The Hitchhiker Guide to

X-ray Dichroism

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Hands on spectroscopy calculations of quantum material

12 Oct. 2022
Heidelberg

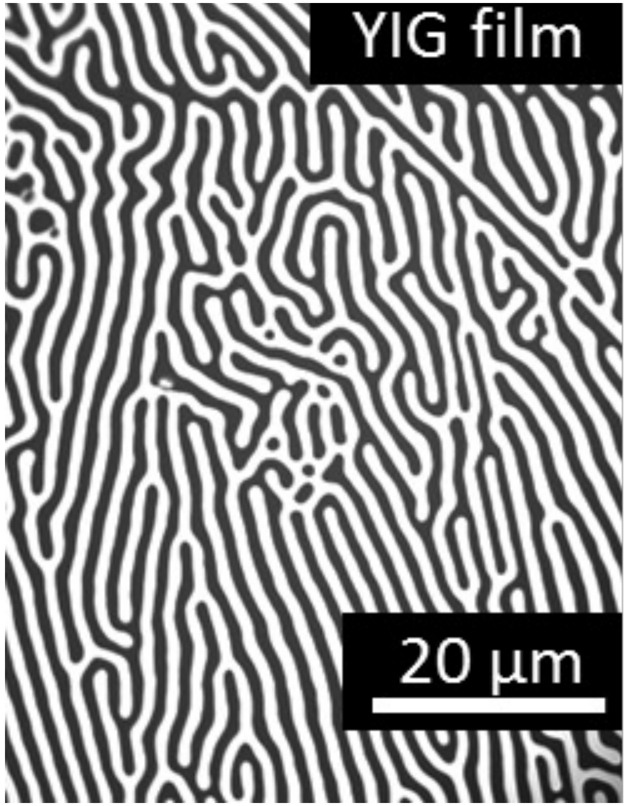
Dichroism

Dichroism:

Dependence of the absorption measured with **two orthogonal polarization** states of the incoming light

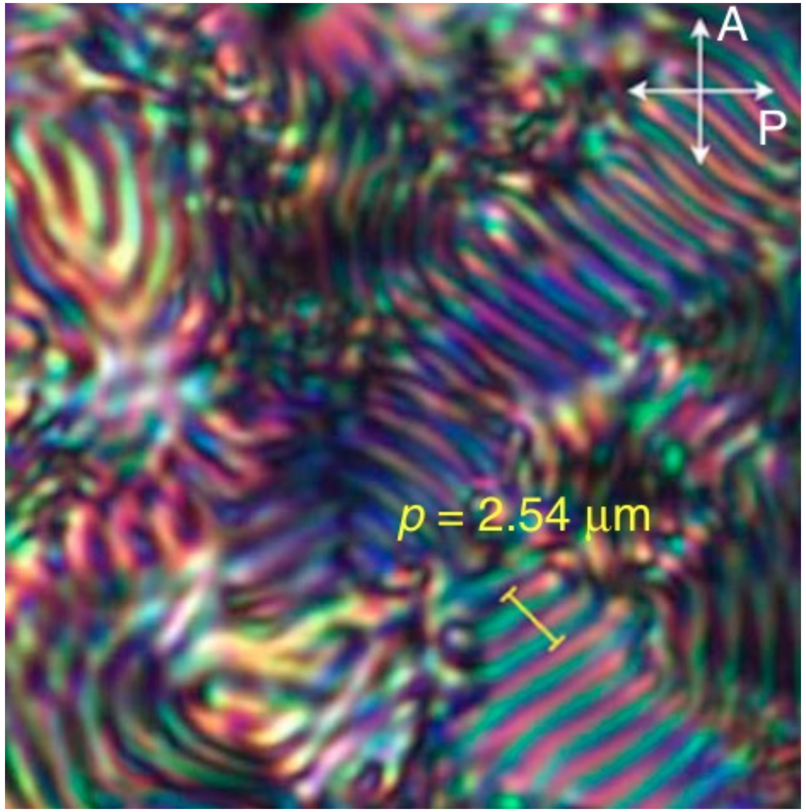
Optical Dichroism

Magnetic domains

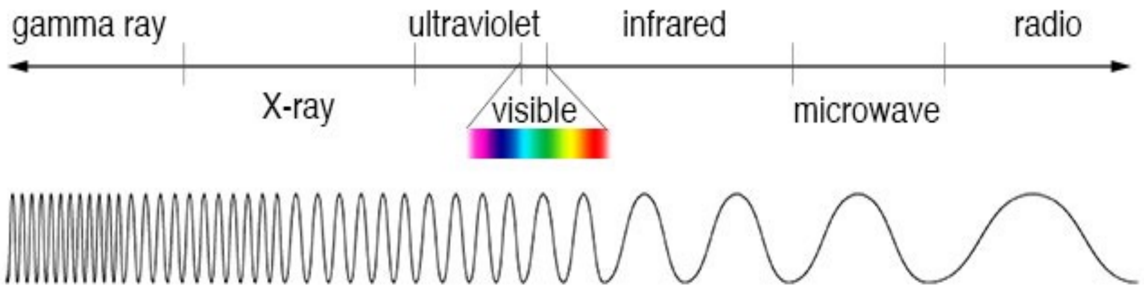


Phase contrast

Liquid crystals



X-ray Dichroism



Measurement:

Linear Dichroism (LD): Difference measured with **LH / LV**

Circular Dichroism (CD): Difference measured with **CR / CL**

Origin:

Magnetic Dichroism (MD): Difference in **magnetic** system

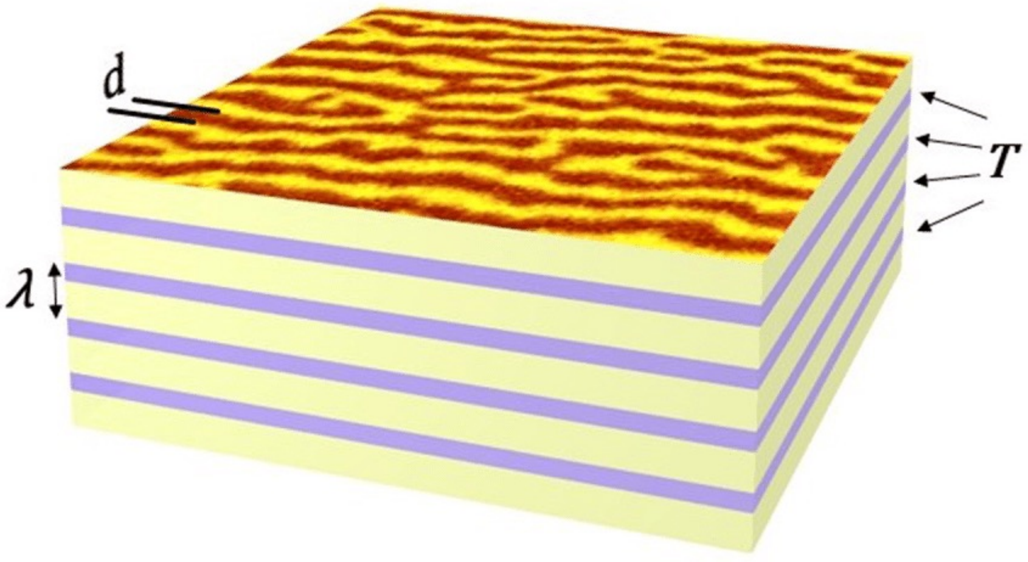
Natural Dichroism (ND): Difference in **distorted** system

Magneto-chiral Dichroism (MχD): Difference in **a magnetic + chiral** system

And more …

X-ray Dichroism

Magnetic Multilayers



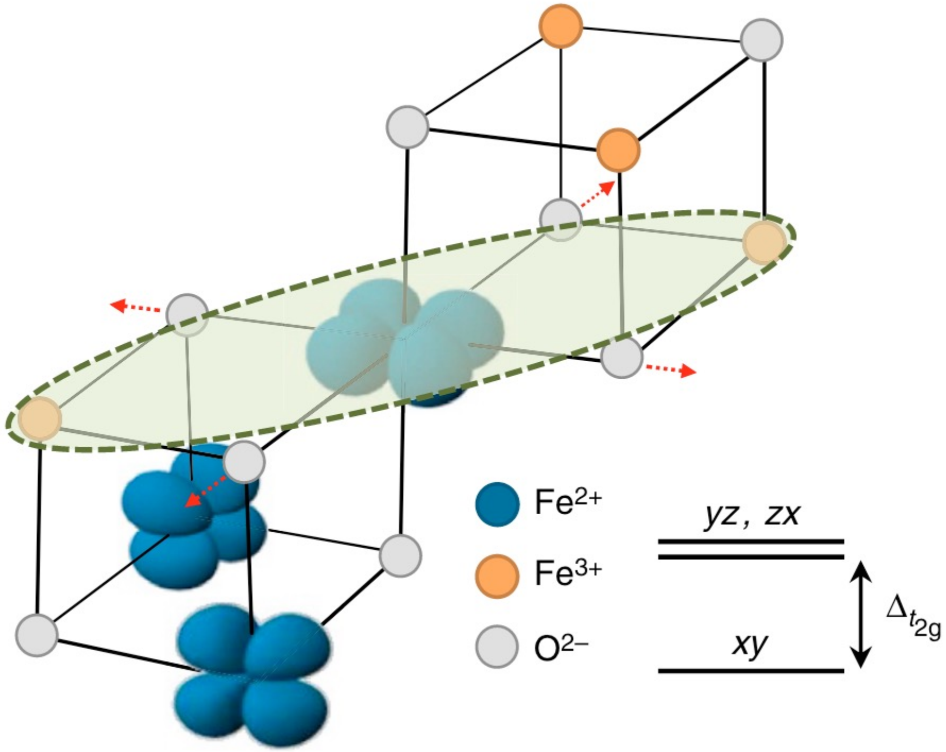
X-rays = Element Selective

- Can study magnetism from different elements

- e.g., Co and Fe multilayers, coupling?

