Soft X-ray emission study on electronic structure and Fermiology of transition metal compounds

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Motivation

Resolution of PES has been developed very rapidly

⬇

High resolution PES is one of the most powerful method for the Fermiology of solids, such as semiconductors, strongly correlated materials, nanomaterials

⬇

It is known that SXES is useful for the electronic structure.
Though the resolution is still low, is it powerful for the Fermiology?

contents

1. Introduction

2. Experimental
   New beamline and SXES spectrometer in SPring-8

3. Materials

   - TiO_2, ScF_3, $ScBr_3$, Cr_2O_3 Polarization dependence of resonant SXES
     $Sr_2CuO_2Cl_2$

   - $La_XSr_{1-X}TiO_3$ Metal-insulator transition by electron filling
     Photo-induced phenomena

   - V_6O_{13} Metal-insulator transition by temperature, 1D

4. Conclusion

Collaborators

Experimental

- Y. Harada
- T. Tokushima
- R. Eguchi
- T. Higuchi
- H. Osawa
- Y. Takata
- T. Takeuchi
- M .Watanabe
- Y. Ishiwata
- R.C.C.Perera
- D.Ederer

Theory

- A. Kotani
- M. Matsubara
- T. Uozumi

SXES is powerful for materials science

- **Resonant SXES is powerful for the study of selective excitation**
  1.What is the elementary excitation of Raman scattering?
  2.What is the resonant state of Raman scattering ?

- **Polarization dependence gives the new information**
  → symmetry of electronic states ($^1A_{1g}$)

- **High resolution SXES and its temperature dependence are useful**
  → the study of magnetic and transport properties (Fermiology)

Polarization dependence

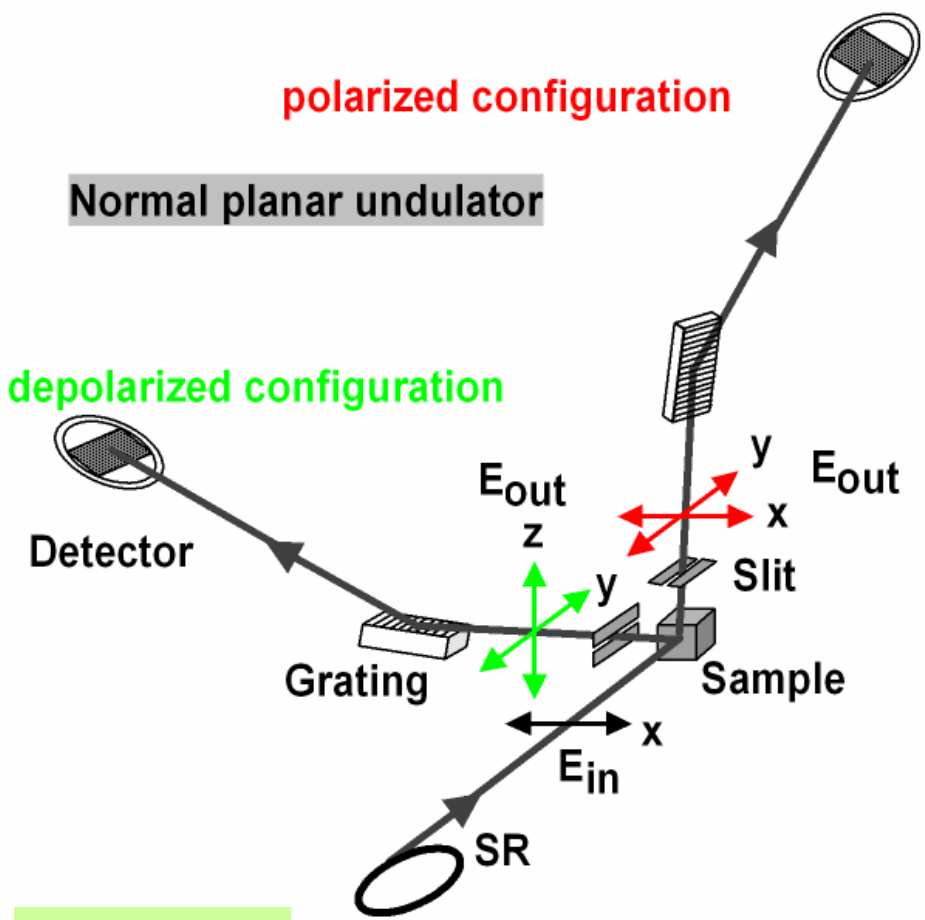
↓

New information
to the orbital symmetry of 3d states

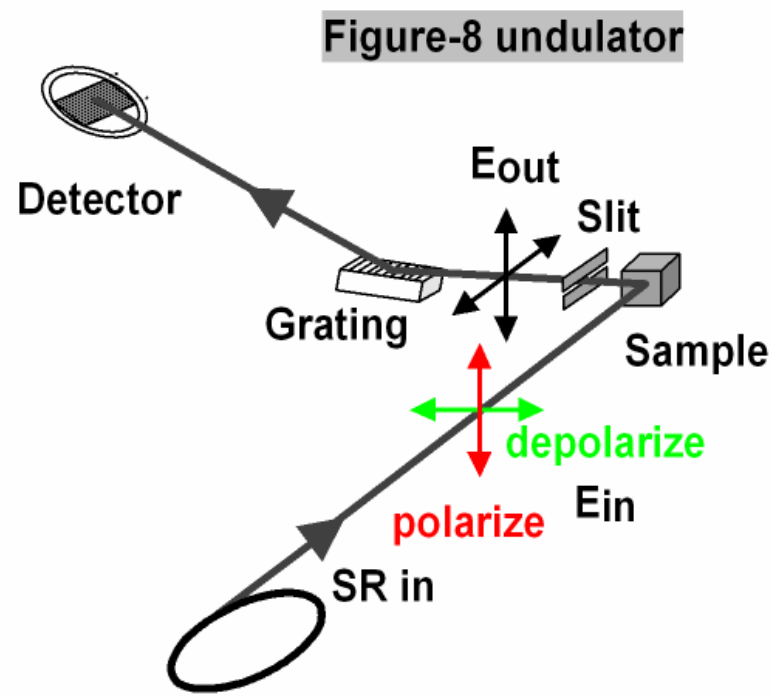
Raman tensors

$$\begin{pmatrix} a & \cdot & \cdot \\ \cdot & b & \cdot \\ \cdot & \cdot & c \end{pmatrix} \qquad \begin{pmatrix} \cdot & d & f \\ d & \cdot & e \\ f & e & \cdot \end{pmatrix}$$

polarized depolarized

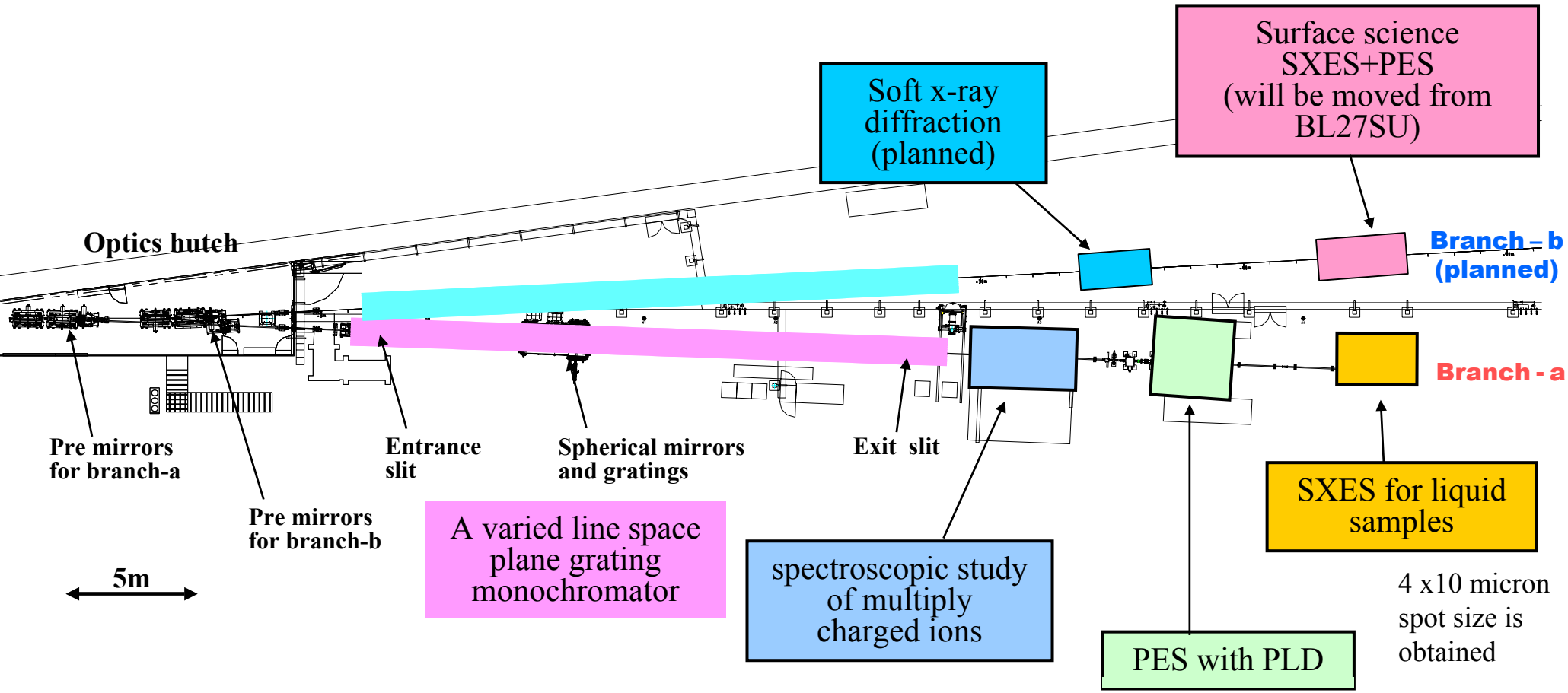


PF BL2C



SPring-8 BL27SU, BL17SU

Beamline layout of RIKEN beamline BL17SU in SPring-8



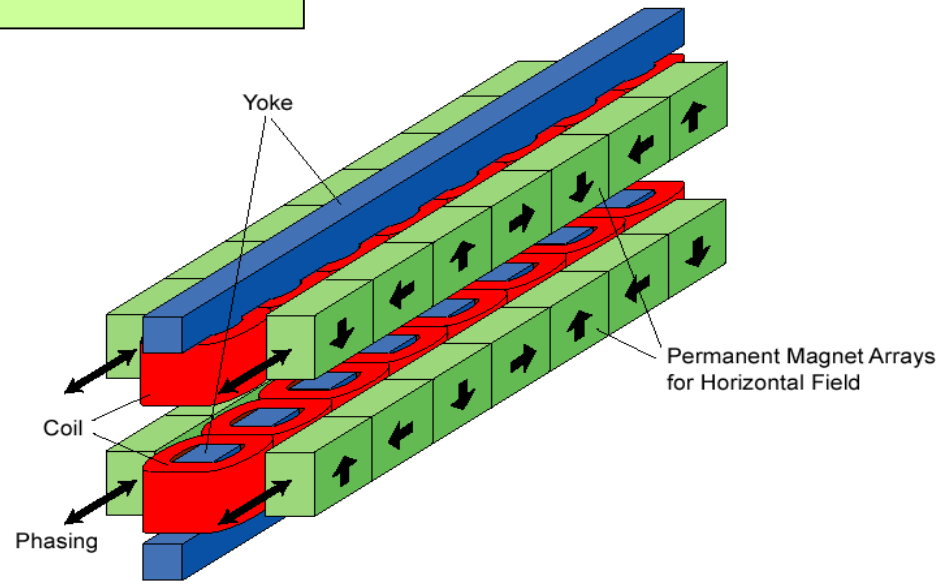
drawn by Dr.H.Ohashi (JASRI / BL-division)

Insertion device; Variably polarized undulator

Permanent magnet ＋ Electromagnet

→ Asymmetric figure-8 undulator

Various operational mode can be achieved by adjusting the phase of <u>permanent magnet</u> arrays and the current intensity of <u>electromagnet</u>.



