Characterization of Fe 3d states in $CuFeS_2$ by resonant X-ray emission spectroscopy

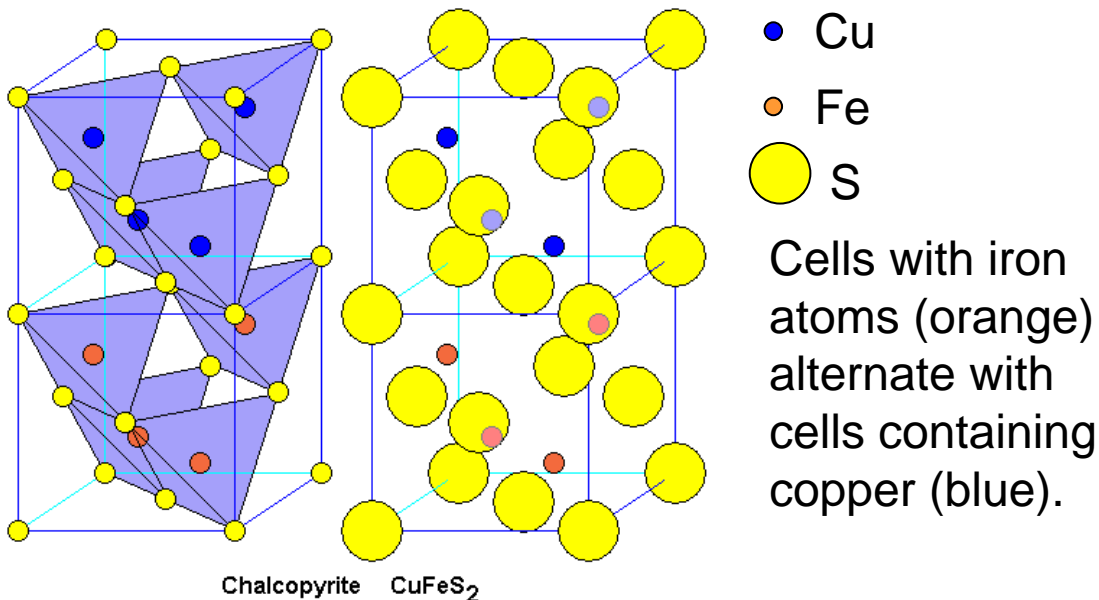K. Sato[1,2], Y. Harada[3], M. Taguchi[3], S. Shin[3] and A. Fujimori[4]

1. Tokyo University of Agriculture and Technology
2. Japan Science and Technology Agency
3. RIKEN/Spring-8
4. University of Tokyo

CONTENTS

1. Introduction

- Chalcopyrite $CuFeS_2$ is a mineral compound with golden luster and is often referred to as "fool's gold". Why is it golden in color even though it is a semiconductor?

- Cu
- Fe
- S

Cells with iron atoms (orange) alternate with cells containing copper (blue).

Chalcopyrite $CuFeS_2$

http://www.uwgb.edu/dutchs/PETROLGY/Sphal-Chalc%20Structure.HTM

www.asahi-net.or.jp/~ug7s-ktu/e_odo.htm

Mystery of CuFeS$_2$

- Chalcopyrite, CuFeS$_2$ is a semiconductor with an antiferromagnetic ordering. The local magnetic moment of Fe has been known to be as small as 3.85 μ_B from neutron scattering experiments[1].

- The result is conflicting with ionic bonding model of Cu$^+$Fe^{3+}S$_2$ in which high spin Fe^{3+}(3d^5) with local moment of 5 μ_B is expected.

- The observed reduction of Fe moment is consistent with the model proposed by Pauling and Brockway, who concluded that chalcopyrite is a mixture of two extreme ionic states, Cu$^+$Fe^{3+}S$_2$, and Cu^{2+}Fe^{2+}S$_2$ [2]

[1] G.Donnay, L.M. Corliss, J.D.H. Donnay, N. Elliot and J.M. Hastings: Phys. Rev. 112 (1958) 1917.
[2] L. Pauling, and L. O. Brockway, Z. Krist. 82, 188 (1932).

# Optical study of electronic structure of $CuFeS_2$, $CuAlS_2$:Fe and $CuGaS_2$:Fe

- In order to elucidate electronic structures of Fe in $CuFeS_2$, Teranishi and Sato studied optical spectroscopy in Fe-doped chalcopyrite-type semiconductors, $CuAlS_2$ and $CuGaS_2$, and found broad and strong absorption band with two peaks around 1.3 eV and 1.9 eV [2]

[2] T. Teranishi and K. Sato:
J. Phys. Soc. Jpn. 36 (1974) 1618-1624.

Optical absorption spectrum in CuFeS$_2$ and CuGaS$_2$:Fe and CuAlS$_2$:Fe
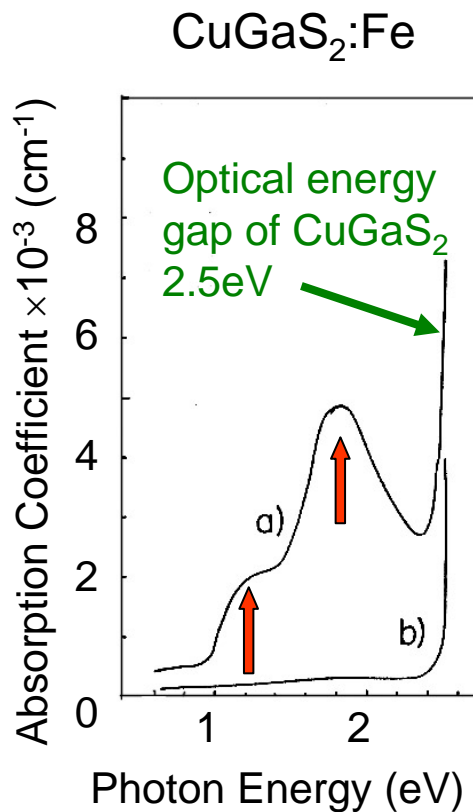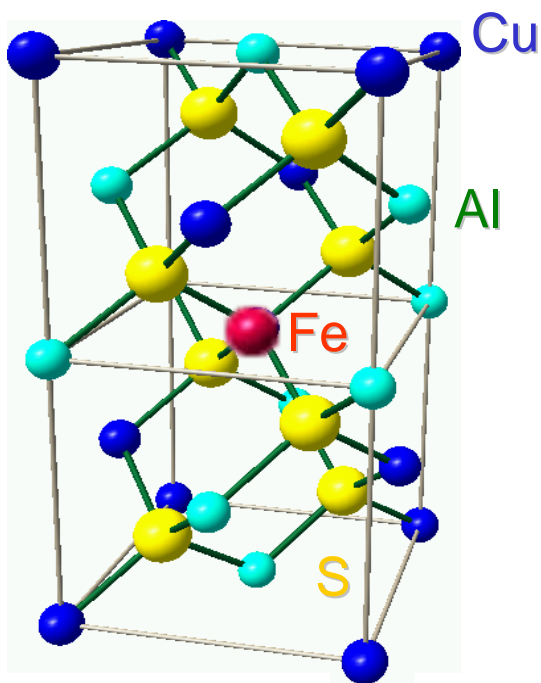
a) CuGaS$_2$:Fe$_{0.006}$, b) CuGaS$_2$
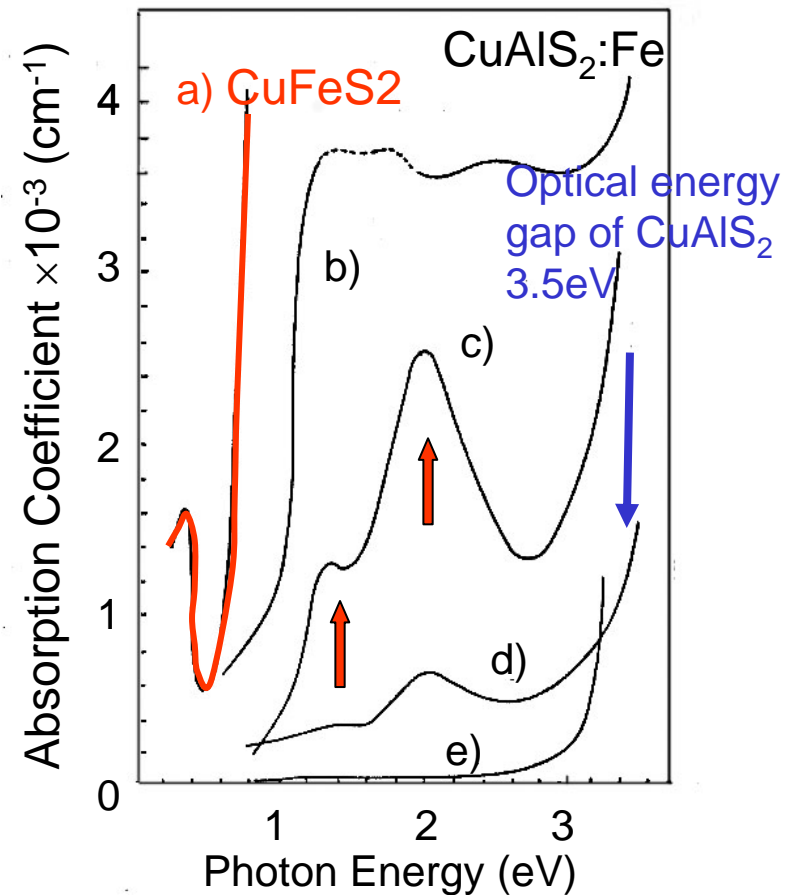
a) CuFeS$_2$, b) CuAlS$_2$:Fe$_{0.07}$, c) CuAlS$_2$:Fe$_{0.006}$, d) CuAlS$_2$:Fe$_{0.0008}$, e) CuAlS$_2$
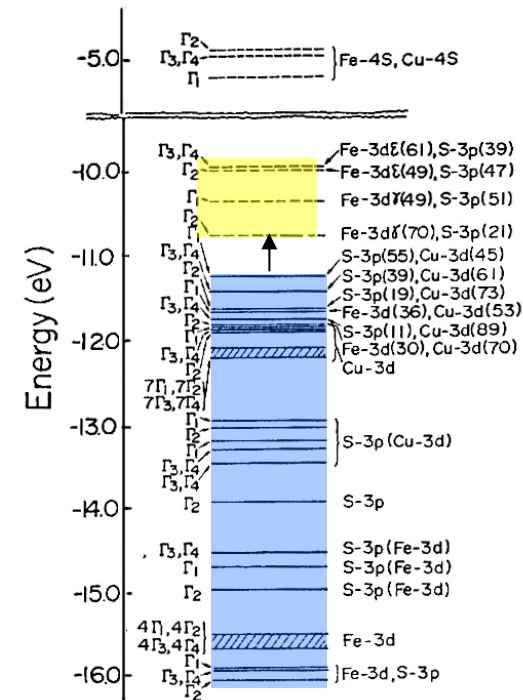
Molecular-orbital calculation of electronic structure in 17-atom cluster

- Kambara calculated absorption spectra of $CuFeS_2$ and $CuGaS_2$:Fe using a model cluster consisting of 17 atoms.

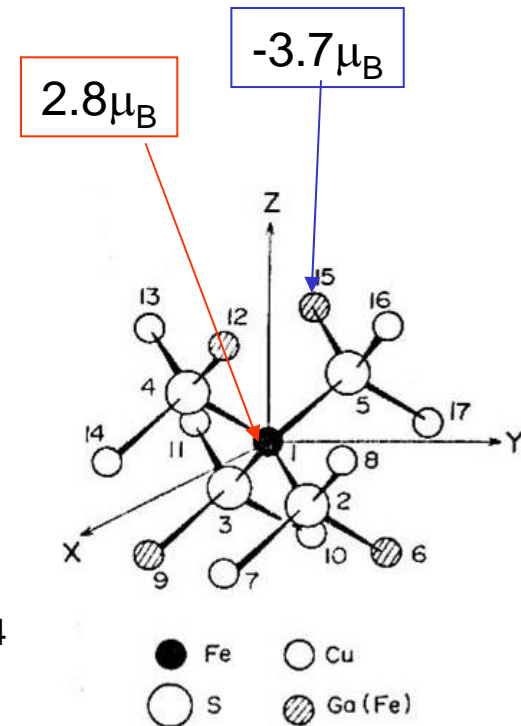**CuGaS₂:Fe**

CuFeS₂

T. Kambara: J. Phys. Soc. Jpn. 36 (1974) 1625-1634
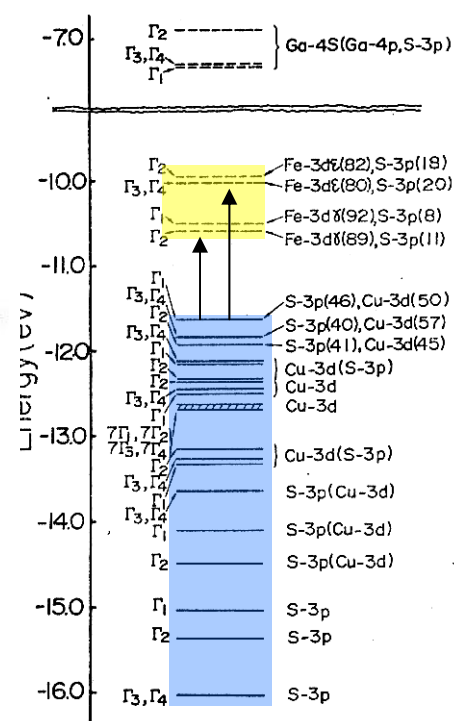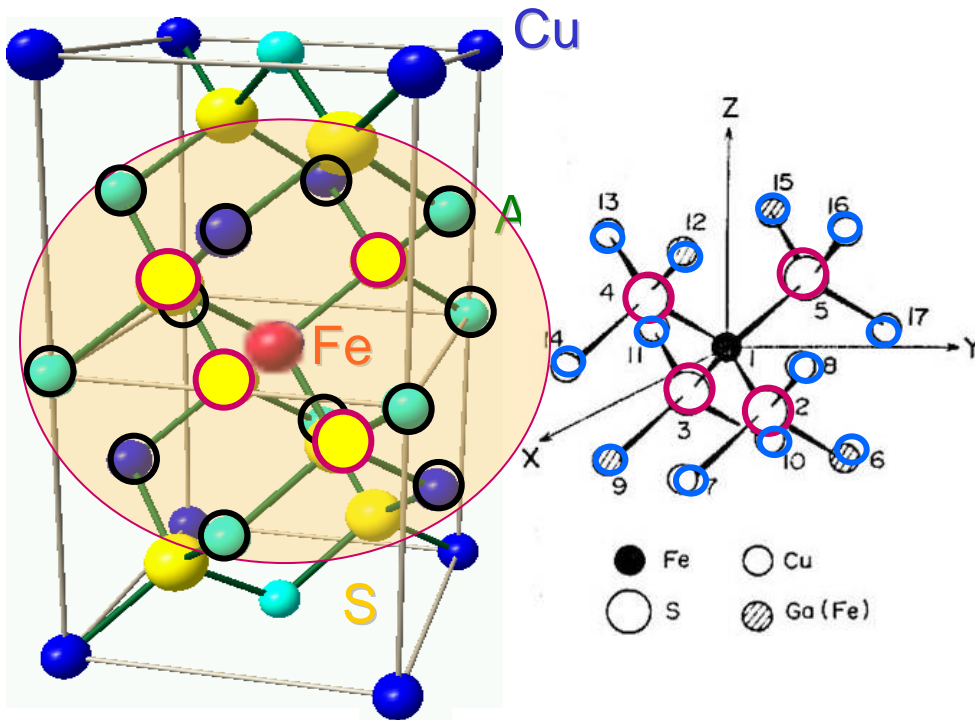
Results of the molecular-orbital calculation

- Energy difference of 1.0eV and 1.5eV between occupied and unoccupied levels in $CuGaS_2$:Fe, the band gap of 0.5 eV in $CuFeS_2$ was obtained explaining the experimental results.

