sigma})$$

TM3d-O2p混成

$$+ U_{dd} \sum_{(\Gamma,\sigma)\neq(\Gamma',\sigma')} d^+_{\Gamma,\sigma} d_{\Gamma,\sigma} d^+_{\Gamma',\sigma'} d_{\Gamma',\sigma'}$$

TM3d
オンサイトクーロン

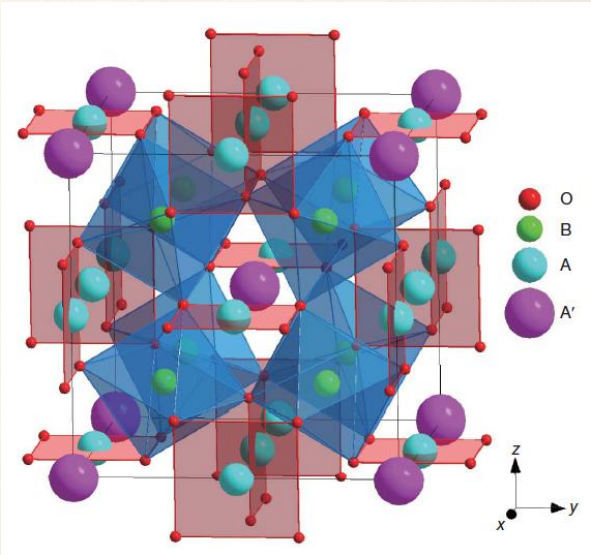
$$- U_{dc}(2p) \sum_{(\Gamma,m,\sigma,\sigma')} d^+_{\Gamma,\sigma} d_{\Gamma,\sigma} (1 - p^+_{m,\sigma} p_{m,\sigma}) + H_{multiplet}$$

TM 2p-3d コアホールポテンシャル

unit : eV	Δ	U	U_{dc}	V	10Dq
Mn^{3+}	-3.0	7.0	8.24	2.0	2.0
Cr^{3+}	5.5	5.5	6.5	2.8	1.5

Mn @D_{4h}

Cr @O_h



RXES formula

$$F(\Omega,\omega)=\sum_f\left|\sum_m\frac{\langle f|T^\dagger|m\rangle\langle m|T|g\rangle}{E_g+\Omega-E_m-i\Gamma_L}\right|^2$$

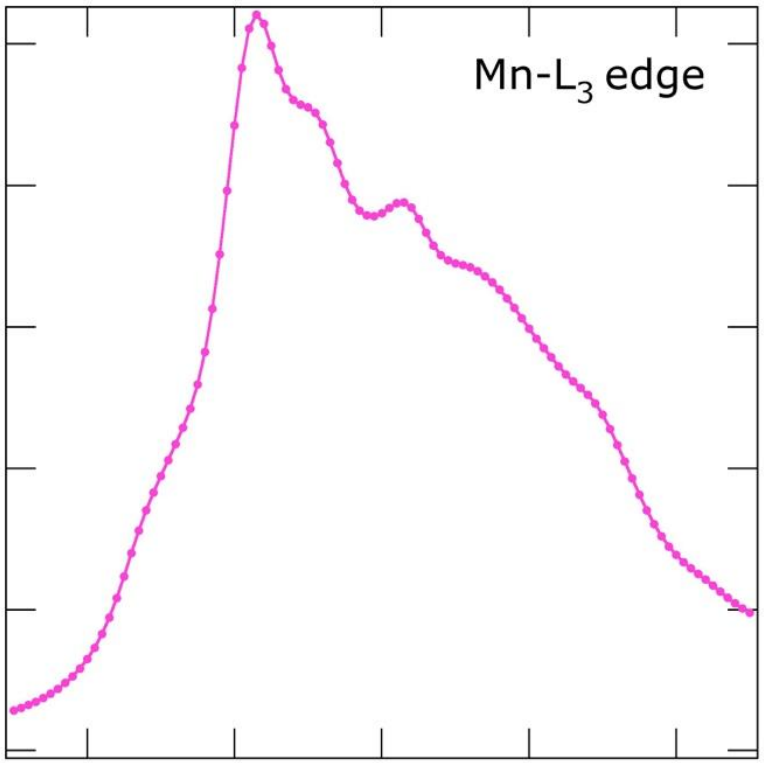
T , $T^\dagger$: 遷移行列演算子(双極子)