X-ray Dichroism

Multi-Site/ and Oxidations

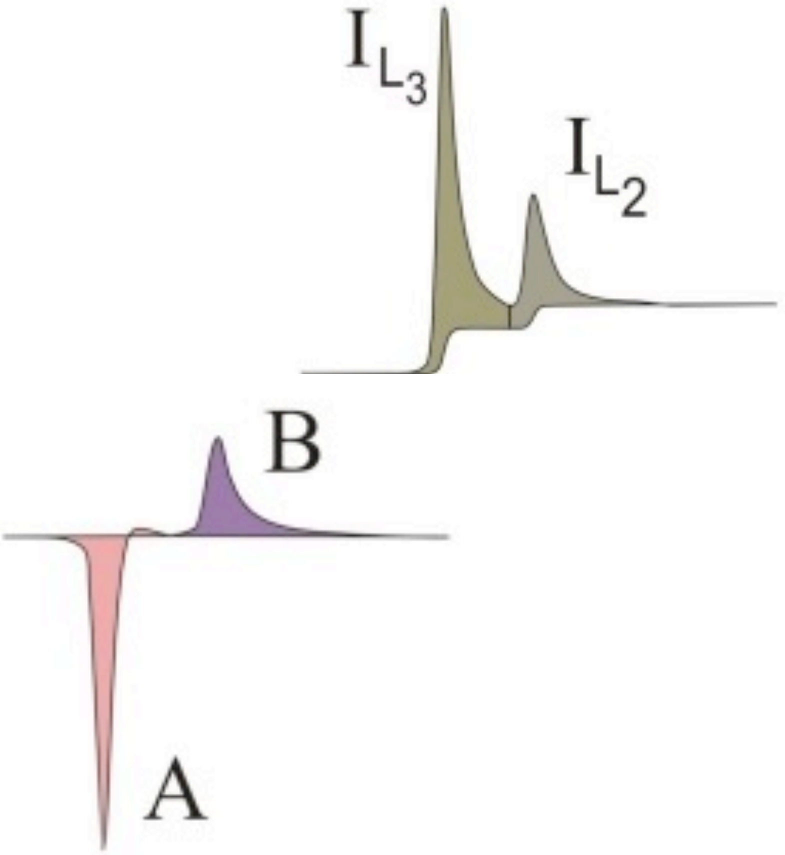


X-rays = Chemical & Site Selective

- Can study one species in a complex system
- e.g., $[Fe^{2+}, Fe^{3+}]_{Oh}\ Fe^{3+}_{Td}\ O_4$

X-ray Dichroism

Magnetic Textures



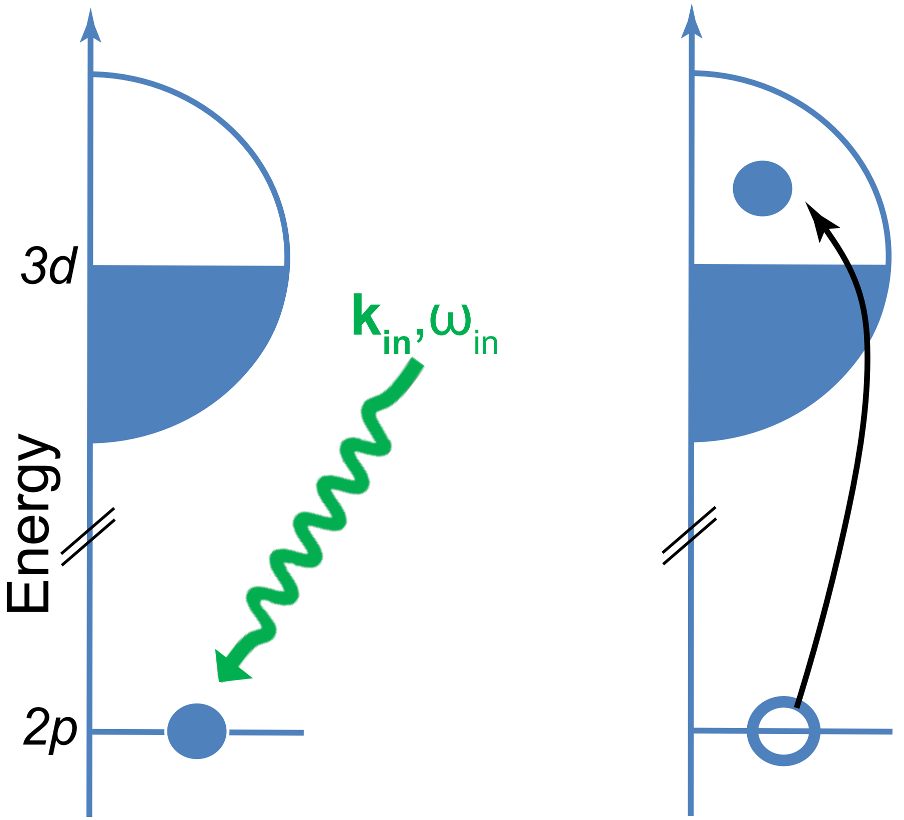
X-rays = Quantification

- Can quantify the magnetic moments using simple rules for ferro, ferri and anti-ferromagnetic systems
- e.g., Sum rules

So, what is the origin of X-ray Dichroism?

Let’s take a step back…

X-ray Absorption Spectroscopy



Fermi golden rule

Transition operator

Final state

Initial state

Remember the square!

$$\sigma(\omega) = \sum_f \left| \langle f | T | i \rangle \right|^2 \frac{\imath/\pi}{\omega - E_f + \imath\Gamma/2}$$

X-ray Absorption Spectroscopy

$$\sigma(\omega) = \sum_f \left| \langle f | T | i \rangle \right|^2 \frac{\imath/\pi}{\omega - E_f + \imath\Gamma/2}$$

$$T = (\boldsymbol{\epsilon}.\boldsymbol{r})\, e^{i\,\boldsymbol{k}.\boldsymbol{r}}$$

polarization — position — wave-vector

Taylor expansion:

$$T = (\boldsymbol{\epsilon}.\boldsymbol{r})e^{i\,\boldsymbol{k}.\boldsymbol{r}} = (\boldsymbol{\epsilon}.\boldsymbol{r}).1 + i(\boldsymbol{\epsilon}.\boldsymbol{r})\frac{\boldsymbol{k}.\boldsymbol{r}}{2!} + \cdots$$

dipole — quadrupole

Selection Rules

Transition operators can be expressed in real spherical harmonics

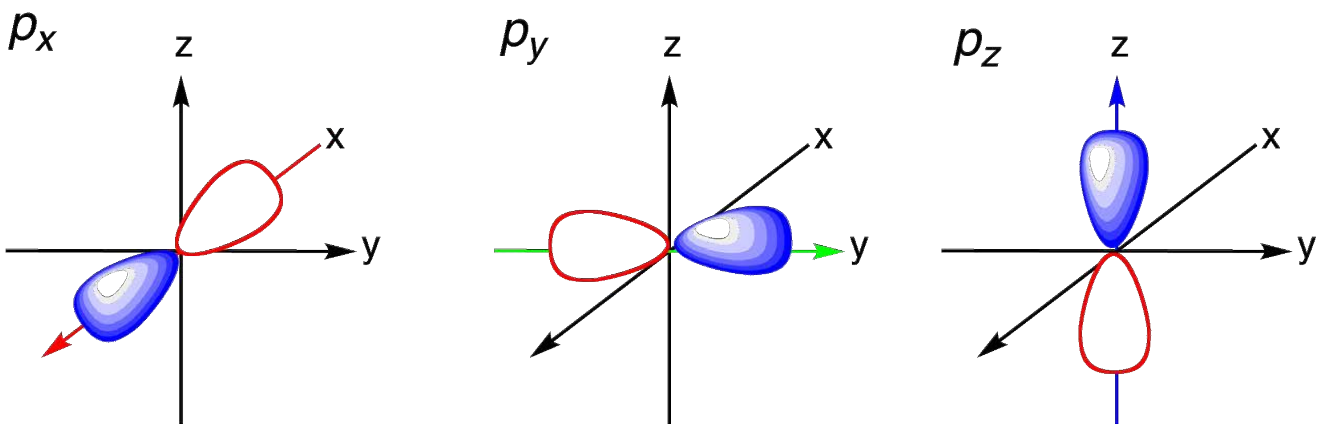
Dipole:

$$\vec{\varepsilon}.\vec{r} = (-1)^m \sqrt{\frac{4\pi}{3}} r Y_1^m(\Omega) \qquad \Omega = (\theta, \varphi)$$

$$\epsilon || z \rightarrow Y_1^0$$

$$\epsilon || y \rightarrow i(Y_1^1 + Y_1^{-1})/\sqrt{2}$$

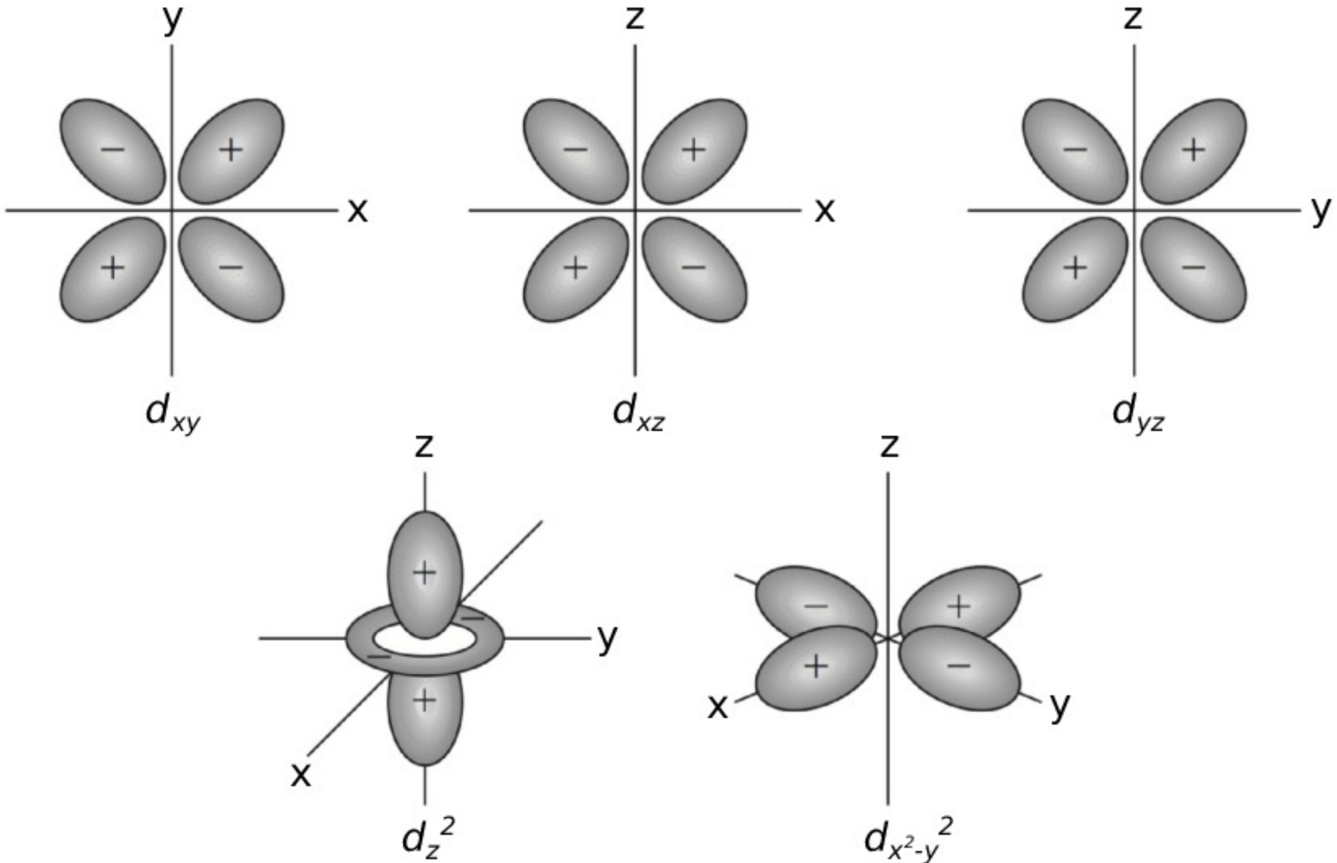
$$\epsilon || x \rightarrow (Y_1^1 - Y_1^{-1})/\sqrt{2}$$



Transition operators can be expressed in real spherical harmonics

Quadrupole:

$$\epsilon || x, \boldsymbol{k} || y \rightarrow i(Y_2^{-2} - Y_2^{2})/\sqrt{2}$$



Fermi Golden Rule

Transition operator

Final state

Initial state

$$\sigma(\omega) = \sum_f \left|\langle f|T|i\rangle\right|^2 \frac{\imath/\pi}{\omega - E_f + \imath\Gamma/2}$$

From previous talks

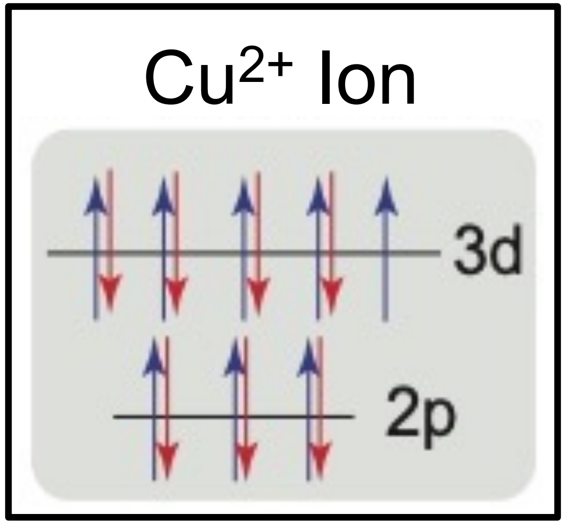
Probes the empty density of states!

From previous talks

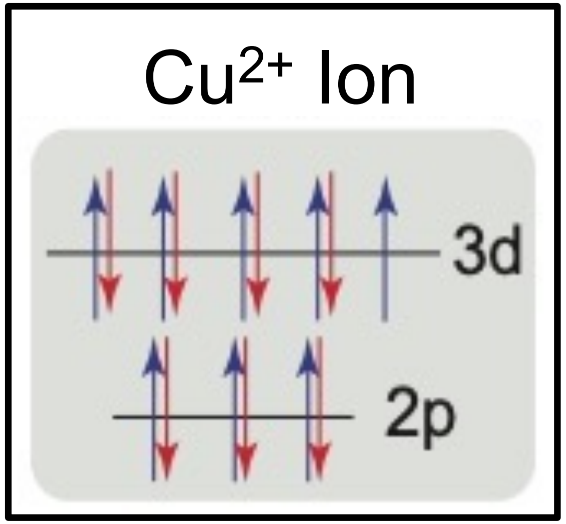
Given by electronic interactions, magnetism, symmetry…