- If antiferromagnetic configuration is assumed Fe moment is $2.8\mu_B$ at the center Fe and $-3.7\mu_B$ at the corner Fe. Overlap of 3d orbitals is responsible to the reduction.

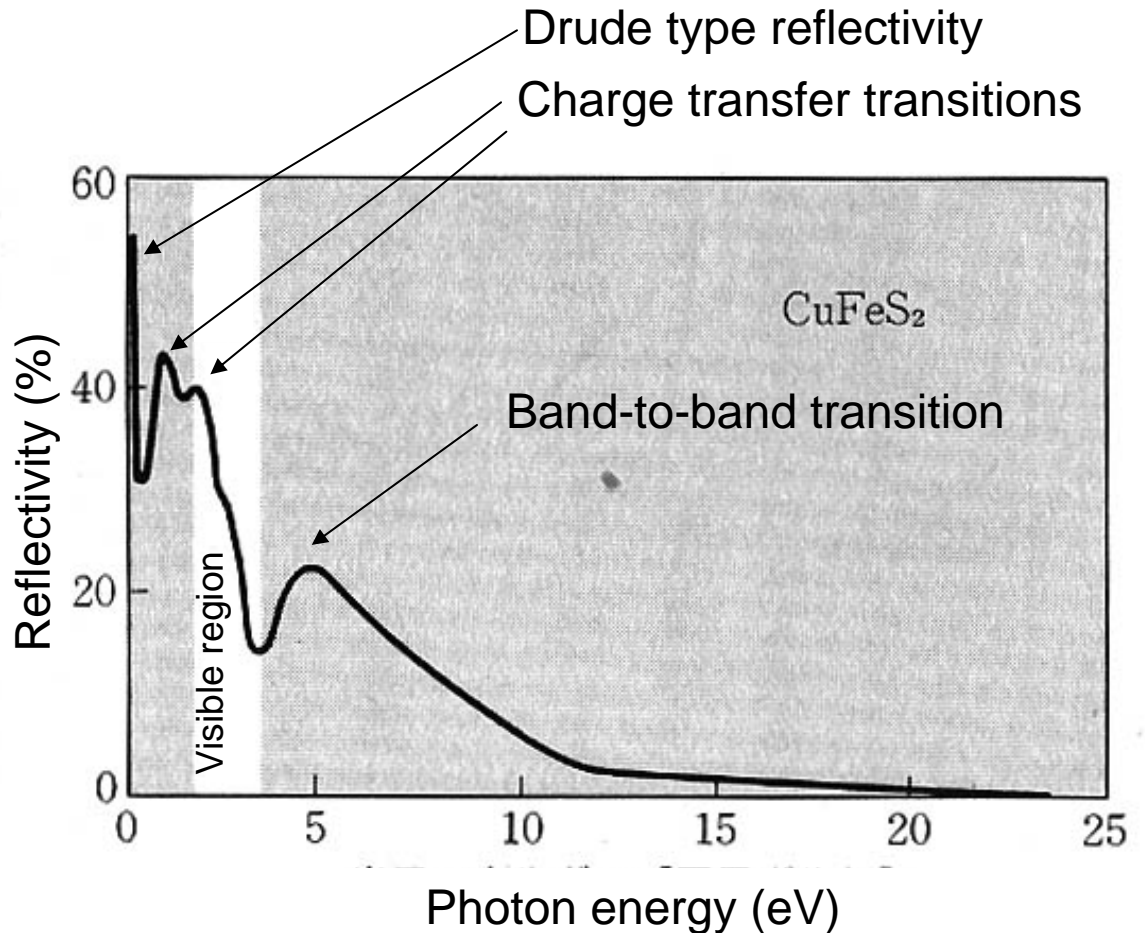 T. Kambara: J. Phys. Soc. Jpn. 36 (1974) 1625-1634

- *Cf*: An energy band calculation was performed for $CuFeS_2$ using a DV-Xα technique, which gives a band gap value of 0.72 eV and a magnetic moment of 3.88 μ_B.

$2.8\mu_B$

$-3.7\mu_B$

Fe ○ Cu
○ S ⊘ Ga (Fe)

T. Hamajima, T. Kambara, and K. I. Gondaira, Phys. Rev. B 24, 3349 (1981)

Is the origin of the golden luster elucidated?

- Reflectivity spectrum of $CuFeS_2$ was measured between 0.2 and 25 eV.

- It is found that the golden color is a consequence of existence of strong absorption band with two peaks around 1 and 2 eV, which have been assigned to the charge transfer type transitions from valence band to Fe 3d-origined conduction band.

Drude type reflectivity

Charge transfer transitions

$CuFeS_2$

Band-to-band transition

Reflectivity (%)

Visible region

Photon energy (eV)

Additional mystery!
Low energy d-d transitions

- Infrared photoluminescence was measured in slightly Fe-doped $CuAlS_2$ and $CuGaS_2$.
- A sharp photoluminescence (PL) line with phonon replicas has been observed at quite low energy position in slightly Fe-doped $CuGaS_2$ and $CuAlS_2$, i.e., at 4942 cm^{-1}=0.613 eV for $CuGaS_2$:Fe, and 5804 cm^{-1}=0.720 eV for $CuAlS_2$:Fe [1].
- PL excitation band of the IR PL overlaps the strong absorption band due to p-d charge transfer.[2]
- Theoretical analysis in terms of the ligand-field theory leads to an assignment of the infrared PL line to $^4T1$ to $^6A1$ transition in the $3d^5$ manifold in Fe^{3+}.
- It is found from PLE and thermal treatment studies in $CuAl_xGa_{1-x}S_2$:Fe that the low energy PL line is derived from the Fe-ion occupying the Cu-site [3,4].

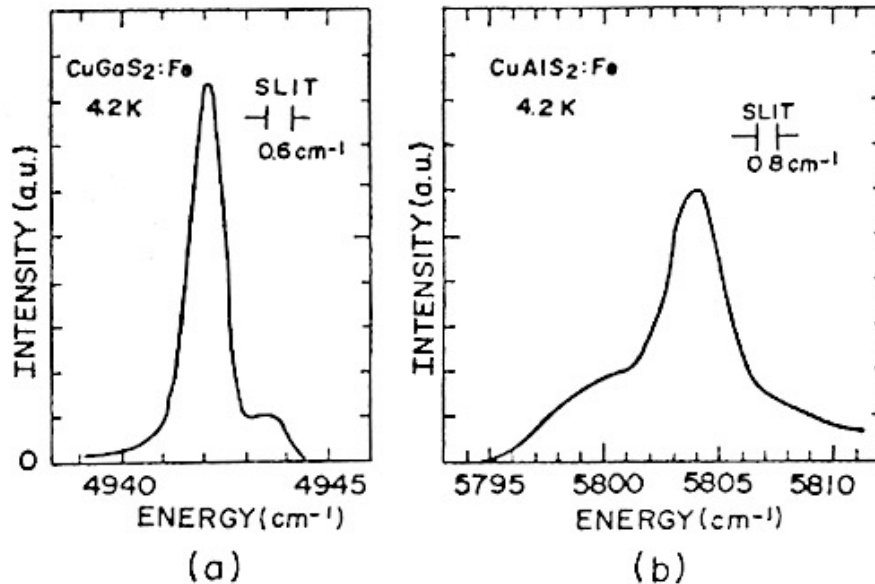[1] K.Sato and T.Teranishi: J. Phys. Soc. Jpn. 37 [2] (1974) 415-422.

[2] K.Tanaka, K.Ishii, S.Matsuda, T.Hasegawa and K.Sato: Jpn. J. Appl. Phys. 28 [1] (1989) 12-15.

[3] K. Sato et al., J. Cryst. Growth **99**, 772 (1990).

[4] X.-J. Li et al., Jpn. J. Appl. Phys. **31**, L303 (1992)

Infrared photoluminescence spectra in CuGaS$_2$:Fe and CuAlS$_2$:Fe

- Sharp photoluminescence (PL) peak was found around 0.61 eV (CuGaS$_2$) and 0.72 eV (CuAlS$_2$) .

PL excitation band of the IR PL overlaps the strong absorption band due to p$\rightarrow$d charge transfer.

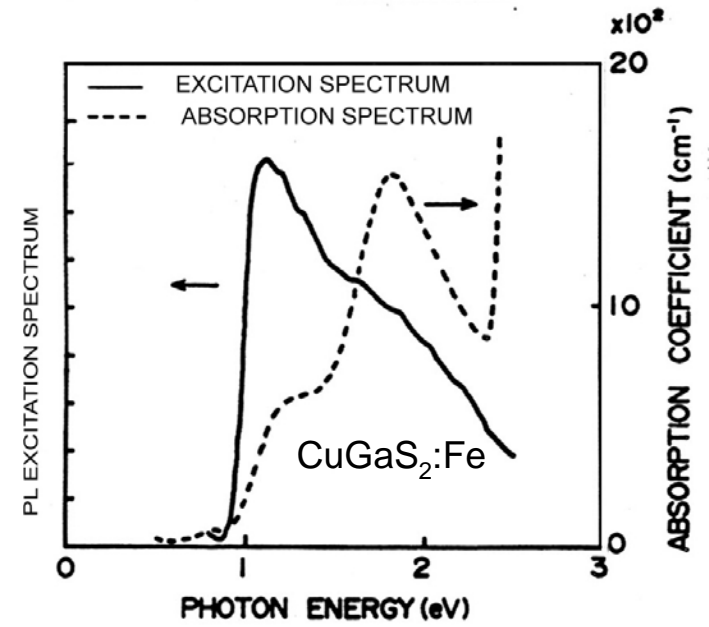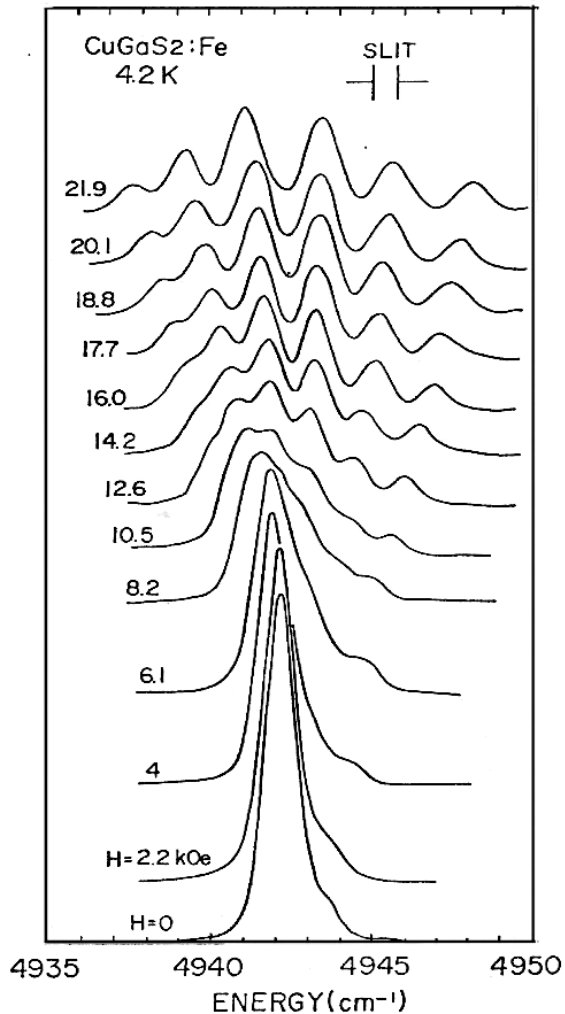Fig. 1. The luminescence spectra of (a) CuGaS$_2$: Fe and (b) CuAlS$_2$:Fe at 4.2 K.

K.Sato and T.Teranishi: Infrared Luminescence of Fe3+ in CuGaS$_2$ and CuAlS$_2$; J. Phys. Soc. Jpn. 37 [2] (1974) 415-422.

Characterization of the IR PL

Fig. 4. The Zeeman spectra of the zero line of $CuGaS_2$:Fe at 4.2 K. The spectra are arbitrarily shifted for the sake of clarity.

- A Zeeman spectrum of the IR-PL line showed that the ground state of the Fe in $CuGaS_2$ is in the sextet state, consistent with the ESR result that Fe is trivalent and belongs to $^6A_1$ symmetry.

- The theoretical analysis of the six-line split Zeeman lines in terms of the ligand-field theory leads to an assignment of the infrared PL line to $^4T_1$ to $^6A_1$ transition in the $3d^5$ manifold in Fe^{3+}.

Interpretation of the IR luminescence spectrum by ligand-field theory

Mn III : $3d^4(^5D)4s, ^6D\sim$?

