放射光を用いた強相関薄膜実験に期待すること

Department of Physics
Tohoku University

Sumio Ishihara

物講研シンポジウム
放射光・中性子・ミュオンを用いた表面・界面科学の最前線
つくばエポカル　Nov. 17-18, 2009

TOHOKU UNIVERSITY

Outline

Introduction

Calculation of $(SrMnO_3)_n/(LaMnO_3)_n$ superlattice & SHG

A perspective

Collaborators

T. Satoh (Tokyo), K. Miyano (Tokyo)

Acknowledgements

H. Nakao (KEK)

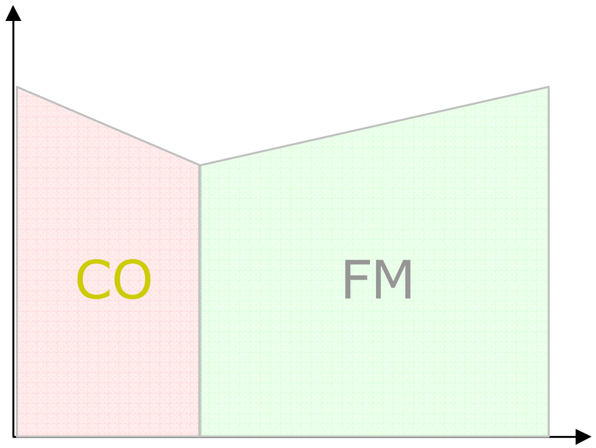
Reference

T. Satoh, K. Miyano, Y. Ogimoto, H. Tamaru, and SI,
Phys. Rev. B 72, 224403 (2005).

Introduction

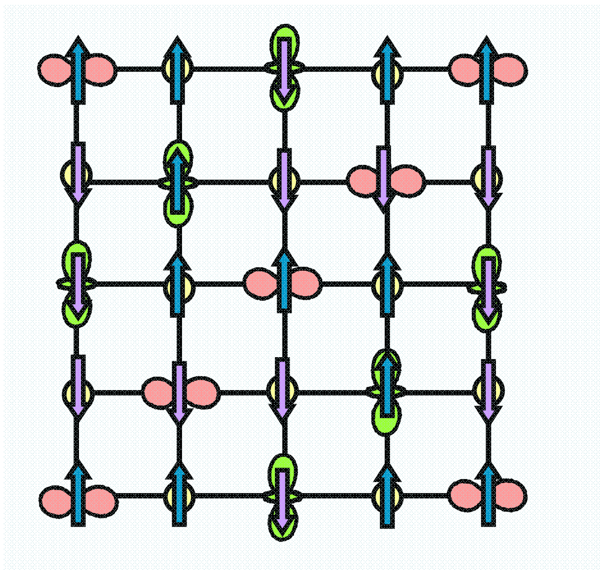
Correlated electron systems

High Tc superconductivity
Colossal magneto resistance
Multiferroics
Heavy fermion state
Quantum Hall effect
etc



[1] Strong electron correlation

Competition between itineracy / localization

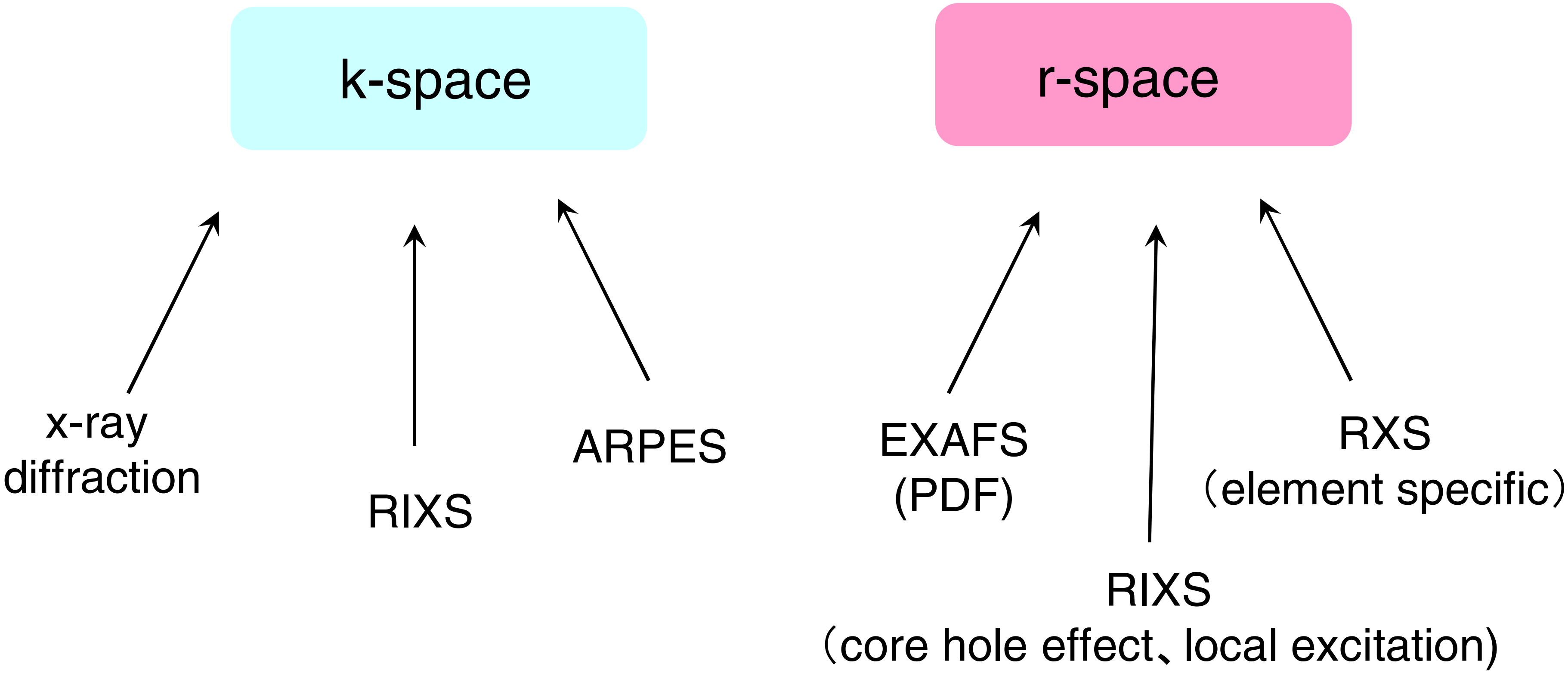


[2] Multi degrees of freedom
& their coupling/separation

charge, spin, orbital, lattice

X-ray diffraction/spectroscopy

[1] X-ray detects both the k-space and real-space nature of electron



X-ray diffraction/spectroscopy

[2] X-ray accesses to charge/spin/orbital degrees

Charge

X-ray diffraction
Resonant x-ray scattering
Resonant inelastic x-ray scattering

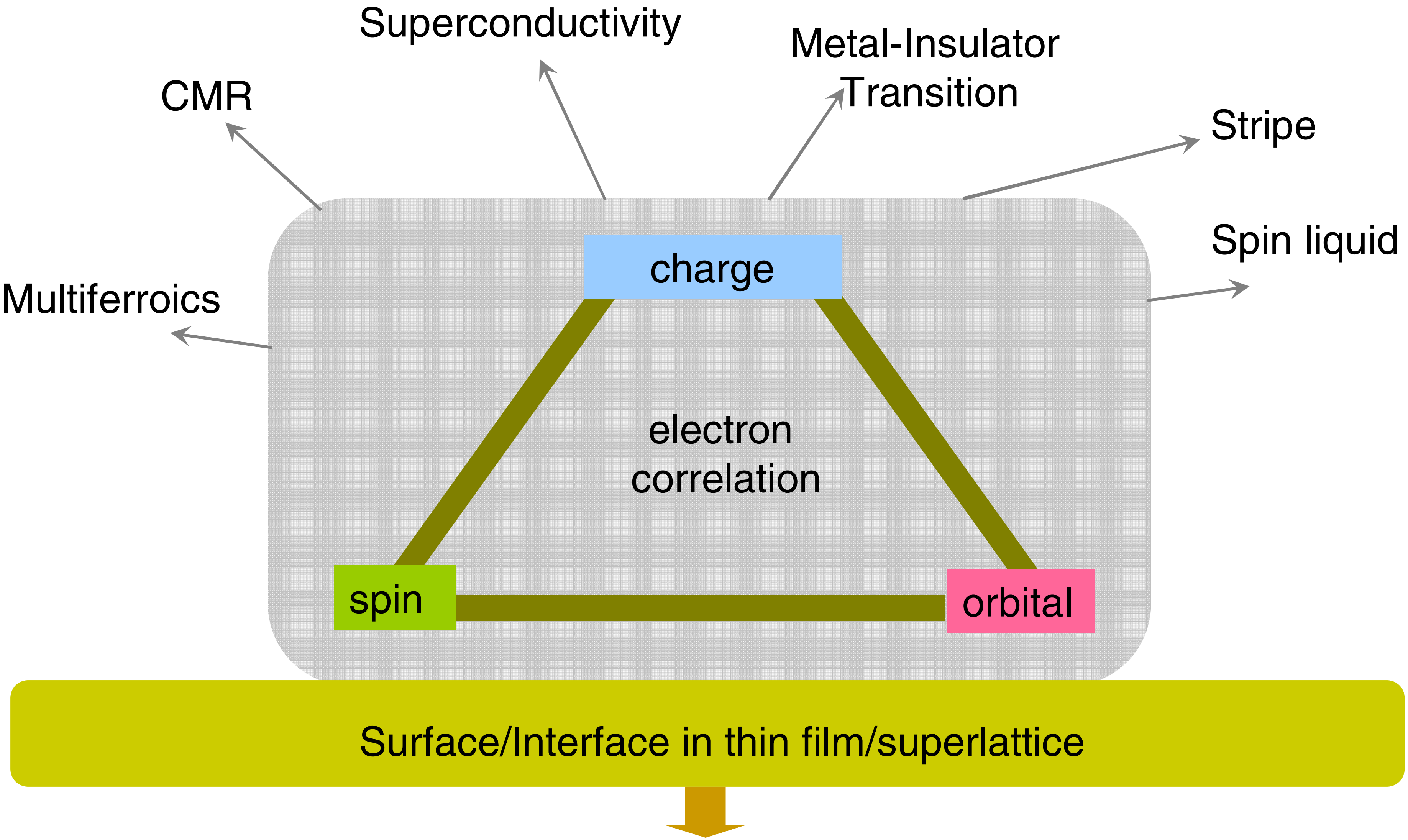
spin

Magnetic x-ray scattering
Magnetic compton scattering
MCD

orbital

Resonant x-ray scattering

Correlated electron systems



Novel phenomena, Colossal response, New functions
(which do not appear in bulk)