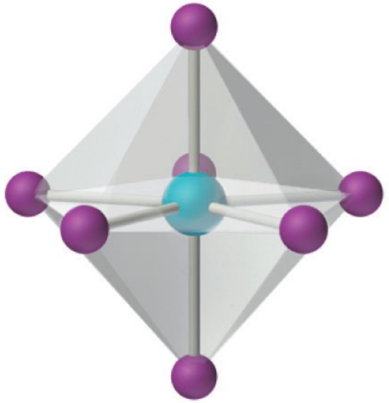
Expressed as spherical harmonic

Simple example: Cu^{2+}

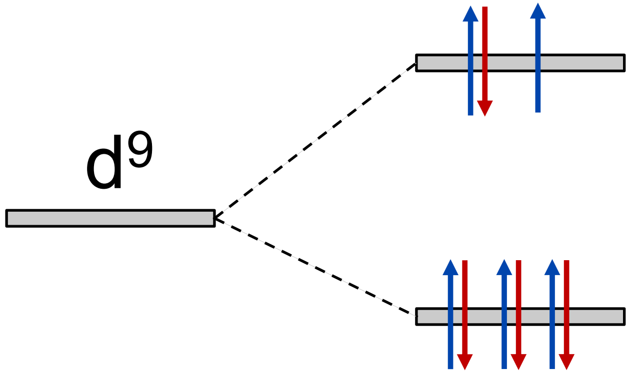


One hole= no multiplets



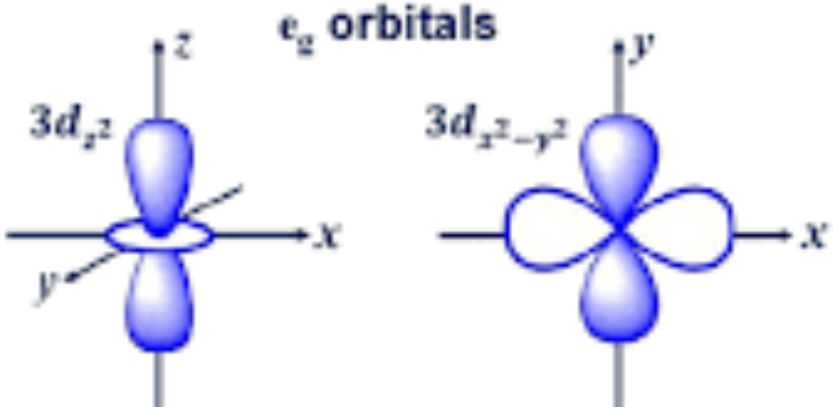


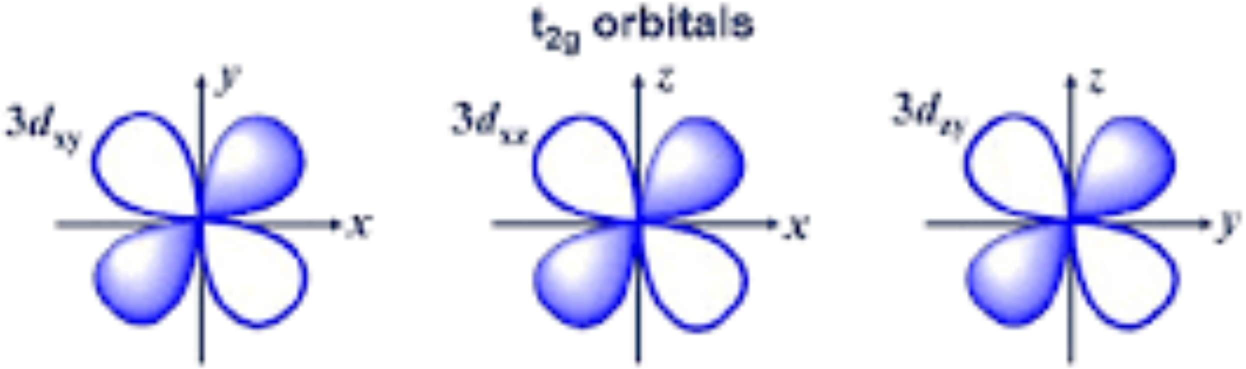
HOLE: $\sim \frac{d_{x^2-y^2}}{\sqrt{2}} + \frac{d_{z^2}}{\sqrt{2}}$

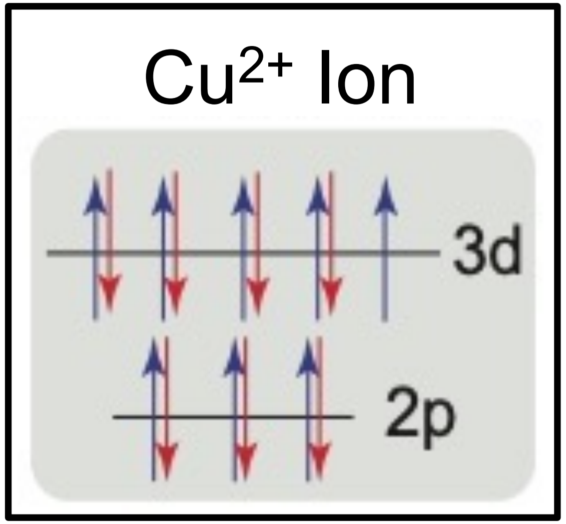


e_g:$(d_{x^2-y^2}, d_{z^2})$

t_{2g}:(d_{xy}, d_{zy}, d_{zx})







Cu^{2+} L_3-edge XAS

$$\sigma(\omega) = \sum_f \left| \langle f | T | i \rangle \right|^2 \frac{\imath/\pi}{\omega - E_f + \imath\Gamma/2}$$

3d orbitals

Dipole
(think p orbitals)

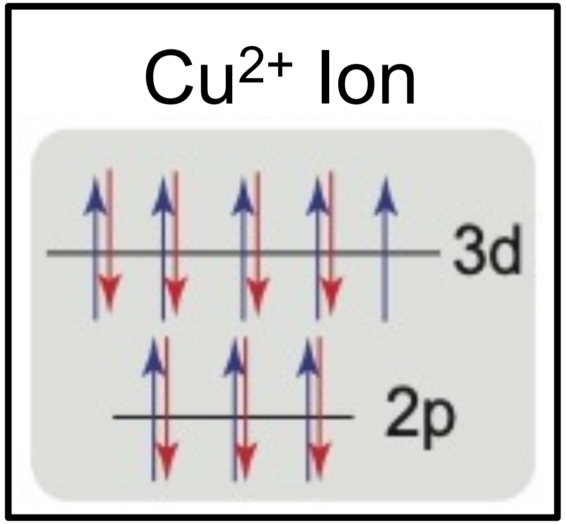
2p orbital

Qeustion:

Do you expect dichroism effects?

(i.e.: would it make a difference if you use x,y,z polarized light?)

Cu d^9 L-edge: $\epsilon || x$



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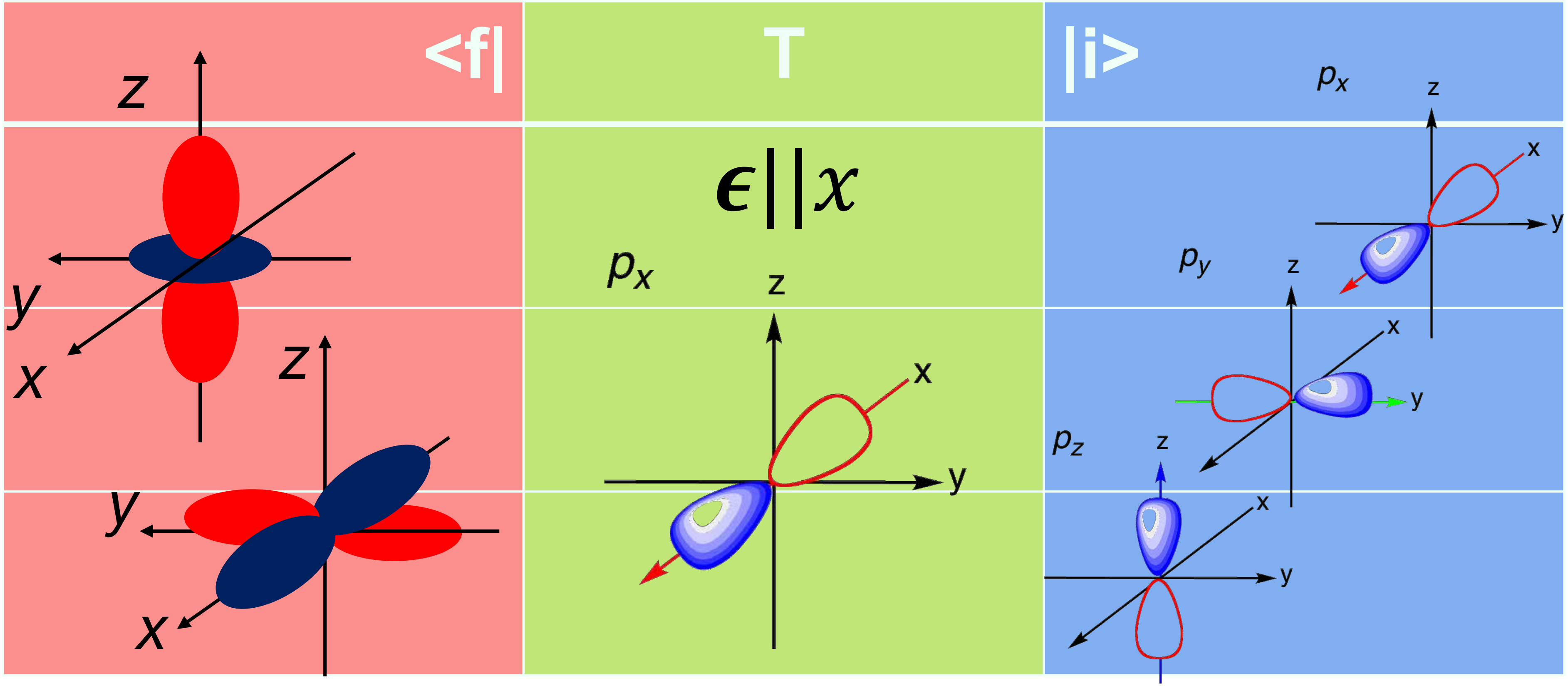