B=860

High spin

Low spin

S=1/2

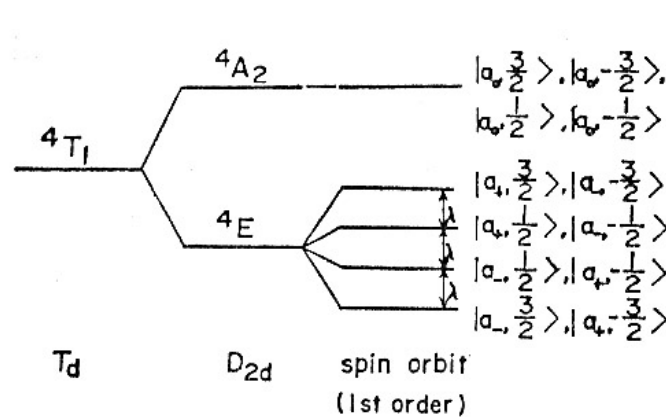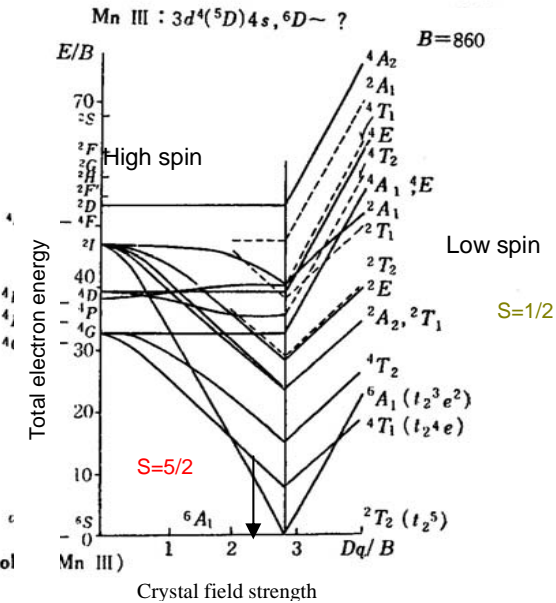Total electron energy

S=5/2

Crystal field strength

Sugano-Tanabe diagram

Fig. 7. A proposed energy level scheme for the excited state ($^4T_1$) of Fe^{3+} with a tetragonal distortion (D_{2d}) and a spin-orbit interaction. In this figure $a_{\pm} = \mp 1/\sqrt{2}(\alpha \pm i\beta)$ and $a_0 = \gamma$.
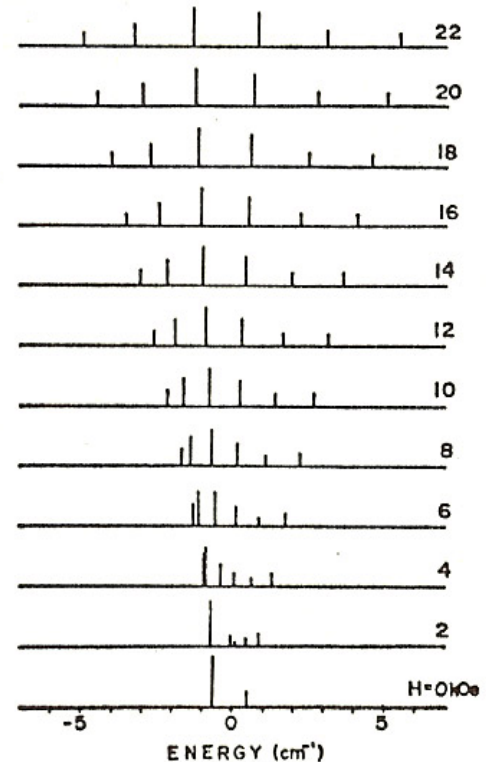
Fig. 8. The predicted Zeeman spectra for various magnitudes of the magnetic field. The excited state is assumed to be represented by $|a_-, +3/2\rangle$ and $|a_+, -3/2\rangle$.

- Extremely reduced values of the Racah parameters were necessary to account for the energy position of the IR photoluminescence.

IR photoluminescence is ascribed to Fe which occupies the Cu site

- It is found from PL studies in $CuAl_xGa_{1-x}S_2$:Fe that the low energy PL line is derived from the Fe-ion occupying the Cu-site [1].

- Results of thermal treatment of $CuGaS_2$:Fe in different atmosphere also support that the infrared PL is originated from the Fe occupying the Cu-site [2].
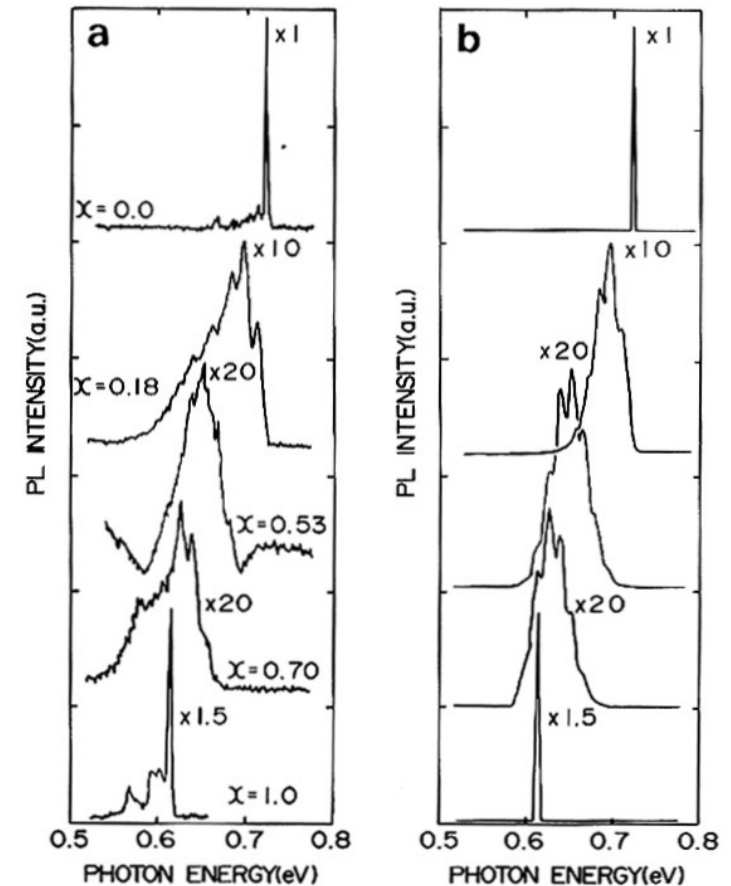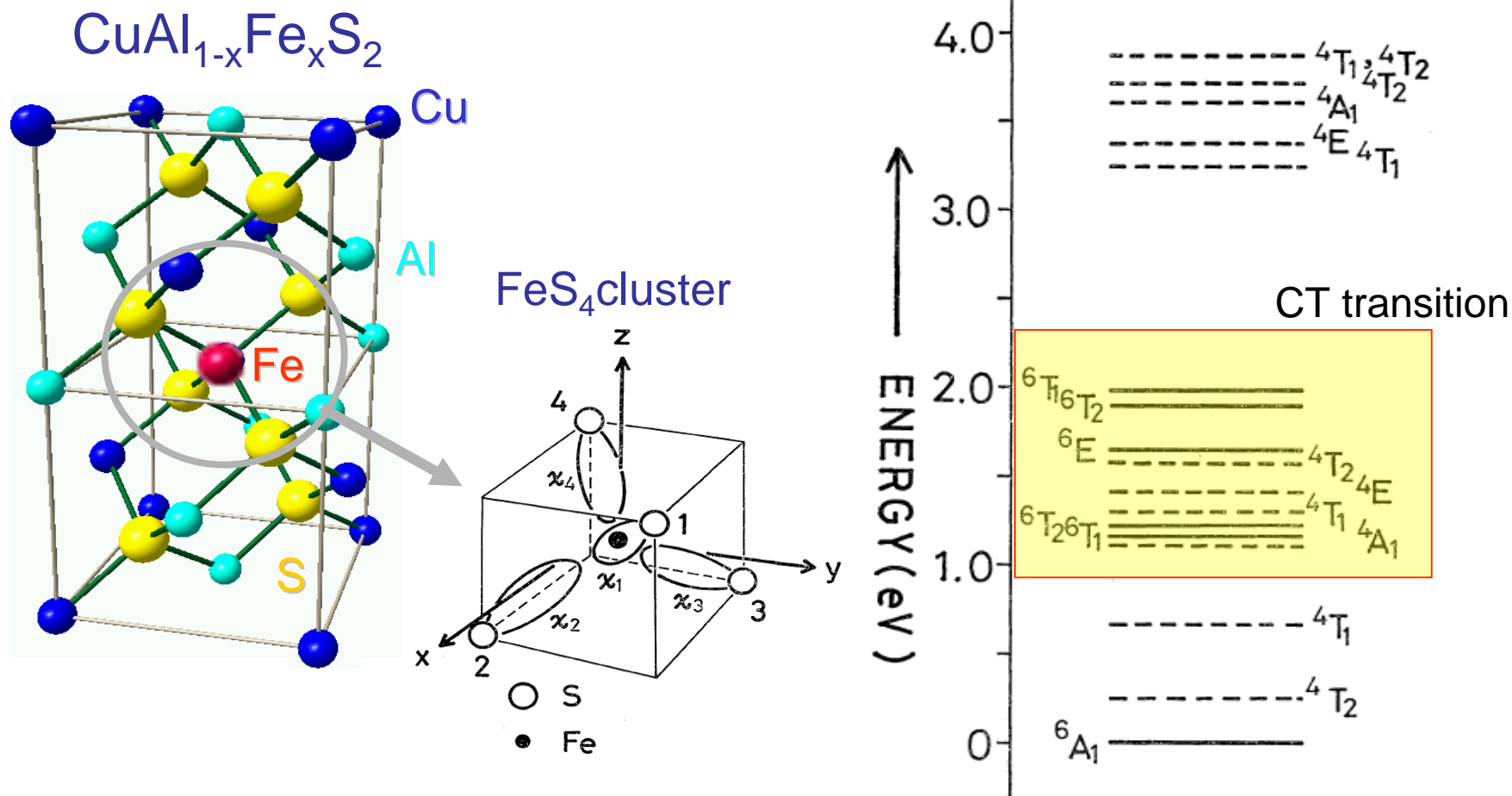

Fig. 1. (a) Photoluminescence spectra associated with the ligand-field transition $^4T_1 \rightarrow {}^6A_1$ of $3d^5$ manifold in Fe^{3+} ion in single crystals of $CuAl_{1-x}Ga_xS_2$ (x = 0, 0.18, 0.53, 0.70 and 1.0) measured at 20 K. (b) Spectra simulated by nine equally spaced Gaussian lines with intensities given by the binomial distribution (see section 3).

[1] K. Sato et al., J. Cryst. Growth **99**, 772 (1990).
[2] X.-J. Li et al., Jpn. J. Appl. Phys. **31**, L303 (1992)
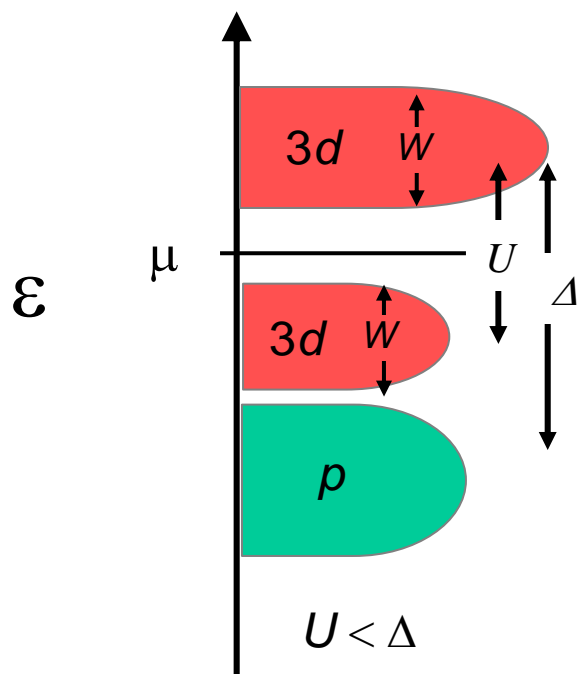
Molecular orbital + CI calculation in the Fe-S$_4$ cluster

CuAl$_{1-x}$Fe$_x$S$_2$

Cu

Al

Fe

S

FeS$_4$cluster

CT transition

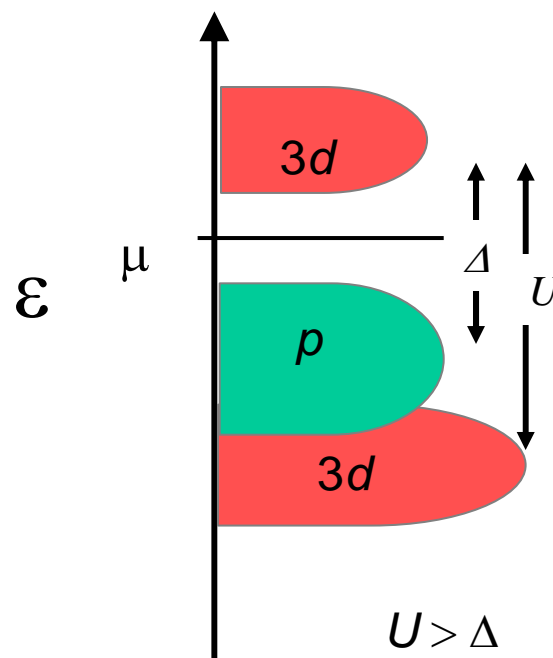T. Kambara, K. Suzuki and K. Gondaira, Electronic States of Fe in I-III-VI2 Compounds, JPSJ 39 764-771 (1975)