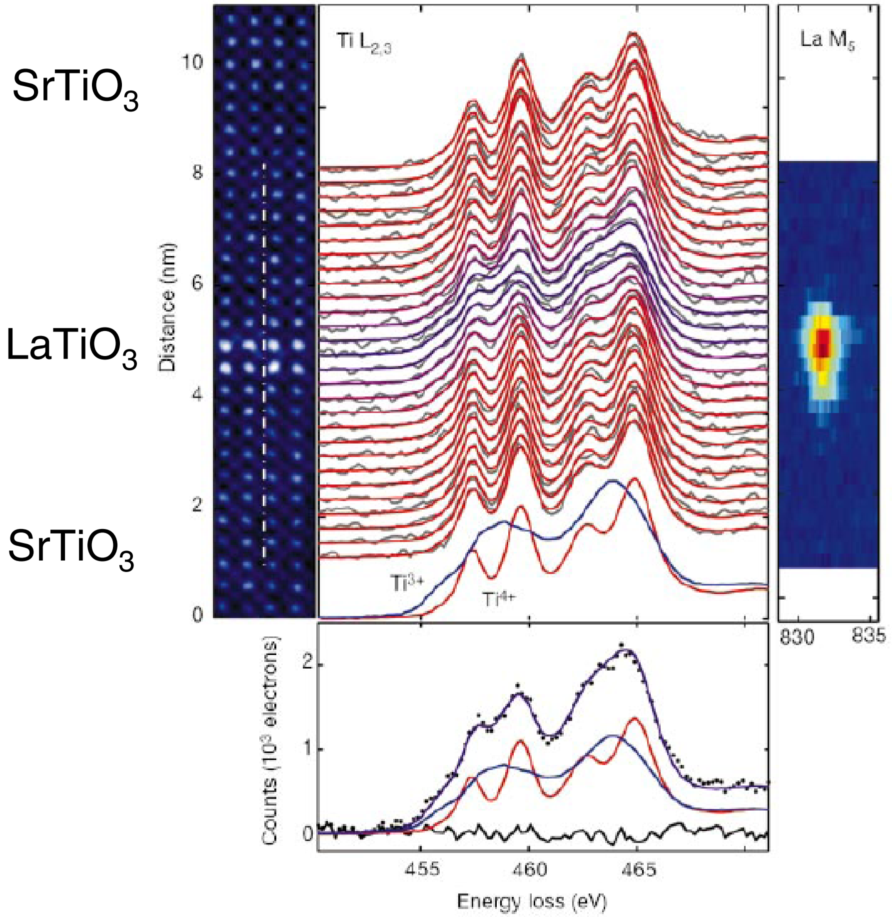
Correlated electron superlattice

$(SrTiO_3)_m$-$(LaTiO_3)_n$ superlattice

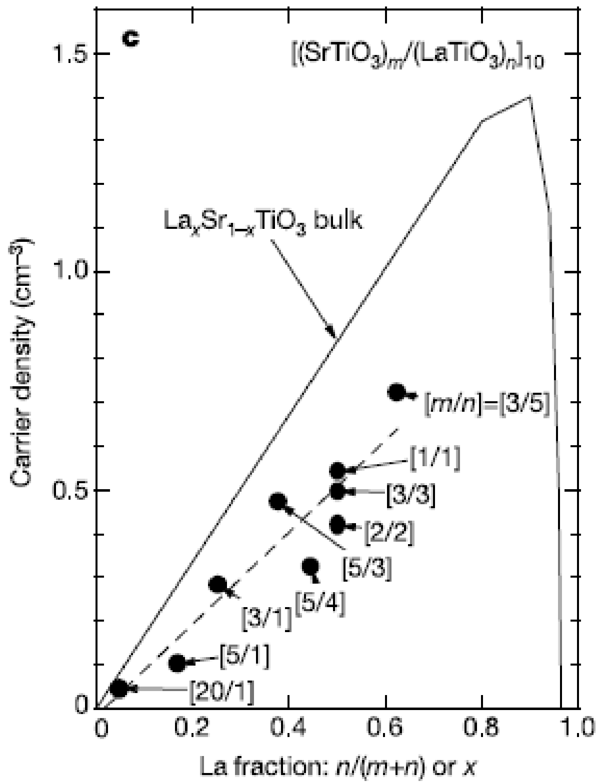
A. Ohtomo, D. A. Muller, J. L. Grazul & H. Y. Hwang,
NATURE 419, 378(2002)

Band insulator (d^0) / Mott insulator (d^1) → metallic interface

EELS



Carrier density from Hall effect

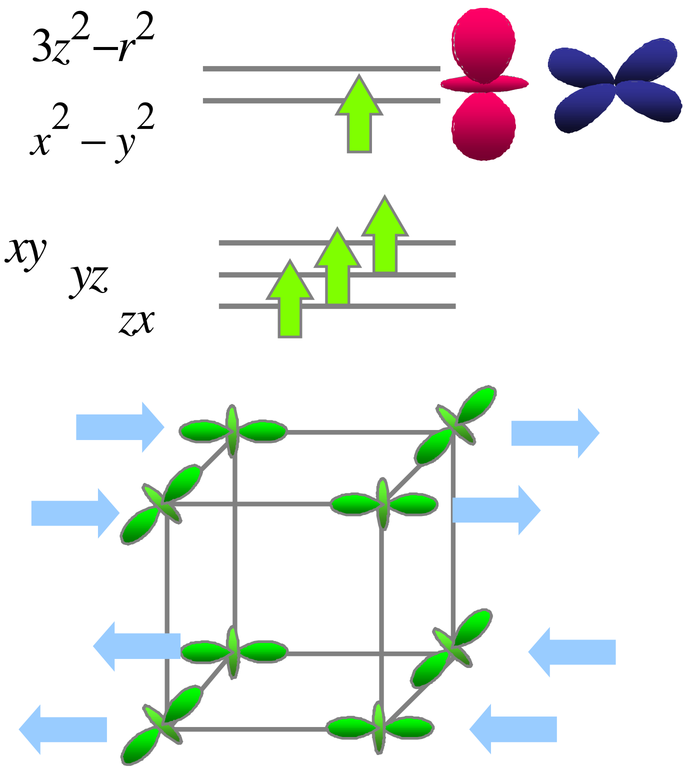


insulator + insulator = metal

Correlated electron superlattice

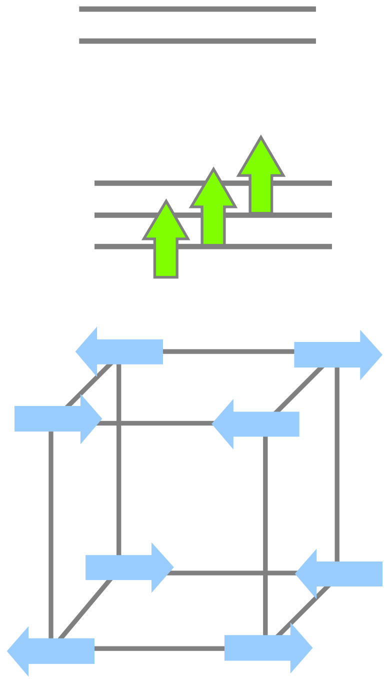
$(SrMnO_3)_m$-$(LaMnO_3)_n$ superlattice

Mott insulator (d^4)



$d(3x^2-r^2)/d(3y^2-r^2)$ orbital order
with Jahn-Teller distortion
A-type Antiferromagnetic order

Mott insulator (d^3)

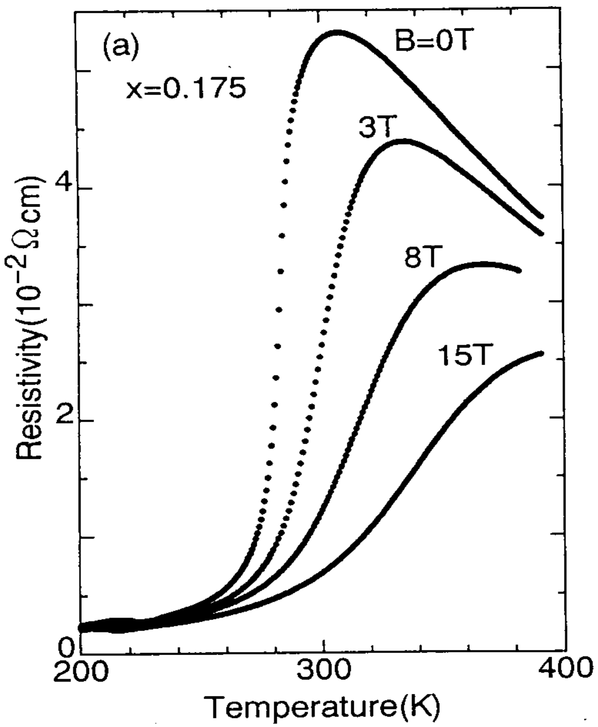


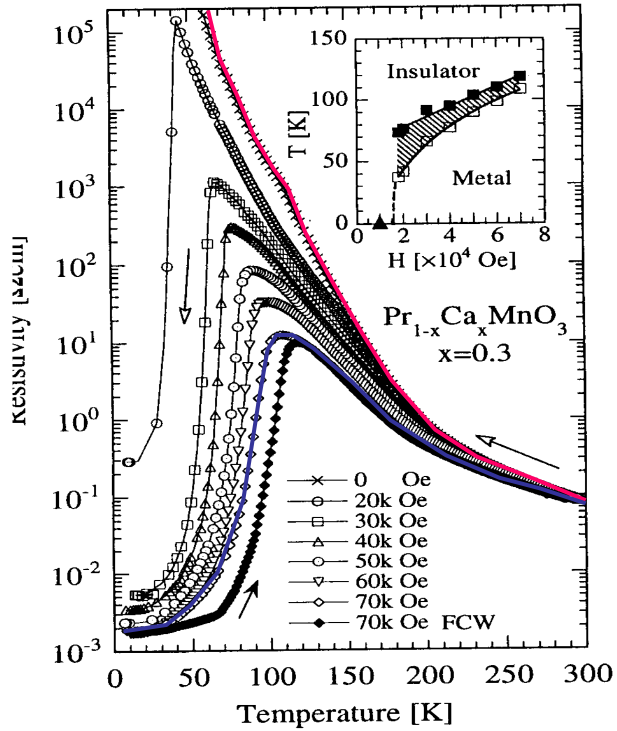
G-type AF order

Colossal Magneto Resistance

Colossal Magneto Resistance (CMR)

$La_{1-x}Sr_xMnO_3$ $Pr_{1-x}Ca_xMnO_3$

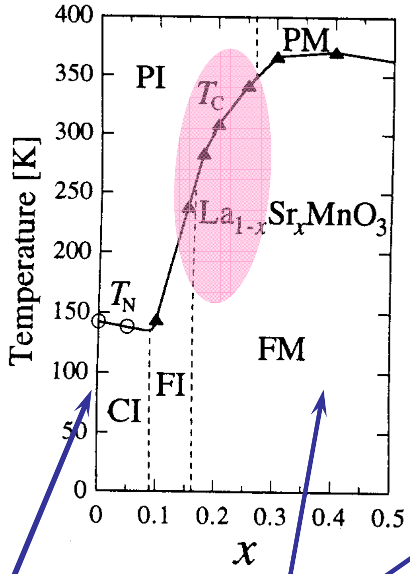


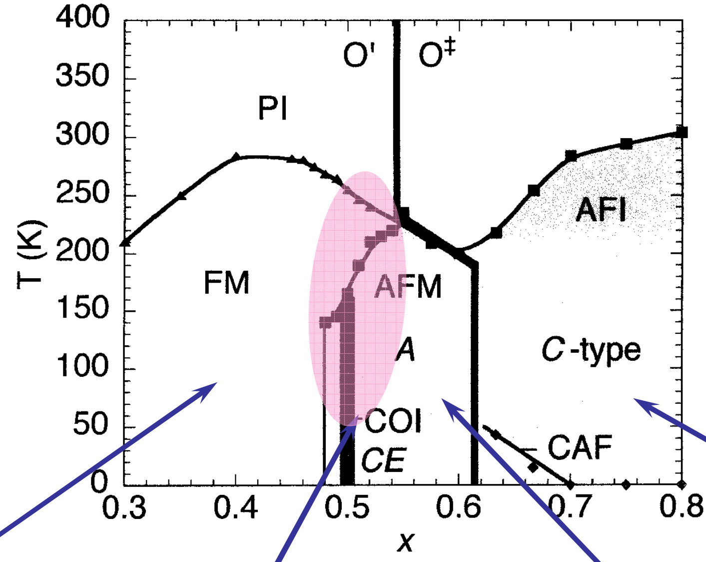


(Tokura group)