Operation mode & energy range

1. Asymmetric figure-8 undulator (λ_u = 13cm)

Horizontal polarization : 230 ～ 2000eV

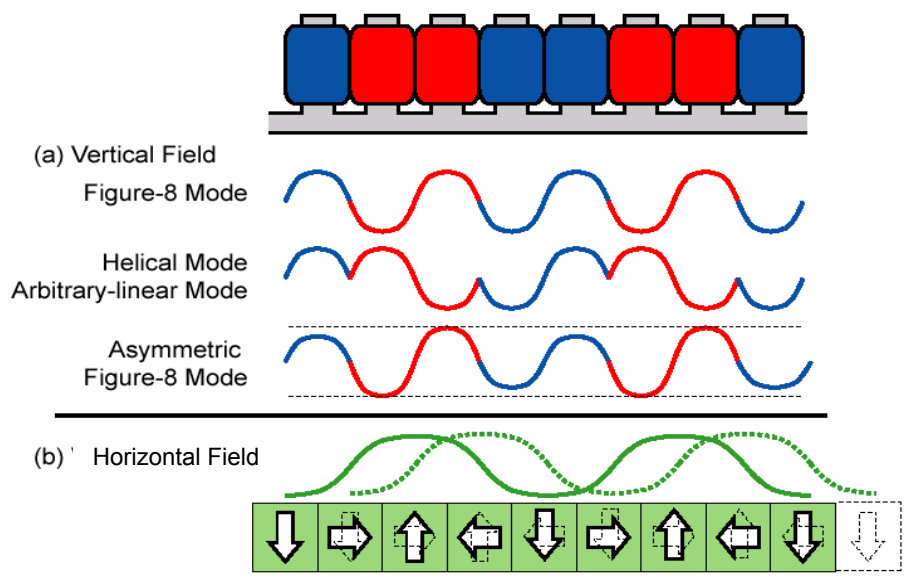
Vertical polarization : 120 ～ 2000eV

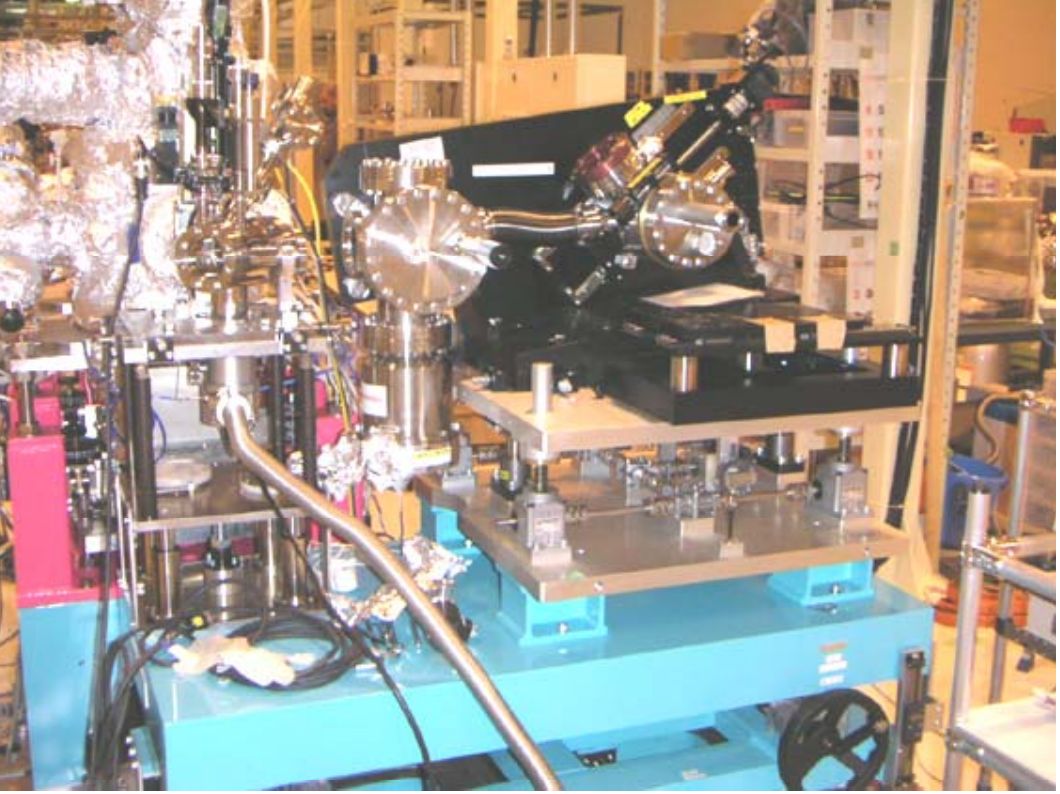
Circular polarization : 460 ～ 2000eV

fast switching of circular polarization

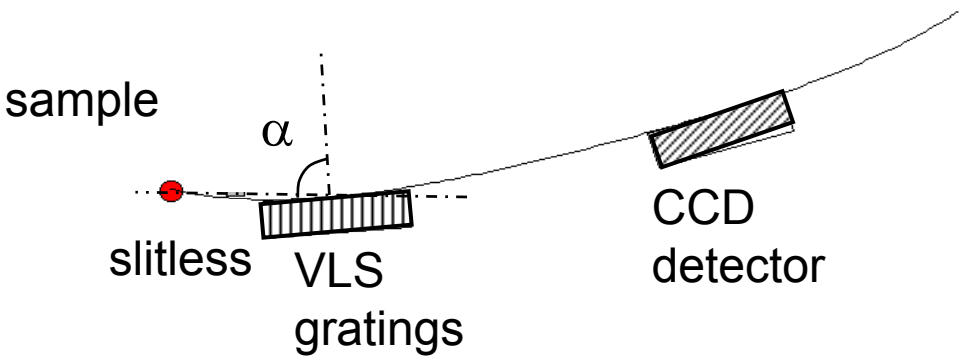
2. Helical undulator (λ_u = 26cm)

Circular polarization : 90 ～ 2000eV





SXES spectrometer at BL27SU, BL17SU in SPring-8



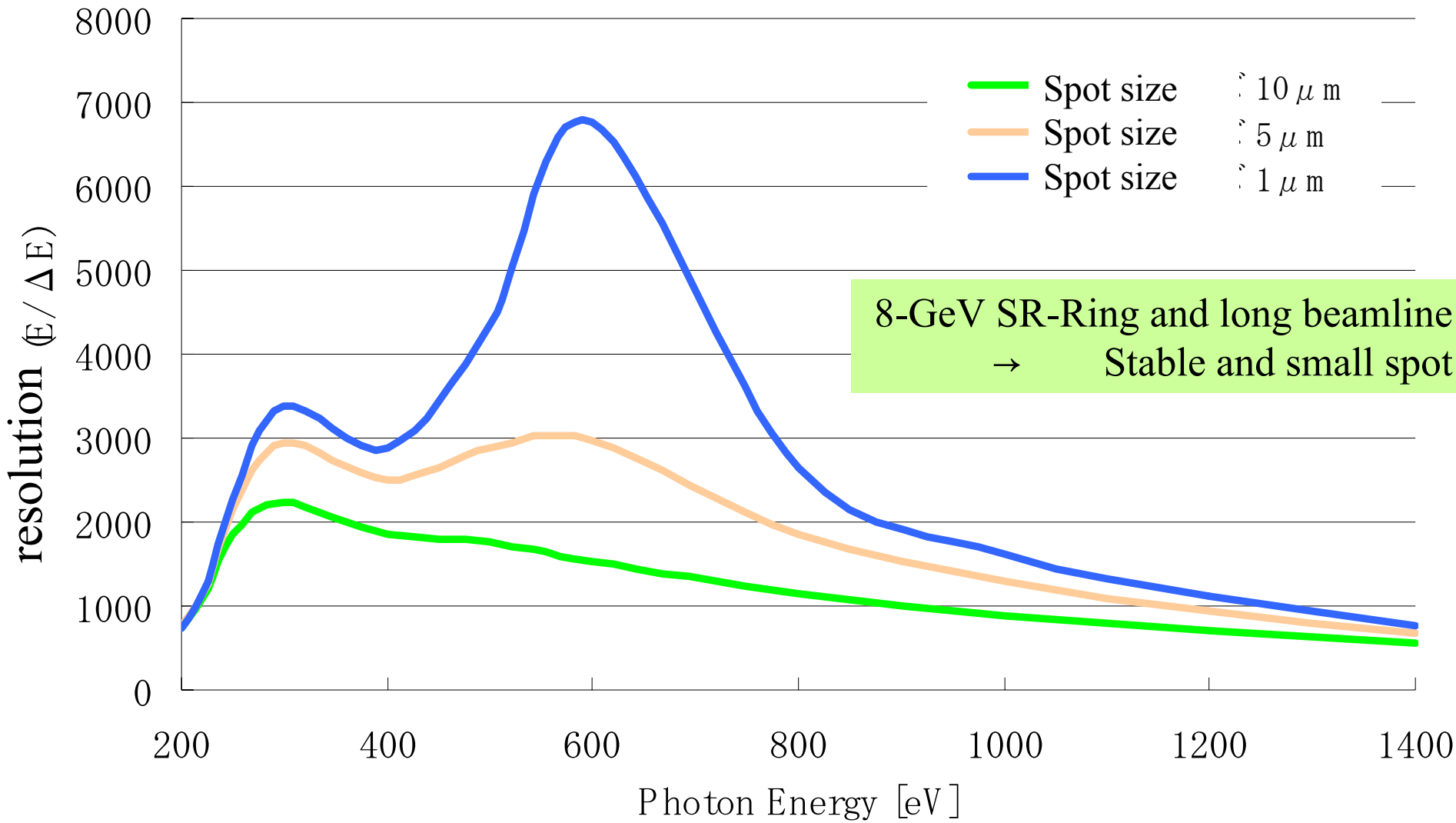
- Slitless
- VLS grating
  (flat focal plane)
- CCD detector

} High efficiency

- Small spot size ⇨ High resolution

Surface Review and Letters **9**(2002)503

High Resolution SXES

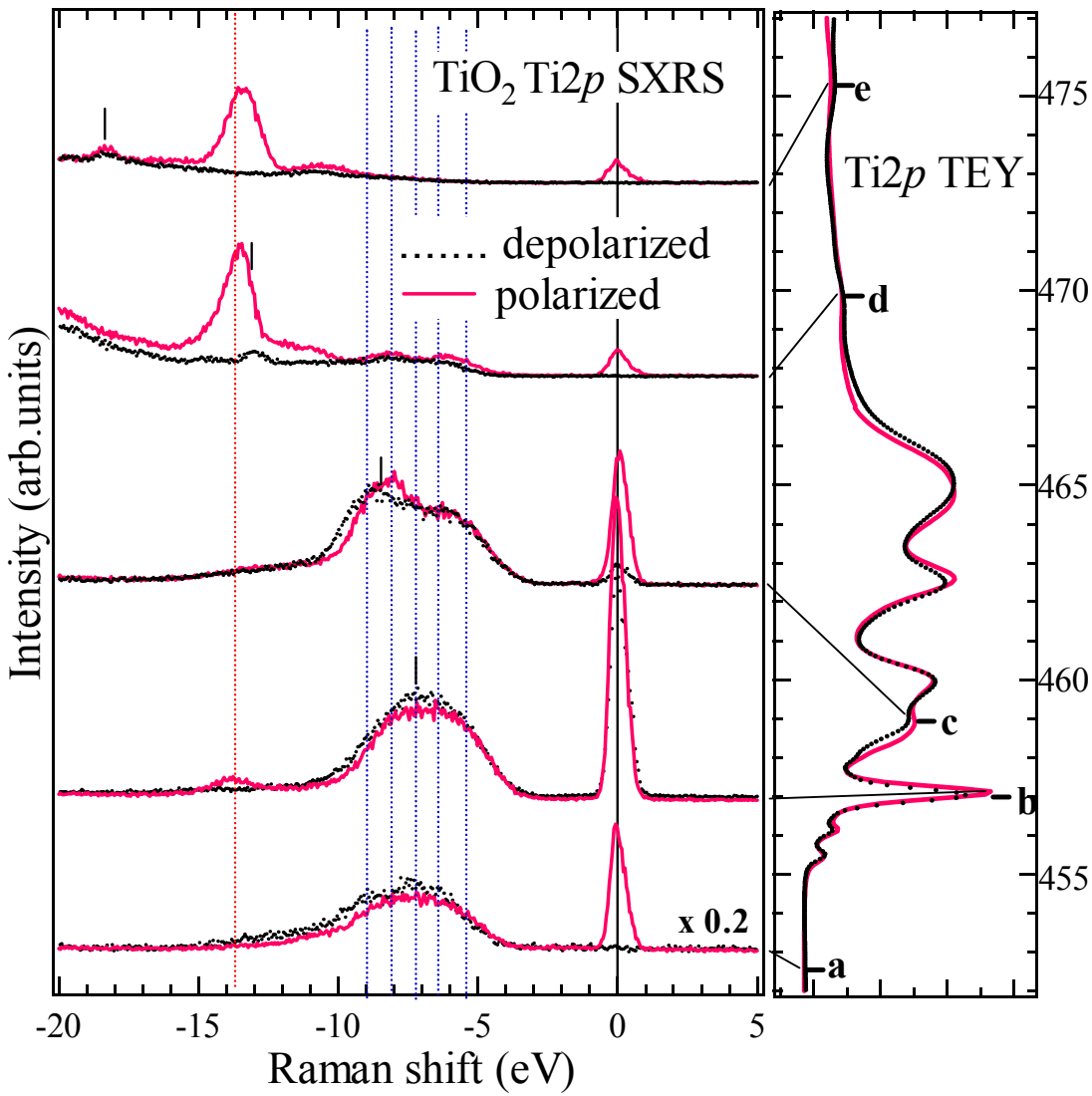


Tokushima and Harada et al

Polarization dependence in resonant SXES of $3d^n$ system

SXES of TiO_2 ; Typical example of the polarization dependence of SXES

TiO_2 is the intermediate compound between the transition metal compounds and semiconductors



13-eV structure can not be elucidated by the band picture but shows strong polarization dependence