Electronic structure of transition-metal compounds

Mott-Hubbard type insulator   **Charge-transfer-type insulator**

W: bandwidth ~3 eV
U : Coulomb energy ~7 eV
Δ: Charge-transfer energy

Chemical trend in charge-transfer energy Δ
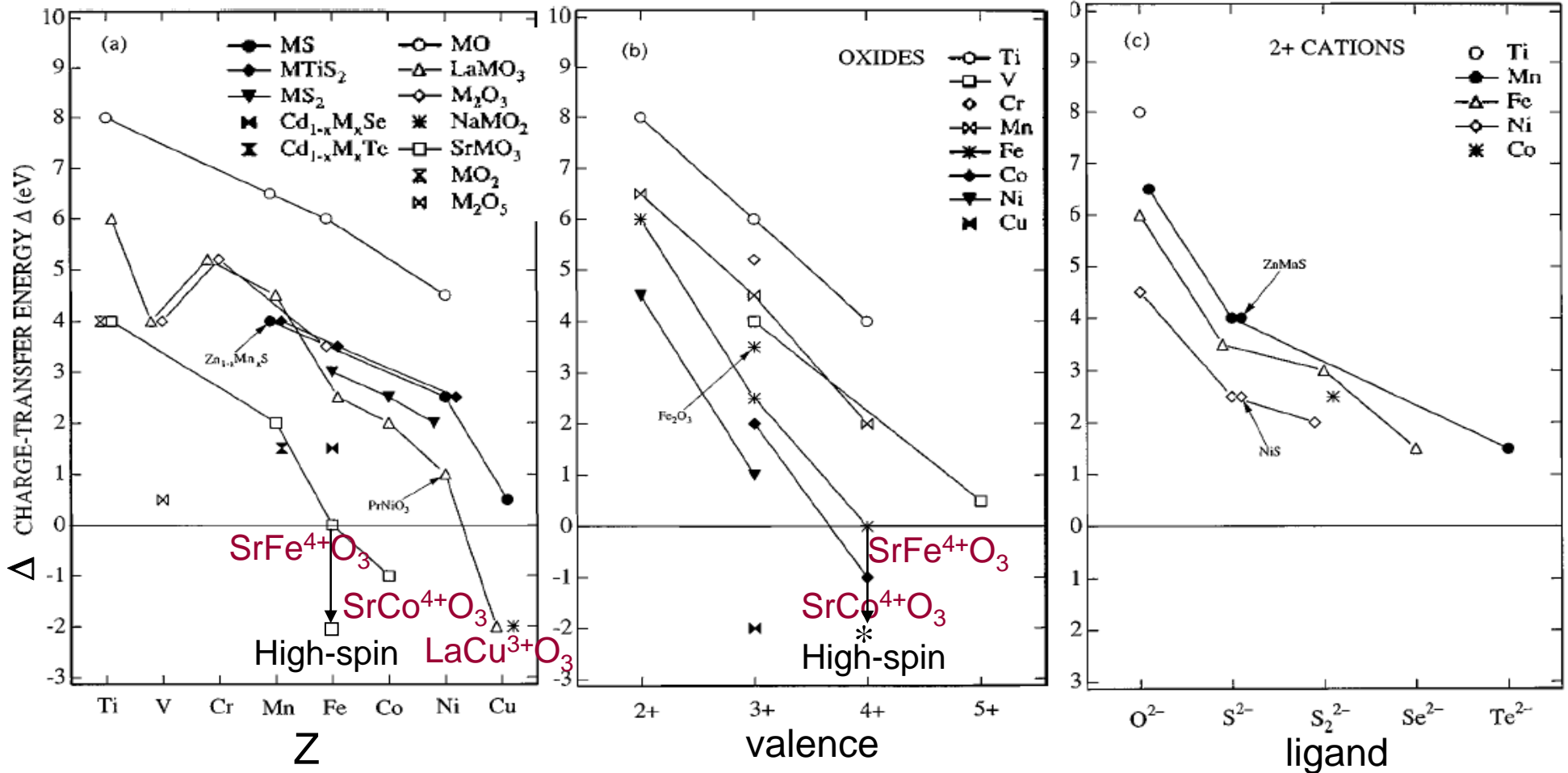
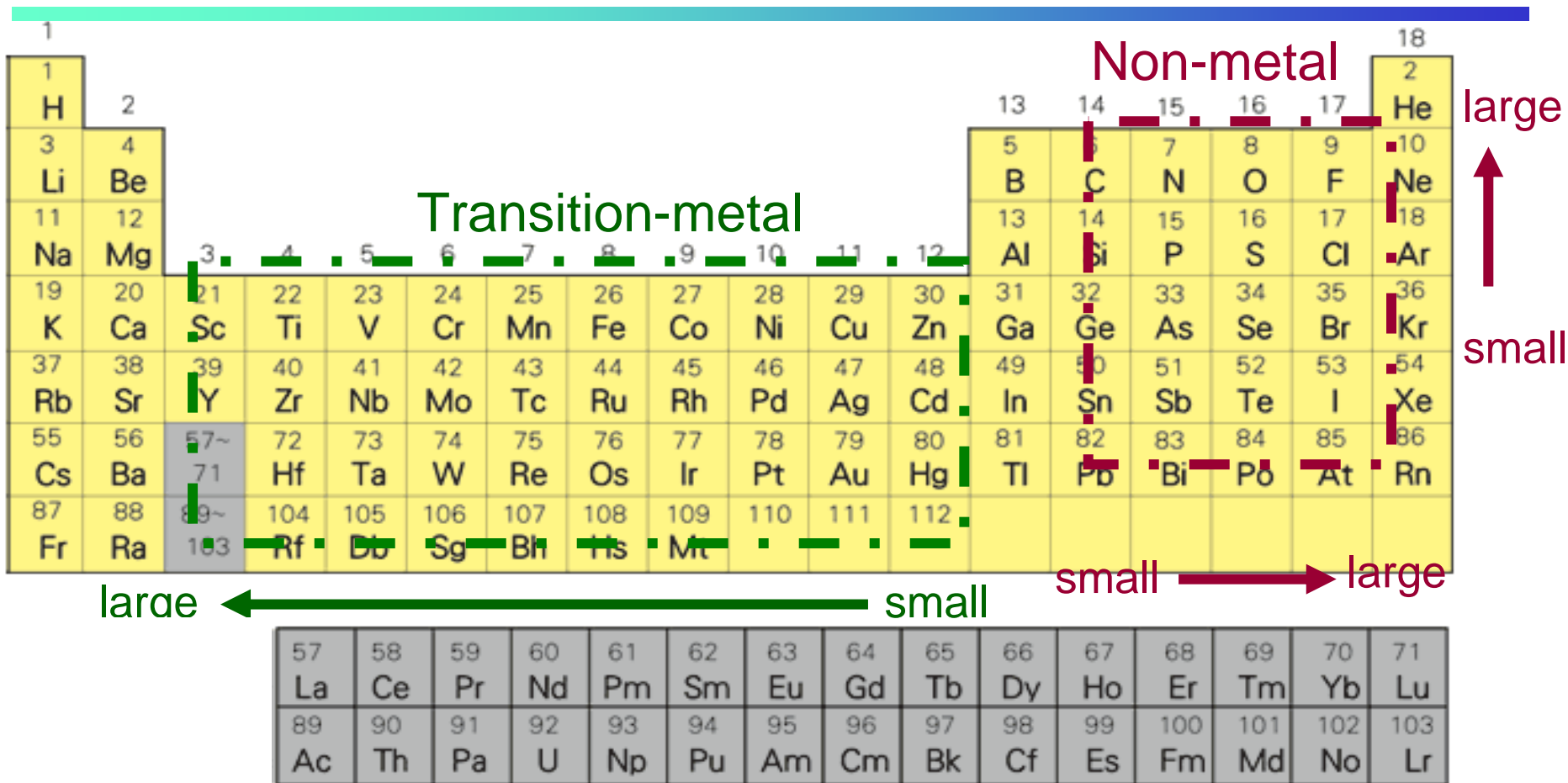

$\Delta = E(d^{n+1}\underline{L}) - E(d^n)$: Charge-transfer energy

A.E. Bocquet et al., PRB '92
M. Imada, A. Fujimori, Y. Tokura, RMP '98

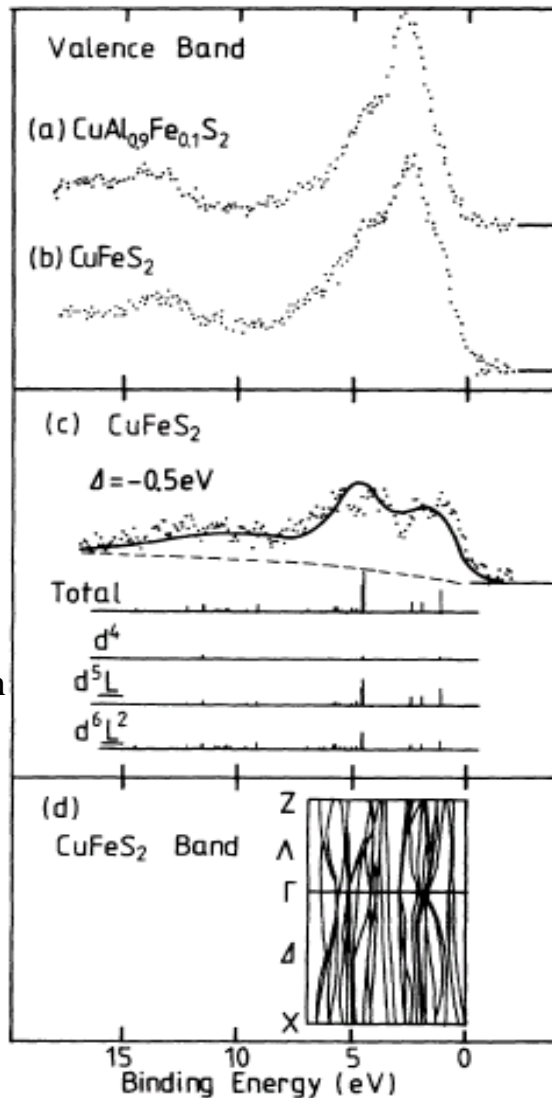# Chemical trend in charge-transfer energy Δ

Chalcopyrite $CuFeS_2$–Magnetic semiconductor with negative charge transfer energy Δ

Valence band photoelectron spectrum

Valence Band

(a) $CuAl_{0.9}Fe_{0.1}S_2$

(b) $CuFeS_2$

(c) $CuFeS_2$

$\Delta = -0.5\,eV$

Total

d^4

$d^5\underline{L}$

$d^6\underline{L}^2$

(d) $CuFeS_2$ Band

Z
Λ
Γ
Δ
X

15   10   5   0
Binding Energy (eV)

Cluster model calculation with CI

Fe 2p-core photoelectron spectrum

$CuFeS_2$ Fe 2p XPS

$\Delta = -0.5\,eV$

plasmon

740   720   700
Binding Energy (eV)

Intensity (arb. units)

d^5

$d^6\underline{L}$

$d^7\underline{L}^2$

Cluster model Calculation with CI
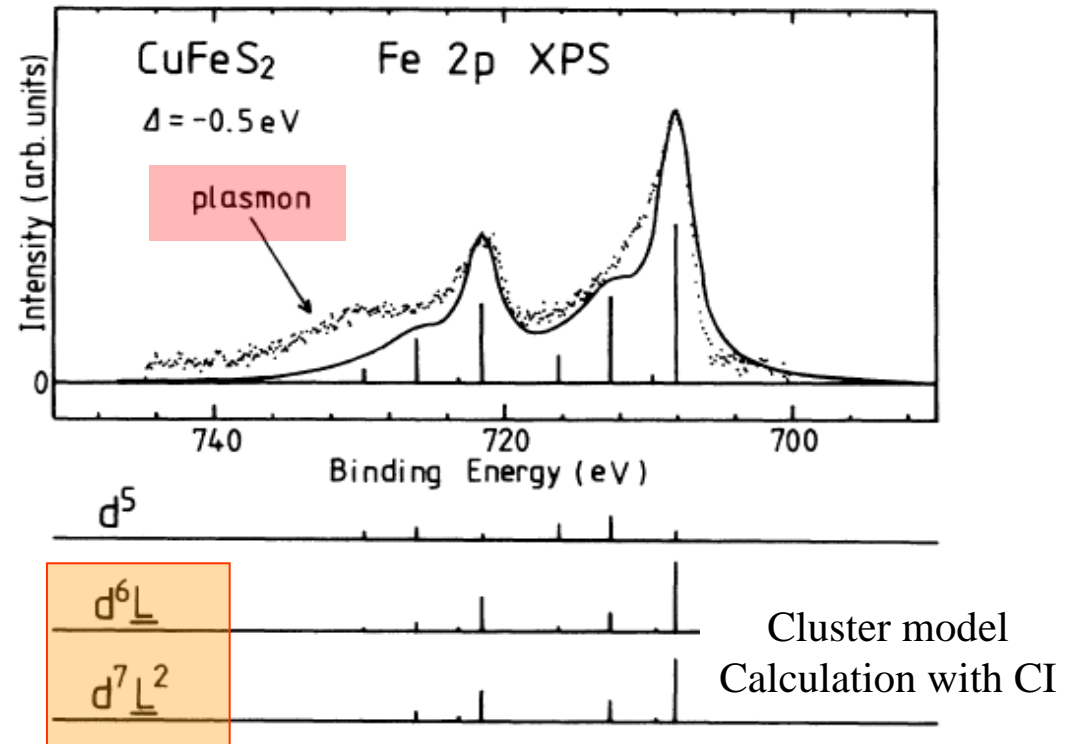
Mixture of charge transferred states

ICTMC16
Berlin 2008

Electronic structure of transition-metal compounds

Mott-Hubbard type insulator **Charge-transfer-type insulator**
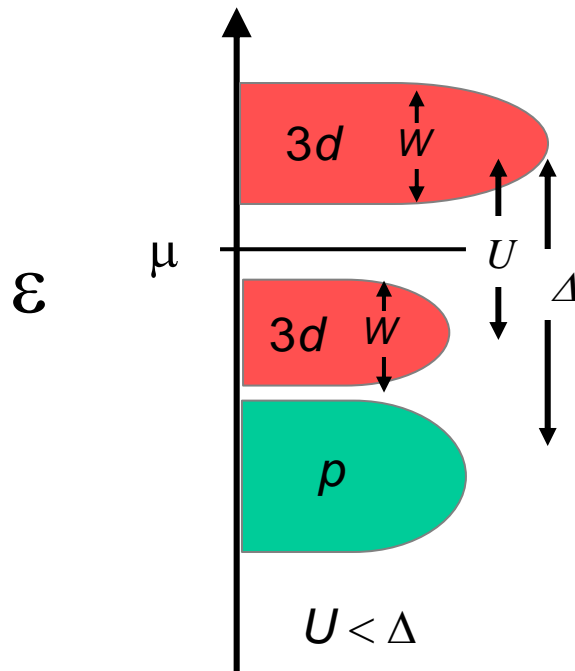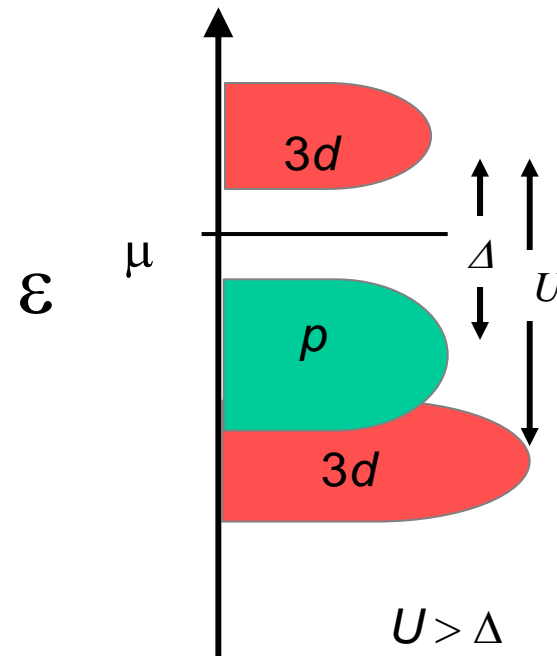
W: bandwidth ~3 eV
U : Coulomb energy ~7 eV
Δ: Charge-transfer energy

Haldane-Anderson mechanism for the formation of localized "d" states in negtive-Δ systems

$\Delta = E(d^{n+1}\underline{L}) - E(d^n)$: Charge-transfer energy

M. Imada, A. Fujimori, Y. Tokura, RMP '98

Chemical trend in charge-transfer energy Δ

CuFeS$_2$

Non-metal

Transition-metal

large

small

large ← small

small → large

large ← small

valence: 2-   - …. + 2+ 3+ 4+ 5+

large ← small

Zaanen-Sawatzky-Allen Phase Diagram

Why insulator?