Phase Diagram

$La_{1-x}Sr_xMnO_3$

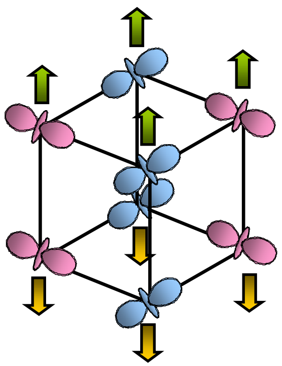


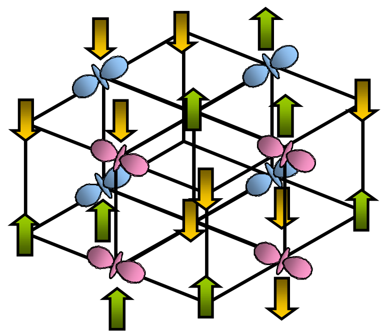


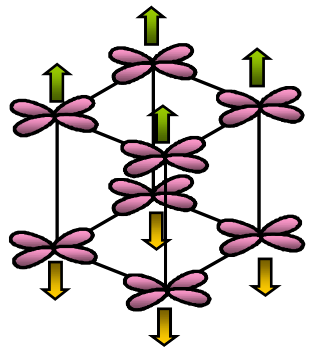
$Nd_{1-x}Sr_xMnO_3$

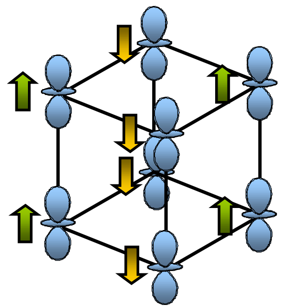
(Tokura group)

電荷	絶縁体	金属	電荷秩序	金属	絶縁体
スピン	A−型反強磁性	強磁性	CE−型反強磁性	A−型反強磁性	C−型反強磁性
軌道	$3x^2-r^2$/ $3y^2-r^2$型 軌道秩序	軌道液体	$3x^2-r^2$/ $3y^2-r^2$型 軌道秩序	x^2-y^2型 軌道秩序	$3z^2-r^2$型 軌道秩序





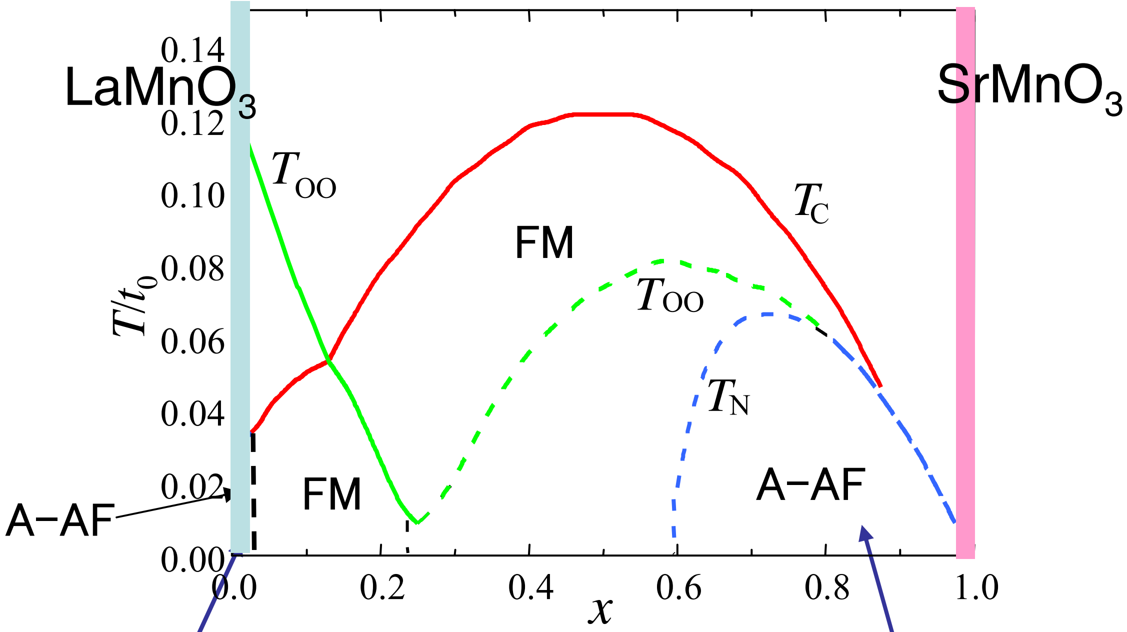




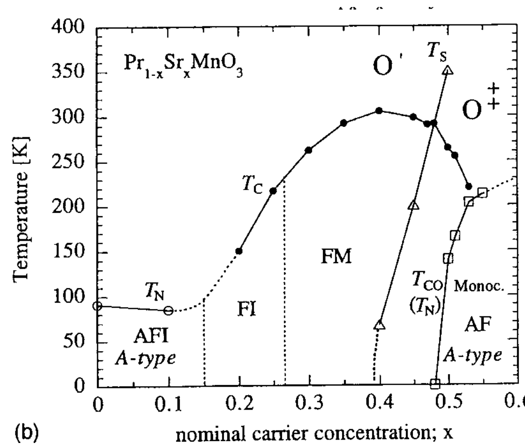
Theoretical Phase Diagram

S. Okamoto, SI, S. Maekawa,
Phys. Rev. B 61, 14647 (‘00).

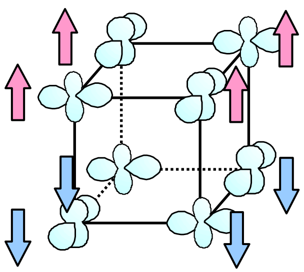
Hartree-Fock approx.



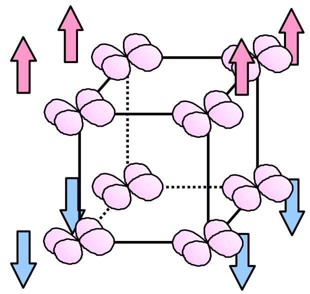
Experiment



$Pr_{1-x}Sr_xMnO_3$
(Tokura Group)



Staggered orbital
(Super-exchange)

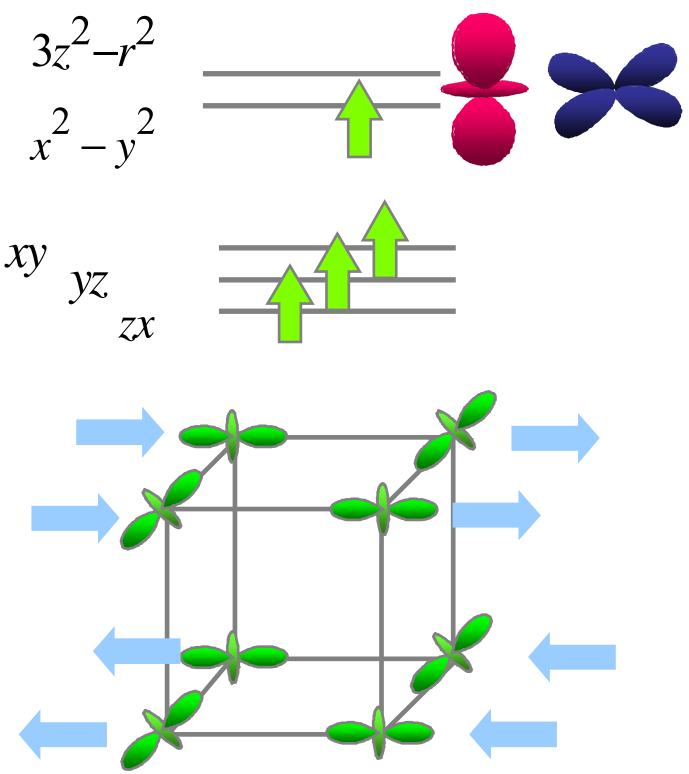


Uniform orbital
(Double exchange)

Correlated electron superlattice

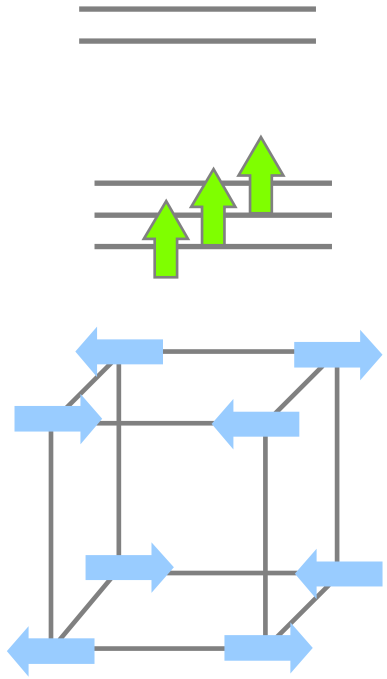
$(SrMnO_3)_m$-$(LaMnO_3)_n$ superlattice

Mott insulator (d^4)



$d(3x^2-r^2)/d(3y^2-r^2)$ orbital order
with Jahn-Teller distortion
A-type Antiferromagnetic order

Mott insulator (d^3)



G-type AF order

Correlated electron superlattice

$(SrMnO_3)_m$-$(LaMnO_3)_n$ super-lattice

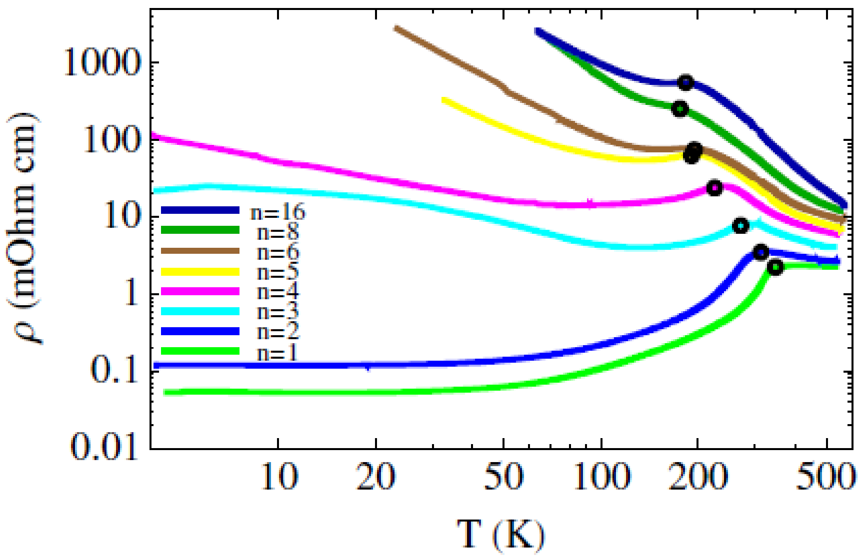
P. A. Salvador et al. APL 75, 2638, ('99)
n/(n+m)=0.26, m=1-15, STO substrate

J. Verbeeck et al. APL 79, 2037, ('01)
n=8, m=4, STO substrate

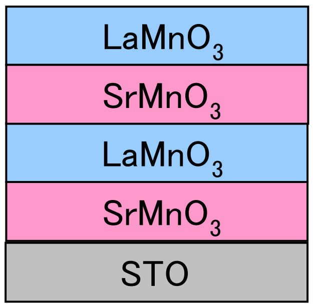
T. Koida et al. PRB 66, 144418, ('02)
n=m, m=1-32, STO[100] substrate

and more

Theory:
C. Lin, A. Millis, PRB 78, 184405('08) DMFT
S. Dong, et al. PRB 78, 201102(R) ('08) MC



