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# Magnetic Circular Dichroism in X-ray Fluorescence

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# Collaborators

Theory : T. Uozumi (Osaka Pref. University)

Instrumentation (New spectrometer) :
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Sample (Electrical steel) :
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Y. Sakaguchi (JFE-TEC)
S. Takahashi (JFE-TEC)

# Fluorescence X-rays

X-ray fluorescence has a long history. It has been widely used as an excellent analytical tool.

You may think that there is nothing to explore in x-ray florescence , nothing interesting in x-ray fluorescence.

The state of a photon is described by its energy (wave length), direction of propagation, and polarization.

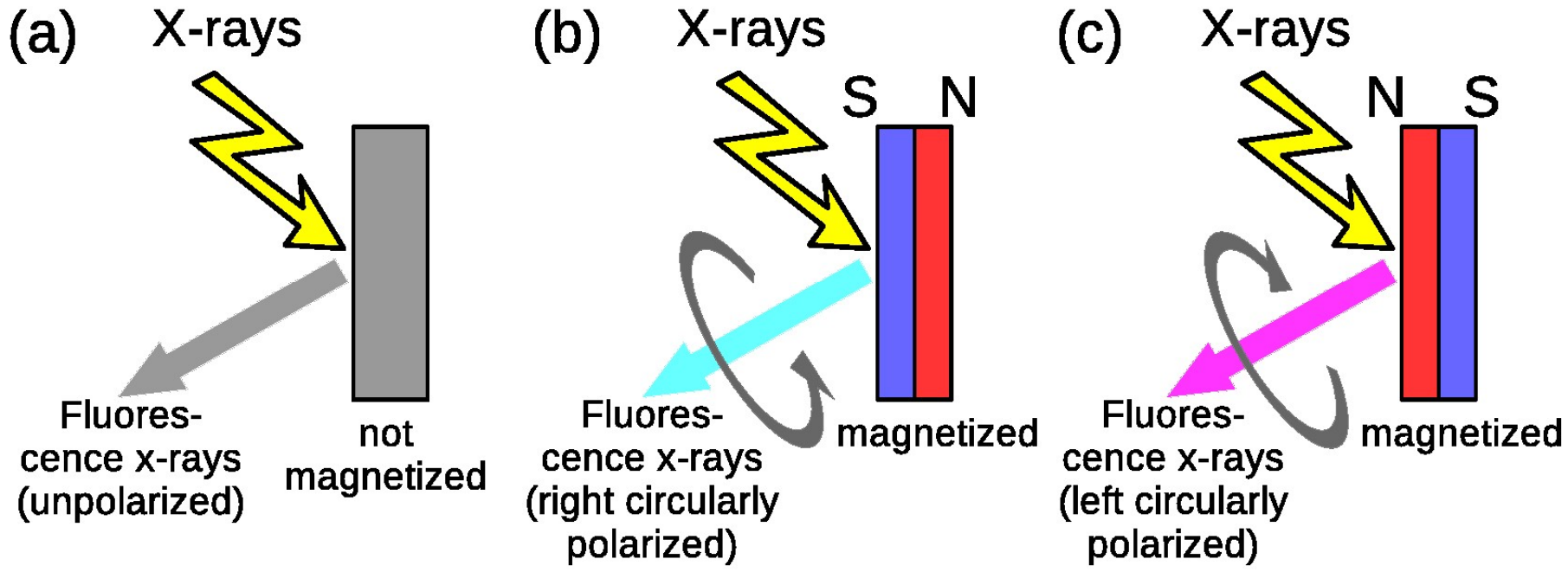
It seems that the last property of fluorescence x-rays has not been investigated in detail so far.

In this study, I measured the circular polarization of $K\alpha$ emission of Iron and obtained very new results.

# X-ray magnetic circularly polarized emission (XMCPE)

## New magnetooptical effect in the x-ray region

T. Inami, Phys. Rev. Lett. **119** 137203 (2017).




(i) Magnetic circular dichroism exists in x-ray emission.
(ii) Large circular polarization (12%) at the Fe *Kα* emission.

# Outline

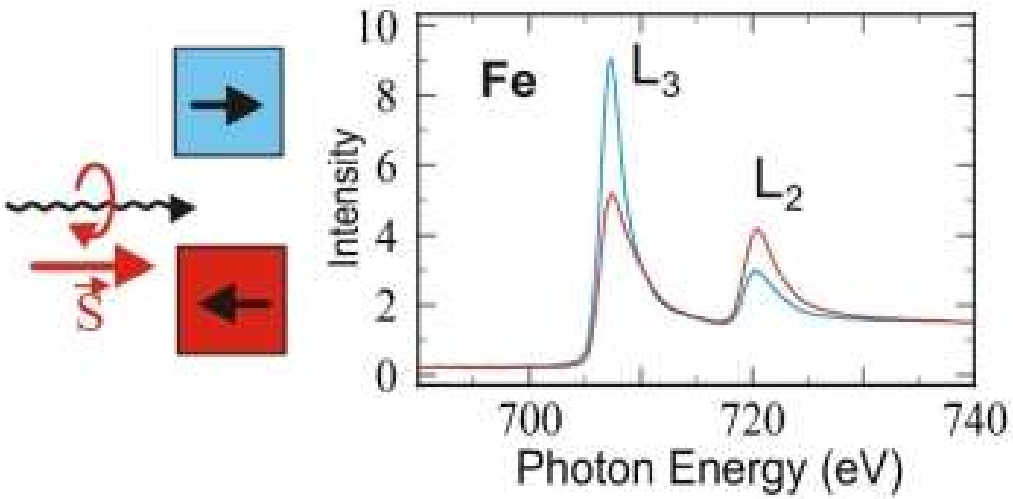
- Introduction
- ➢ Motivation
- Spectrometer & Experimental results
- XMCPE in other emissions (multiplet calculations)
- Domain observation (magnetic microscope)
- Summary

# Motivation

Synchrotron x-ray based magnetic measurements :

(non-)resonant x-ray magnetic diffraction,
magnetic Compton scattering,
x-ray magnetic circular dichroism (XMCD),
XMCD photoemission electron microscopy, etc.