Harada et al, Phys. Rev. B 61(2000)12854

Selection rule of the Raman scattering

Kramers-Heisenberg formula

$$\frac{d\sigma}{d\Omega} \propto \sum_f \left| \sum_m \frac{\langle f | \mathbf{e}_{out} \cdot \mathbf{r} | m \rangle \langle m | \mathbf{e}_{in} \cdot \mathbf{r} | i \rangle}{E_m - E_i - h\nu_{in} - i\Gamma} \right|^2 \cdot \delta(E_f + h\nu_{out} - E_i - h\nu_{in}),$$

Excitation to the intermediate states

$$A_{1g} \otimes T_{1u}(z) = T_{1u}(z)$$

ground state e**r**(z) intermediate state

Emission to final states

- Polarized configuration:

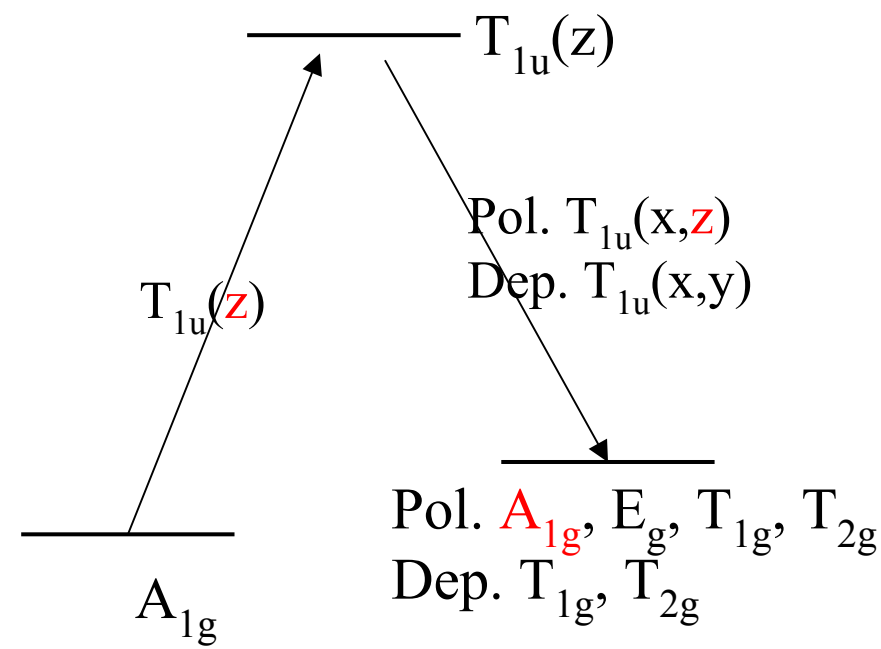
$$T_{1u}(z) \otimes T_{1u}(x,z) = A_{1g}, E_g, T_{1g}, T_{2g}$$

intermediate state e**r**(x,z) final state

- Depolarized configuration:

$$T_{1u}(z) \otimes T_{1u}(x,y) = T_{1g}, T_{2g}$$

intermediate state e**r**(x,z) final state

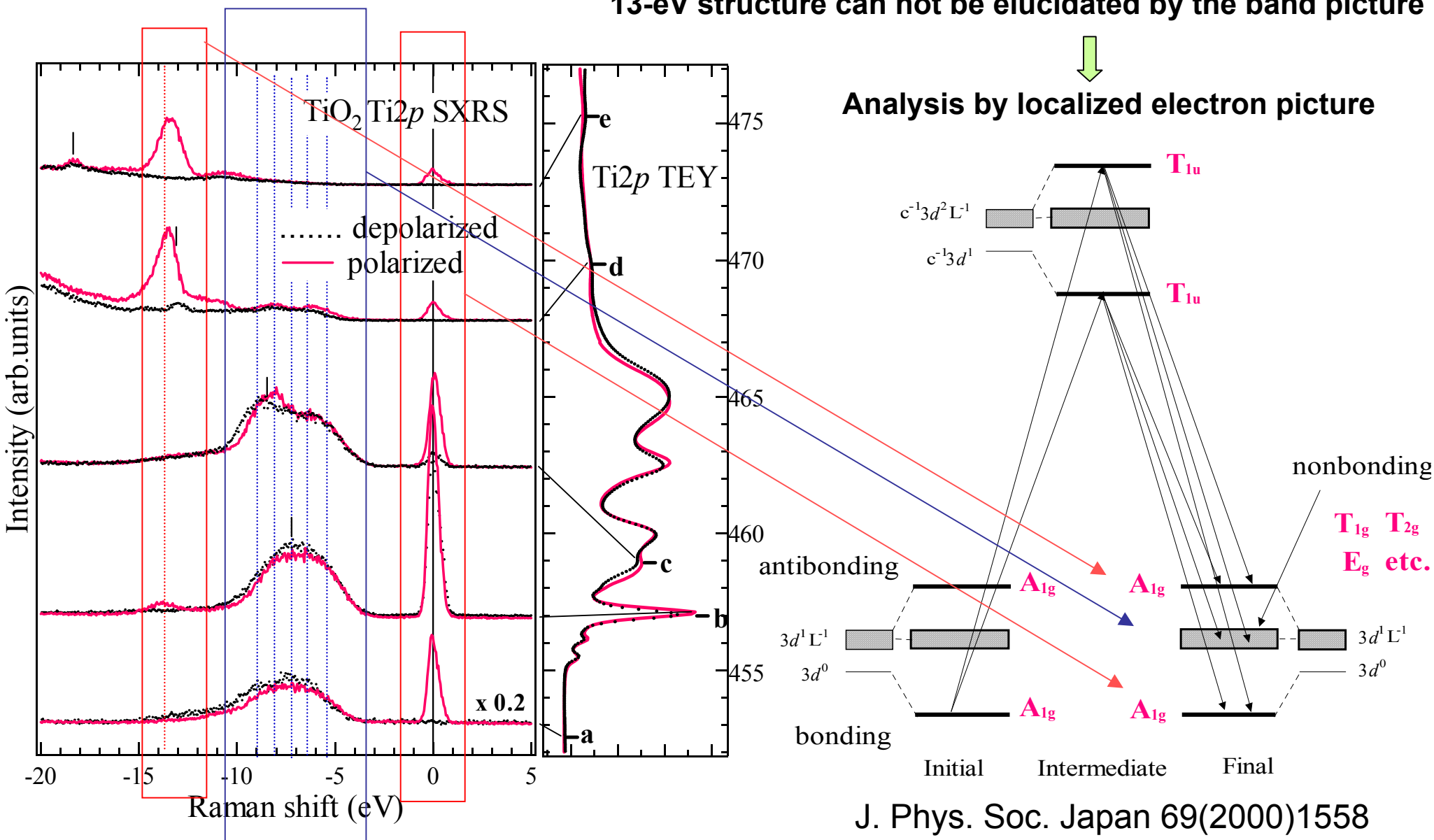


SXES of TiO_2 ; Typical example of the polarization dependence of SXES

TiO_2 is the intermediate compound between the transition metal compounds and semiconductors

13-eV structure can not be elucidated by the band picture

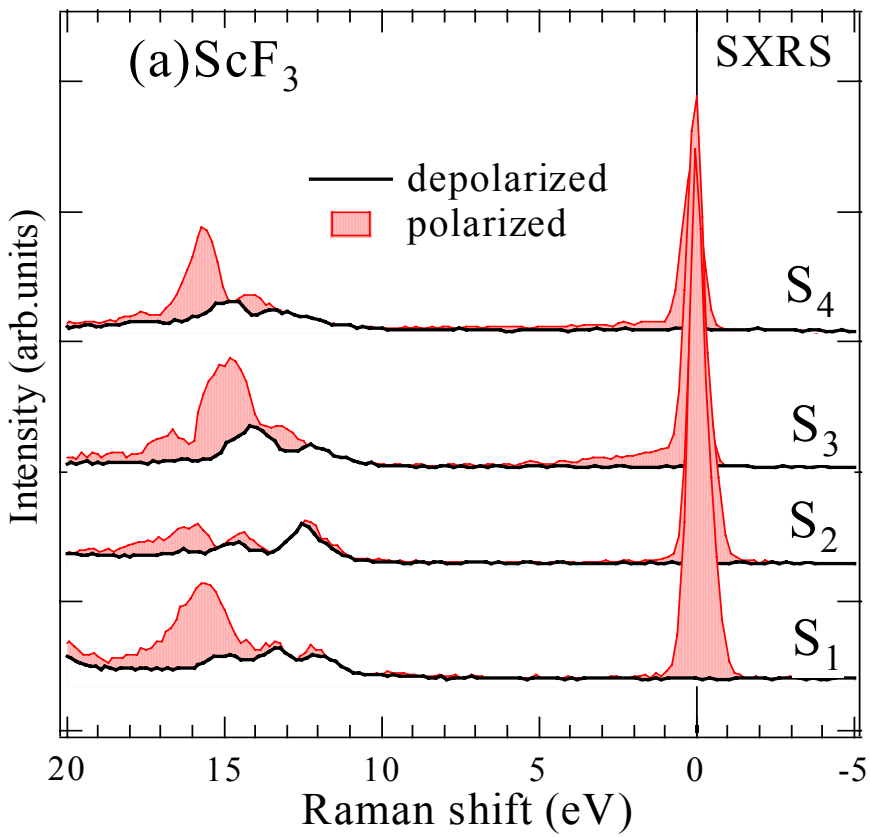
Analysis by localized electron picture

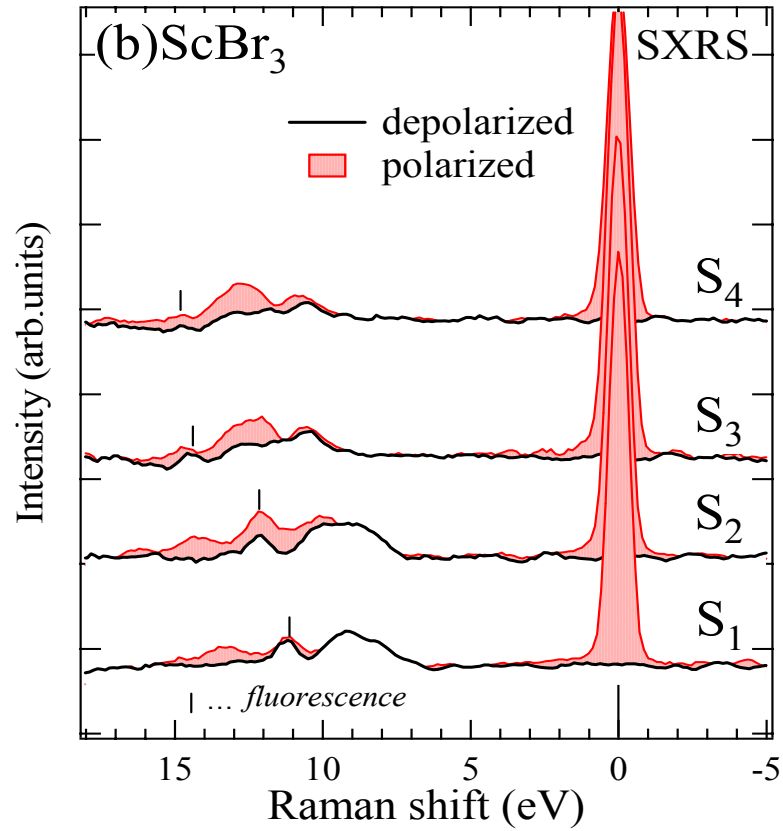


J. Phys. Soc. Japan 69(2000)1558

ScF_3, $ScBr_3$ Sc2*p* SXES

Y. Harada et al., J. Electron. Spectrosc. Relat. Phenom. ***136*** *143 (2004)*
M. Matsubara et al., J. Phys. Soc. Jpn. ***71*** *347 (2002)*





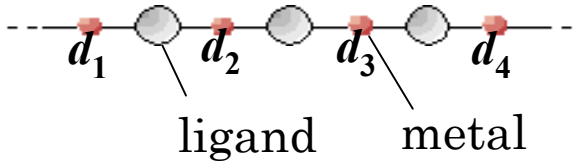
Rayleigh (ScF_3) < Rayleigh ($ScBr_3$)

Raman (ScF_3) > Raman ($ScBr_3$)

Δ (ScF_3) > Δ ($ScBr_3$)

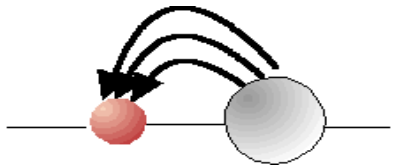
V_{eff} (ScF_3) < V_{eff} ($ScBr_3$)