C. Adamo et al. PRB 79, 045125, ('09)
n=2m, m=1-16, STO substrate



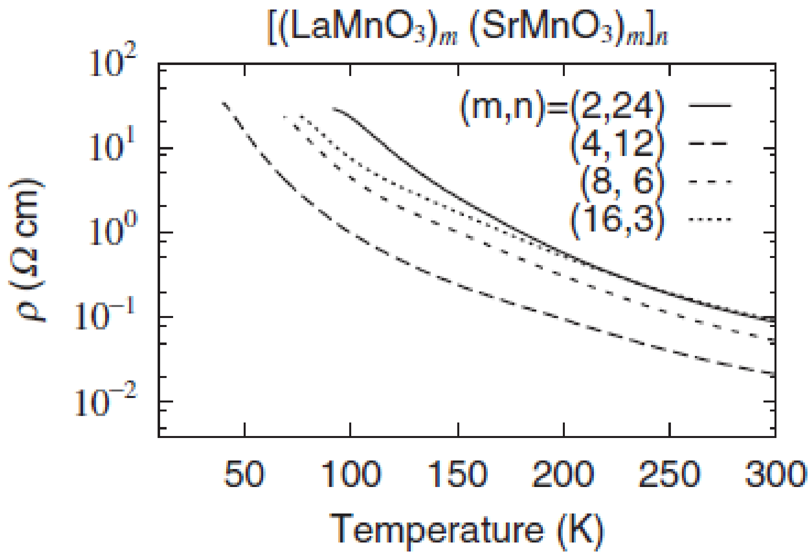
Ferromagnetic metallic behavior with decreasing m and n

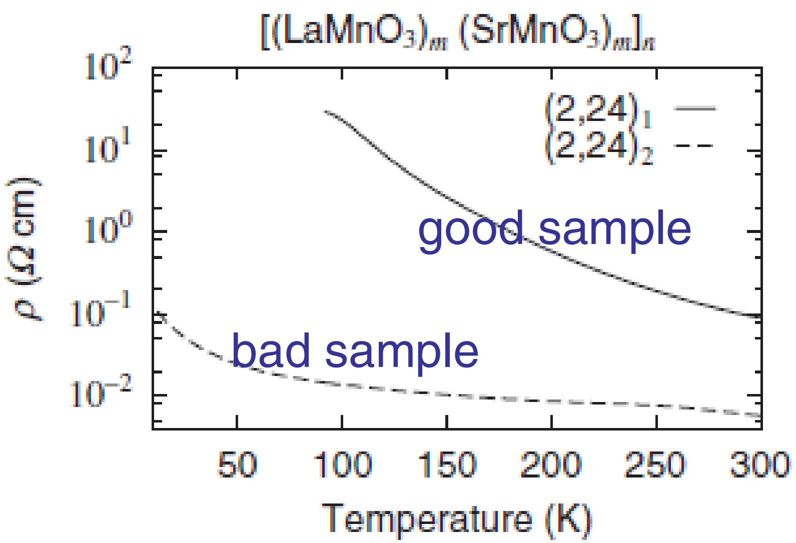
Correlated electron superlattice

$(SrMnO_3)_m$-$(LaMnO_3)_n$ superlattice

H. Nakao et al. JPSJ 78, 024602, ('09)
$n=m$, $m=1$-16. STO substrate

sample quality is important
Insulating behavior for all *m*





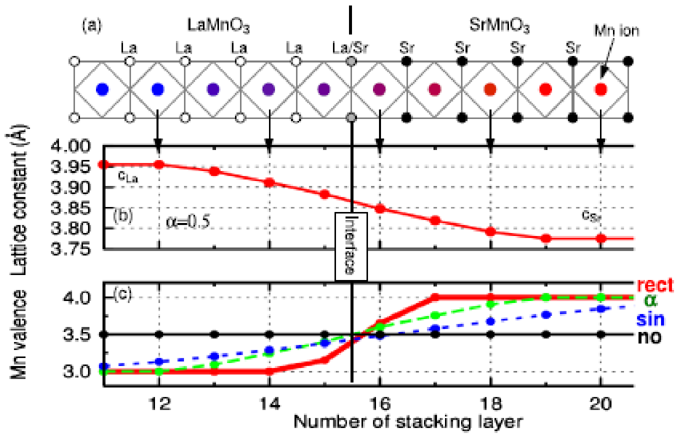
Correlated electron superlattice

$(SrMnO_3)_m$-$(LaMnO_3)_n$ superlattice

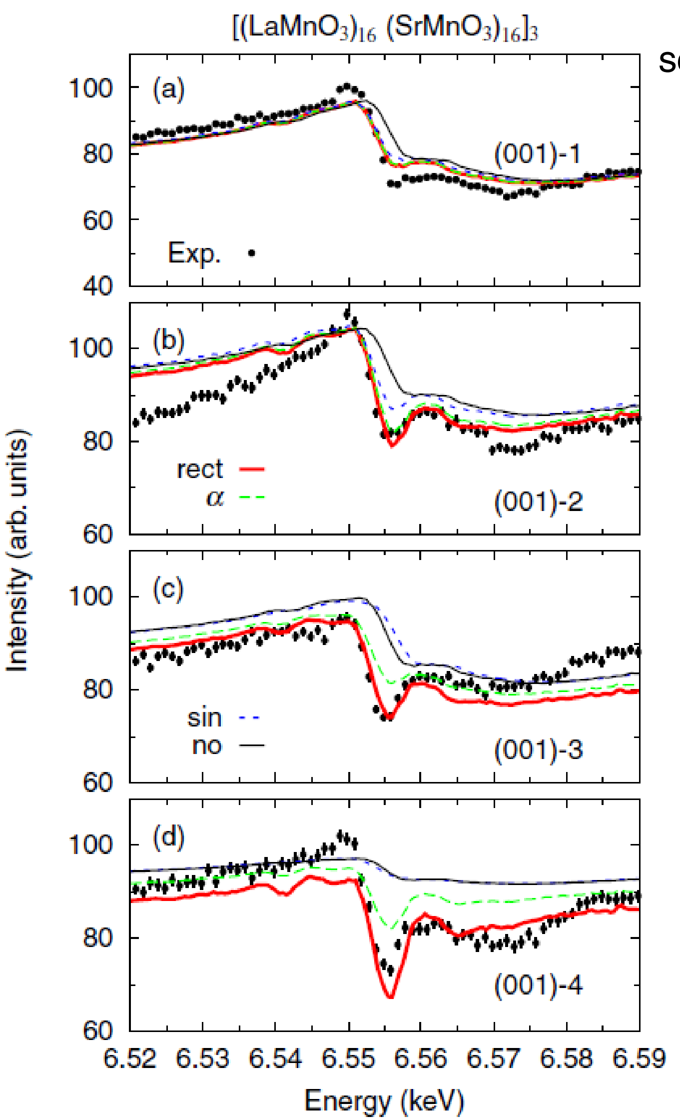
H. Nakao et al. JPSJ 78, 024602, ('09)
$n=m$, $m=1$-16. STO substrate
Intermediate valence of Mn^{3+} and Mn^{4+}
(consistent with present calculation ?)

A. Sawa (previous talk)
H. Yamada (CMRC meeting)
LSAT substrate

AFM-Insulator → FM-Insulator



Resonant x-ray scattering @ Mn K



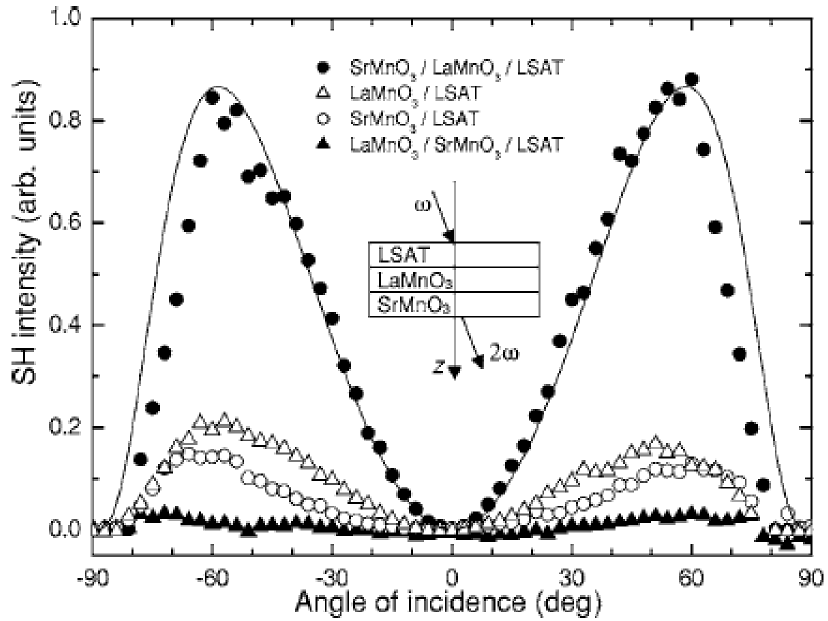
SHG and electronic structure

in $(LaMnO_3)_n/(SrMnO_3)_n$ interface

SH Experiments

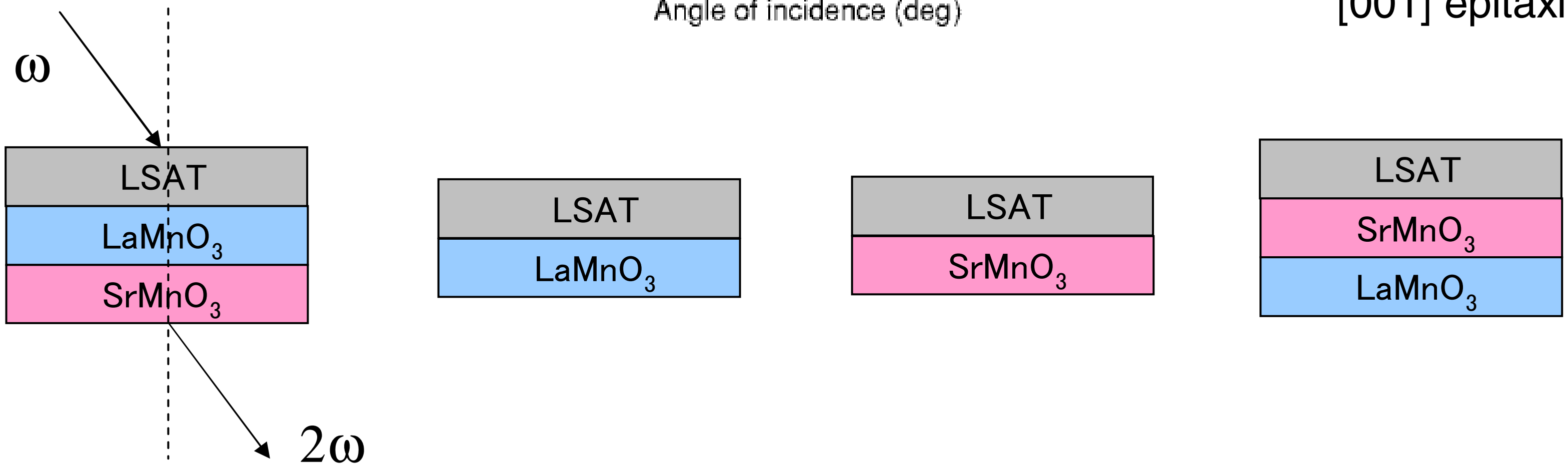
T. Satoh, K. Miyano, Y. Ogimoto, H. Tamaru & SI
PRB ('05)