XMCD: standard tool




www-ssrl.slac.stanford.edu/stohr/xmcd.htm

Element selective, highly sensitive (small samples and small moments), magnetooptical sum rules are applicable for several edges, etc.

# Motivation

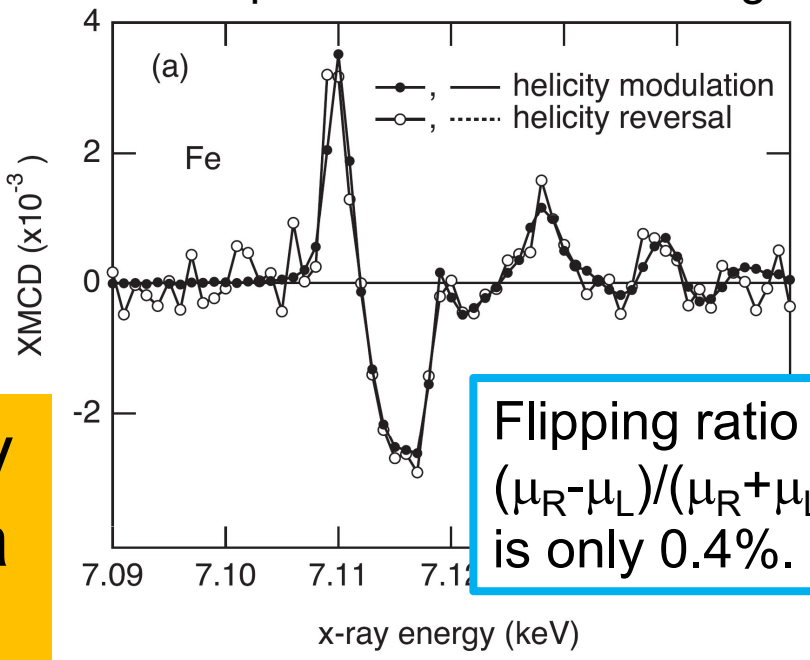
XMCD in the hard x-ray region :

☺ Long penetration depth. Bulk sensitive. (~10μm)

☹ Insensitive to 3d transition metals (Fe, Co, Ni, etc). (< 0.5%)

A new magnetic spectroscopy in the hard x-ray region with a large dichroic effect for 3d TMs is necessary.

XMCD spectrum at the Fe *K*-edge.




Flipping ratio $(\mu_R-\mu_L)/(\mu_R+\mu_L)$ is only 0.4%.

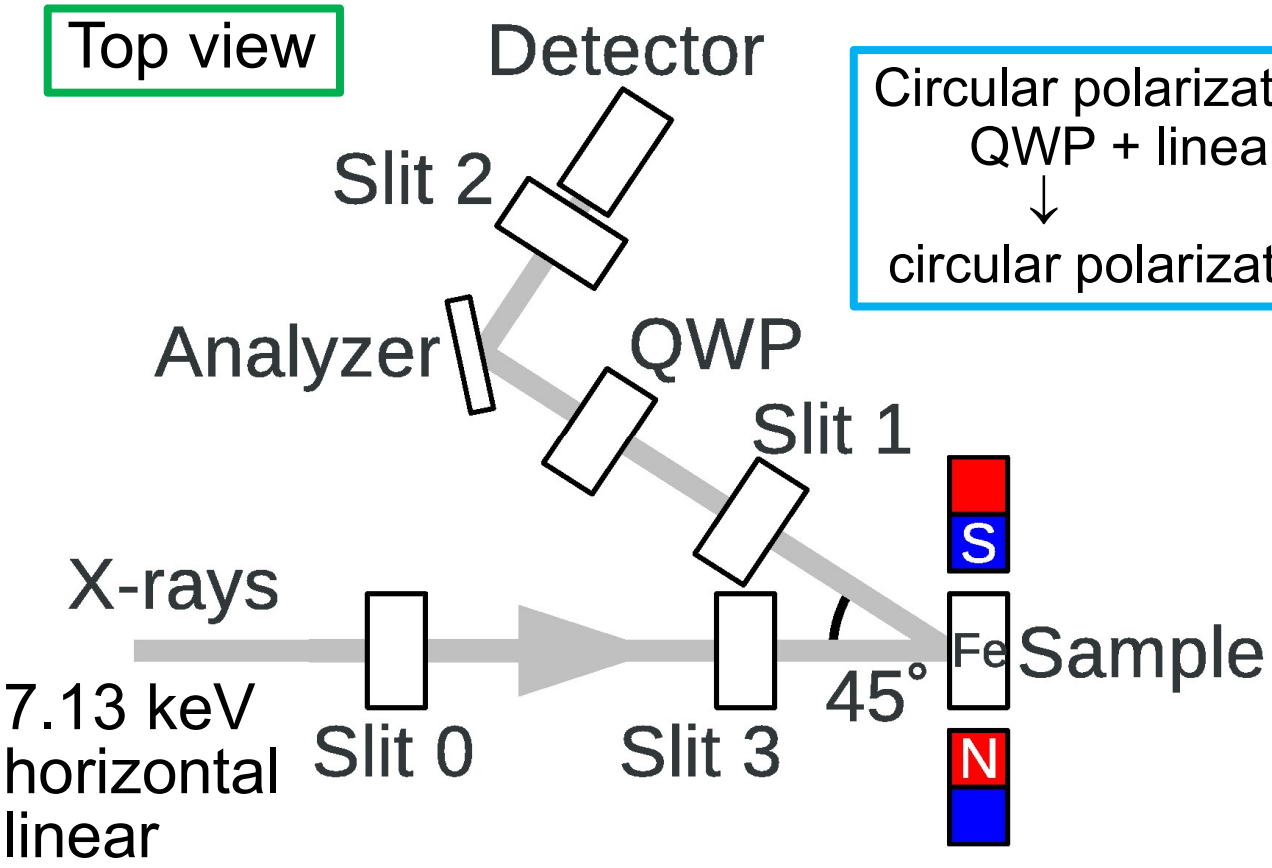
T. Nakamura and M. Suzuki, JPSJ 82 021006 (2013)