Multi-site effect

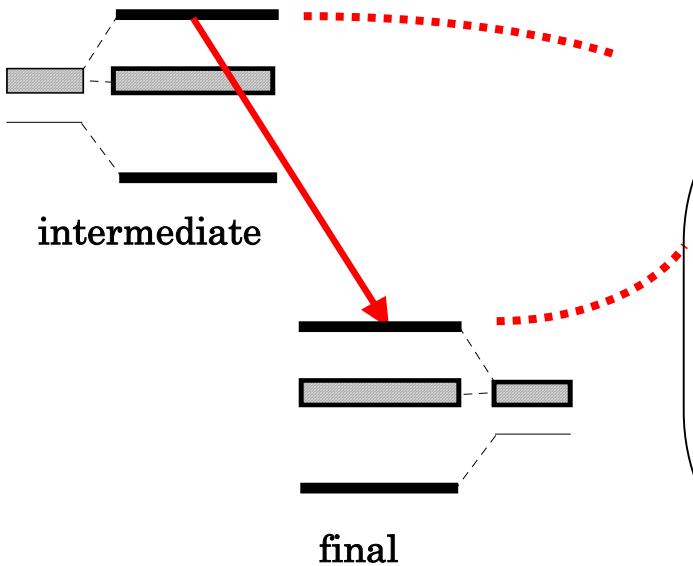


ex. $3d_1{}^1\underline{L}$, $3d_2{}^1\underline{L}$, $3d_3{}^1\underline{L}$, $3d_4{}^1\underline{L}$, …

Multi-CT excitation effect



ex. $3d^1\underline{L}$, $3d^2\underline{L}^2$, $3d^3\underline{L}^3$, $3d^4\underline{L}^4$, …



Phase shift of the antibonding state

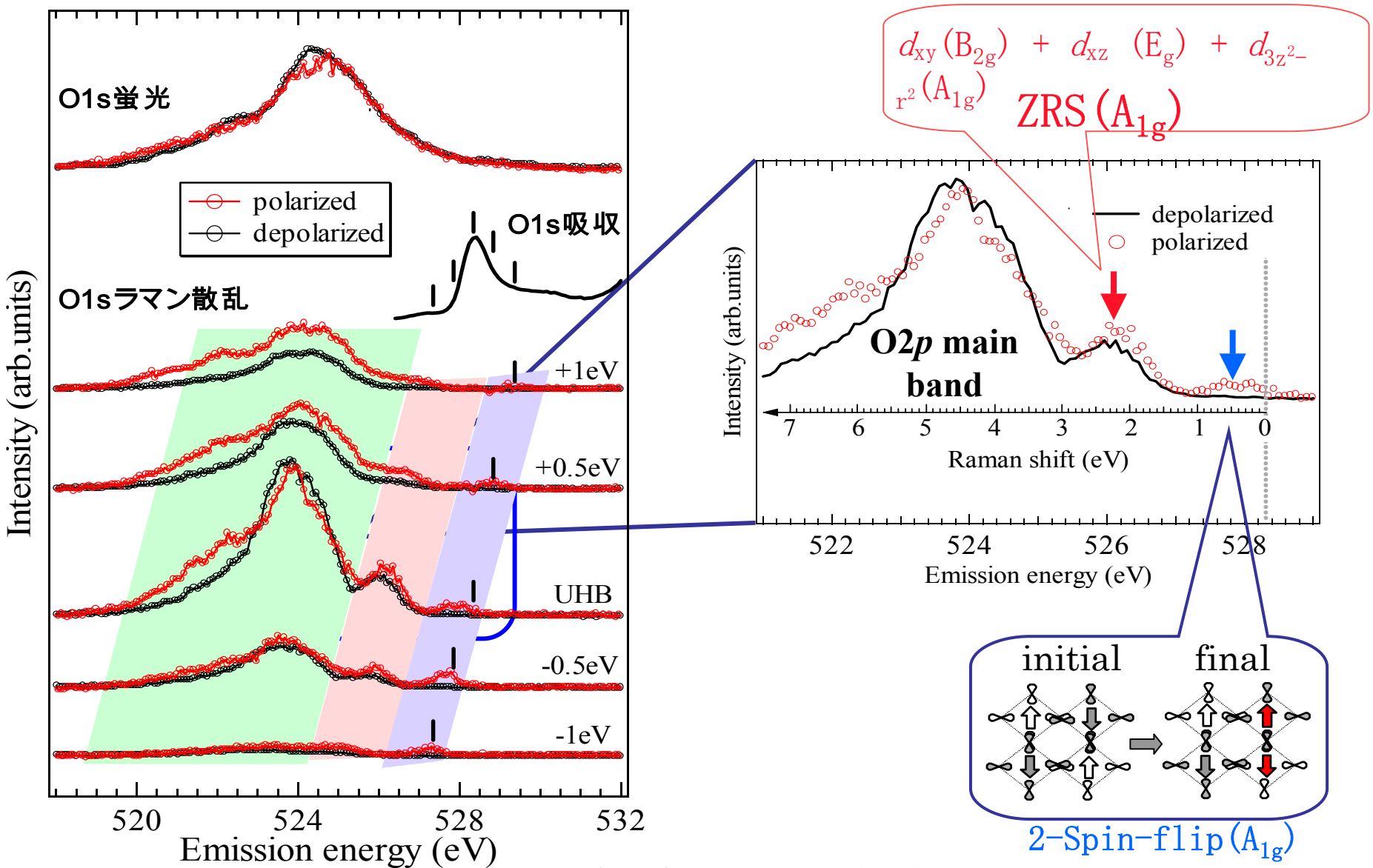
⇩

Phase miss-matching

⇩

weak polarization dependence

Experimental results for O1s SXES of $Sr_2CuO_2Cl_2$



Harada et al, PRB**66,**165104(2002)

Selection rule for $3d^n$ systems

n=1 $$R_{3d^1} = T_{2g} \times T_{1u} \times T_{1u}$$

$$= \begin{cases} A_{1g}, A_{2g}, T_{1g}, T_{2g}, E_g & \text{(polarized)} \\ A_{1g}, A_{2g}, T_{1g}, T_{2g}, E_g & \text{(depolarized)} \end{cases}$$

n=2 $$R_{3d^2} = T_{1g} \times T_{1u} \times T_{1u}$$

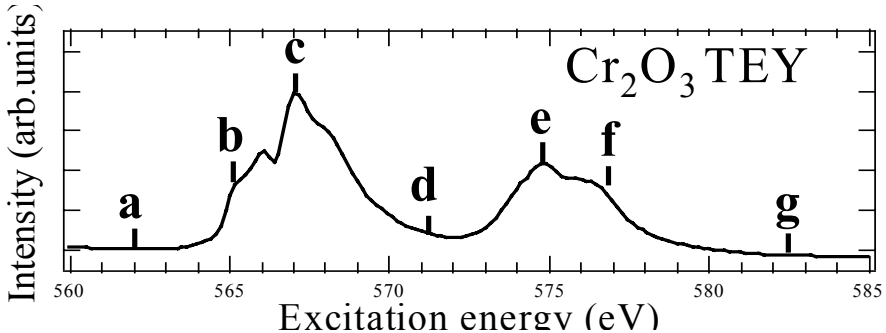
$$= \begin{cases} A_{1g}, T_{1g}, T_{2g}, E_g & \text{(polarized)} \\ A_{1g}, A_{2g}, T_{1g}, T_{2g}, E_g & \text{(depolarized)} \end{cases}$$

n=3 $$R_{3d^3} = A_{2g} \times T_{1u} \times T_{1u}$$

$$= \begin{cases} A_{2g}, T_{1g}, T_{2g}, E_g & \text{(polarized)} \\ T_{1g}, T_{2g} & \text{(depolarized)} \end{cases}$$

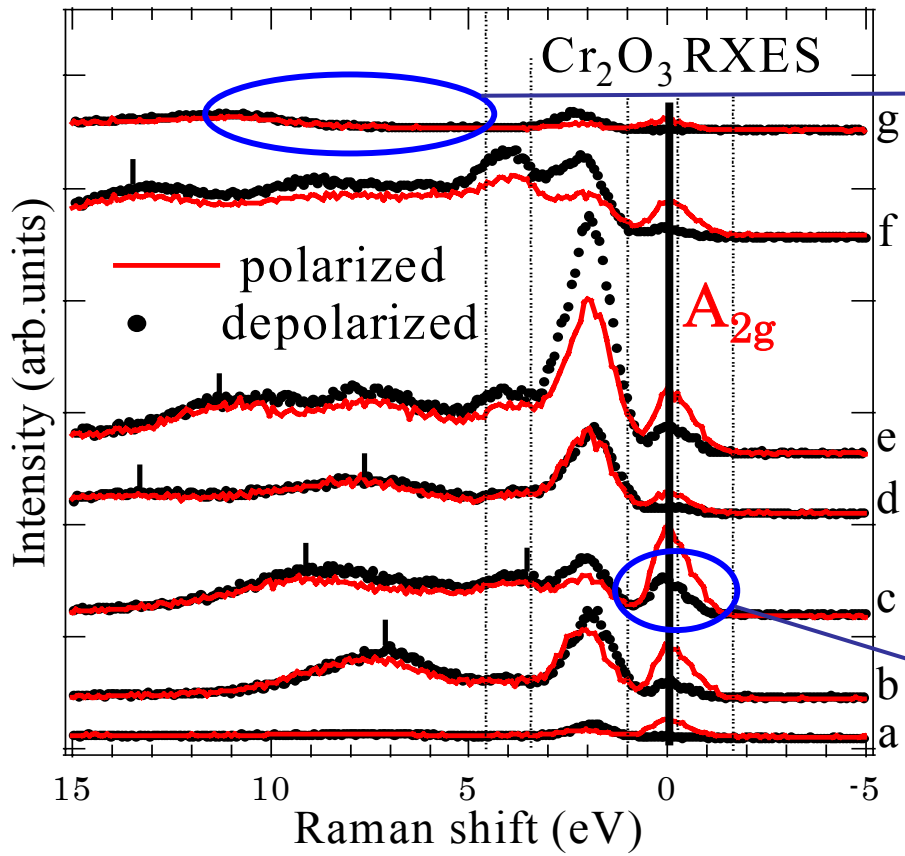
Cr_2O_3 Cr2*p* SXES ($3d^3$)

*M. Matsubara et al., J. Phys. Soc. Jpn., **71**, 347 (2002).*

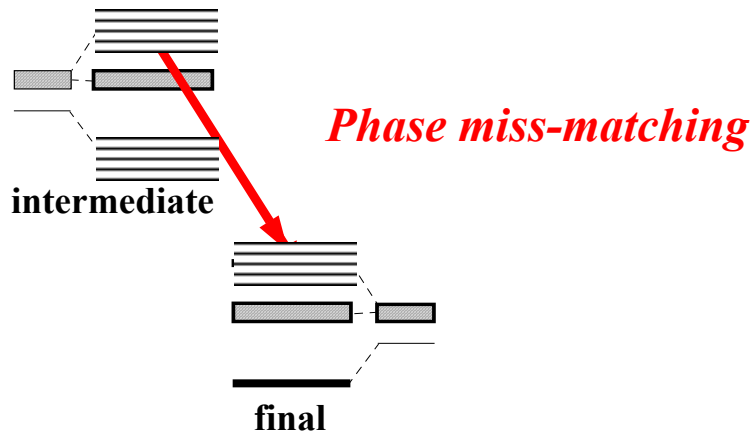


$$R_{3d^3} = A_{2g} \times T_{1u} \times T_{1u}$$

$$= \begin{cases} A_{2g}, T_{1g}, T_{2g}, E_g & \text{(polarized)} \\ T_{1g}, T_{2g} & \text{(depolarized)} \end{cases}$$



negligible polarization dependence due to multiplet of the antibonding state



breakdown of symmetry selection due to spin-orbit interaction

Metal-Insulator transition in La-doped $SrTiO_3$

SXES study on $Sr_xLa_{1-x}TiO_3$

Metal-insulator transition by 3d electron filling

Evidence of Mott-transition by SXES

- $SrTiO_3$; Band insulator
- $LaTiO_3$; Mott insulator

- $La_{1-X}Sr_XTiO_3$;Metal insulator transition at x=0.05 ➡ typical Mott transition?