Maker fringe pattern



$$P_i(2\omega) = \varepsilon_0 \chi^{(2)}_{ijk} E_j(\omega) E_k(\omega)$$

[001] epitaxial growth

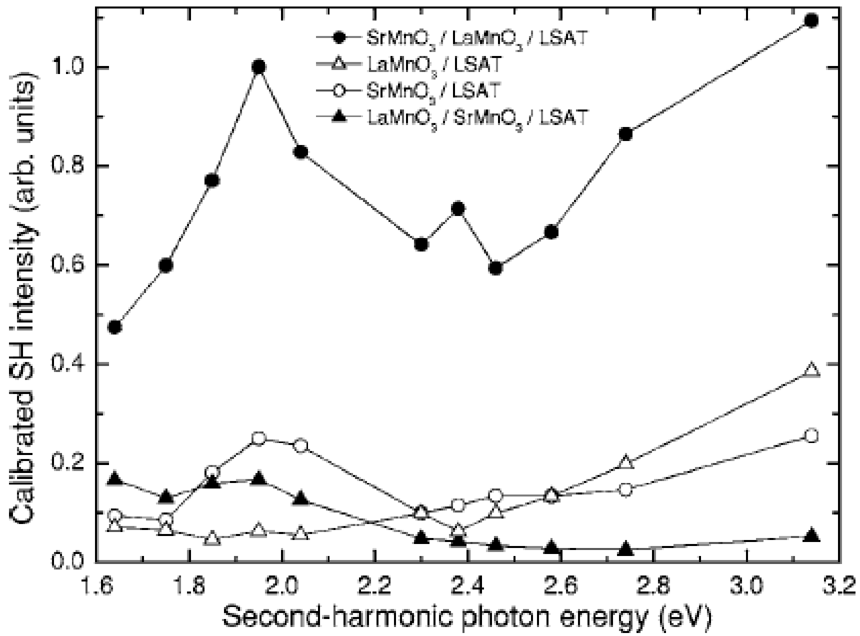


3-4 units

SH Experiments

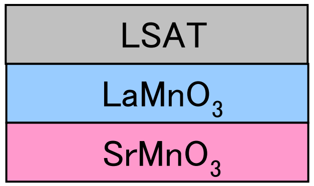
SH spectra v.s. photon energy

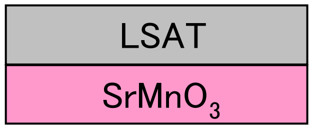
insulator

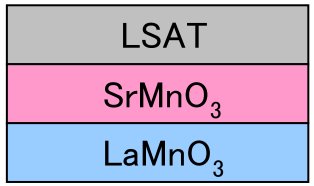


$|\chi^{(2)}| \sim 10^{-6}$

10 times larger than $\chi^{(2)}$ in $BaTiO_3$







$|\chi^{\mathrm{air-SMO}} + \chi^{\mathrm{SMO-LMO}}|^2$ $|\chi^{\mathrm{air-LMO}}|^2$ $|\chi^{\mathrm{air-SMO}}|^2$ $|\chi^{\mathrm{air-LMO}} + \chi^{\mathrm{LMO-SMO}}|^2$

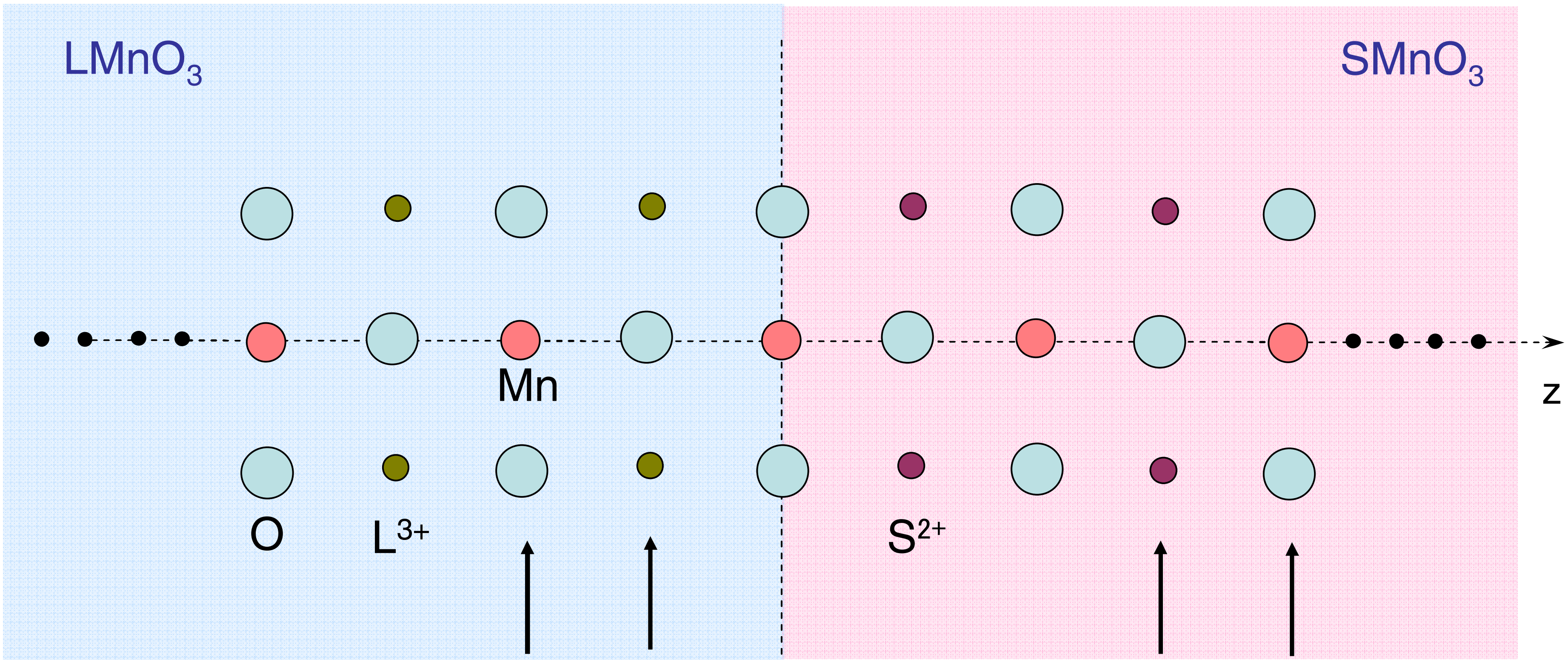
$\chi^{\mathrm{LSAT-SMO}}, \chi^{\mathrm{LSAT-LMO}} \sim 0$

Model

$(LMnO_3)_n$-$(SMnO_3)_n$ super lattice

Tight binding model for O 2p & Mn 3d electrons
Extended d-p model

L (La): trivalent cation
S (Sr): divalent cation



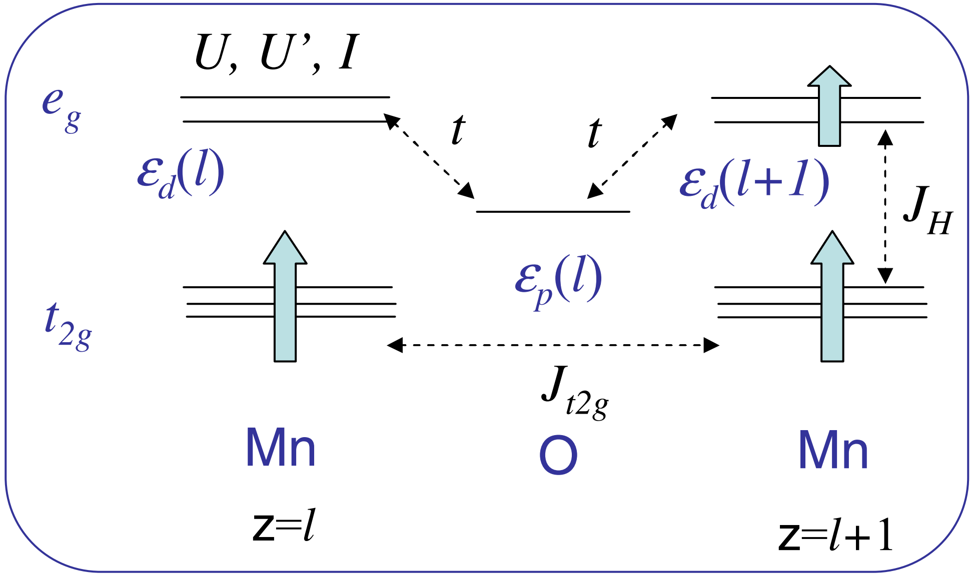
L, S: point charge
O : bonding orbital
Mn : e_g orbitals + t_{2g} localized spin

MnO_2 LO SO MnO_2

layers

Model

Extended d-p model



$$H = H_d + H_p + H_{pd}$$

$$\begin{aligned}
H_d &= \sum_{il\sigma\gamma} \varepsilon_d(l) d^\dagger_{il\sigma\gamma} d_{il\sigma\gamma} \\
&+ U \sum_{il\gamma} n_{il\uparrow} n_{il\downarrow} + U' \sum_{il} n_{ilu} n_{ilv} \\
&+ (1/2) \sum_{il} d^\dagger_{il\uparrow u} d^\dagger_{il\downarrow v} d_{il\uparrow v} d_{il\downarrow u} \\
&+ J_H \sum_{il} \vec{s}_{il} \cdot \vec{S}_{il} + J_{t_{2g}} \Big(\sum_{<ij>l} \vec{S}_{il} \cdot \vec{S}_{jl} + \sum_{i<lm>} \vec{S}_{il} \cdot \vec{S}_{im} \Big)
\end{aligned}$$

(Mn 3d electron)

$$H_p = \sum_{il\sigma\alpha} \varepsilon_p(l) p^\dagger_{il\sigma\alpha} p_{il\sigma\alpha}$$

(O 2p electron)

$$H_{pd} = \sum_{<ij>l\sigma\gamma\alpha} t^{\gamma\alpha}_{iljl} d^\dagger_{il\sigma\gamma} p_{jl\sigma\alpha} \sum_{i<lm>\sigma\gamma\alpha} t^{\gamma\alpha}_{ilim} d^\dagger_{il\sigma\gamma} p_{im\sigma\alpha} + H.c.$$

(Mn 3d –O 2p transfer)

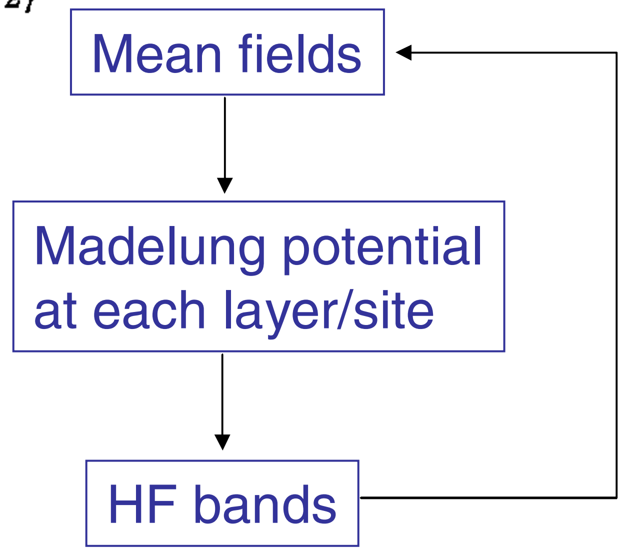
$$H_{JT} = g \sum_{iln=(2,3)} Q_{iln} T_{iln}$$

(Jahn-Teller coupling)