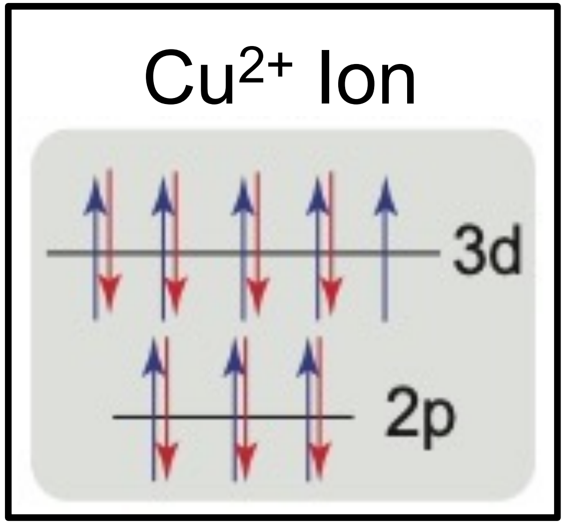

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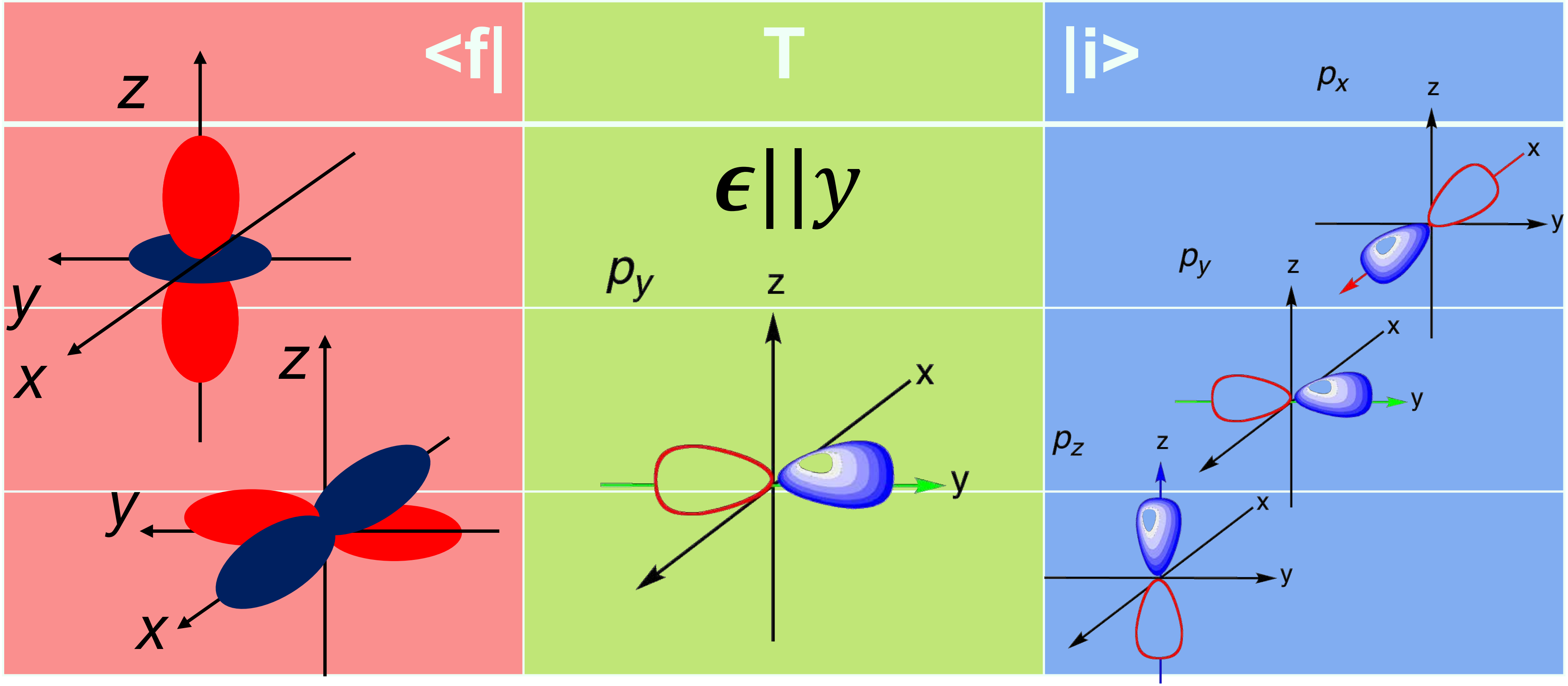
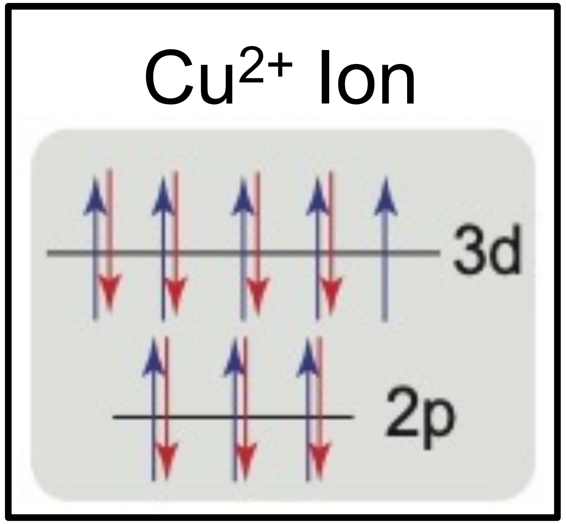
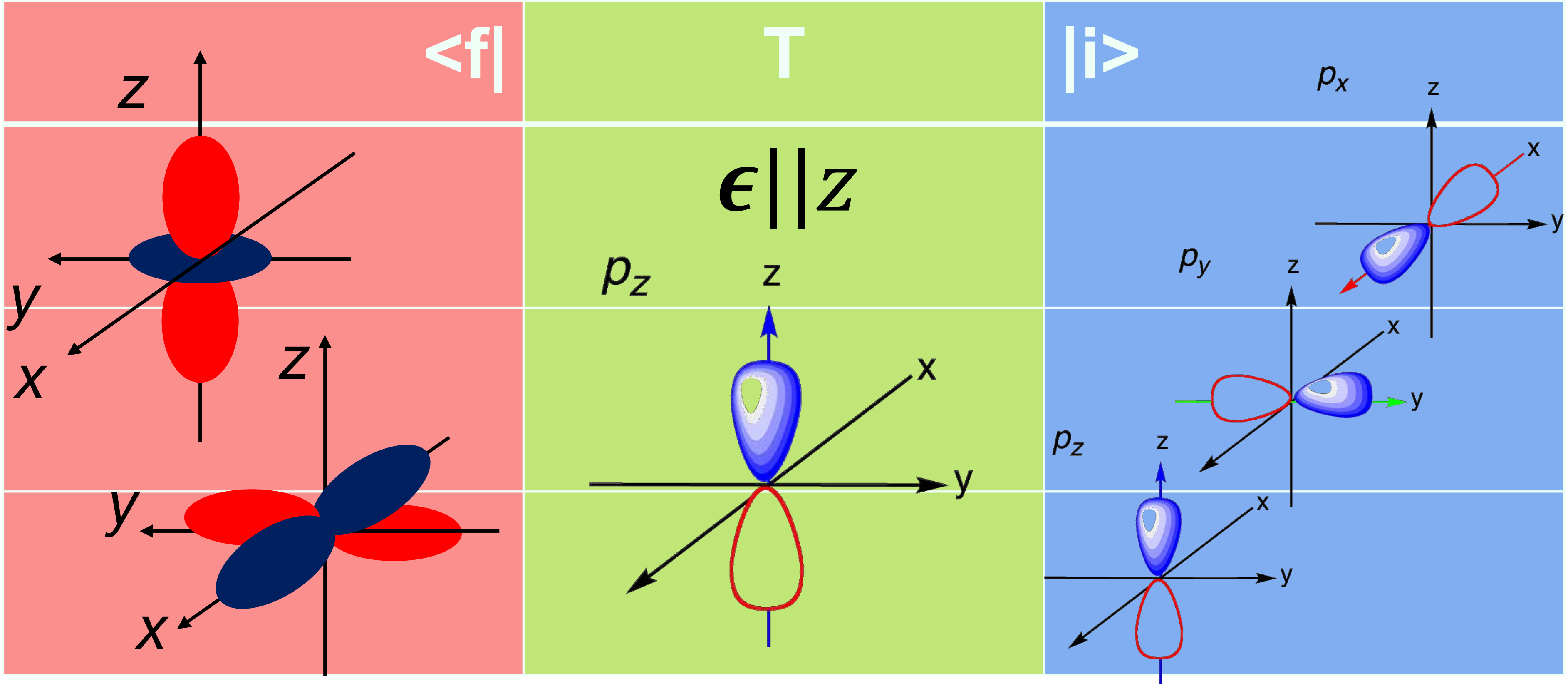