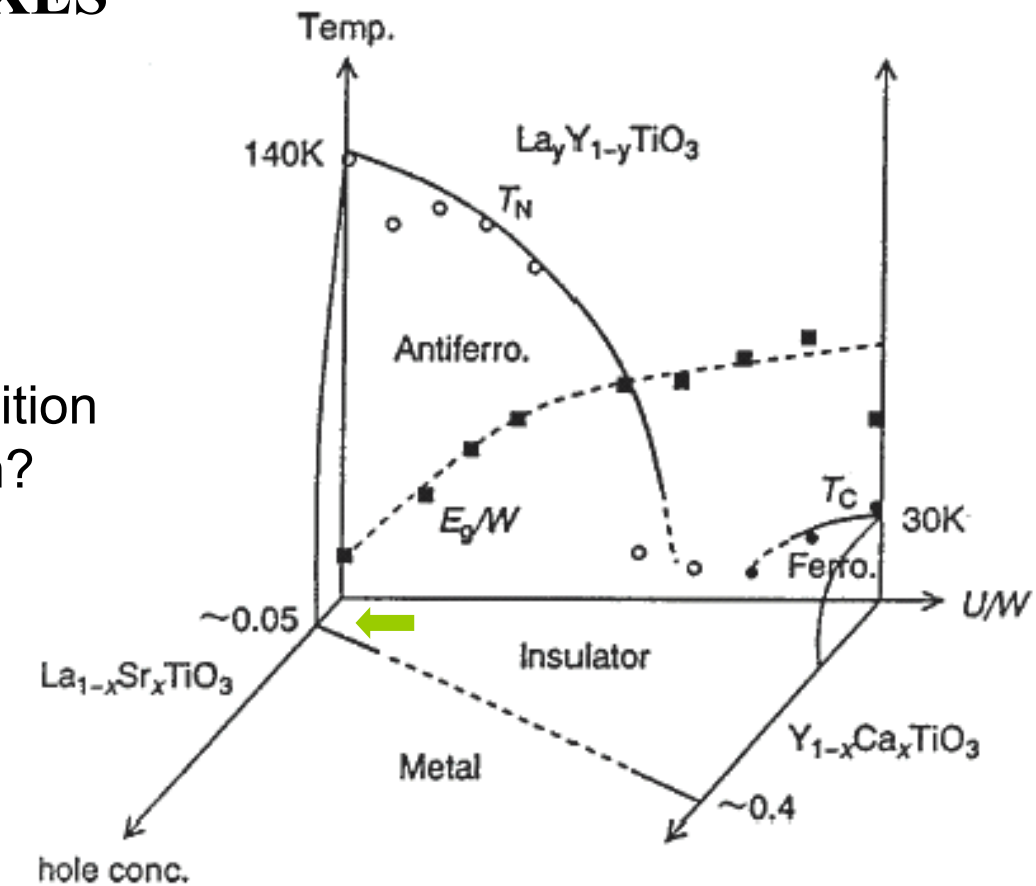
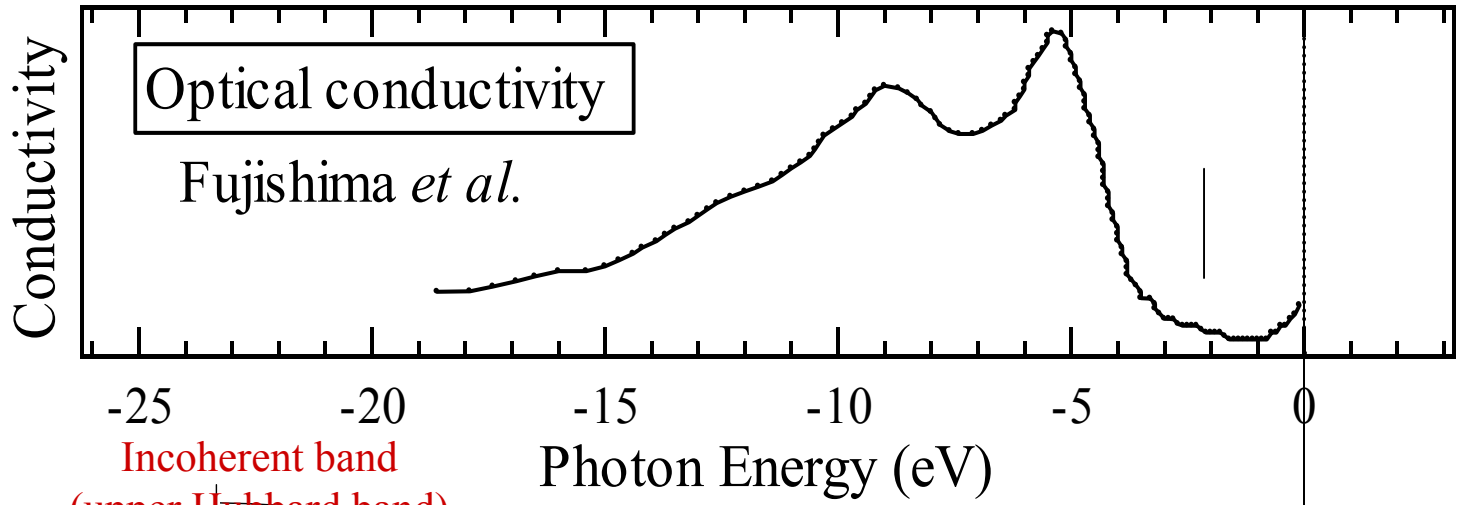
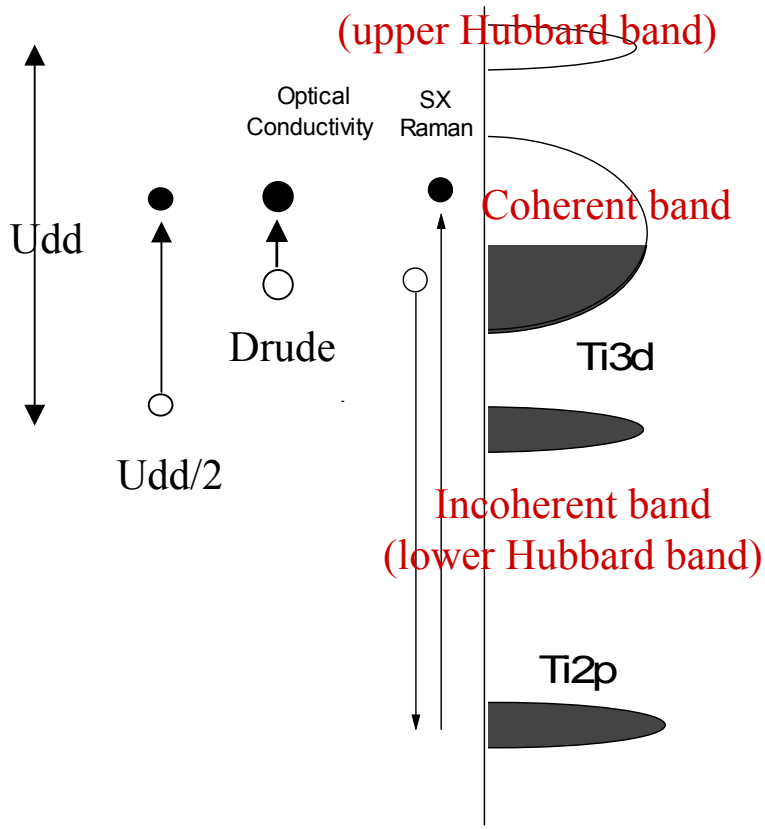
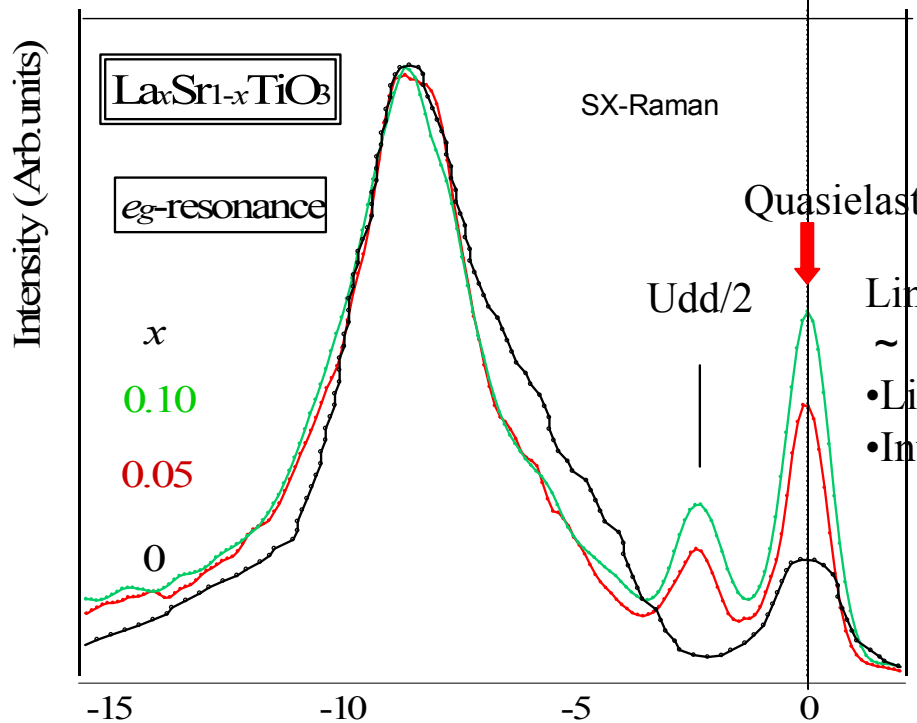


FIG. 101. Electronic and magnetic phase diagram for the $R_{1-x}Sr_xTiO_3$.







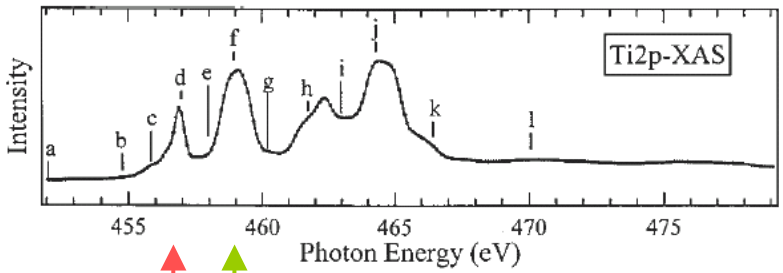
Quasielastic(Drude) + elastic

Line width of Drude
~ 100 meV
•Line width ~ τ
•Intensity ~ n

Higuchi et al,
Phys.Rev.B60(1999)7711

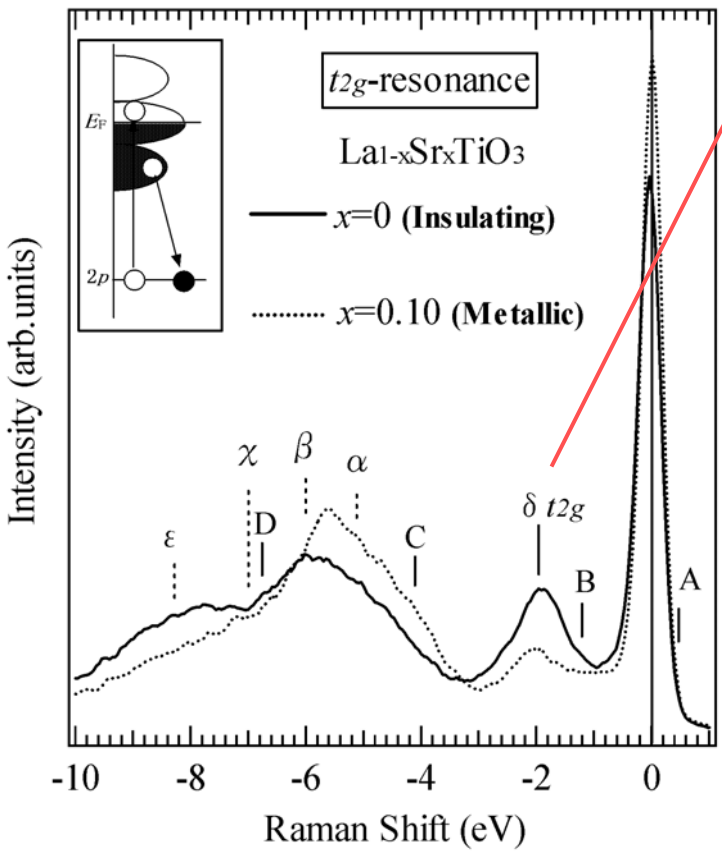
Estimation of

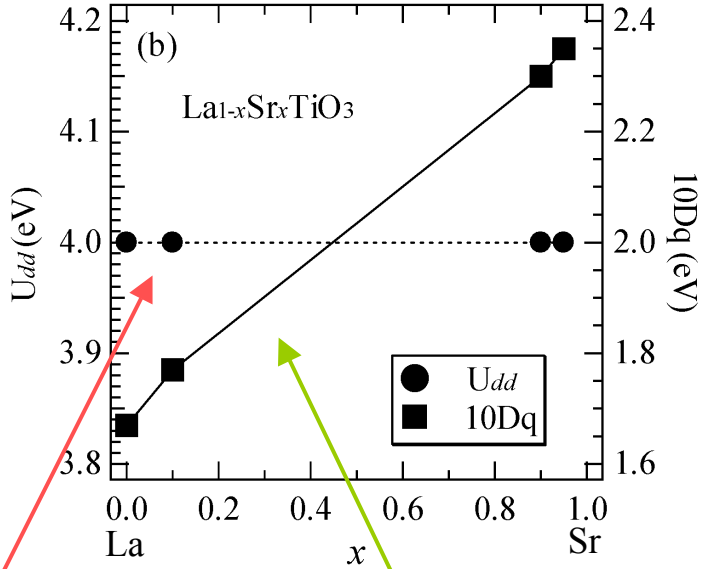
1. **Electron correlation energy U_{dd}**
2. **Crystal field splitting 10Dq**