Method

Hartree-Fock approximation

$$d_1^\dagger d_2 d_3^\dagger d_4 \rightarrow \langle d_1^\dagger d_2 \rangle d_3^\dagger d_4 + d_1^\dagger d_2 \langle d_3^\dagger d_4 \rangle - \langle d_1^\dagger d_4 \rangle d_3^\dagger d_2 - d_1^\dagger d_4 \langle d_3^\dagger d_2 \rangle$$



Order parameters (at each layer)

d electron number
$$N_d(l) = N^{-1} \sum_{\vec{k}_\parallel \gamma \sigma} \langle d^\dagger_{\vec{k}_\parallel l \sigma \gamma} d_{\vec{k}_\parallel l \sigma \gamma} \rangle$$

p electron number
$$N_p(l) = N^{-1} \sum_{\vec{k}_\parallel \gamma \sigma} \langle p^\dagger_{\vec{k}_\parallel l \sigma \gamma} p_{\vec{k}_\parallel l \sigma \gamma} \rangle$$

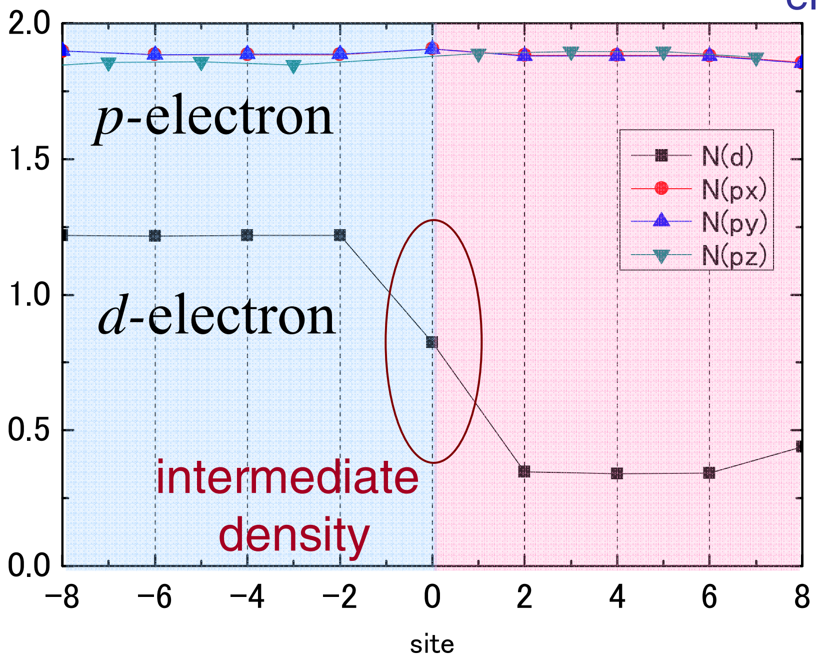
Magnetic order
$$M(q_\parallel, l) = N^{-1} \sum_{\vec{k}_\parallel \sigma \gamma} \langle d^\dagger_{\vec{k}_\parallel l \gamma \sigma} d_{\vec{k}_\parallel + \vec{q}_\parallel l \sigma \gamma} \varepsilon_\sigma \rangle$$

Orbital order
$$\vec{T}(\vec{q}_\parallel, l) = N^{-1} \sum_{\vec{k}_\parallel \gamma \gamma' \sigma} \langle d^\dagger_{\vec{k}_\parallel l \sigma \gamma \sigma} \vec{\sigma}_{\gamma \gamma'} d_{\vec{k}_\parallel + \vec{q}_\parallel l \sigma \gamma'} \rangle$$

Madelung potential (Ewald method)
$$\varepsilon_d(l),\ \varepsilon_p(l) \leftarrow N_d(l),\ N_p(l),\ \mathrm{R}^{3+},\ \mathrm{A}^{2+}$$

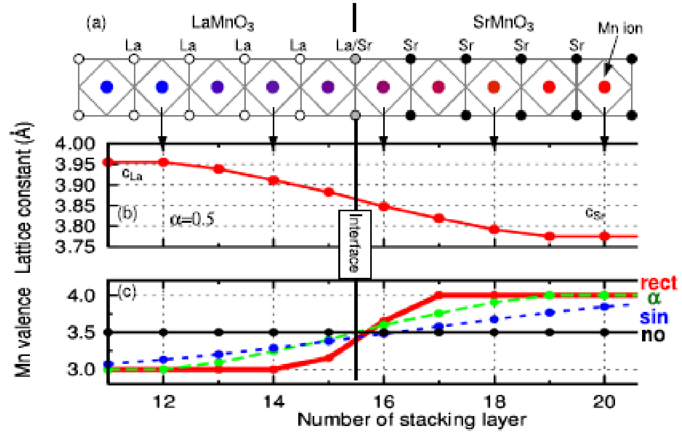
Electronic structure

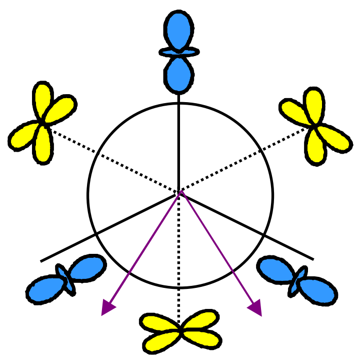
electron density

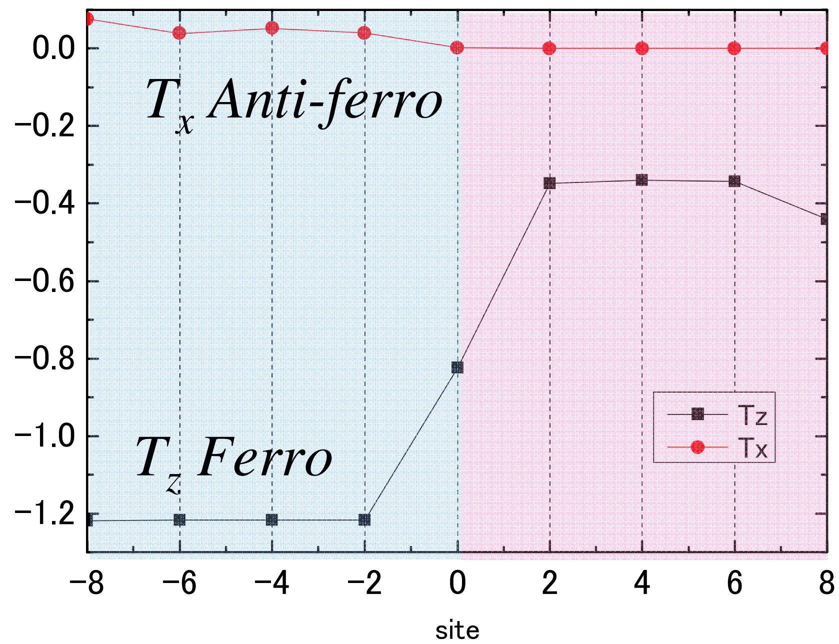


$LMnO_3$ $SMnO_3$

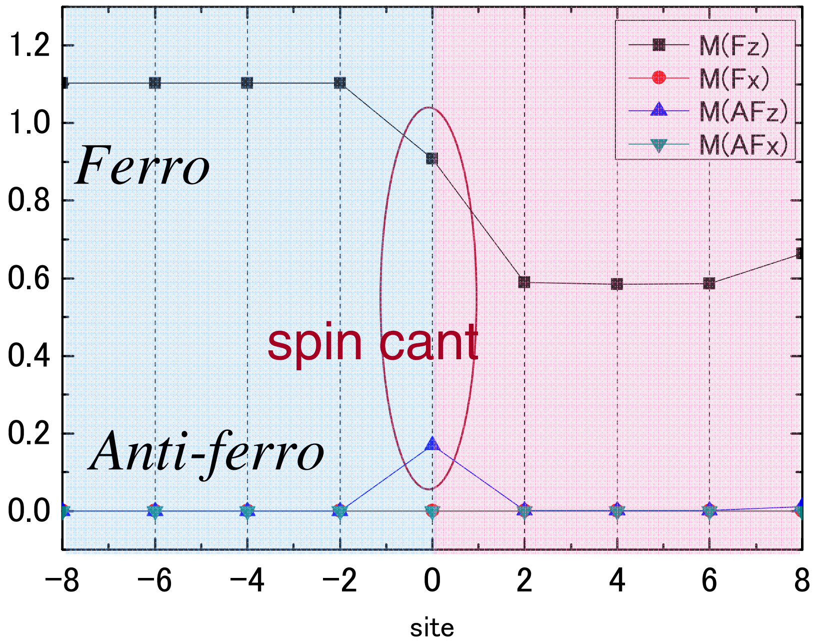
H. Nakao et al. JPSJ 78, 024602, ('09)







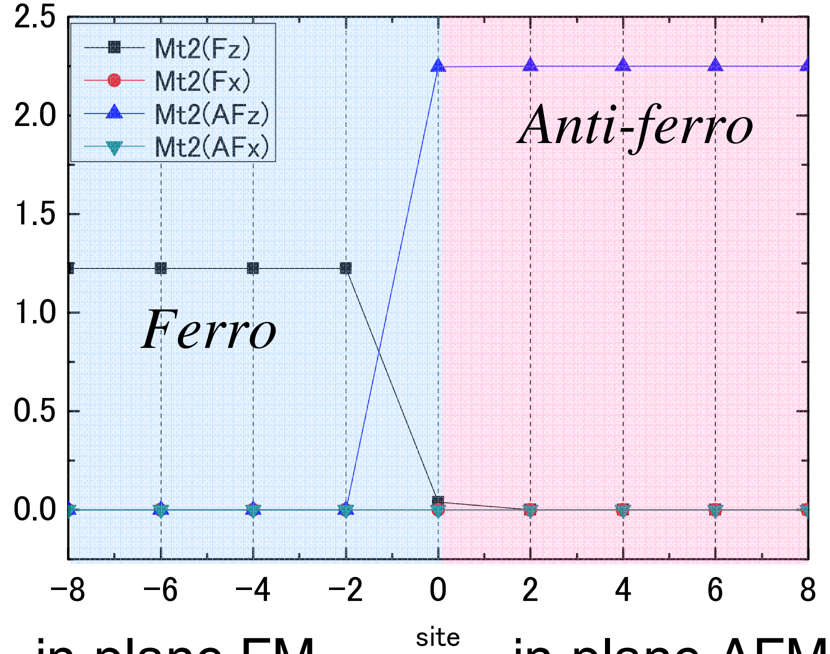
Electronic structure



$LMnO_3$ $SMnO_3$

e_g spin
(in-plane component)

t_{2g} spin
(in-plane component)