Schematic diagram
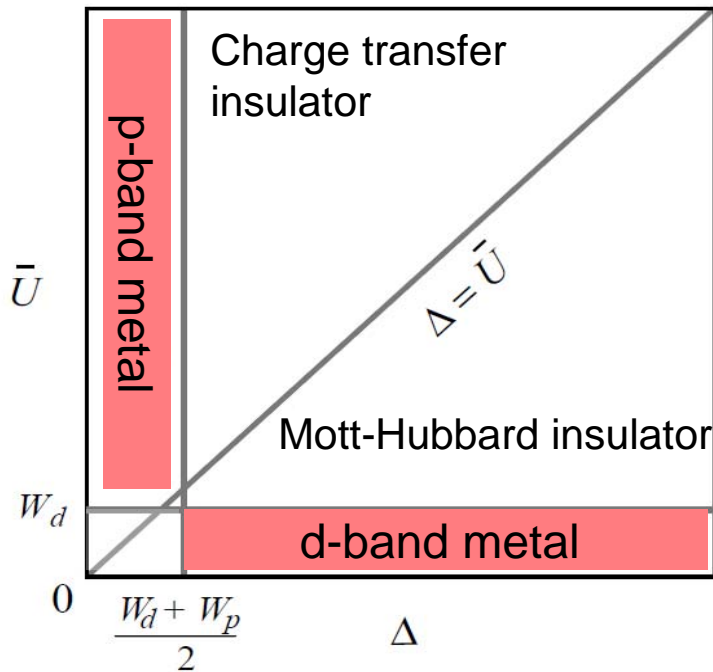
Actual materials
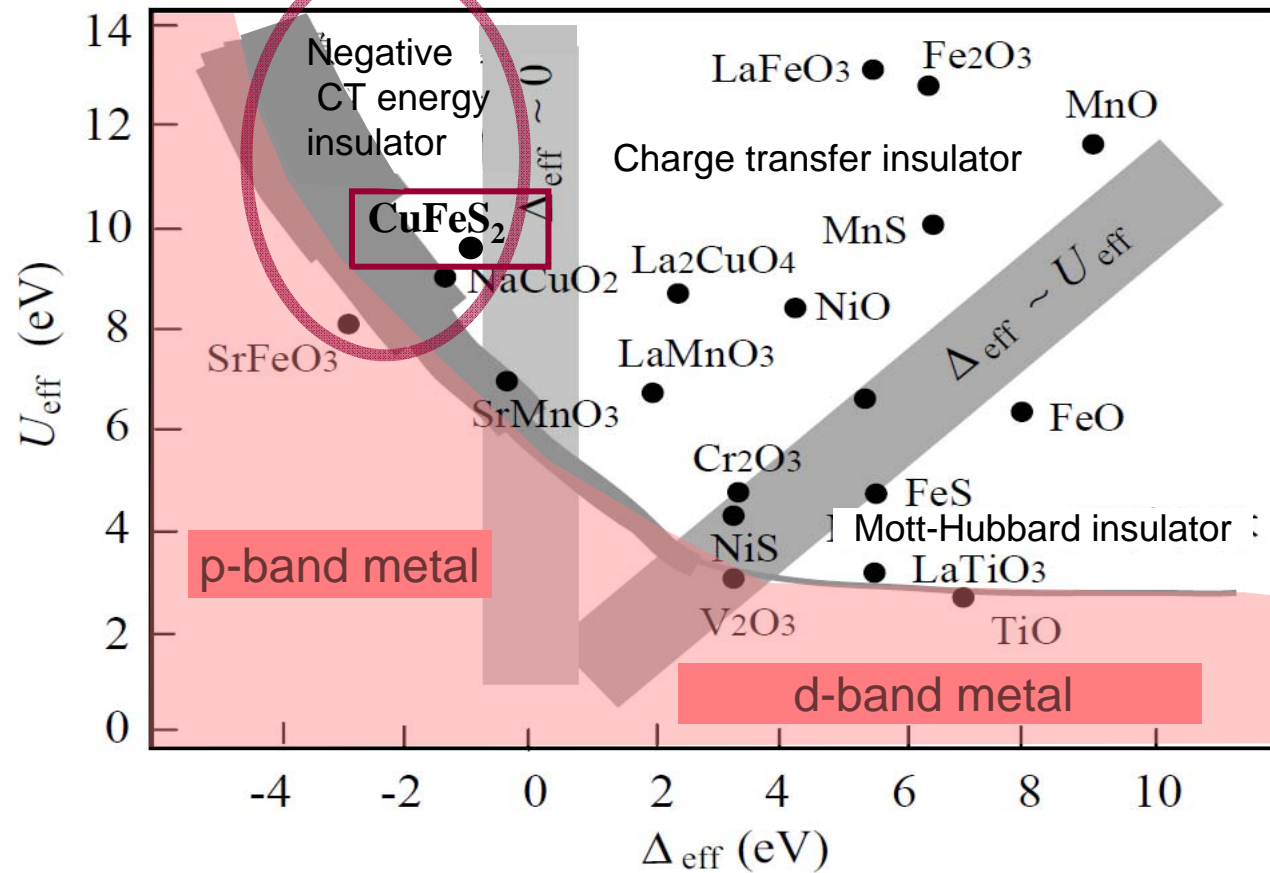
Charge transfer energy : Δ
Intraatomic Coulomb energy : U

Summary of previous studies

- By plotting in the ZSA diagram the considerably large U and the negative Δ determined above, it is suggested that $CuFeS_2$ is in the intermediate region, in which there are strong fluctuations between the states d^n, $d^{n+1}\underline{L}$, $d^n\underline{L}$, and d^{n+1}.

- This leads to a conclusion that $CuFeS_2$ is an unusual insulator of Haldane-Anderson type brought about by the strong p-d hybridization.

Purpose of the present study

- If the CT energy Δ is negative, the d-d multiplets become pushed down from the CT continuum, as illustrated in the right.

- In order to get further information on the 3d states of Fe in $CuFeS_2$, resonant X-ray emission spectroscopy (RXES) has been carried out

- The present paper describes experimental results and theoretical analysis on the resonant XES result.

$\Delta < 0$

$E - N\mu$

d^n

Δ

Charge-transfer state

$d^{n+1}\underline{L}$

Opt abs

$p\text{-}d$ hybridization
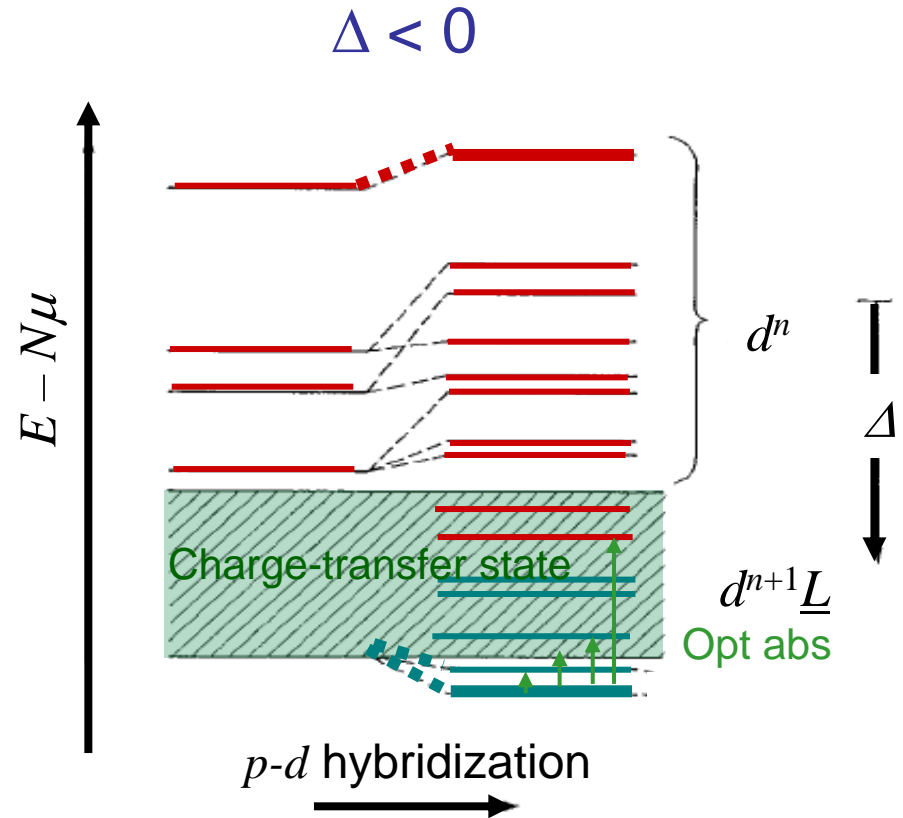
2.Resonant X-ray Emission Spectroscopy

- In the XAS process, absorption of incident X-ray excites an electron to empty valence state leaving a hole at the core state, providing information on unoccupied states.
- In the XES process, an electron in the filled valence state recombines the core hole produced by the precedent XAS and emits an X-ray photon, giving information on the occupied states.
- Thanks to this property, XES is applicable to solids ranging from metals to wide gap insulators.
- This technique has the advantage that it can probe electronic states at larger depth than the photoemission spectroscopy (PES) which can only probe electronic states near the surface.

X-ray absorption(XAS) and X-ray emission (RXES) spectroscopy

XAS **XES**

valence

$h\nu_{in}$

$h\nu_{out}$

core

$\sim f\,sec$
(core hole lifetime)
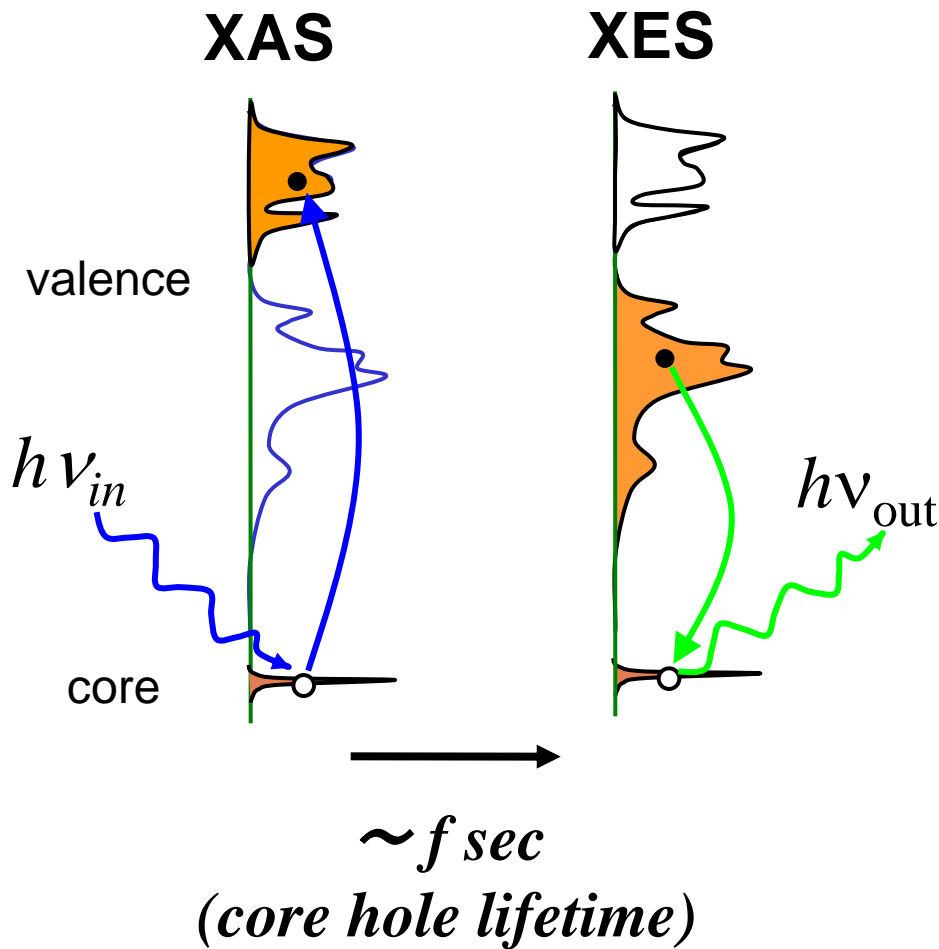
- XAS probes unoccupied electronic states
- XES probes occupied electronic states
- Applicable to solids ranging from metals to wide gap insulators
- Large probing depth
- Element specificity

Unraveling hidden *d-d* transitions by resonant x-ray emission spectroscopy (RXES)

Resonant x-ray emission spectroscopy (RXES)
Resonant inelastic x-ray scattering（RIXS）

$2\underline{p}3d^{n+1}$ — Core excited state

E

Soft X-ray emission

Soft X-ray absorption

$3d^n$

Ground state

RIKEN/SPring8.Group
Fe in hemoprotein
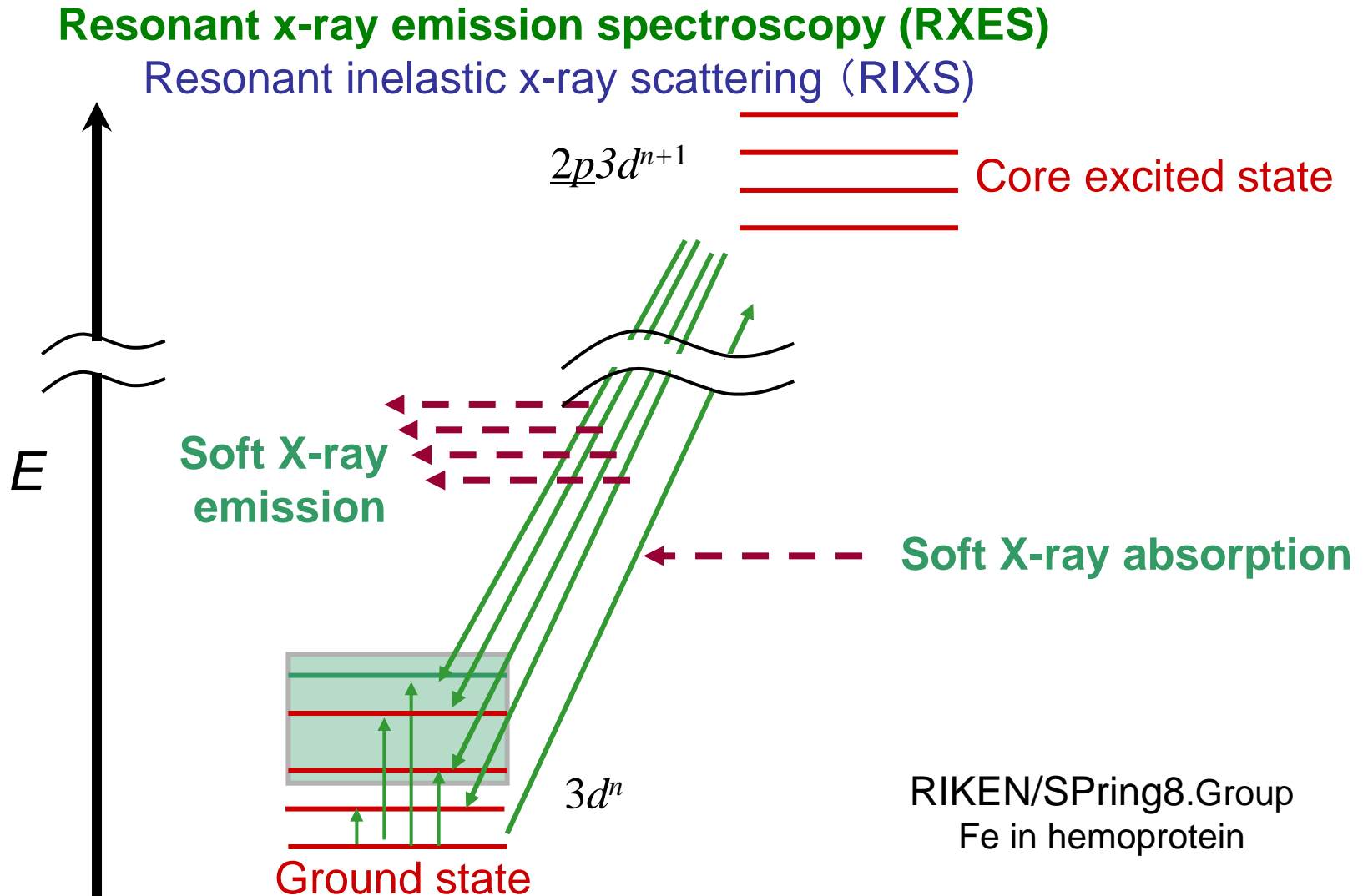
Transition Metal *L*-edge RXES