Fe *Kα* emission must be circularly polarized and exhibit MCD!!

# Contents

# Spectrometer

## Fluorescence spectrometer with circular polarization analysis




Circular polarization analyzer =
QWP + linear polarization analyzer
↓
circular polarization ↔ linear polarization

Crystal optics require well collimated x-rays.
Slit1 – sample : 60 cm
Slit1 75 μm X 75 μm
Slit3 100 μm X 75 μm

- QWP (phase retarder) : 0.5 mm thick diamond single crystal
- Analyzer (linear polarization and energy analyzer) :
  Ge (400) single crystal, $2\theta$=86.4°

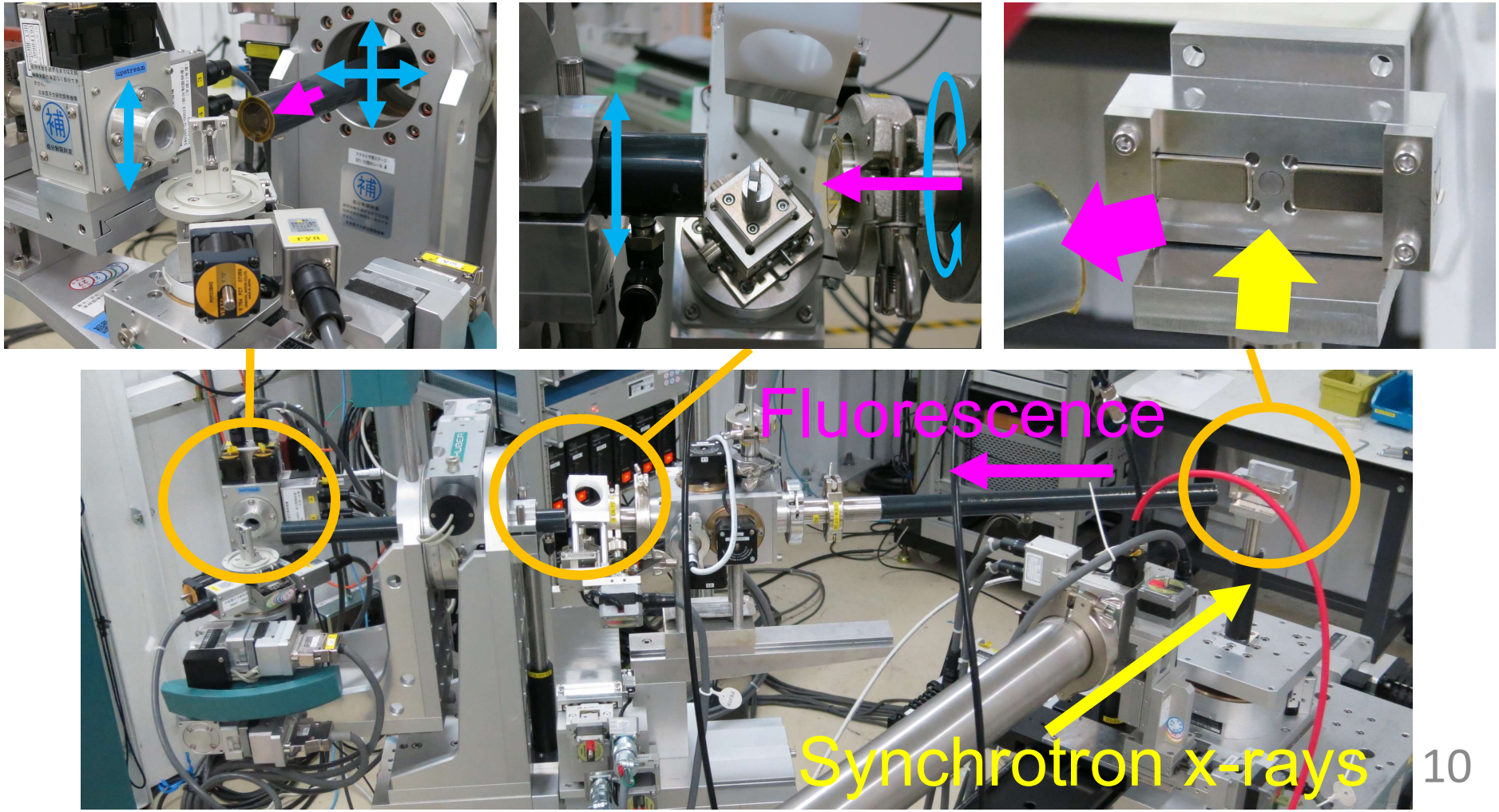
# Spectrometer

SPring-8 BL22XU

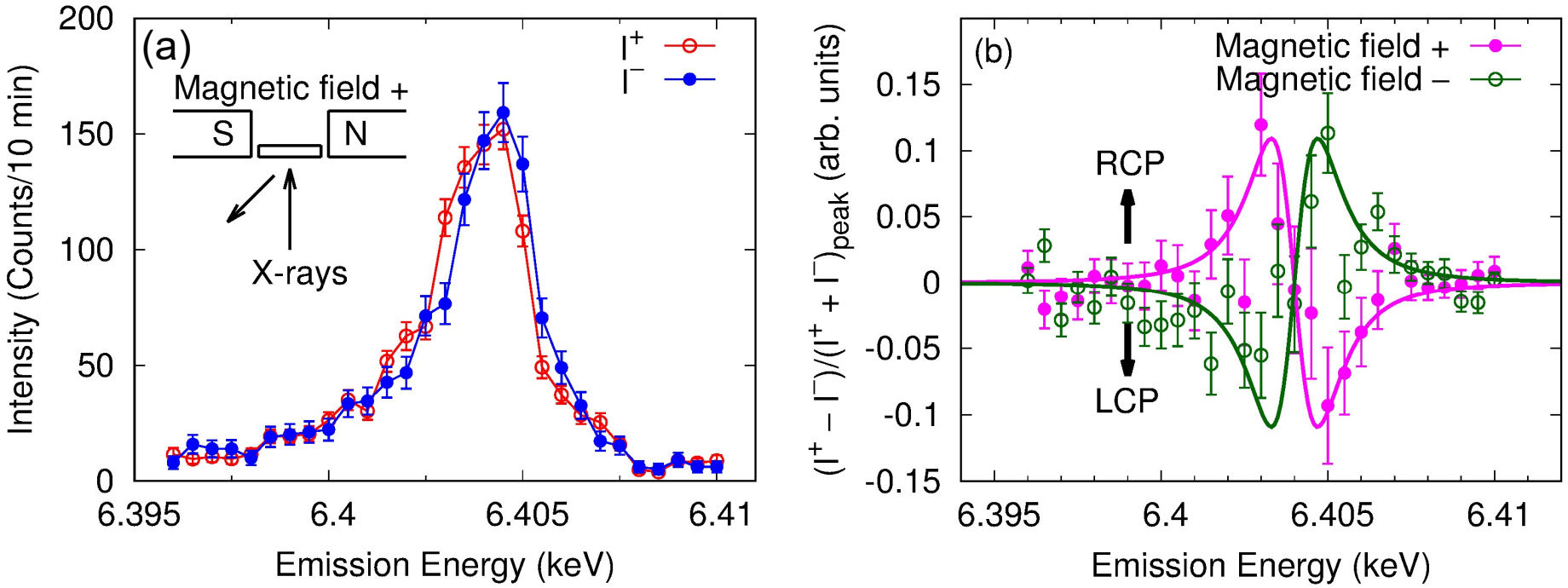
Analyzer

Phase retarder

Sample (Fe)