Cu d^9 L-edge: $\boldsymbol{\epsilon}||z$

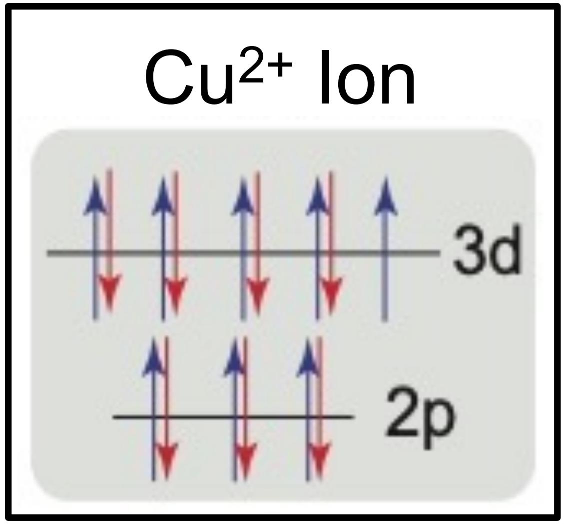


Cu^{2+} L_3-edge XAS

$$\sigma(\omega) = \sum_f \left| \langle f | T | i \rangle \right|^2 \frac{\imath/\pi}{\omega - E_f + \imath\Gamma/2}$$

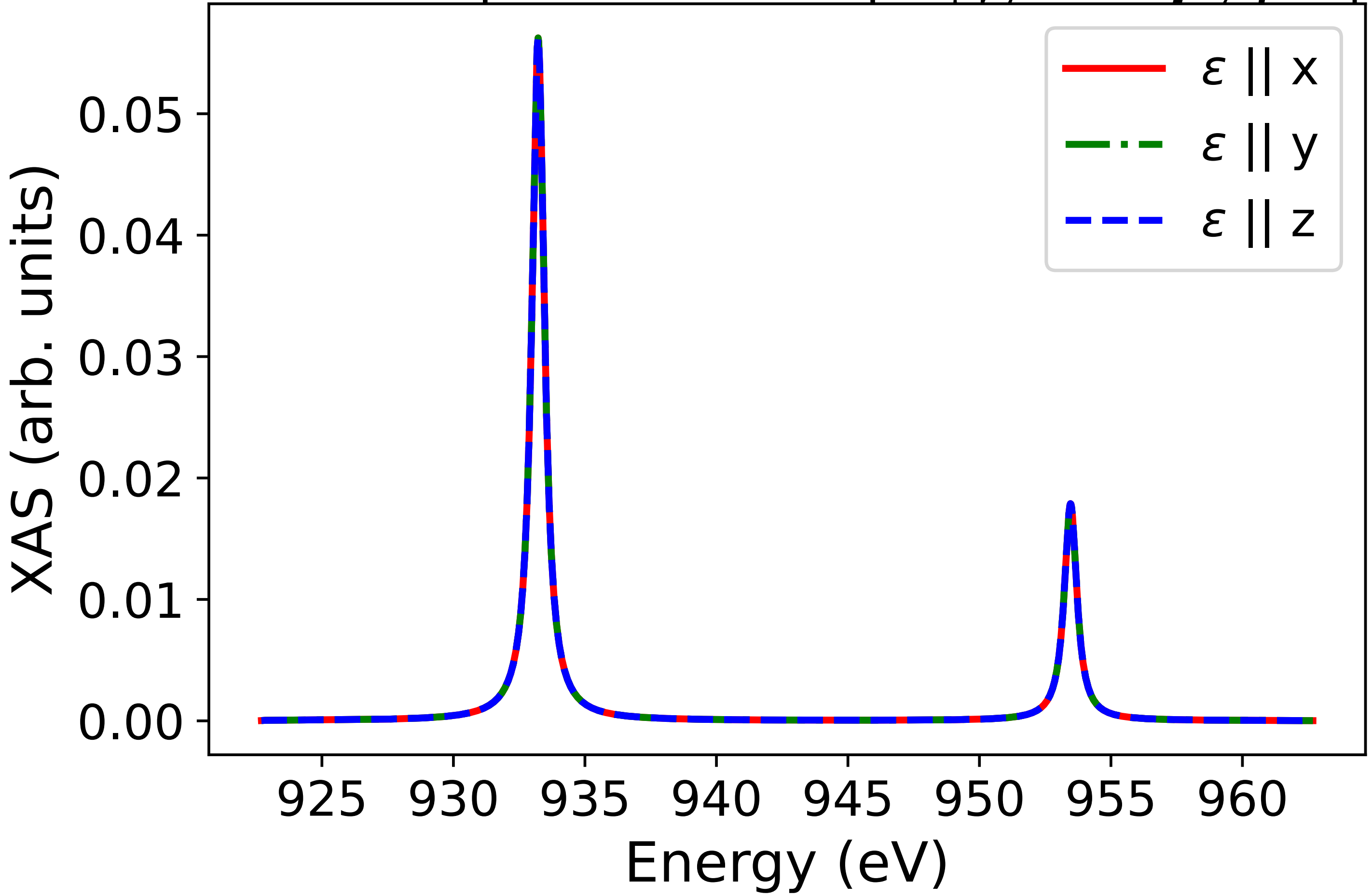


Cu d^9 L-edge: $\boldsymbol{\epsilon}||z$

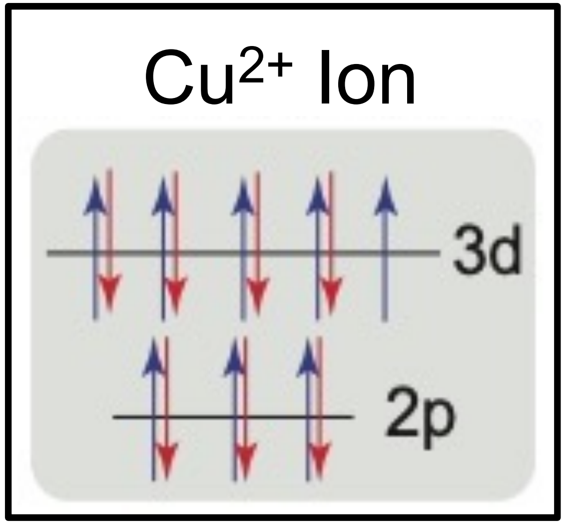


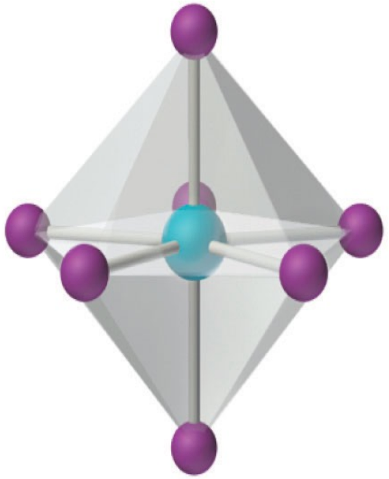
Cu^{2+} L_3-edge XAS

$$\sigma(\omega) = \sum \left| \langle f | T | i \rangle \right|^2 \frac{\imath/\pi}{\omega - E_f + \imath\Gamma/2}$$