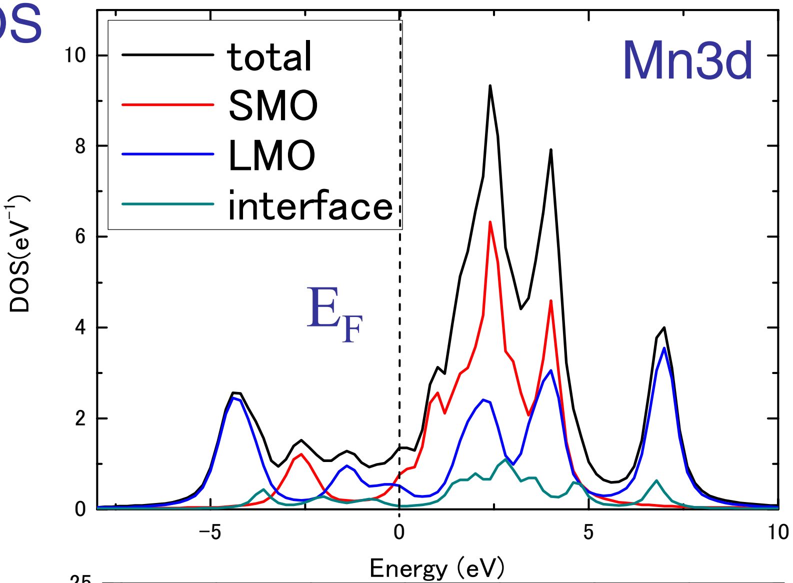


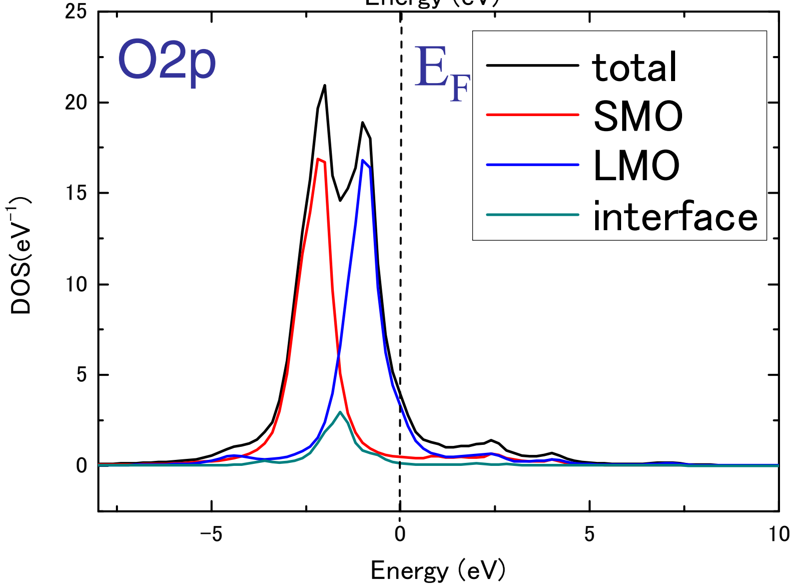
in-plane FM in-plane AFM

Spin cant ~ Phase separation (?)
(c.f. Sawa's talk)

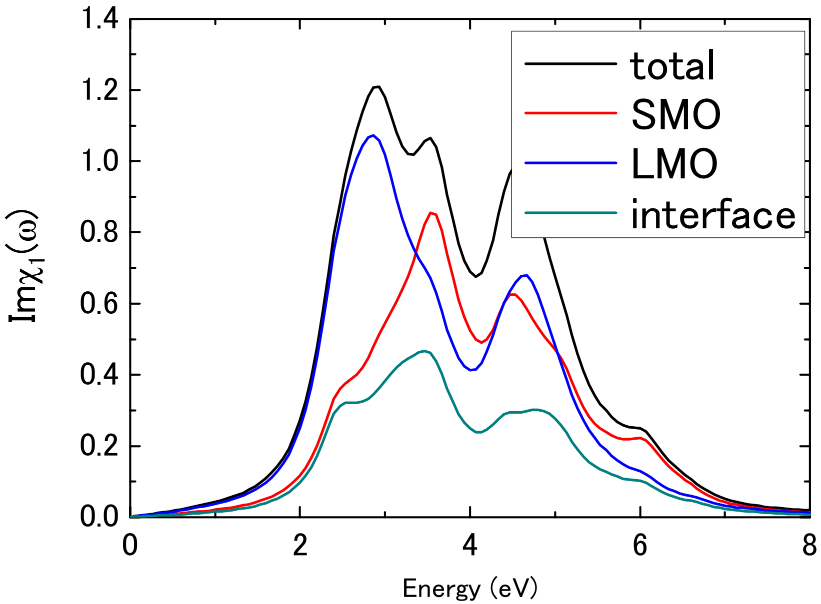
Electronic structure

DOS





linear optical absorption



insulator

SHG spectra

One-body (Hartree-Fock) scheme

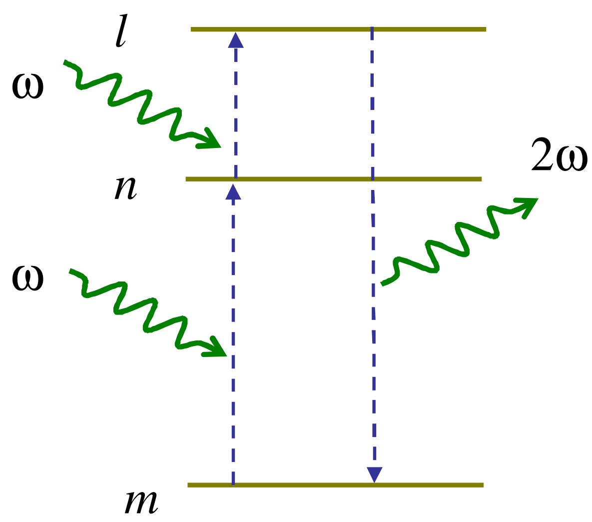
$$\chi^{(2)}_{zzz}(\omega) = -\frac{Ne^3}{\hbar^2} \sum_{m,n(\neq m),l,\vec{k}_\parallel} X_{mn} X_{nl} X_{lm} (F_1 + F_2)$$

$$F_1 = \frac{f_{ml}}{\varepsilon^3_{lm}(2\varepsilon_{lm} - \varepsilon_{nm})(\omega - \varepsilon_{lm})} + \frac{f_{nl}}{\varepsilon^3_{nl}(2\varepsilon_{nl} - \varepsilon_{nm})(\omega - \varepsilon_{nl})}$$

$$F_2 = \frac{16}{\varepsilon^3_{mn}(2\omega - \varepsilon_{mn})} \left\{ \frac{f_{ml}}{\varepsilon_{nm} - 2\varepsilon_{lm}} + \frac{f_{nl}}{\varepsilon_{nm} - 2\varepsilon_{nl}} \right\},$$

$$X = -t \sum_{i,\delta=\pm a\hat{z},\sigma} \delta \left\{ d_{3z^2-r^2\sigma}(i)^\dagger p_{z\sigma}(i+\delta) - H.c. \right\},$$

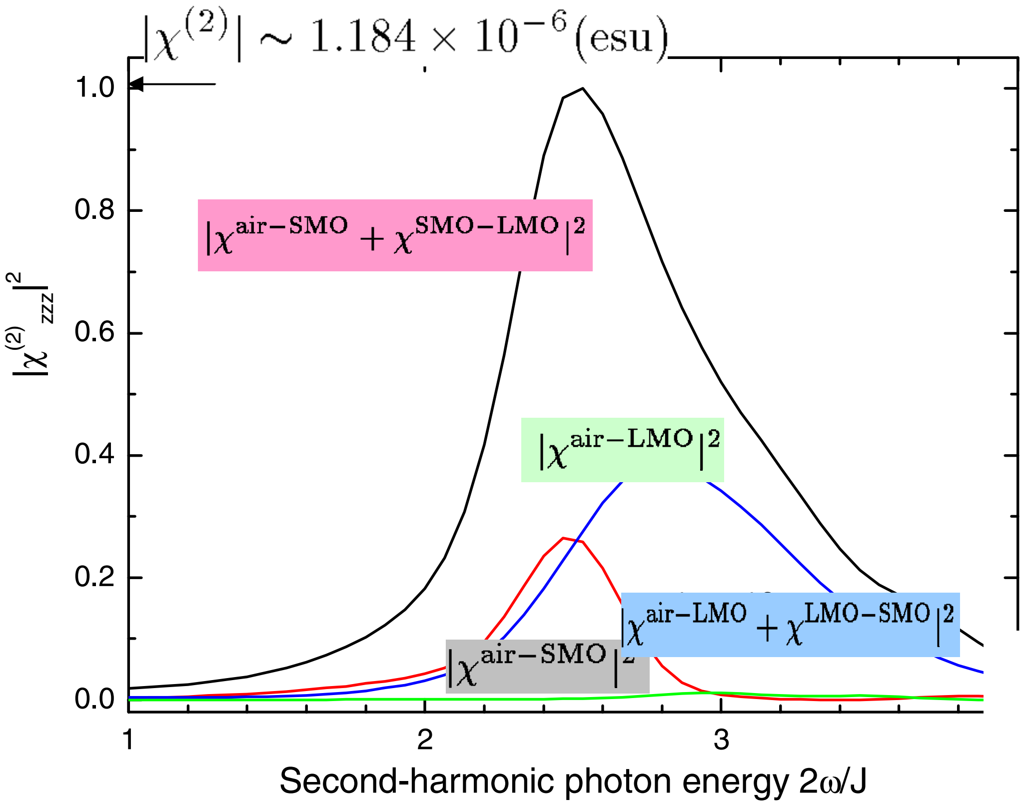
$$f_{ij} = f_F(\varepsilon_i) - f_F(\varepsilon_j) \qquad \varepsilon_{ij} = \varepsilon_i - \varepsilon_j$$



SHG spectra

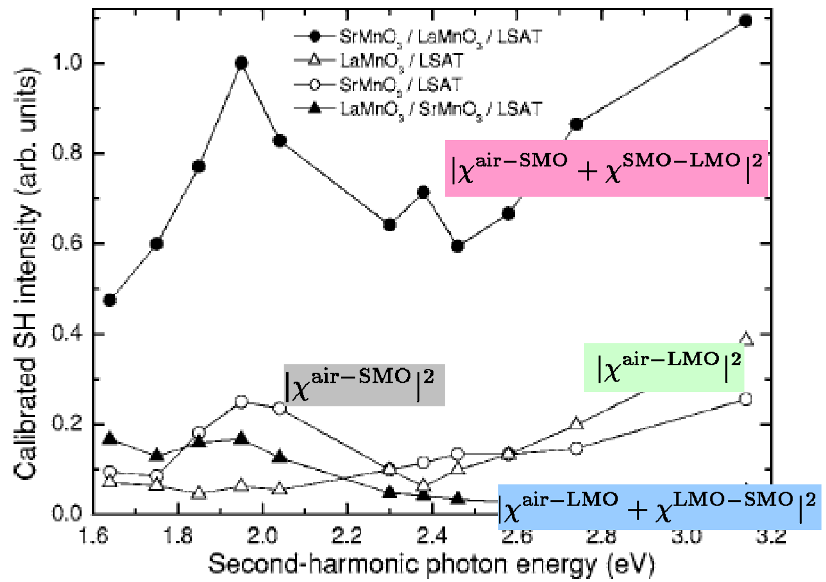
$$n = 4,\ U = 6eV,\ J = 1rV,\ J_H = 1eV,$$
$$J_{AF} = 0.05eV,\ t = 0.85eV,\ gQ = 0.25eV$$