3d

2p

Initial state

Intermediate state

Final state

$|3d^n\rangle$

$|2p^5 3d^{n+1}\rangle$

$|3d^n\rangle$

dd excitation (3d^5)

Energy

3d

2p core hole

Coulomb interaction between 2p and 3d

spin-orbit interaction of 2p core level

3d

3d

3d

3d

Ground state

2p core hole

3d

Energy

dd excitation

Elastic peak
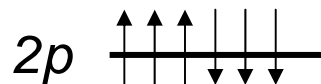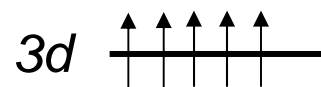
Initial state
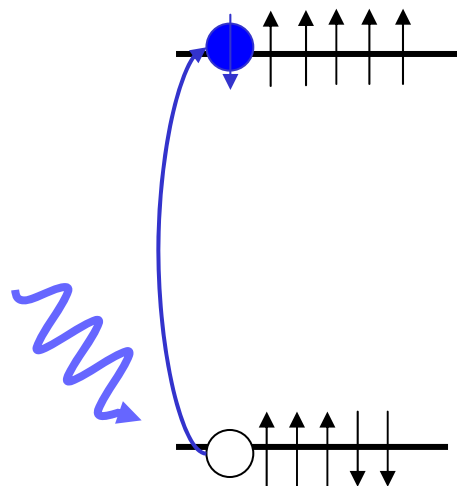
Intermediate state
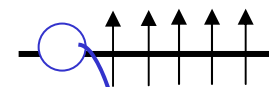
Final state
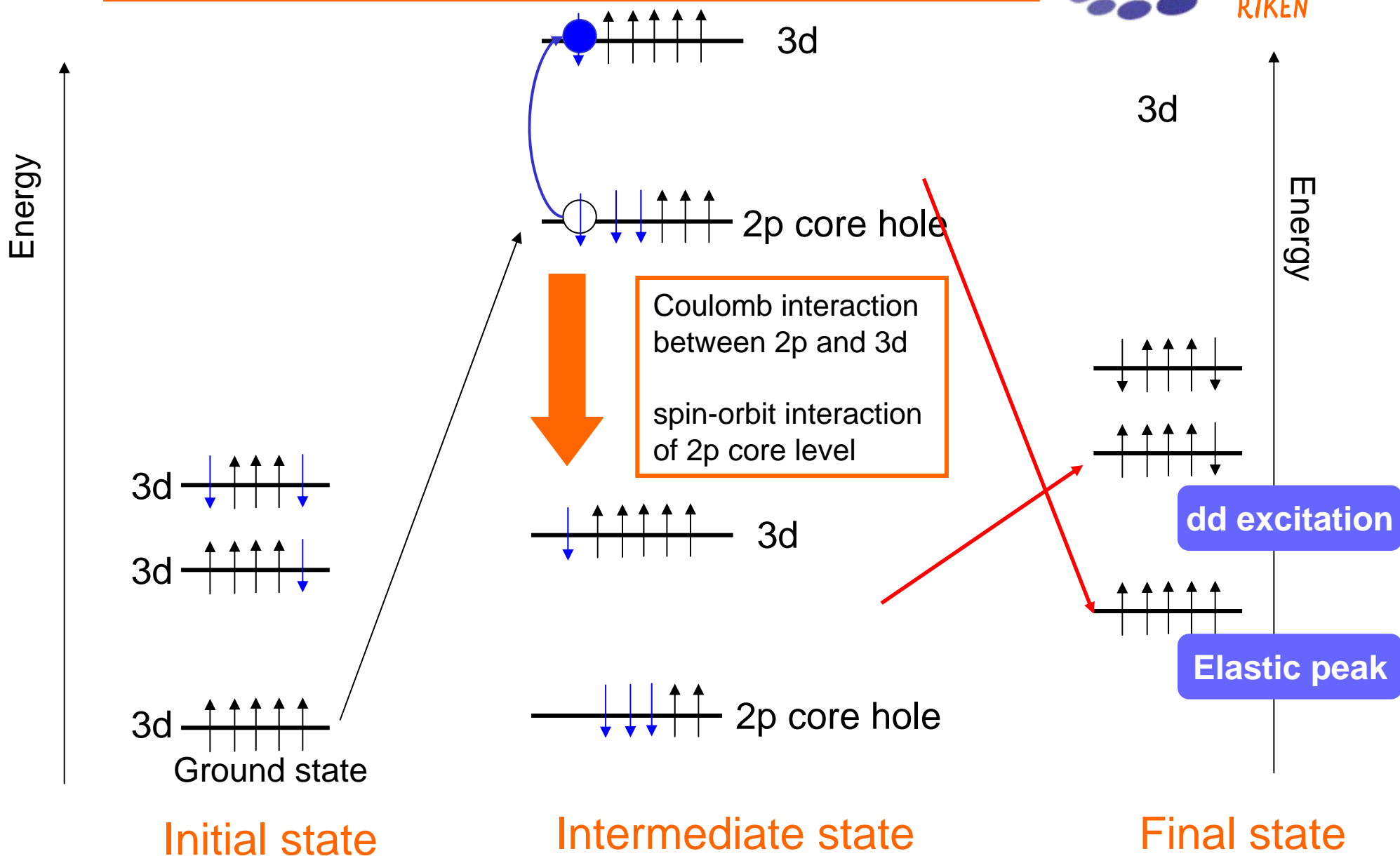
SPring-8 BL27SU c3 station

CCD Detector with super-resolution reconstruction

Cylindrical VLS Grating

750mm

450mm

m

Slit-less
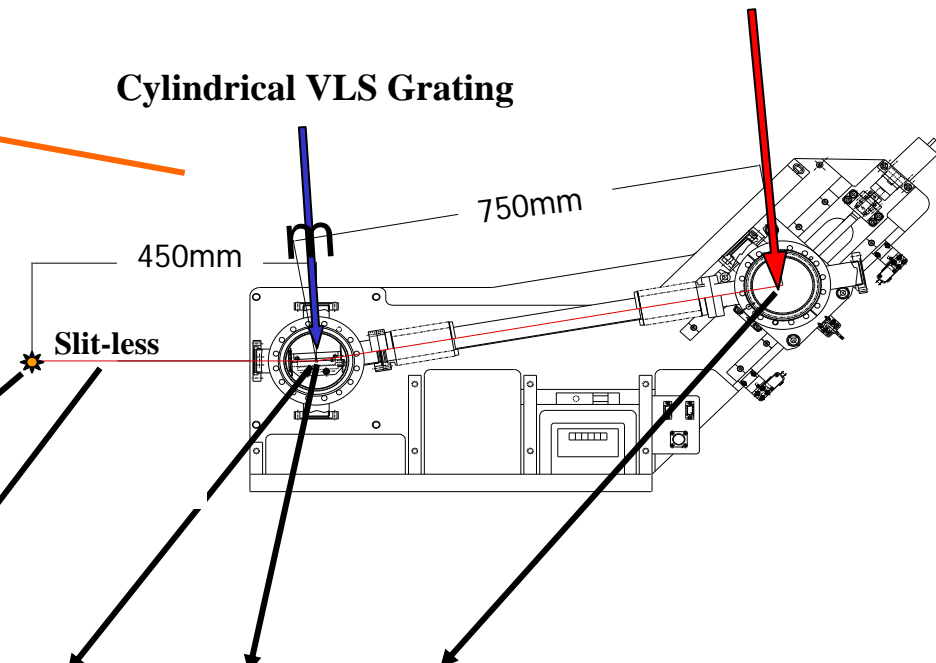
	Mount type	Spot size (μm)	Slit width (μm)	Lines/mm & α (deg.)	Radius (mm)	Detector type	Resolution(eV) @ Fe 2p edge
BL27SU	Flat Field type	7~10	None	Valid line 2200 & 87.5	8940	背面照射型 CCD(2k x 2k)	0.6

3. RXES Experiments in CuFeS$_2$

- XES experiments: using a synchrotron radiation beam line BL27SU at SPring-8.
 The spectrometer employed in this study: a specially designed flat-field-type slit-less type.

- The energy resolution of the incident and detected photons at the Fe 2p edge was 0.2 eV and 1.0 eV, respectively.

- Incident X-rays with two nonequivalent polarization conditions were used: vertically polarized X-rays, where the polarization vector of which are included in emitted photons, and horizontally polarized X-rays that have polarization vectors perpendicular to those in emitted photons.

- The XES spectra: 693 –715 eV
  Incident photon energy: fixed at 710 eV,
  which is 2eV above the reported position of the XAS peak to reduce overlap of the lower end of the intense elastic scattering with the d-d multiplet peaks.

Polarization dependence

**depolarized** and **polarized** configurations for the XES measurement
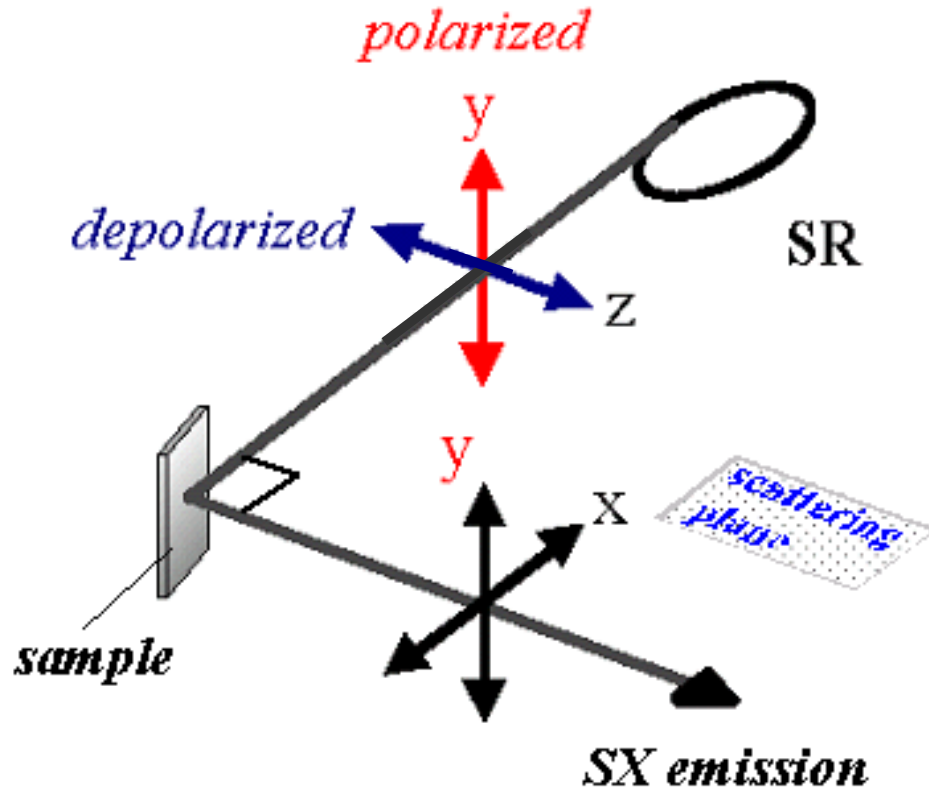
'depolarized' configuration polarization vector of the incident photon is NOT included in detected photons

'polarized' configuration polarization vector of the incident photon is included in detected photons