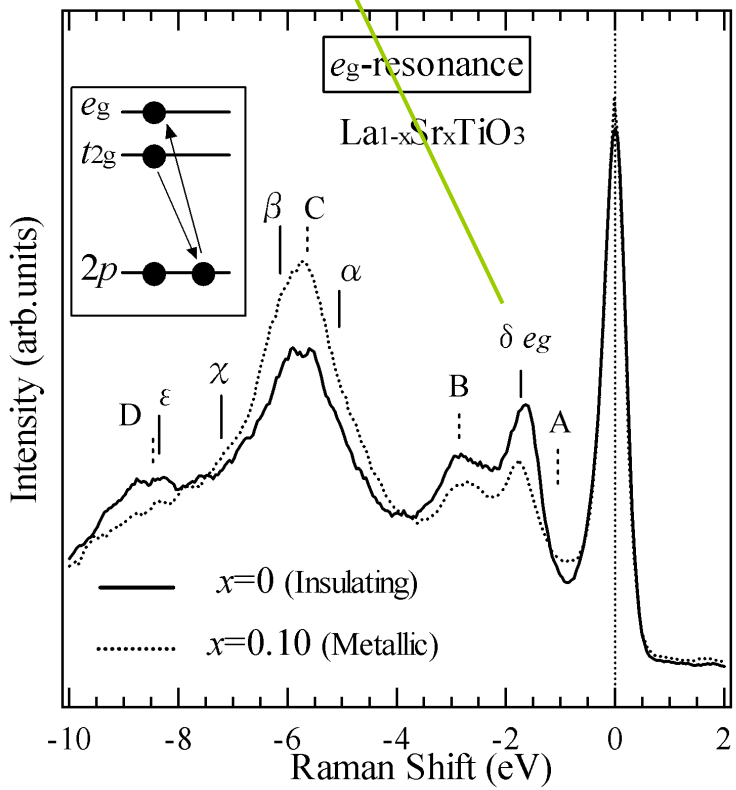


t_{2g} e_g

Resonance







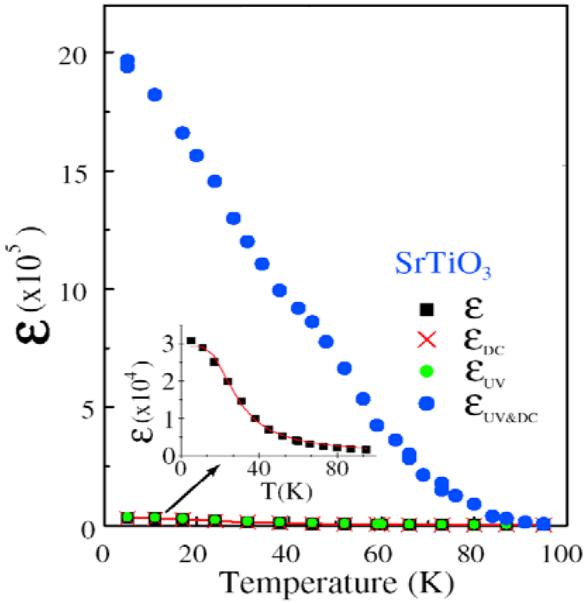
Higuchi et al.,
PRB68,104420('03)

Photo-induced phenomena in $SrTiO_3$

Photo-induced phenomena in $SrTiO_3$

Under the irradiation of the VUV light higher than Band Gap(3.2eV) in low temperature phase of $SrTiO_3$

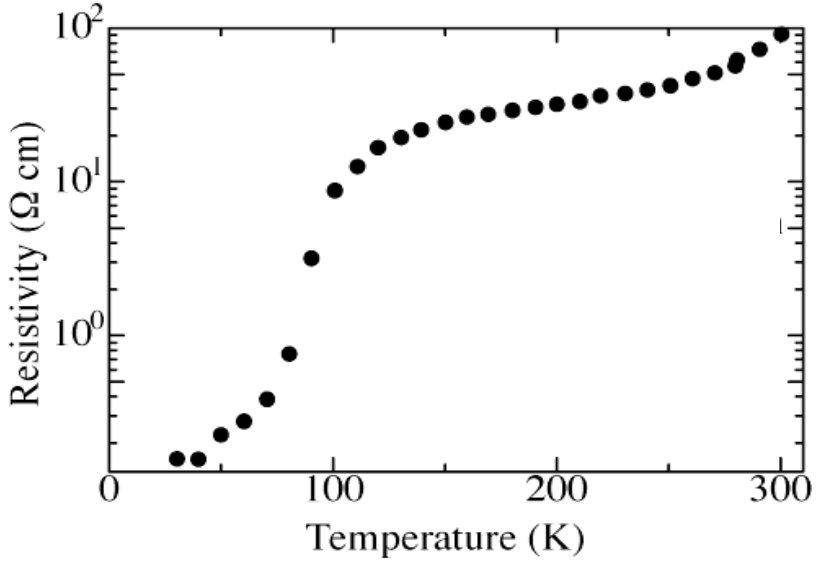
Drastic increase of dielectric constant



M. Takesada, *et al*, JPSJ 72, 37 (2003)
T. Hasegawa, *et al*, JPSJ 72, 41 (2003)

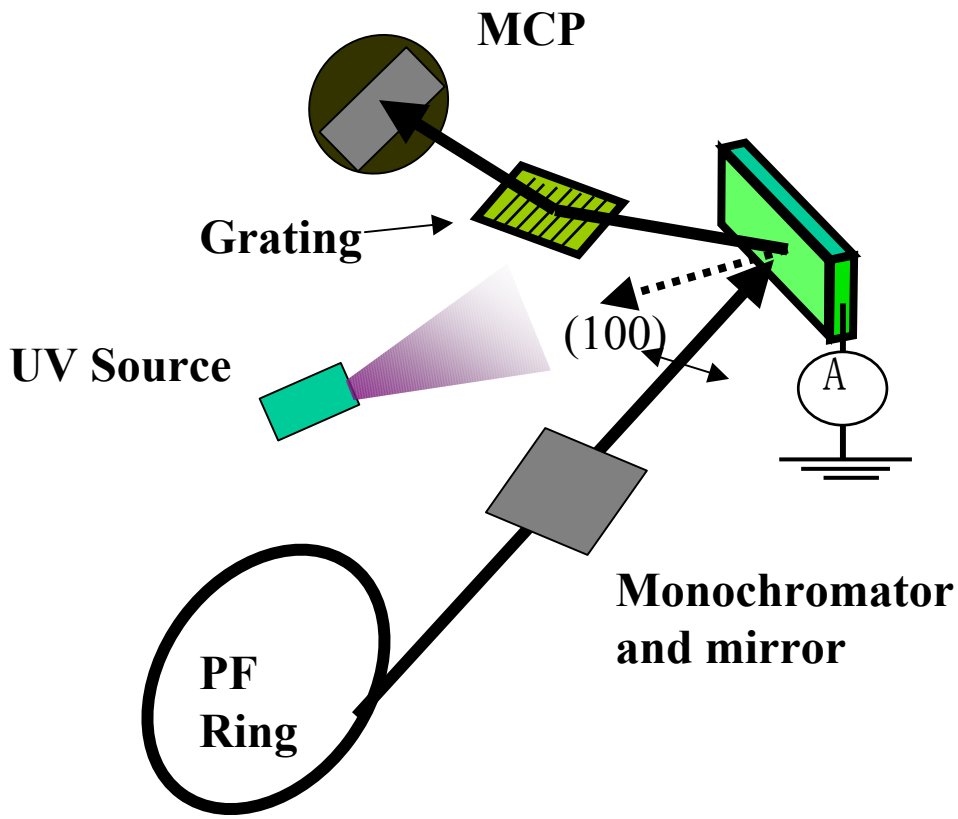
T_C=105K

Drastic increase of conductivity



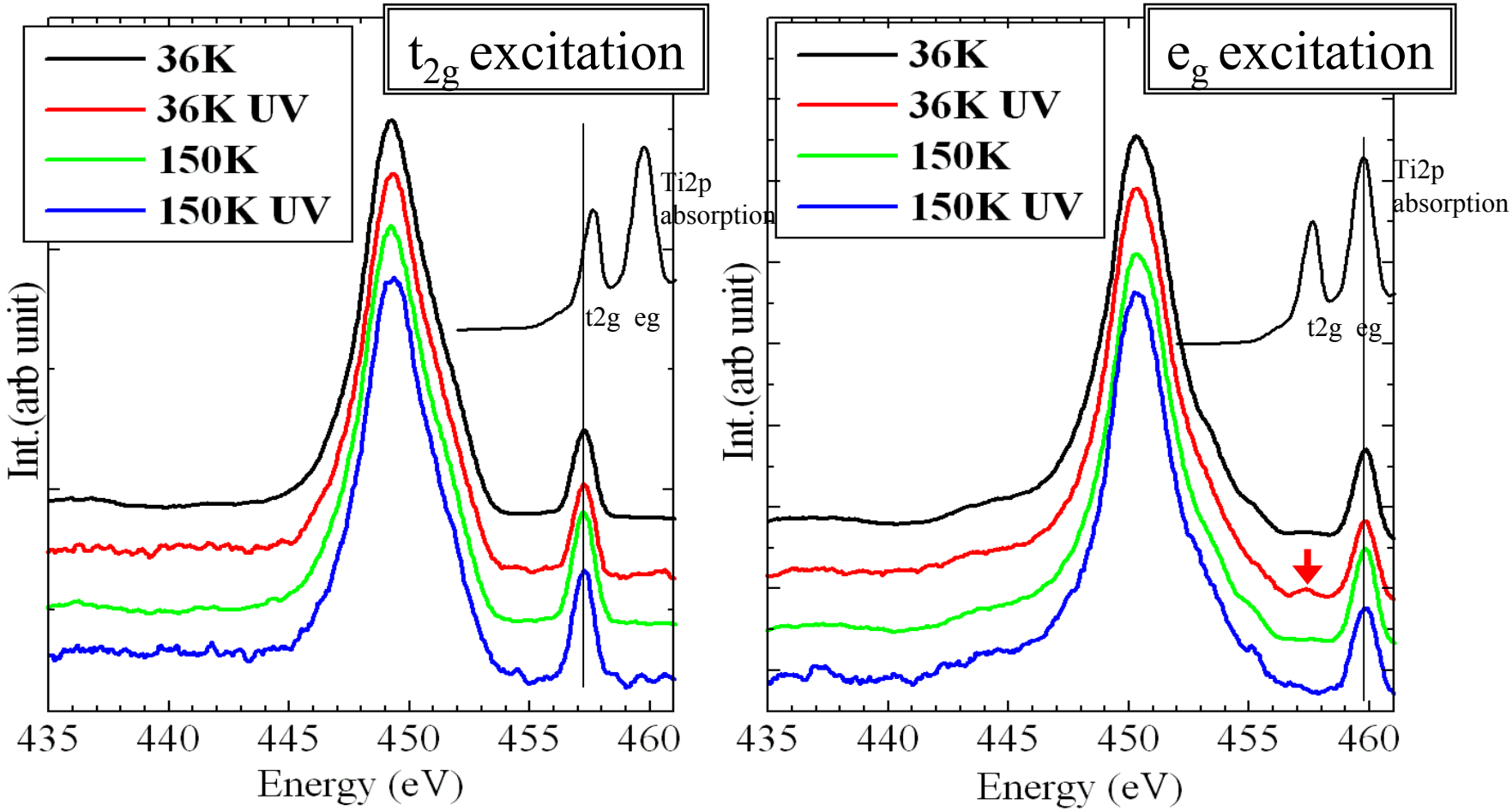
H. Katsu, *et al*, JJAP. 39, 2657 (2000)

KEK, PF BL-19B



- Sample : $SrTiO_3$ (100) single crystal
- UV Source : 3.4 eV, 2 mW/cm^2 on sample
- Temperature : HT phase 150K, LT phase 36K
- Ti 2p XANES : TEY mode