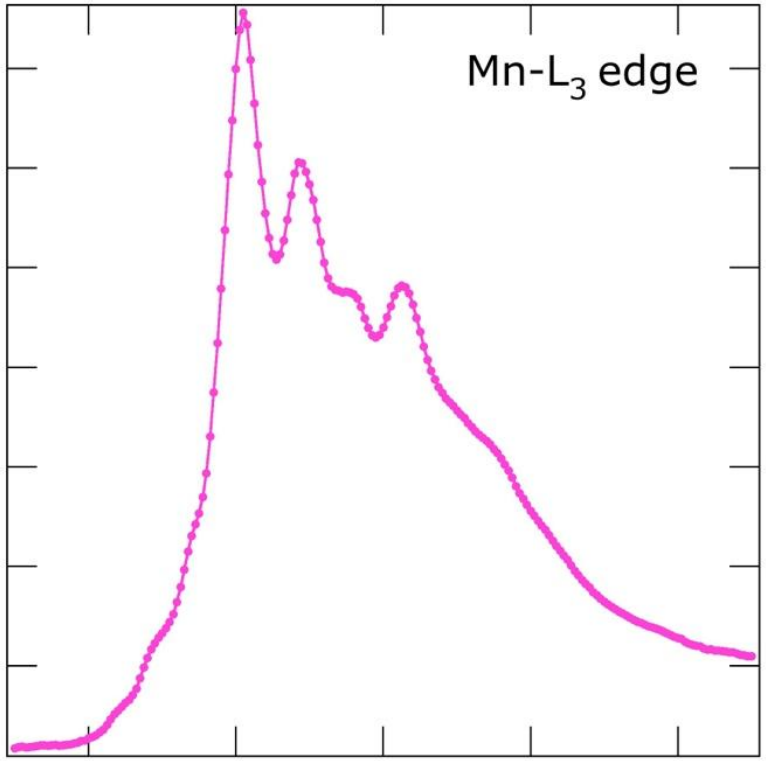
基底状態

d^4 $d^5\underline{L}^1$ $d^6\underline{L}^2$ Mn @D_{4h}

d^3 $d^4\underline{L}^1$ $d^5\underline{L}^2$ Cr @O_h

Mn-2pXAS (理論)


Mn-L_3 edge
-2
0
2
4
6
Energy (eV)


Mn-L_3 edge
638
640
642
644
646
Energy (eV)

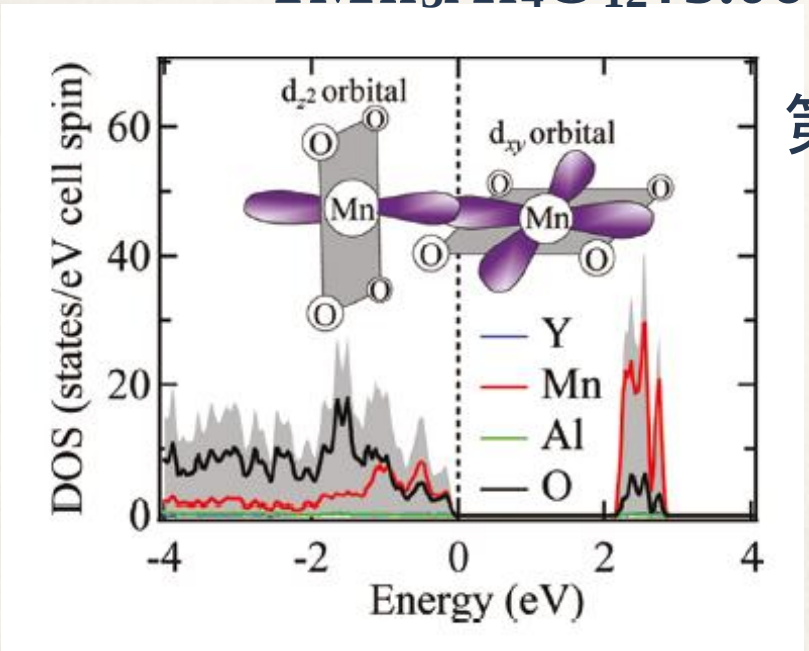
Mn-電子状態

d^4　$d^5\underline{L}^1$　$d^6\underline{L}^2$　**Basis-weights : 0.209 0.713 0.078**　4.87 個