XAS in CuFeS$_2$

Previous XAS experiment : Y. Mikhlin et al., J. Electron Spectrosc.
Relat. Phenom. **142**,83 (2005)
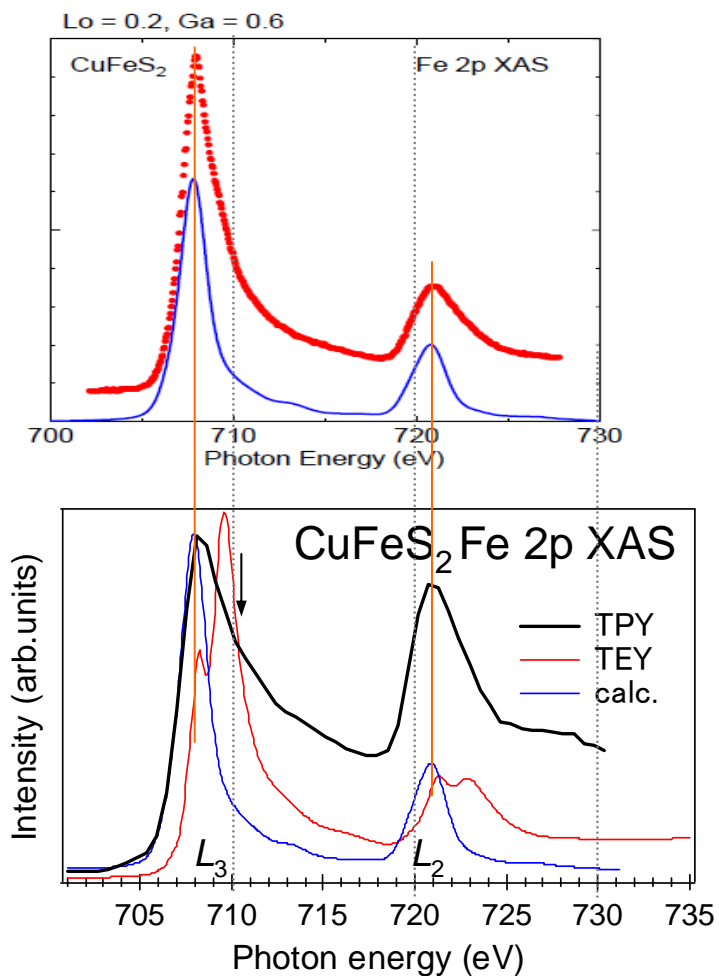
or
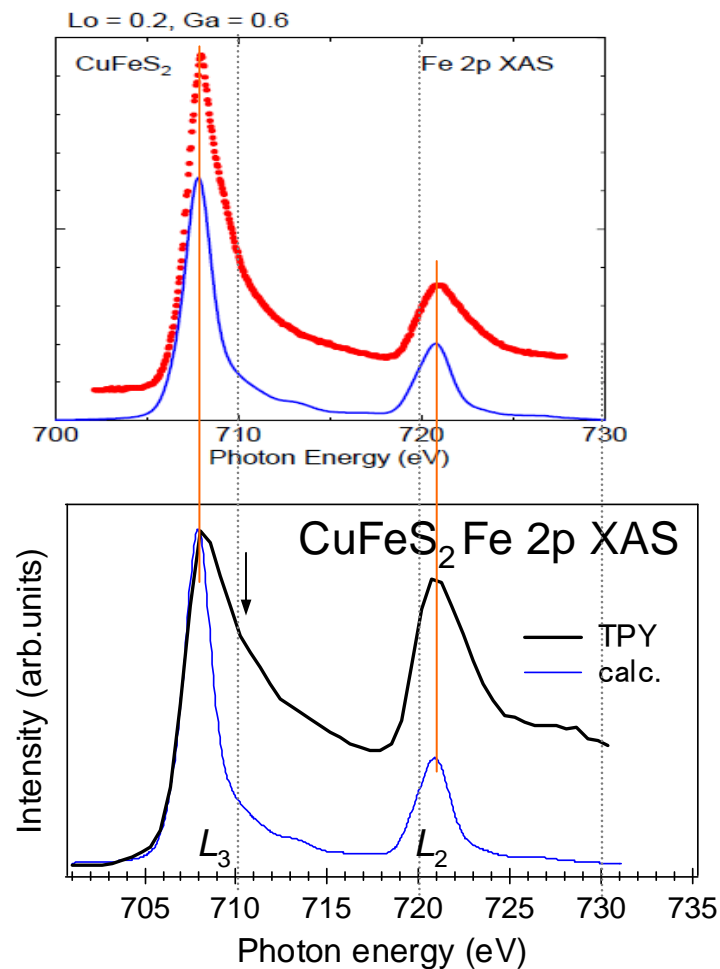
Our work

The raw experimental data

Excitation: 710 eV

CuFeS$_2$ Fe L_3 XES

— horizontal
— vertical

Intensity (arb.units)

Emission energy (eV)
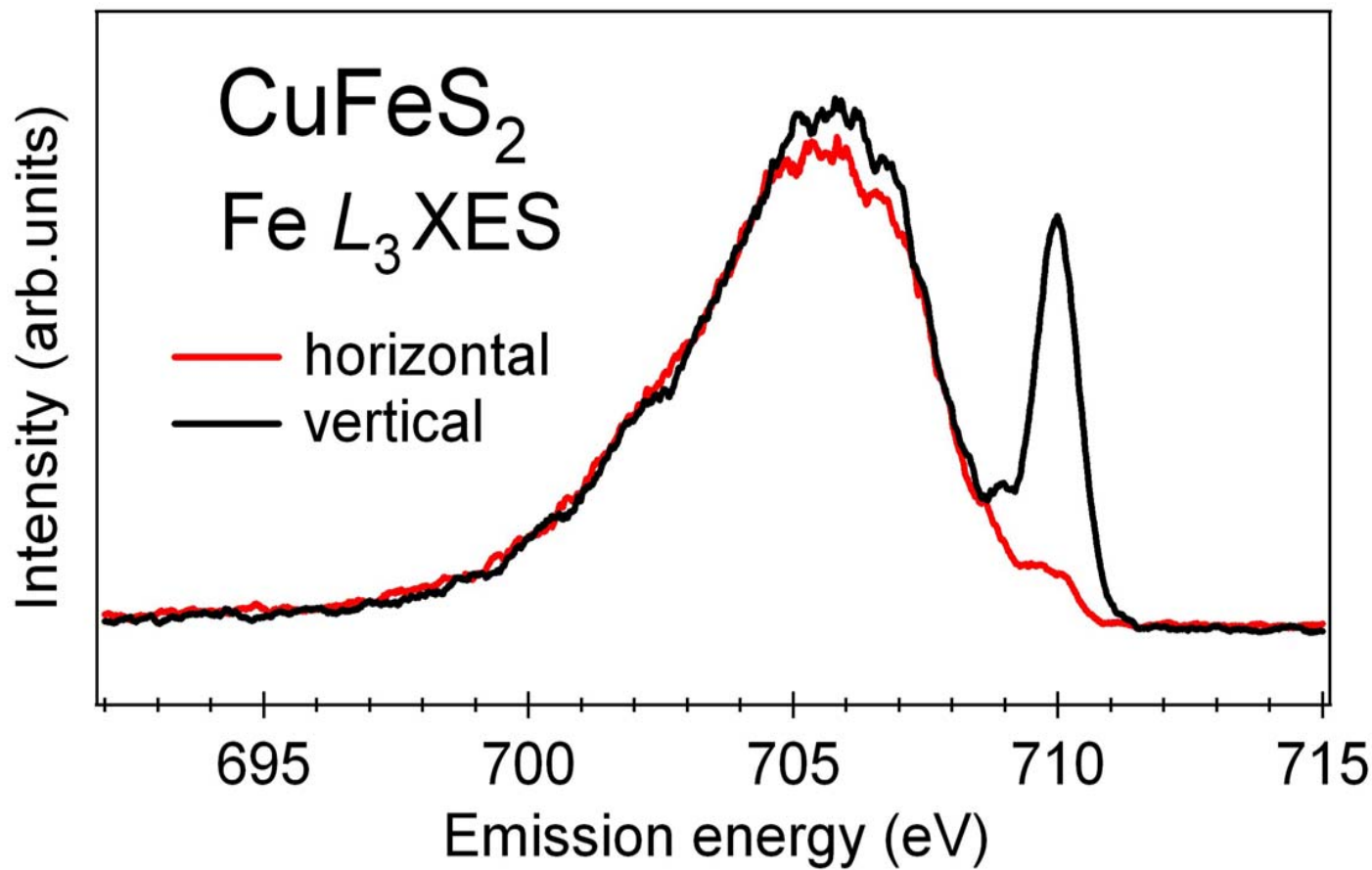
Nonresonant XES spectrum of the Fe L3 edge.

Excitation: 750 nm (off-resonance)
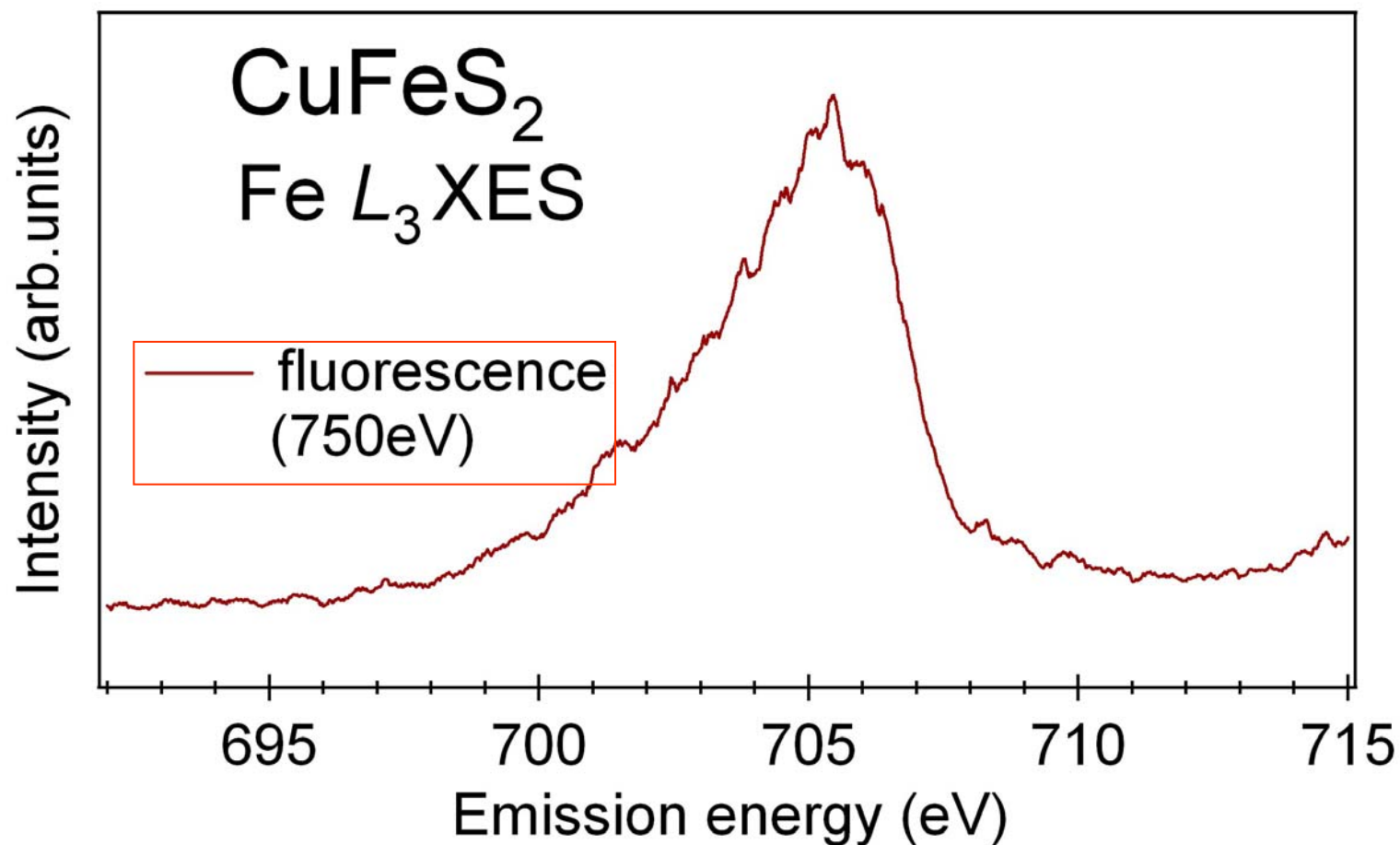
RXES of Fe L_3 edge in $CuFeS_2$ obtained by subtraction of fluorescence from the raw XES data.

4. Analysis of the RXES spectra by cluster-model calculation with a configuration interaction (CI)
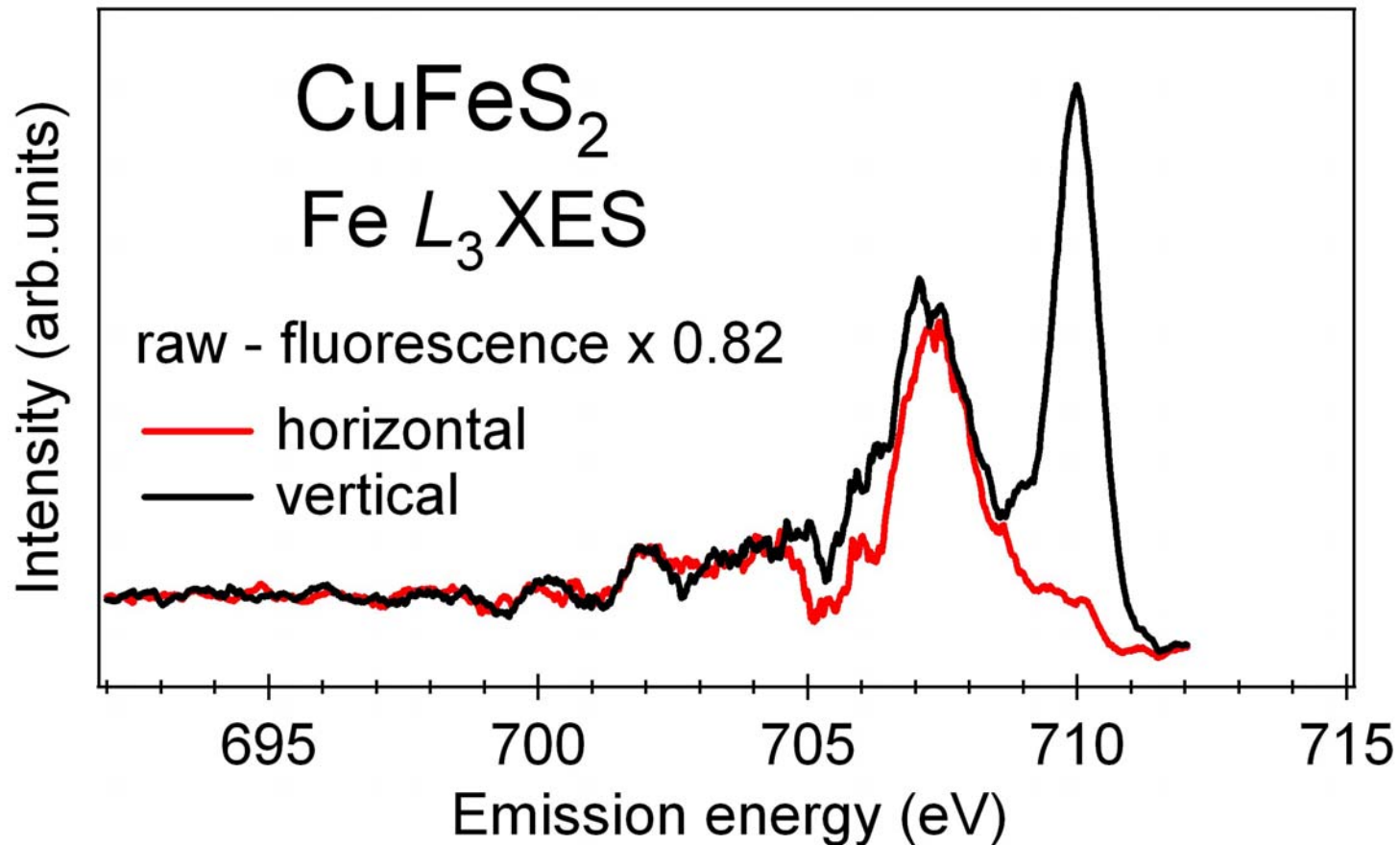
- If a simple ligand-field approach is employed, strongly reduced values of Racah's parameter B and C are necessary to explain the energy position of resonant XES shoulder at 709 eV, and no peaks around 706-707 eV can be predicted.