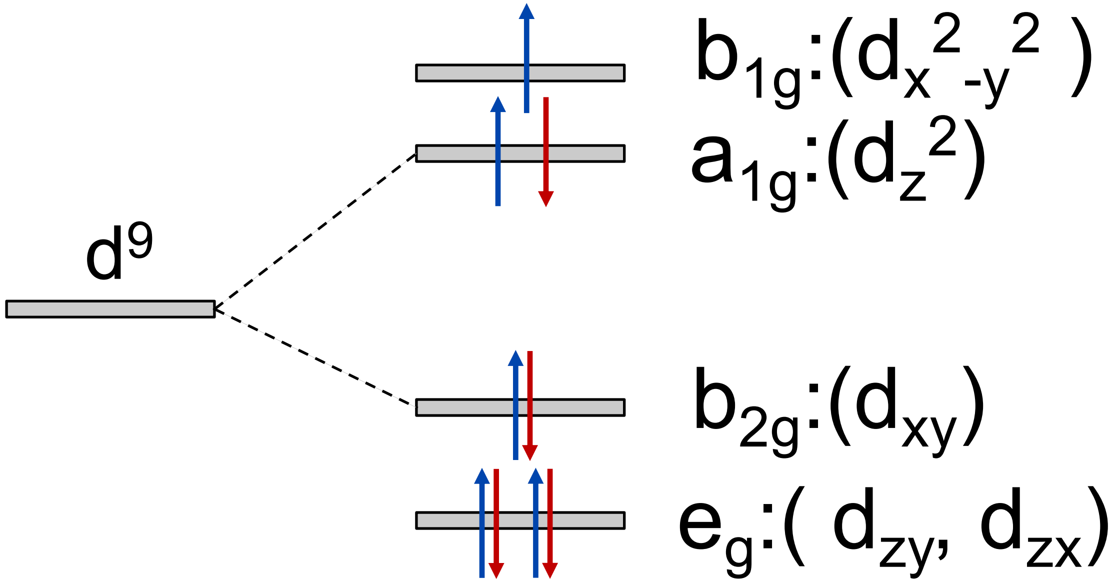


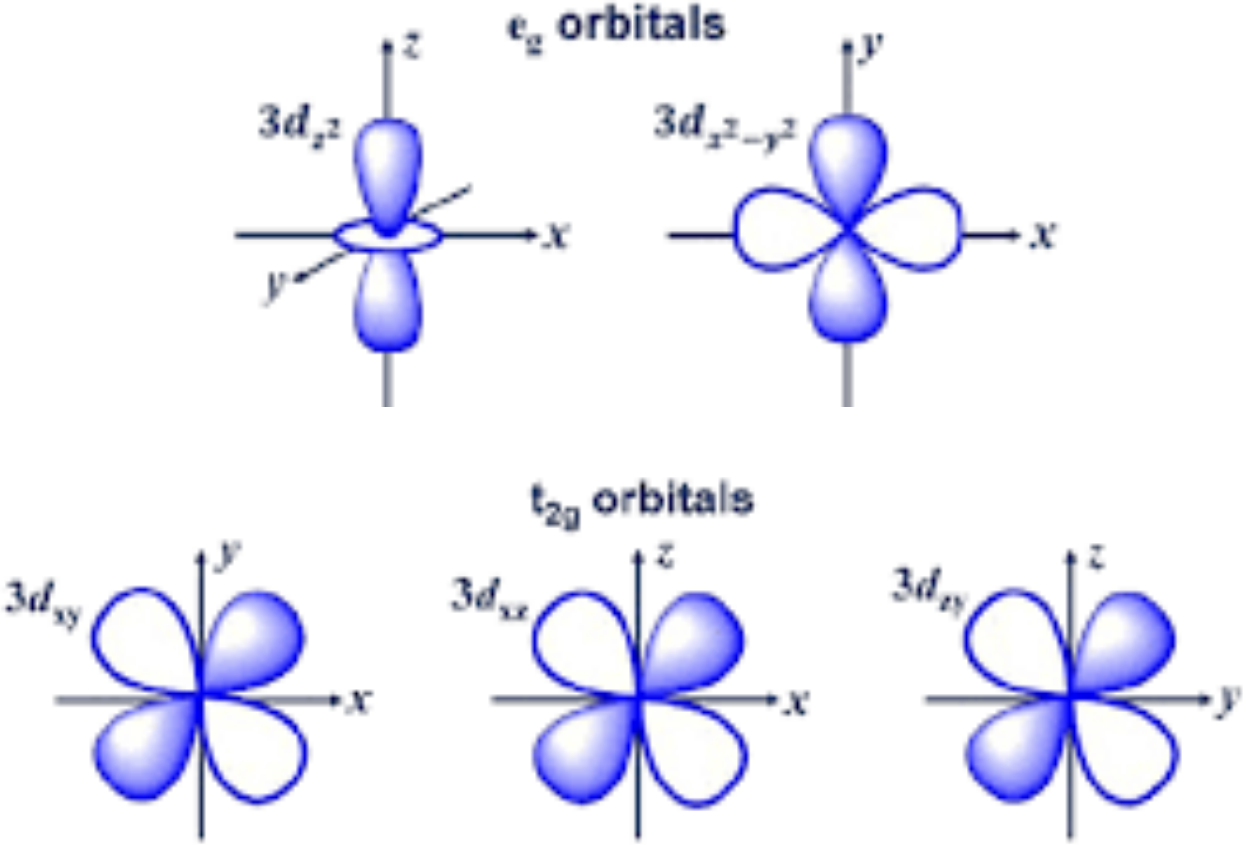
XAS: Cu d^9 ion





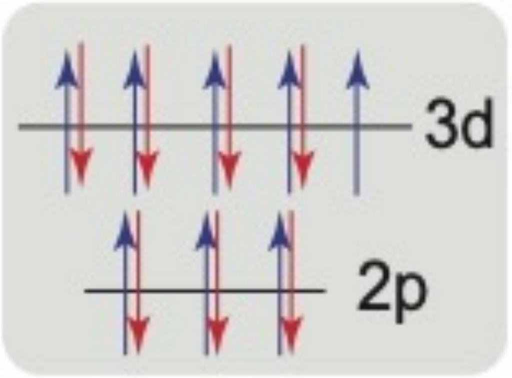
HOLE: ~ $d_{x^2-y^2}$





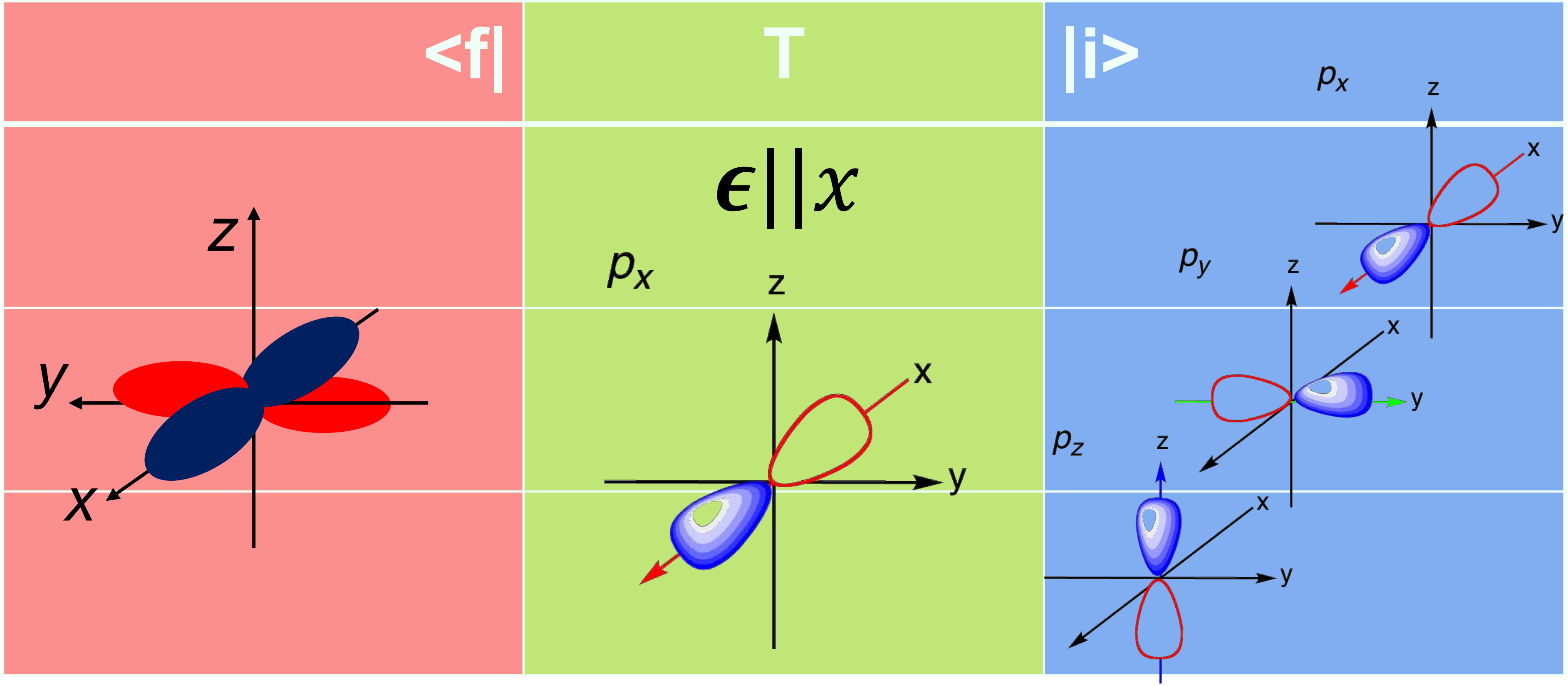
Cu d^9 L-edge: $\epsilon || x$

Cu^{2+} Ion

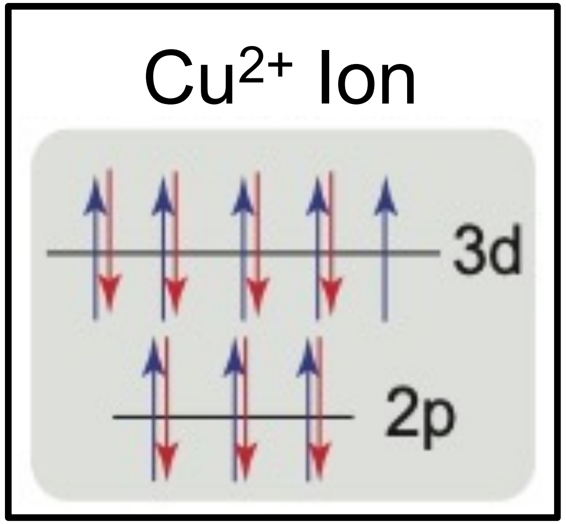


Cu^{2+} L_3-edge XAS

$$\sigma(\omega) = \sum_f \left| \langle f | T | i \rangle \right|^2 \frac{\imath/\pi}{\omega - E_f + \imath\Gamma/2}$$