Theory



$$|\chi^{(2)}| \sim 10^{-6}(\text{csu})$$

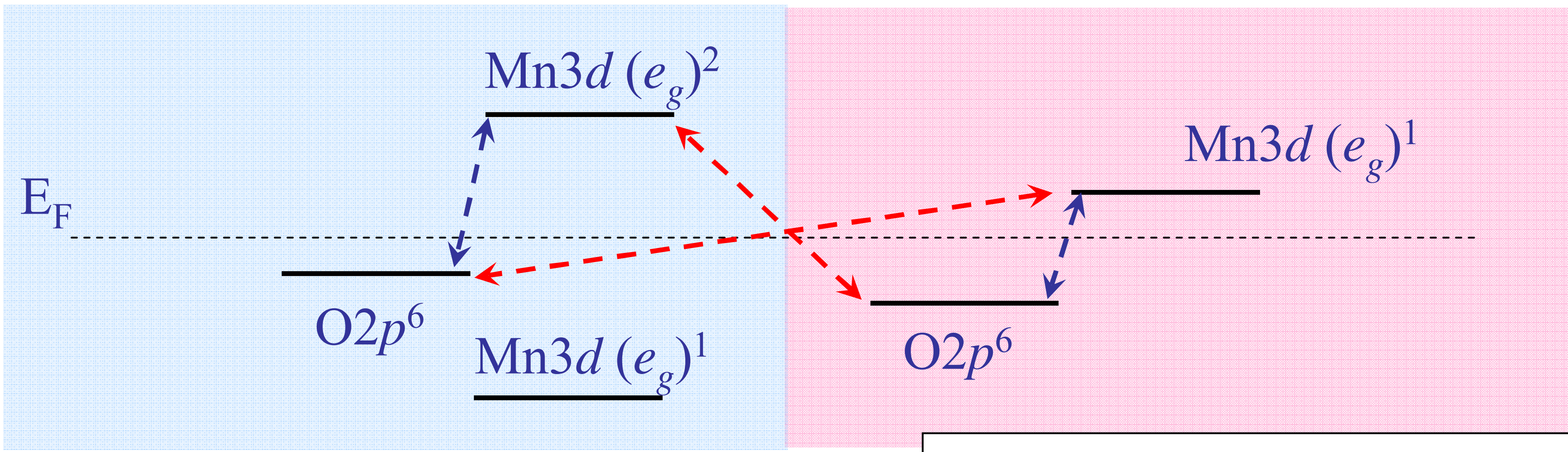
Experiment



T. Satoh, K. Miyano, Y. Ogimoto, H. Tamaru, and SI
Phys. Rev. B 72, 224403 (2005).

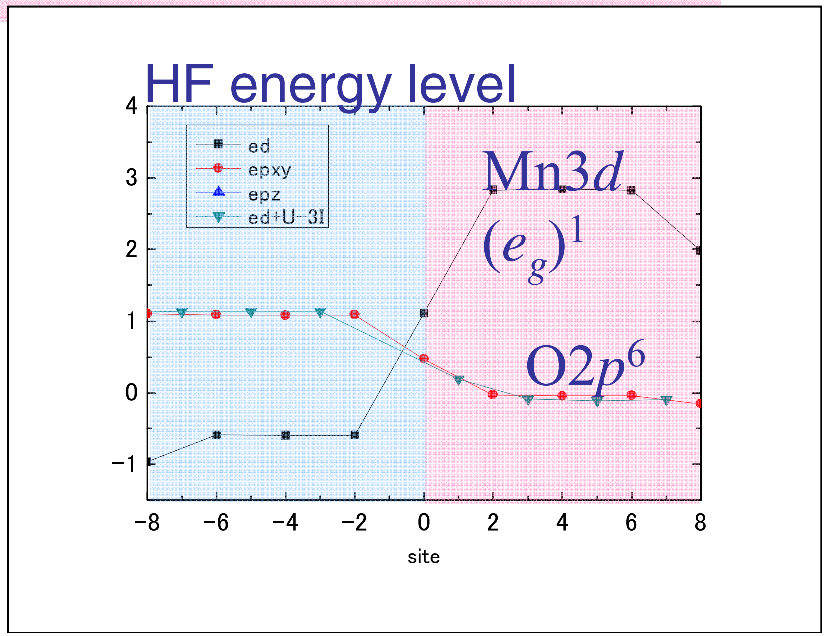
SHG spectra

Charge transfer excitation over interface



LMnO$_3$

Interface



O2p^6 (LMO) / Mn3d (e_g)^0 (SMO) → O2p^5 (LMO) / Mn3d (e_g)^1 (SMO)

O2p^6 (SMO) / Mn3d (e_g)^1 (LMO) → O2p^5 (SMO) / Mn3d (e_g)^2 (LMO)

A perspective

(理論側からの期待)

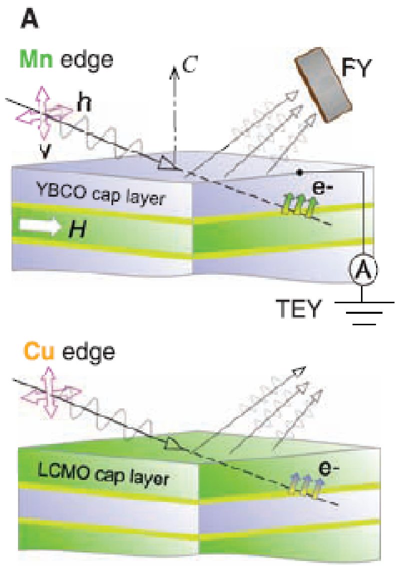
More direct observation

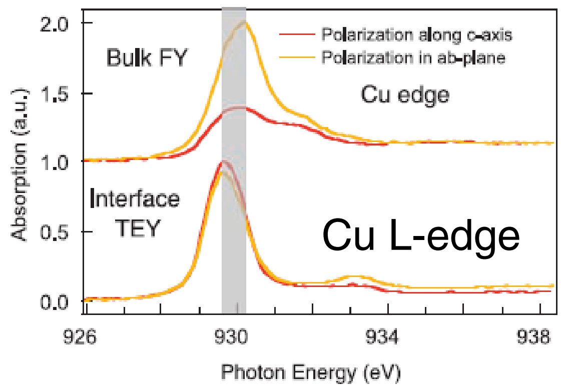
Observation of electronic/lattice structure only at/around interface

X-ray diffraction
- Crystal truncation rods (CTR) measurements
- Grazing incident x-ray scattering (GIXD)

X-ray absorption spectroscopy
- tuned @ absorption edge in deeper layer
- low angle of incident x-ray

Photoemission
- resonant
- penetration depth



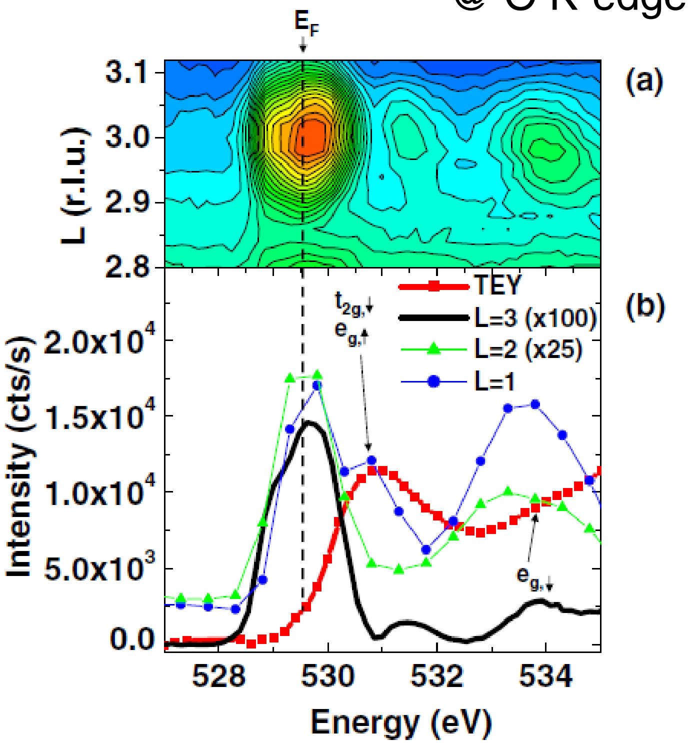


J. Chakhalian, et al. Science 318, 1114 (‘07)

More direct observation

$(SrMnO_3)_n$-$(LaMnO_3)_{2n}$ super lattice
n=4, 5, STO substrate
Resonant soft X-ray scattering

@ O K-edge



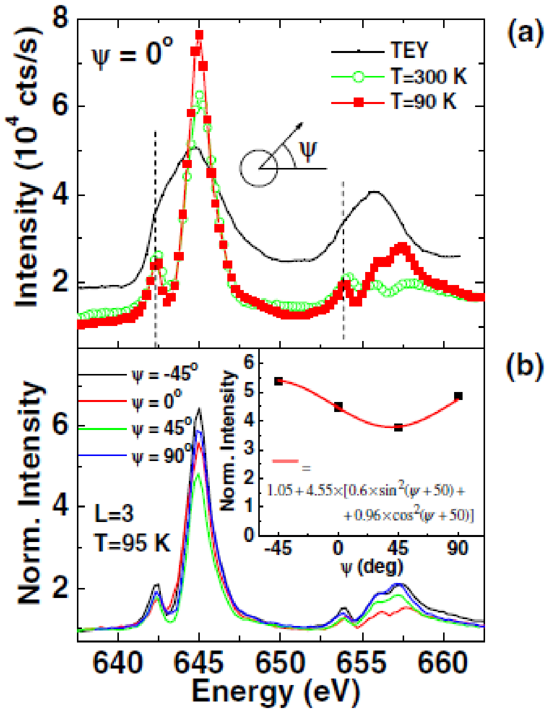
Structure factor

$$F(L=3) = 2f^{\mathrm{MnO_2}}_{\mathrm{interface}} - f^{\mathrm{MnO_2}}_{\mathrm{LMO}} - f^{\mathrm{MnO_2}}_{\mathrm{SMO}}$$

(superlattice forbidden reflection)

S. Smadici, et al. PRL 99, 169404 (2007)

@ Cu L-edge

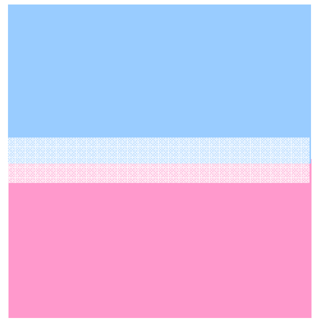


Magnetic scattering

$$I \propto \cos^2\theta\ \sin^2\phi + \sin^2 2\theta\ \cos^2\phi$$

a perspective

Electronic structure (almost) only at interface



Breaking of space inversion symmetry

+

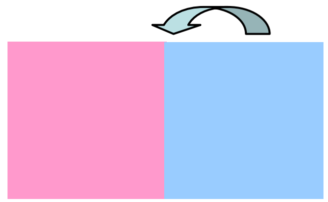
Sometime breaking of

time reversal symmetry (FM)

crystalline symmetry (orbital)

Interference of dipole-quadrupole transition at pre-edge

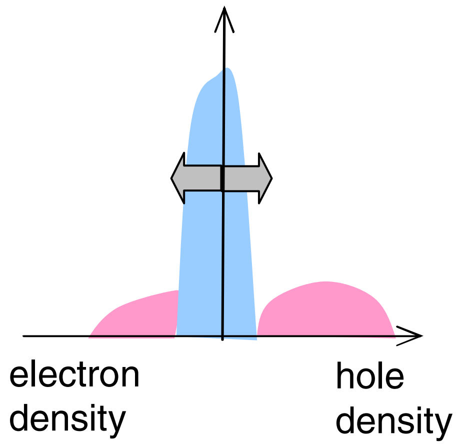
Linear/circular polarization analyses



Intrinsic properties of correlated electron interface

Novel Function attributed to interface
(GMR, SC, SHG etc.)

Differences from (band insulator)/(band insulator) interface
from carrier doping effect in Mott insulator



Summary

SHG and electronic structure
in $(RMnO_3)_n$-$(AMnO_3)_n$ superlattice

Insulating interface：　Almost discontinuous
Large SHG:　New charge transfer channel across interface

T. Satoh, K. Miyano, Y. Ogimoto, H. Tamaru, and SI,
Phys. Rev. B 72, 224403 (2005)

A perspective from a theoretical side（理論家からの期待）

More direct observation of electronic state @ interface
breaking of
(space inversion)+ (time reversal / crystal symmetries)
Interference of dipole+quadrupole transitions

Intrinsic properties in correlated electron interface