- Therefore we adopted a full multiplet cluster calculation with configuration interaction (CI) in FeS_4 cluster. The method of calculation is the same as that described elsewhere.
  -M. Taguchi, P. Krüger, J. C. Parlchas, and A. Kotani, Phys. Rev. B 73, 125404 (2006)

CI model with full multiplet

Parameters

Approximations

(I) Central atom: Fe $3d^5$, $3d^6$
    Neighboring atom: ligand

$V(\Gamma)$: Hybridization

U_{dd} : On-site Coulomb interaction

U_{dc} : Core-hole potential

Δ : Charge transfer energy

Slater Integrals (Racah parameter) are calculated by Hartree-Fock method and are rescaled by 80%
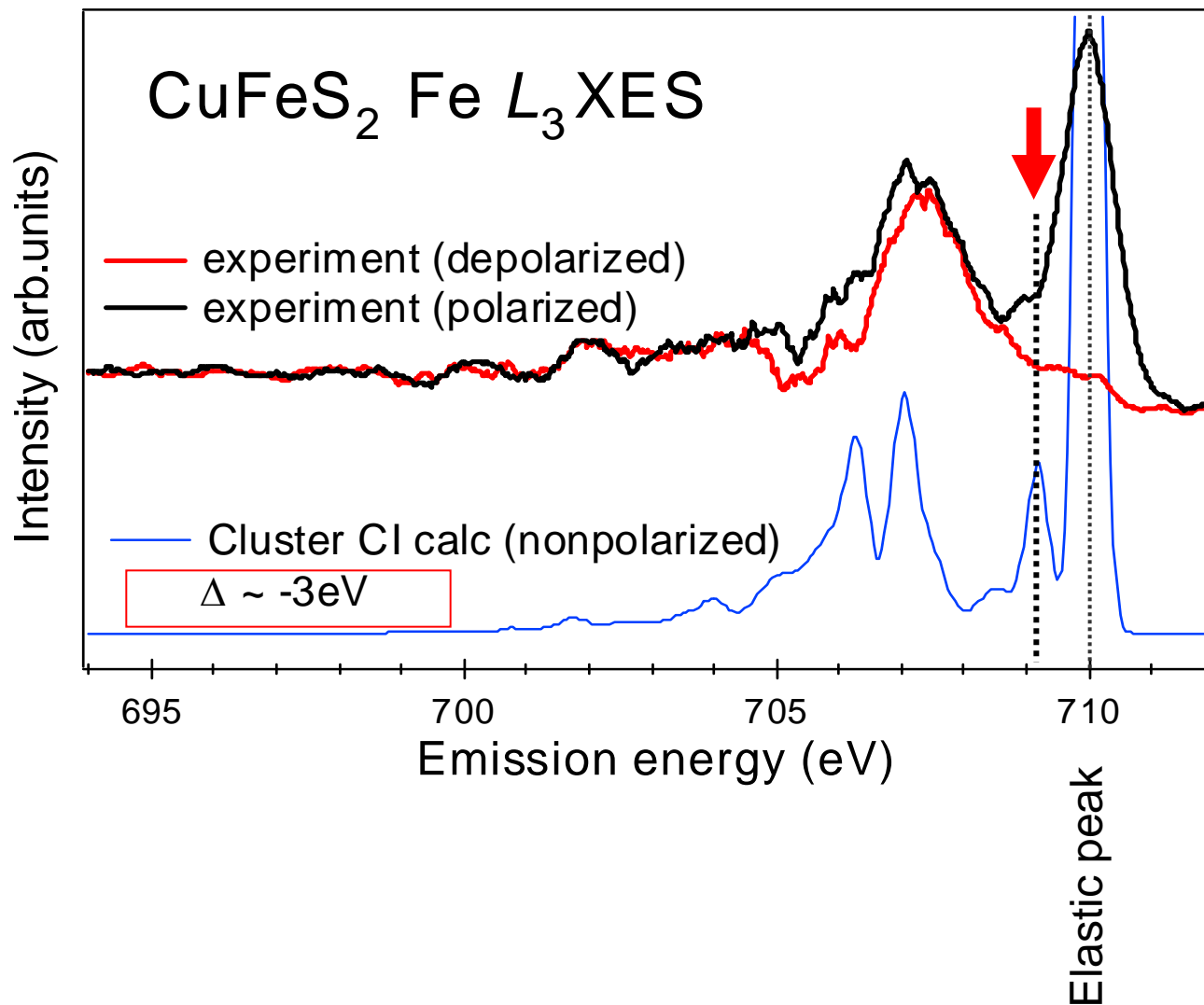
CI model

$$H = \sum_{\Gamma,\sigma} \varepsilon_{3d}(\Gamma) d^\dagger_{\Gamma\sigma} d_{\Gamma\sigma} + \sum_{m,\sigma} \varepsilon_{2p} p^\dagger_{m\sigma} p_{m\sigma} + \sum_{\Gamma,\sigma} \varepsilon_p(\Gamma) a^\dagger_{\Gamma\sigma} a_{\Gamma\sigma}$$

Fe 3d   Fe 2p   ligand

$$+ \sum_{\Gamma,\sigma} V(\Gamma)(d^\dagger_{\Gamma\sigma} a_{\Gamma\sigma} + a^\dagger_{\Gamma\sigma} d_{\Gamma\sigma})$$

Fe3d - ligand charge transfer

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

Fe3d on-site Coulomb interaction

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

Fe 2p-3d core-hole potential

Ground state : linear combination of 3 configurations

$$3d^n \longleftrightarrow 3d^{n+1}\underline{L} \longleftrightarrow 3d^{n+2}\underline{L}^2$$

Experiment and calculation

CuFeS$_2$ Fe L_3 XES

experiment (depolarized)
experiment (polarized)

Cluster CI calc (nonpolarized)

$\Delta \sim -3eV$

Intensity (arb.units)

Emission energy (eV)

Elastic peak
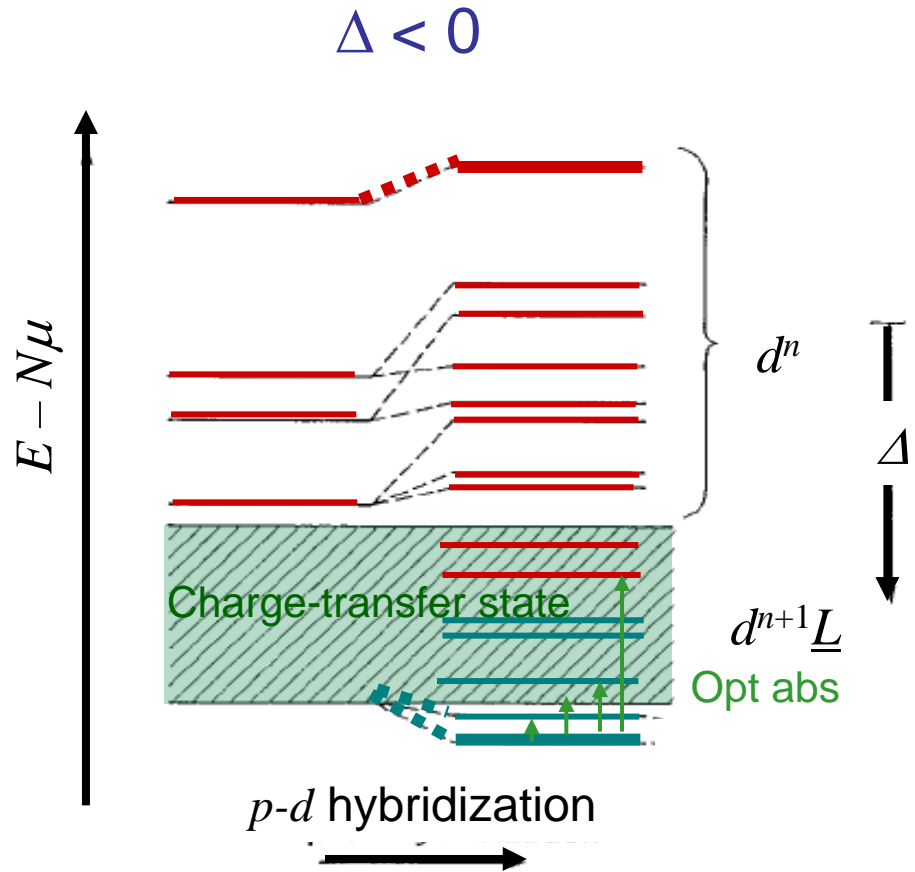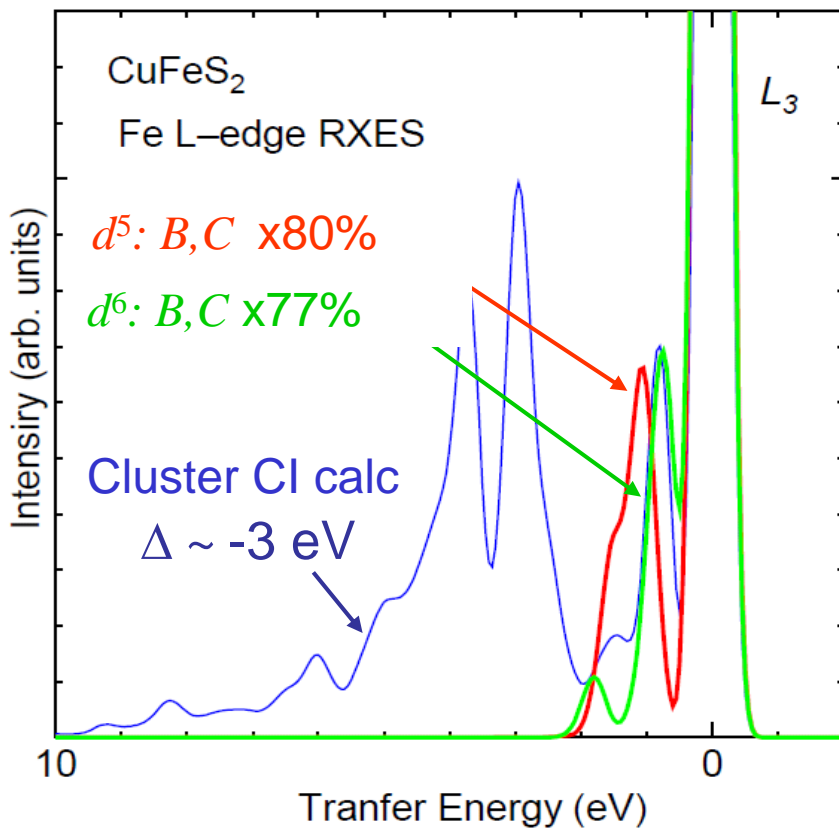
RXES spectra
→ dd excitation

- Parameters: U_{dd}=3.2, Δ=-3.0, U_{dc}=4.0, $V(e_g)$=2.07, $V(t_{2g})$= -1.07, in units of eV.

- The ground state character：
3d^5=22.1%, 3d^6$\underline{L}$=54.6%, and 3d^7$\underline{L}^2$=23.3%.

Energy (eV)

3.0

2.0

1.0

0

$^6T_1$
$^6T_2$
$^4A_2$
$^2E, ^2T_1$
$^6T_1$
$^6T_2$
^4E
$^4T_2$
$^4T_1$
$^6A_1$
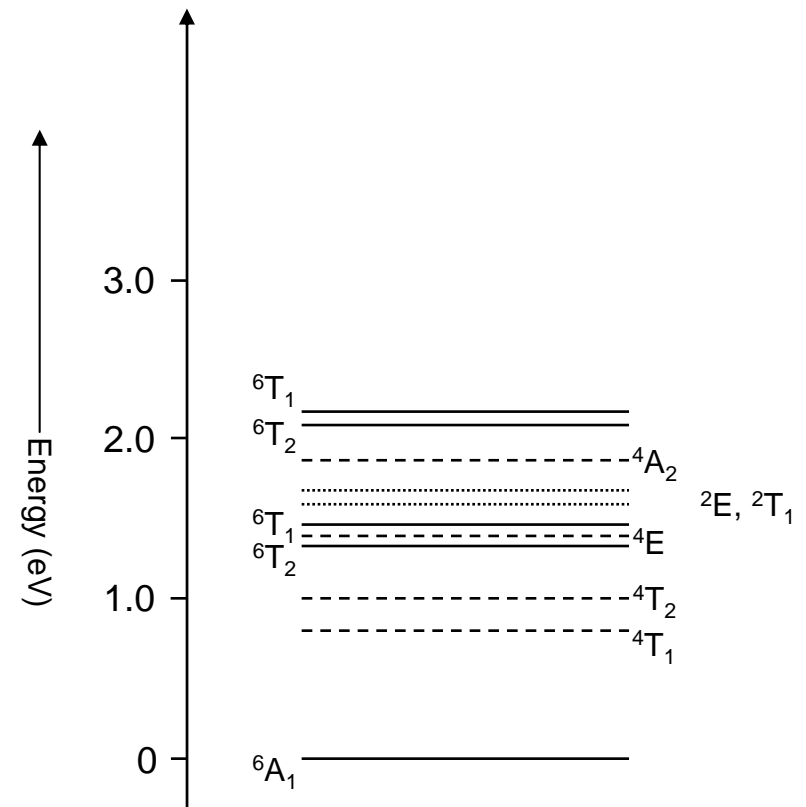
The present study

Unraveling hidden *d-d* transitions by resonant x-ray emission spectroscopy (RXES)

Ligand-field and CI cluster-model calcs

$\Delta < 0$

CuFeS$_2$

Fe L–edge RXES

L_3

d^5: B,C x80%

d^6: B,C x77%

Cluster CI calc

$\Delta \sim$ -3 eV

Intensiry (arb. units)

10   0

Tranfer Energy (eV)

$E - N\mu$

d^n

Δ

Charge-transfer state

$d^{n+1}\underline{L}$

Opt abs

p-d hybridization

Low energy transitions explained?

- Yes!
- Due to strong hybridization, the ground states of Fe 3d are no more a pure d states but are consisting of 80% charge transferred states, leading to a negative Δ situation.

Similarity to hemoprotein problems

- The problems of the electronic states of Fe in $CuFeS_2$ gives much insight to the electronic states of Fe in hemoprotein, since a negative or very small value of Δ is also found in the latter [*], which results in interesting physical properties such as the spin cross-over.
  - Y. Harada, M. Taguchi, Y. Miyajima, T. Tokushima, Y. Horikawa, A. Chainani, Y. Shiro, Y. Senba, H. Ohashi, H. Fukuyama, S. Shin, submitted to Nature.

Summary

- Resonant X-ray emission spectroscopy has been carried out on Fe L3 edge of $CuFeS_2$. The experimental spectrum was compared with theoretical one obtained by cluster CI calculation, from which it is found that the previous assignments of the optical absorption are consistent with that of resonant XES.

- The spectral details are successfully explained by assuming that the charge transfer energy Δ takes a negative value. This result is consistent with the previous consideration that $CuFeS_2$ is a Haldane-Anderson type insulator.

- The strong hybridization is found to be a dominant cause of the mysterious 3d electron behaviours in this material.

Acknowledgment

Thank you for kind attention.

Brandenburger Tor
2008.9.18

Katsuaki