2> <3z2-r2> <xy> 0.0731 0.0731 0.0037 0.0102 0.0737 0.9984 79

磁気モーメント：4.39 μ_B

$YMn_3Al_4O_{12}$：5.06 μ_B

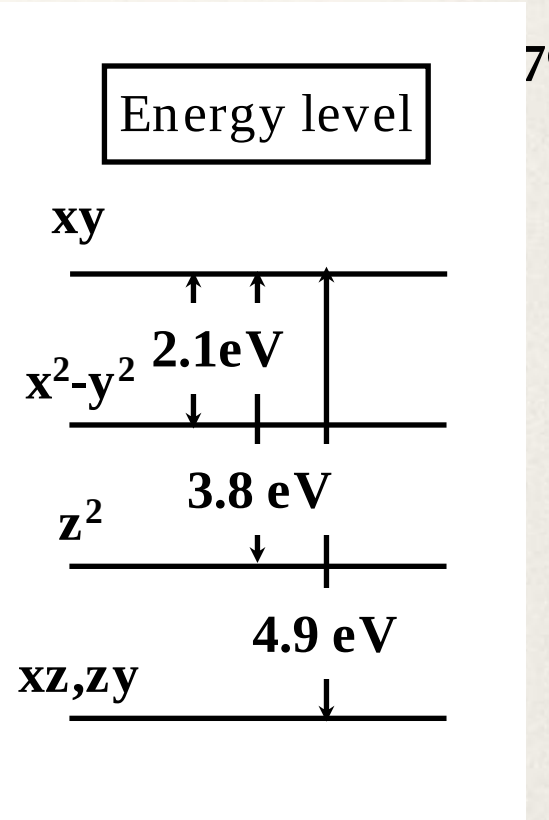


第一原理計算

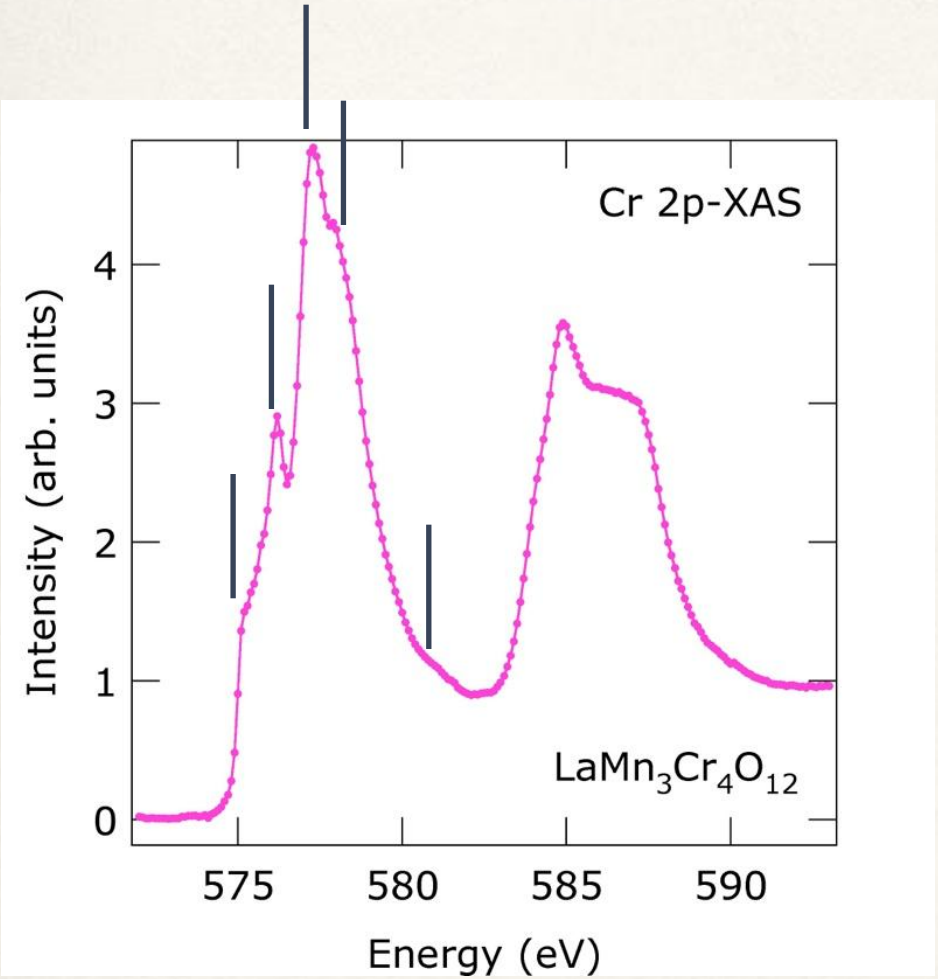
Mn：22.8 個

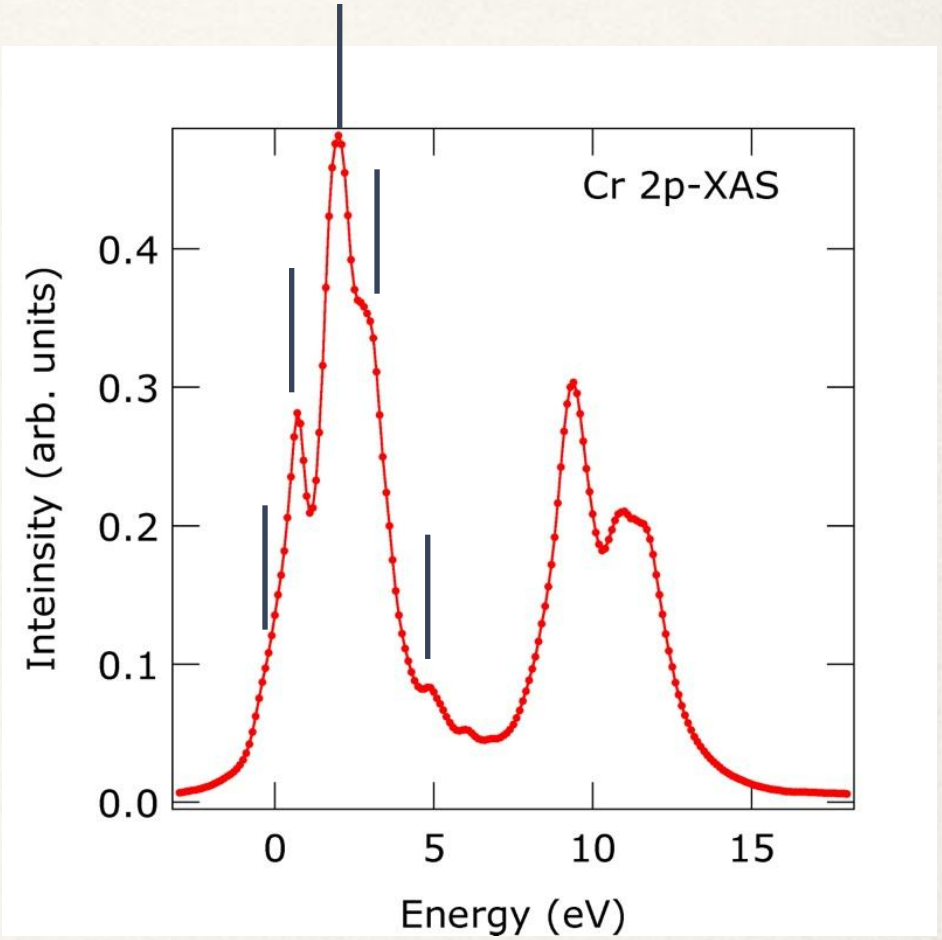
Mn^{2+}：23 個

Mn^{3+}：22 個



Cr-2pXAS (理論)


Cr 2p-XAS
$LaMn_3Cr_4O_{12}$
Intensity (arb. units)
Energy (eV)
0
1
2
3
4
575
580
585
590


Cr 2p-XAS
Inteinsity (arb. units)
Energy (eV)
0.0
0.1
0.2
0.3
0.4
0
5
10
15

まとめ

- ✓ X線吸収・発光分光測定を行った
- ✓ Mnの電子配置は$d^5\underline{L}$
- ✓ Mnは負電荷移動エネルギー

  負電荷移動エネルギー型絶縁体　$YMn_3Al_4O_{12}$
- ✓ サイトにより絶縁化の性質が異なる

  負電荷移動エネルギー型＋中間型絶縁体

  $LaMn_3Cr_4O_{12}$