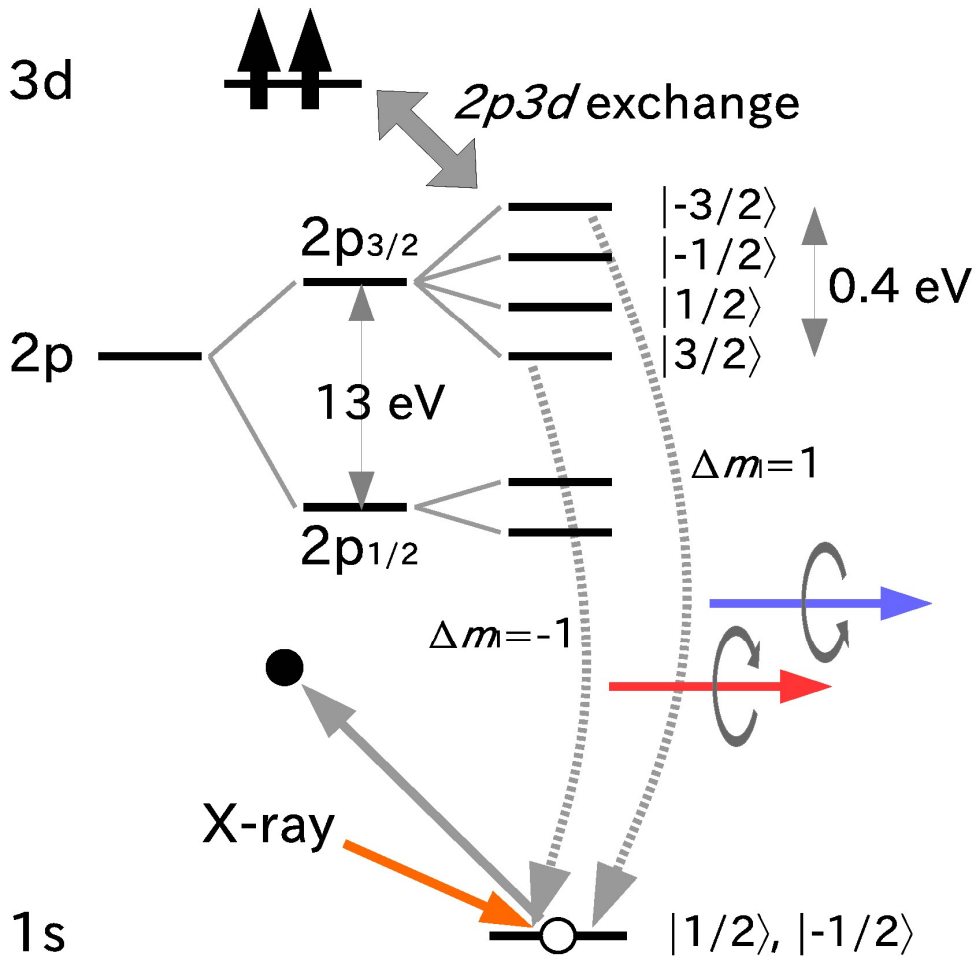
# Experimental results




(a) Iron $K\alpha_1$ fluorescence spectra $I^+$ and $I^-$, measured at configurations sensitive to right- and left-circularly polarized x-rays, respectively. $I^+ = I_0(1+P_C)/2$, $I^- = I_0(1-P_C)/2$, $I_0 = I^+ + I^-$, $P_C$: degree of circular polarization. The $I^+$ spectrum is shifted to the low energy side by about 0.3 eV.

(b) The difference spectra $I^+$-$I^-$ normalized by the peak intensity. The ordinate is approximately $P_C$. The sign of $P_C$ is inverted when the magnetization is inverted. The largest $P_C$ ~12%.

# Qualitative interpretation




1. An incident x-ray photon creates a 1s core hole.
2. A fluorescence x-ray is emitted when a 2p electron occupies the 1s core hole.
