Magnetic Circular Dichroism in X-ray Fluorescence

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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.
(i) Magnetic circular dichroism exists in x-ray emission.
(ii) Large circular polarization (12%) at the Fe $K\alpha$ emission.
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  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

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

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

XMCD in the hard x-ray region:

😊 Long penetration depth. Bulk sensitive. (~10\(\mu\)m)
😊 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.

Fe \(K_{\alpha}\) emission must be circularly polarized and exhibit MCD!!

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

\[\text{XMCD spectrum at the Fe } K\text{-edge.}\]

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

Fluorescence spectrometer with circular polarization analysis

Top view

- X-rays 7.13 keV horizontal linear
- Slit 0
- QWP
- Slit 1
- Analyzer
- Slit 2
- Detector
- Sample

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, 2θ=86.4°
Spectrometer

Analyzer     Phase retarder     Sample (Fe)

Synchrotron x-rays  Fluorescence

SPring-8 BL22XU
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 $P_C \sim 12\%$.
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.
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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  (?)
A program developed by Uozumi was used.

Ionic state: $4f^7$ ($\text{Eu}^{2+}$)
SO: $3\sigma$
Slater integrals: 80%
SO (core, valence): 100%
M: 10 meV
Lorentzian: 5.0 eV (FWHM)
Gaussian: 1.5 eV (FWHM)
Multiplet calculation \((L^{\beta}_{15,2})\)

Uozumi program was used.

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

Eu\(^{2+}\) 4d\(2p_{3/2}\)

6.842 keV
Multiplet calculation \((K\beta_1)\)

Uozumi program was used.

Ionic state \(4f^7 (\text{Eu}^{2+})\)
SO3
Slater integrals 80%
SO (core, valence) 100%
M 10 meV
Lorentzian 28 eV
(FWHM)
Gaussian 5 eV
(FWHM)
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1. Focusing optics for small lateral resolution (refractive lens, 10 μm)
2. Collimating optics for large solid angle (Montel mirror, 21 mrad × 21 mrad)
(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 3d transition metal atoms carry magnetic moments.
3. Observation of magnetic domains well below the surface (and under the coating) is required.
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 30\(\mu\)m (Z) and 65 \(\mu\)m (X). 101 \(\times\) 53 points. The observation time is 4 sec/point. The incident x-ray energy was 17.3 keV. The exit angle was 45\(^\circ\).
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 sign 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.
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