Ti 2p RXESによる比較

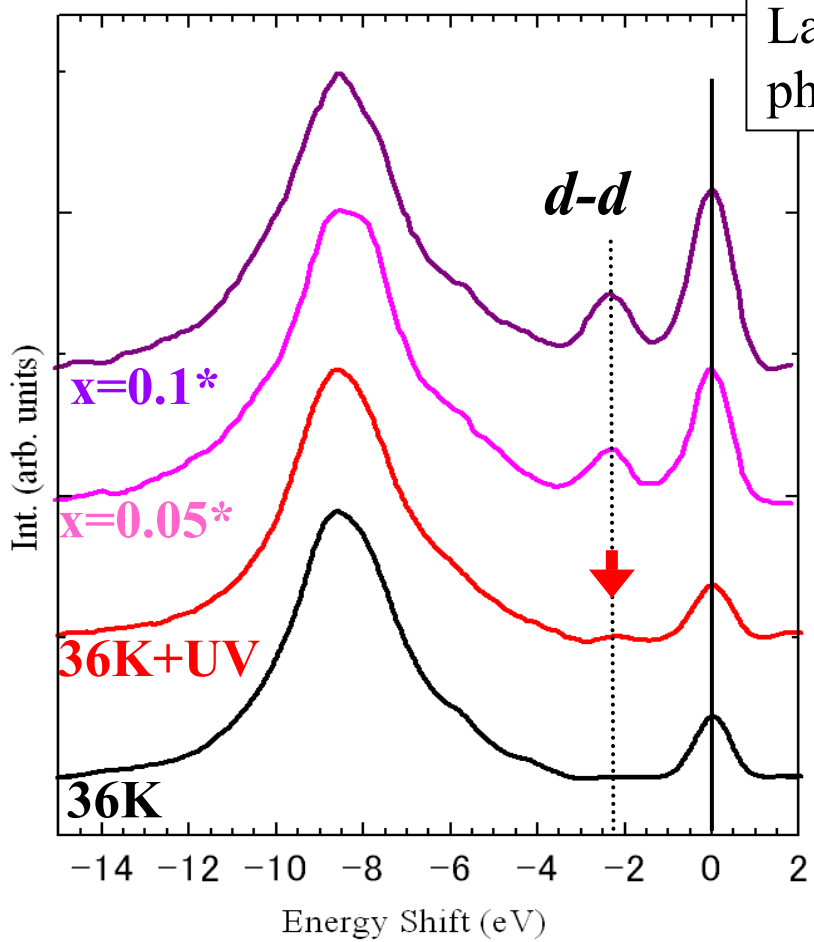


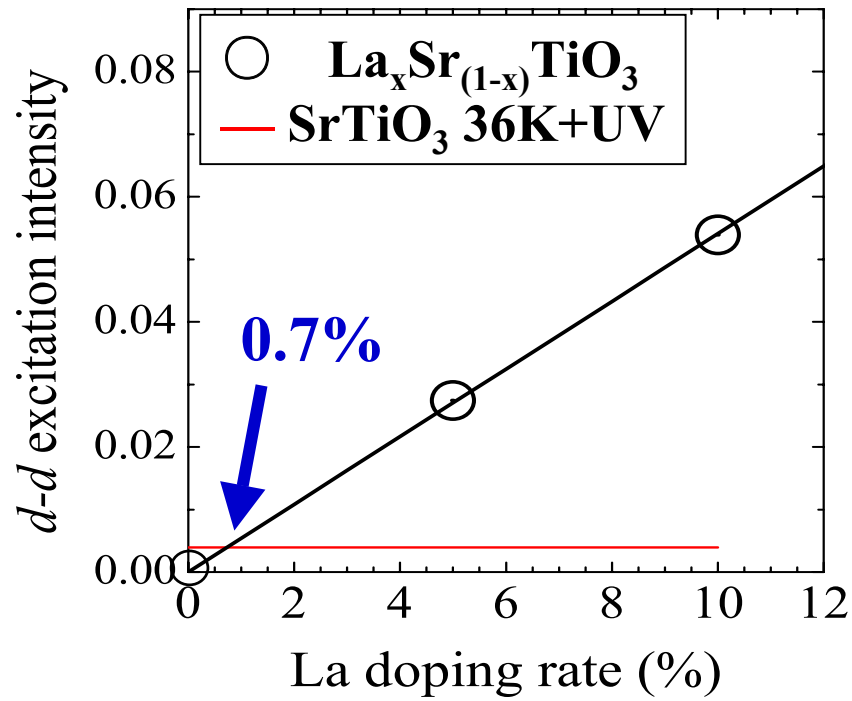
New peak ↓ appears only in the VUV irradiation at low temperature

What is the origin of new peak?

Comparison between chemical doping and photo-induced $SrTiO_3$

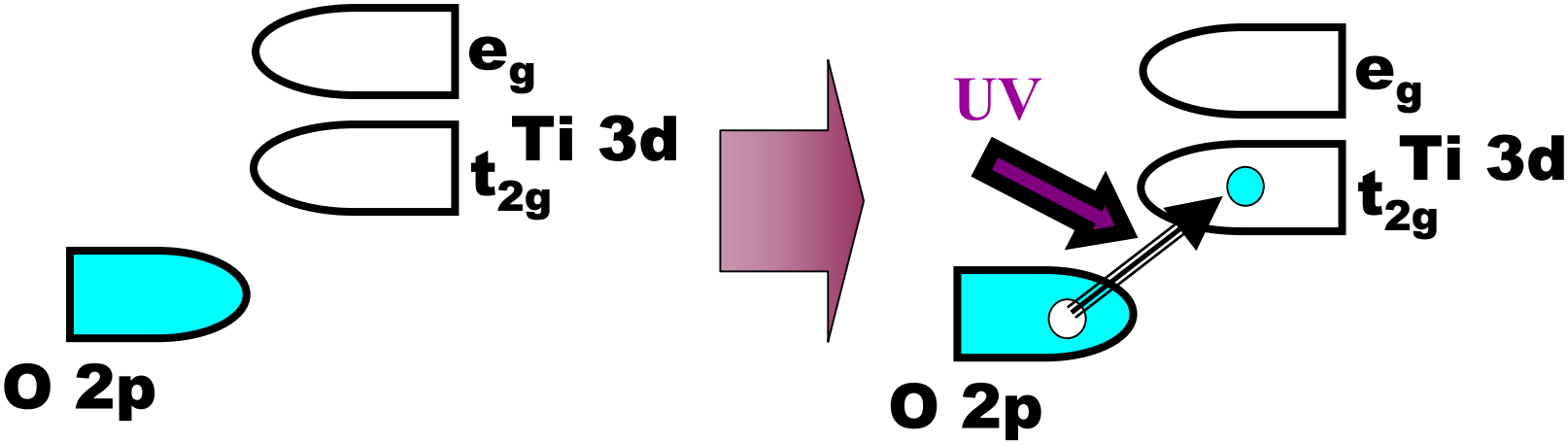
La-doping and photo-induced phenomena have the same origin





*T. Higuchi, *et al*, PRB60, 7711(1999)

Photo-induced phenomena in $SrTiO_3$



$O^{2-}(2p^6)$ — $Ti^{4+}(t_{2g}{}^0 e_g{}^0)$ $O^{-}(2p^5)$ — $Ti^{3+}(t_{2g}{}^1 e_g{}^0)$

Long life time of excited state by 11 minutes

↓

Consistent with high conductivity by the UV irradiation

Polarization dependence in one-dimensional transition metal compounds and Metal-Insulator transition in V_6O_{13}

SXES study on V_6O_{13}
Metal-insulator transition by temperature about 150 K

1. Origin of the metal insulator transition at Tc=150K
   - Mott-transition
   - Band shift (crystal field splitting)
2. One dimensional antiferromagnetic ordering below T_N=50K

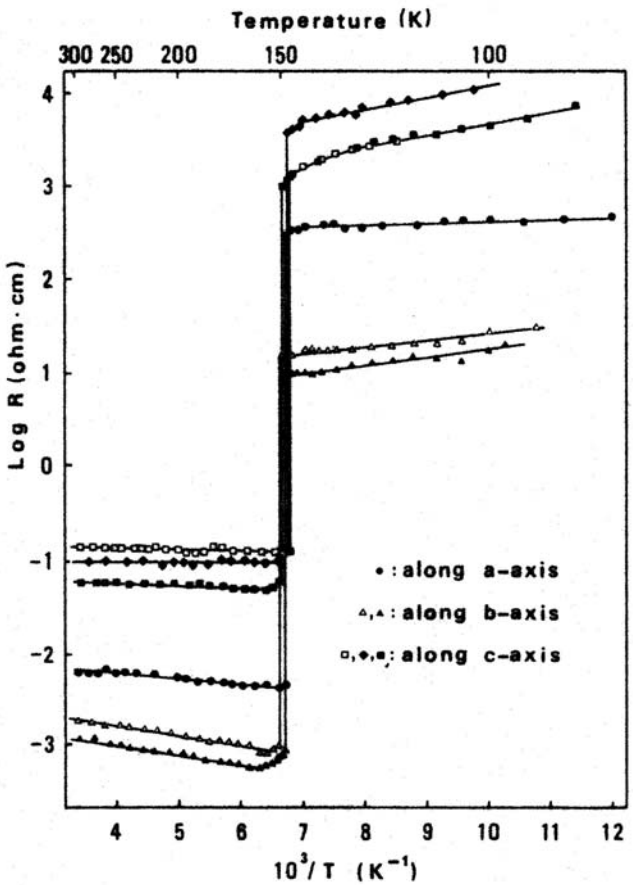


Fig. 2. Temperature dependence of electrical resistivity of single crystal V_6O_{13} along *a*, *b* and *c*-axes.

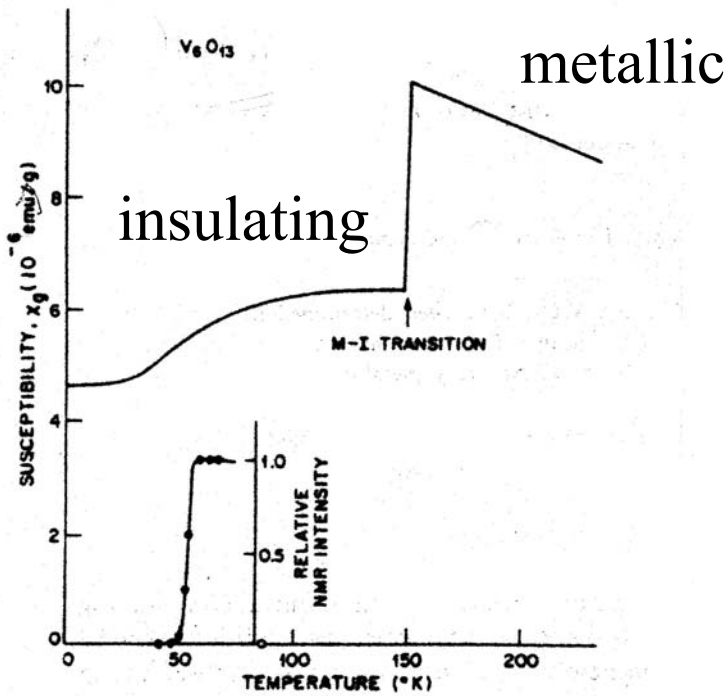
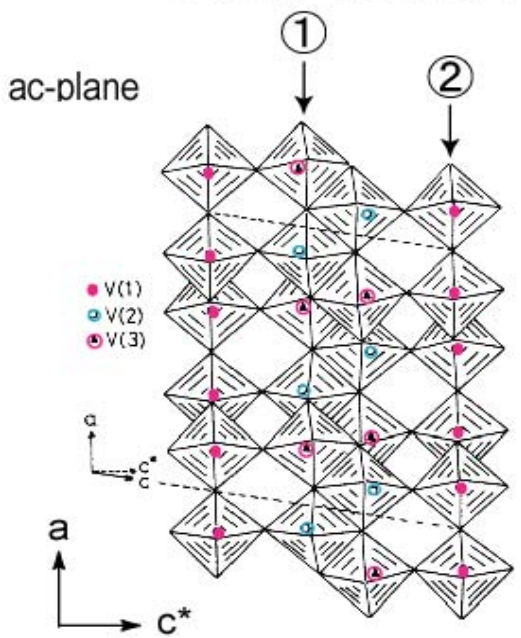


FIG. 1. Magnetic susceptibility vs temperature and relative NMR intensity vs temperature for V_6O_{13}. The decrease in NMR intensity between 50 and 60 °K is caused by the onset of magnetic long-range order. The implied Néel temperature is T_N = 55 °K.

V_6O_{13}

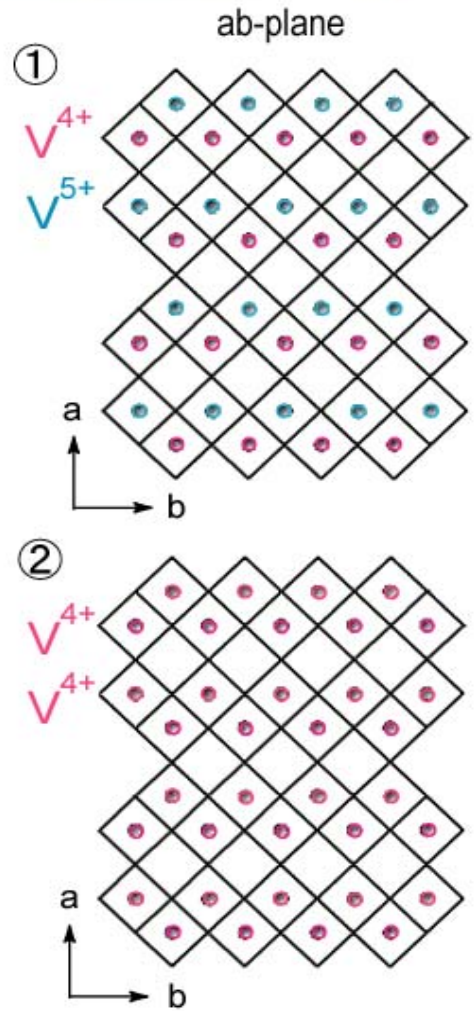
- monoclinic structure
- $3d^1(V^{4+})$: $3d^0(V^{5+})$=2 : 1 mixed valence
- metal-insulator transition at Tc=150K
  antiferromagnetic transition at TN=50K