3. The final $2p^5$ state splits into a $2p_{3/2}$ quartet and a $2p_{1/2}$ doublet because of large spin-orbit coupling.
4. The 2p3d exchange interaction further splits these multiplets when a magnetic moment exists in the 3d orbital, producing spin polarization.
5. Because of the large spin-orbit coupling, the spin polarization results in the orbital polarization, which is the origin of circularly polarized x-rays.

# Contents

# XMCPE at other emissions

XMCPE is expected at many emission lines.

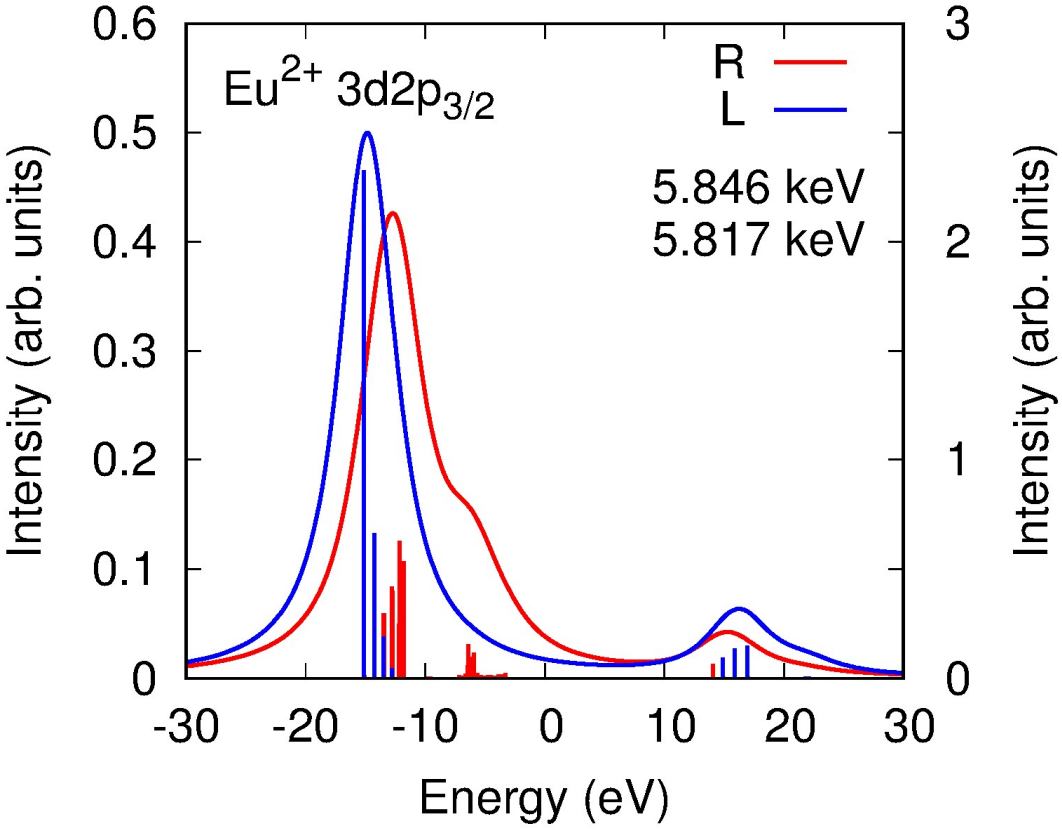
L: Large, M: Moderate, S: Small, N: Nothing

- 3d transition metal
  3p→1s (S)
  3p→2s (S), 3s→2p (N), 3d→2p (?)
- 4f rare earth
  3d→2p (L), 4d→2p (L), 3p→1s (M)
  4p→3s (S), 4d→3p (L), 4f→3d (?)
- 5d transition metal
  4p→2s (?), 4d→2p (?)

# Multiplet calculation ($L\alpha_{1,2}$)

A program developed by Uozumi was used.

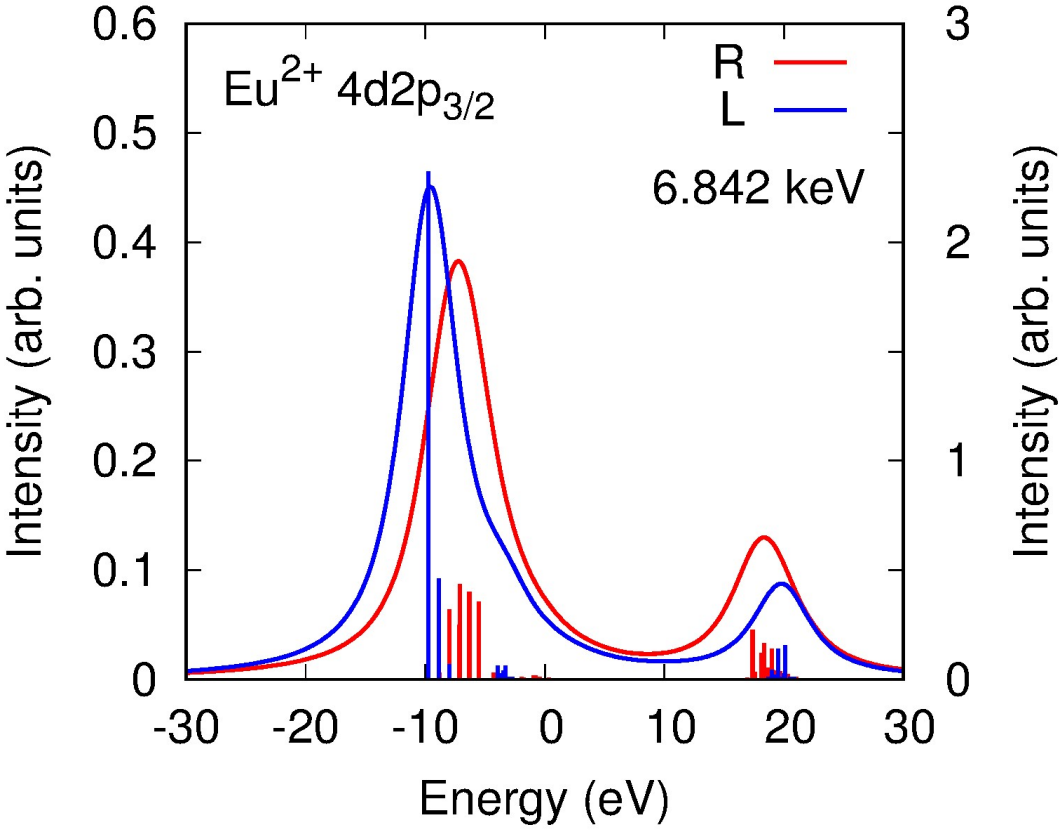
| | |
|---|---|
| Ionic state | $4f^7$ ($Eu^{2+}$) |
| SO3 | |
| Slater integrals | 80% |
| SO (core, valence) | 100% |
| M | 10 meV |
| Lorentzian (FWHM) | 5.0 eV |
| Gaussian (FWHM) | 1.5 eV |



# Multiplet calculation ($L\beta_{15,2}$)

Uozumi program was used.

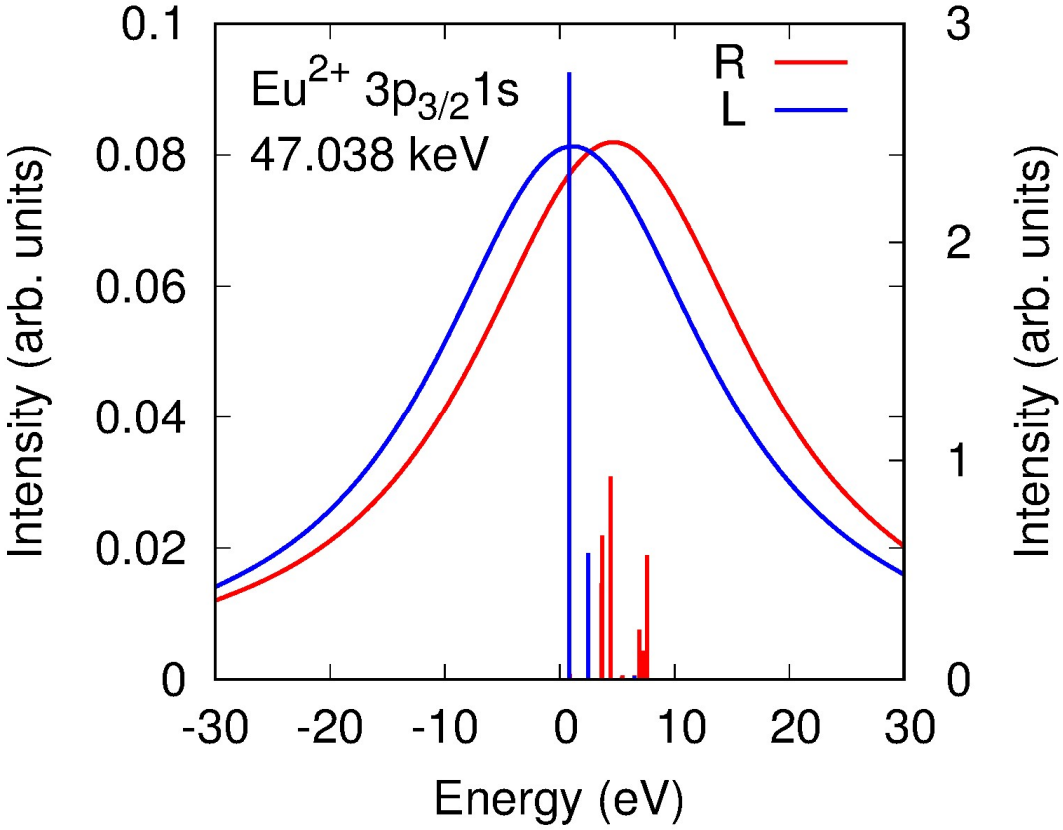
| | |
|---|---|
| Ionic state | $4f^7$ ($Eu^{2+}$) |
| SO3 | |
| Slater integrals | 80% |
| SO (core, valence) | 100% |
| M | 10 meV |
| Lorentzian (FWHM) | 5.0 eV |
| Gaussian (FWHM) | 1.5 eV |