crystal structure



298K		120K
a 11.921(Å)		a 11.963
b 3.6811	→	b 3.707
c 10.147		c 10.064

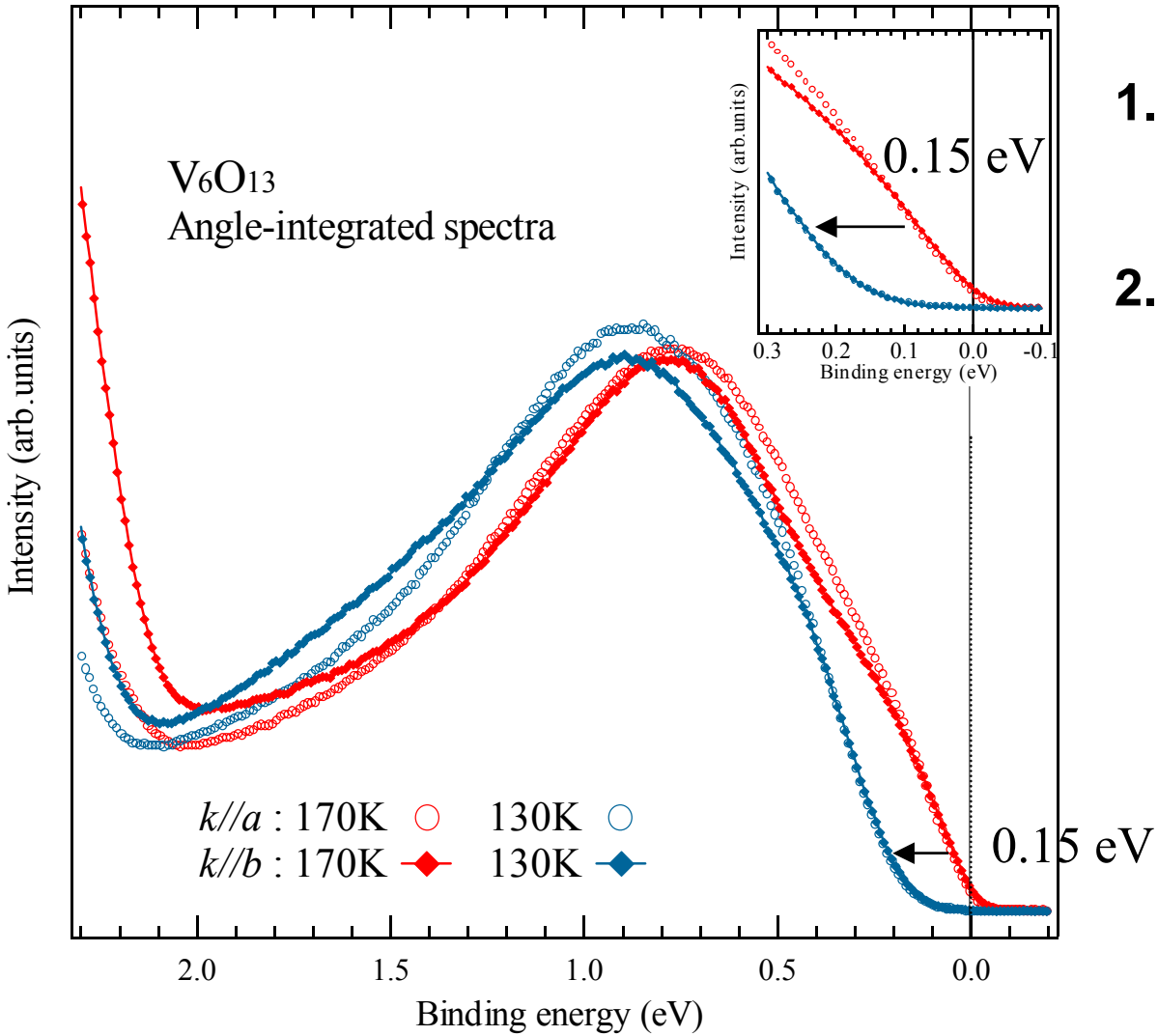
latice constants



One dimensional structure

Eguchi et al, Phys. Rev. B65(2002)205124

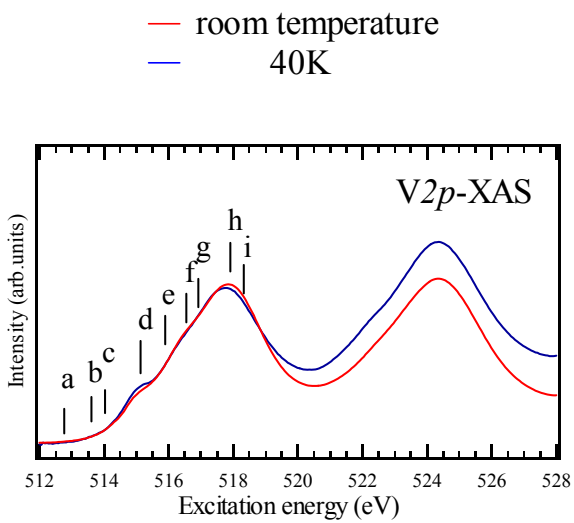
Temperature dependence and polarization dependence of angle-integrated **PES** of V_6O_{13}

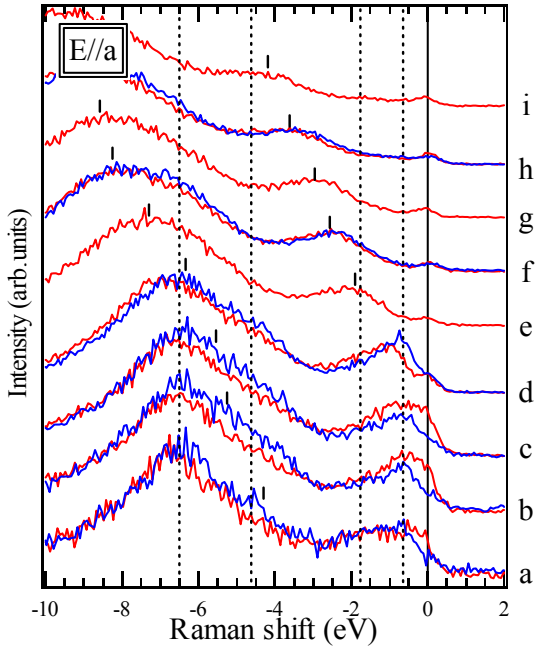


1. **Band shift of about 0.15 eV by metal-insulator transition**

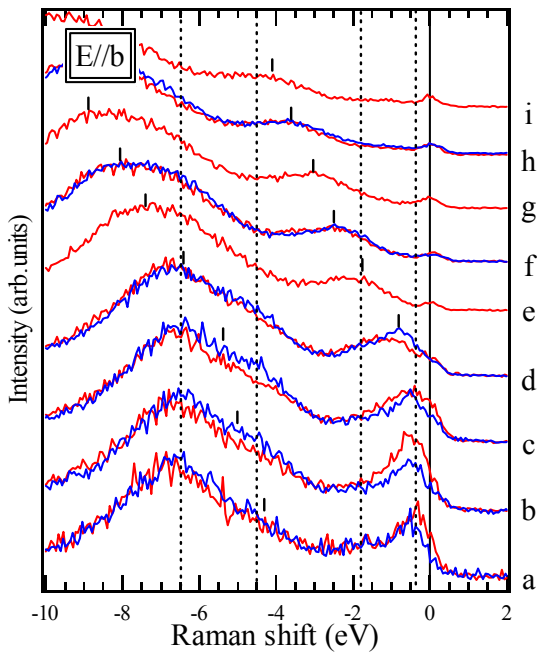
2. **No intensity at Fermi level even in metallic phase is due to the one dimensionality**

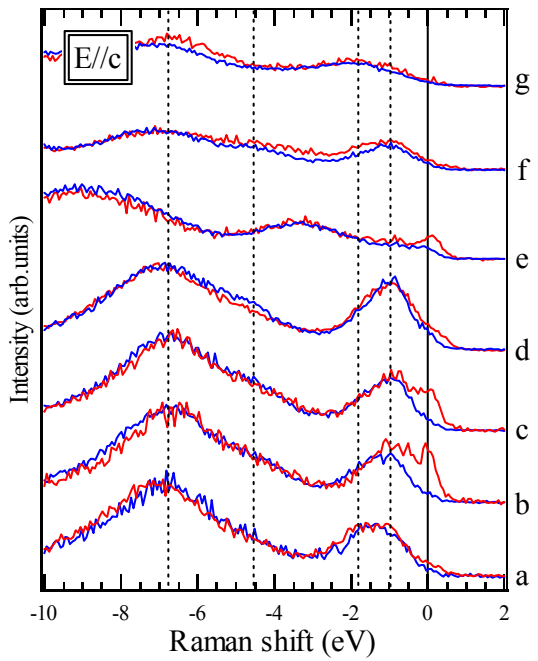
Eguchi et al,
Phys. Rev. B65(2002)205124





Temperature dependence and polarization dependence of V2p-SXES on V_6O_{13}





1. **High conductivity along b axis is consistent with the lowest Raman band of E//b**
2. **Small changes at 0 eV through the metal-insulator transition**

Eguchi et al., unpublished

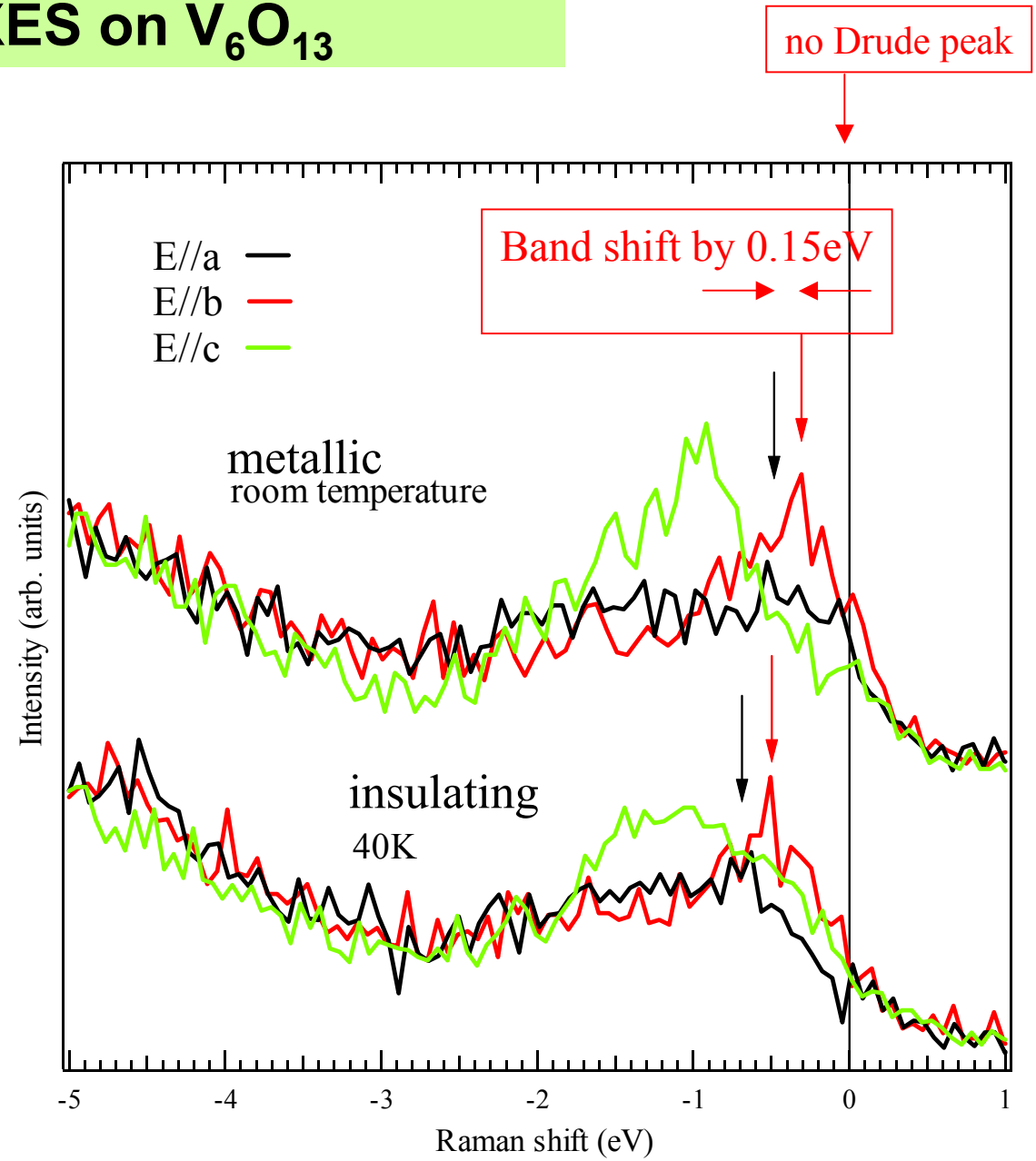
Cf. The spectra are similar to the figures in Schmitt et al., PRB**69**,125103(2004)

Temperature dependence and polarization dependence of SXES on V_6O_{13}

1. The lowest Raman band with E//b is responsible for the transport properties

2. Band shift by 0.15eV through the metal-insulator transition is consistent with the PES results
   ⇨ • Crystal distortion?

3. There is no Drude peak, even though a intensity exists at E_F
   • Inconsistent with DMFT
   ⇨ • Low carrier density?
   • One-dimensionality?



Eguchi et al,

summary

- Resonant SXES is powerful for the study of d-d excitation

- Polarization dependence gives the new information, especially for the singlet A1g electronic states

  ⇨ Undulator technology is important

- Cluster calculations are powerful to elucidate the resonant SXES and their polarization dependence

- High resolution SXES around E_F and its temperature dependence are powerful for the study of transport properties (Fermiology)

  ⇨ We need much higher resolution but possible
  (small and stable spot size is important)
  beamline technology