# Multiplet calculation ($K\beta_1$)

Uozumi program was used.

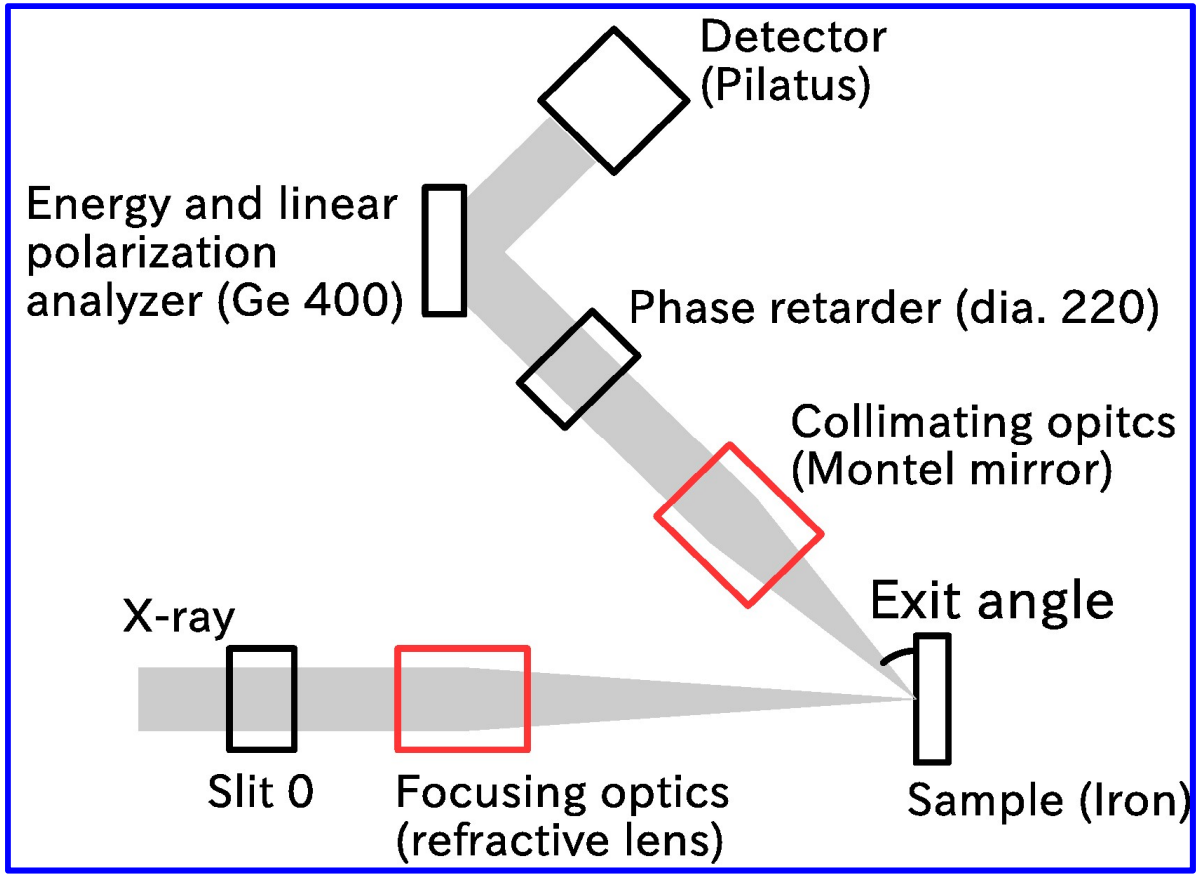
| | |
|---|---|
| Ionic state | $4f^7$ ($Eu^{2+}$) |
| SO3 | |
| Slater integrals | 80% |
| SO (core, valence) | 100% |
| M | 10 meV |
| Lorentzian (FWHM) | 28 eV |
| Gaussian (FWHM) | 5 eV |



# Contents

# SR XMCPE Microscope

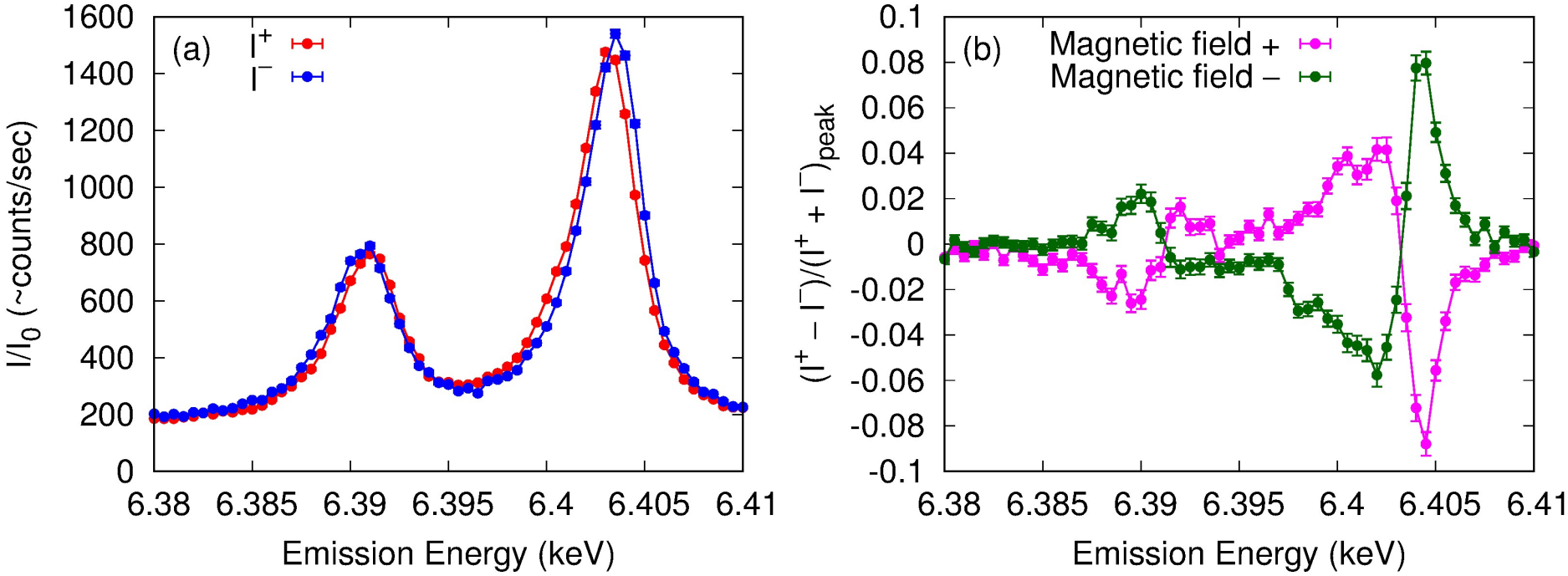
1. Focusing optics for small lateral resolution (refractive lens, 10 μm)
2. Collimating optics for large solid angle (Montel mirror, 21 mrad × 21 mrad)




SPring-8 BL11XU

JTEC & INCOATEC
Laterally graded Ni/C
multi layer mirror

# New spectra

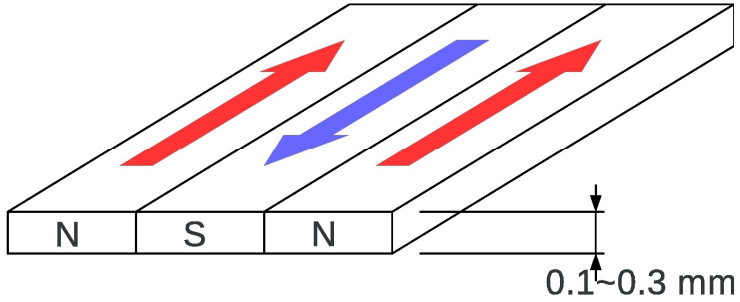



(a) Iron $K\alpha_{1,2}$ fluorescence spectra $I^+$ and $I^-$. The statistics is much improved. Background must be decreased.

(b) The difference spectra ($I^+$- $I^-$) normalized by the peak intensity.

# Electrical steel

Grain oriented electrical steel is a functional material used as magnetic cores in transformers.




Basic magnetic domains are stripe domains.


We measured an electrical steel sheet, because ...

1. Large magnetic domains.
2. Only the 3*d* transition metal atoms carry magnetic moments.
3. Observation of magnetic domains well below the surface (and under the coating) is required.

# Domain Observation

A map of the flipping ratio $(I^+-I^-)/(I^++I^-)$ measured at 6.405 keV. Basic stripe domains and several lancet domains are clearly discernible. Step sizes are 30μm (Z) and 65 μm (X). 101 × 53 points. The observation time is 4 sec/point. The incident x-ray energy was 17.3 keV. The exit angle was 45°.

# Summary

- The degree of the circular polarization ($P_C$) of the $K\alpha_{1,2}$ fluorescence line is measured on metallic iron.
- It is found that (i) the $K\alpha_{1,2}$ spectrum of magnetized iron exhibits finite circular polarization
- And that (ii) the sing of the circular polarization is inverted when the magnetization of the sample is inverted.
- These results indicate that magnetic circular dichroism exists in x-ray emission. Discovery of XMCPE.
- A measure of $2p3d$ exchange. Indirect measurement.
- The observed $P_C$ is 12% and will amount to 18% after corrections. This large value is comparable to flipping ratios in soft x-ray MCD (~30%).
- A preliminary result on XMCPE microscope is presented.
- Large XMCPE signals are expected at various emission lines.

# Acknowledgement

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# Thank you for your attention.