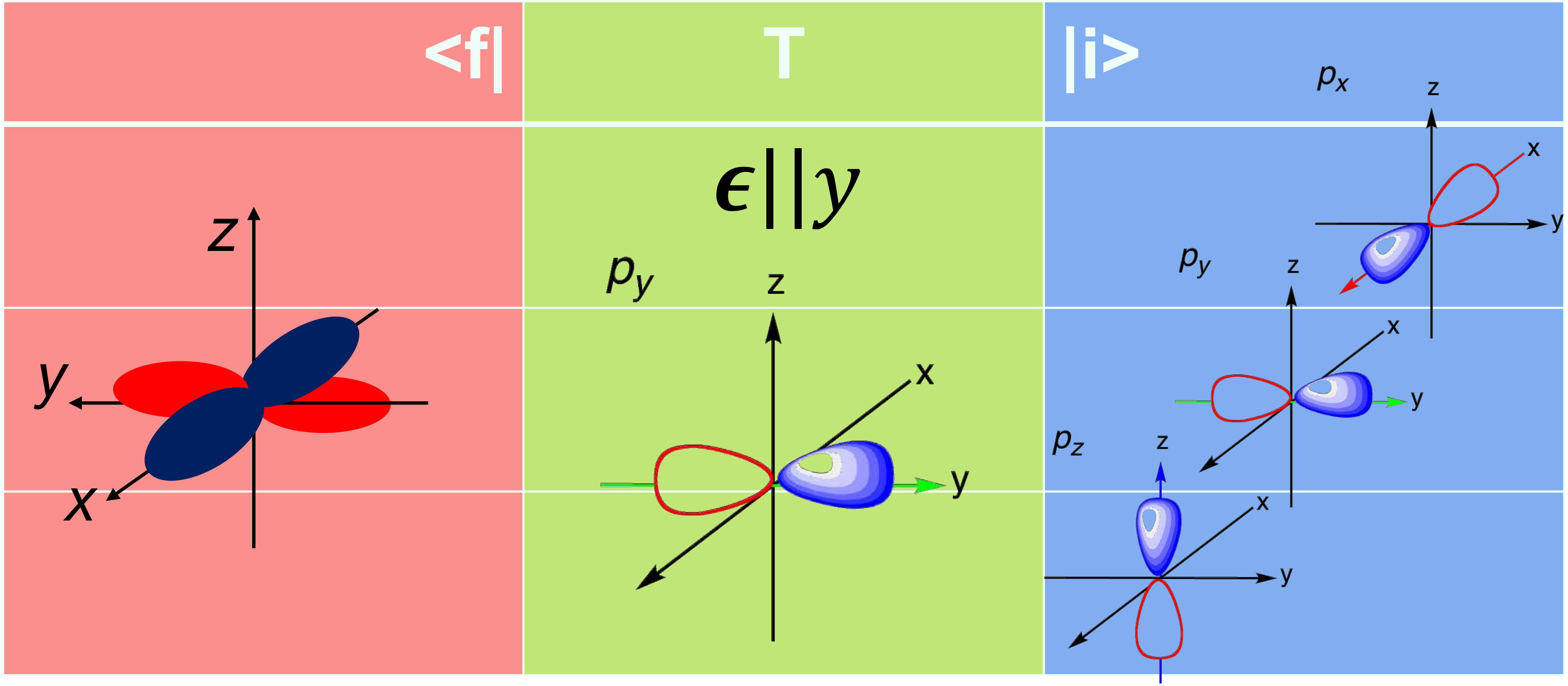


Cu d^9 L-edge: $\boldsymbol{\epsilon}||y$



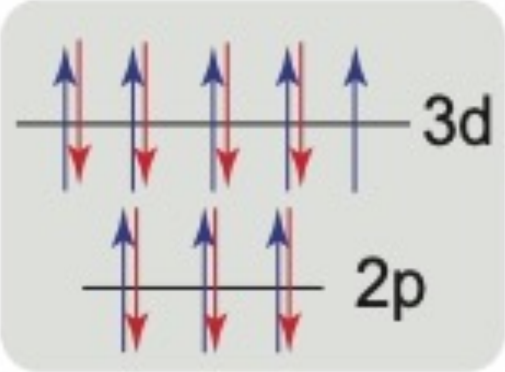
Cu^{2+} L_3-edge XAS

$$\sigma(\omega) = \sum_f \left| \langle f | T | i \rangle \right|^2 \frac{\imath/\pi}{\omega - E_f + \imath\Gamma/2}$$



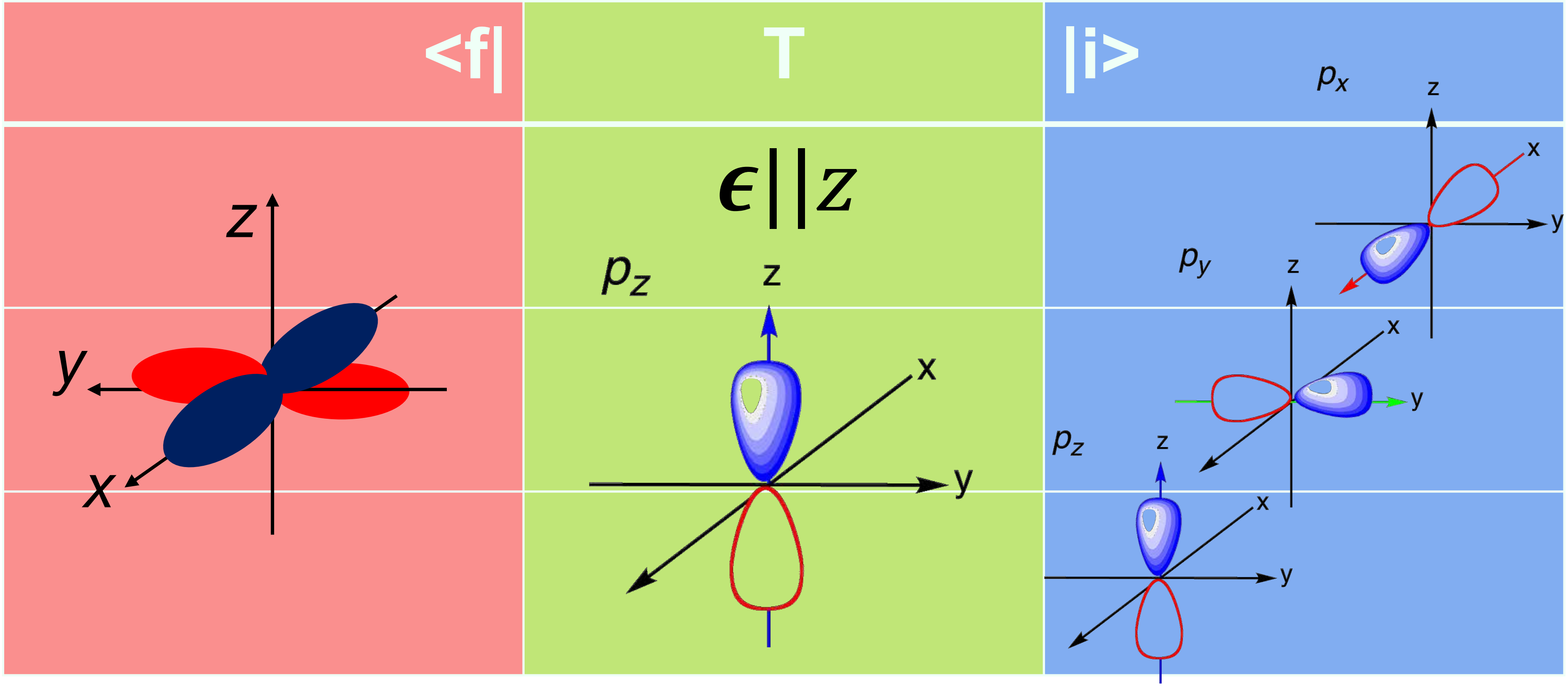
Cu d^9 L-edge: $\epsilon || z$

Cu^{2+} Ion



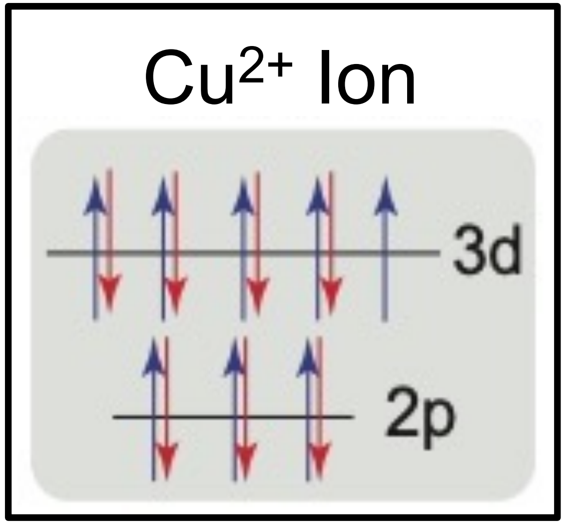
Cu^{2+} L_3-edge XAS

$$\sigma(\omega) = \sum_f \left| \langle f | T | i \rangle \right|^2 \frac{\imath / \pi}{\omega - E_f + \imath \Gamma / 2}$$



No absorption!

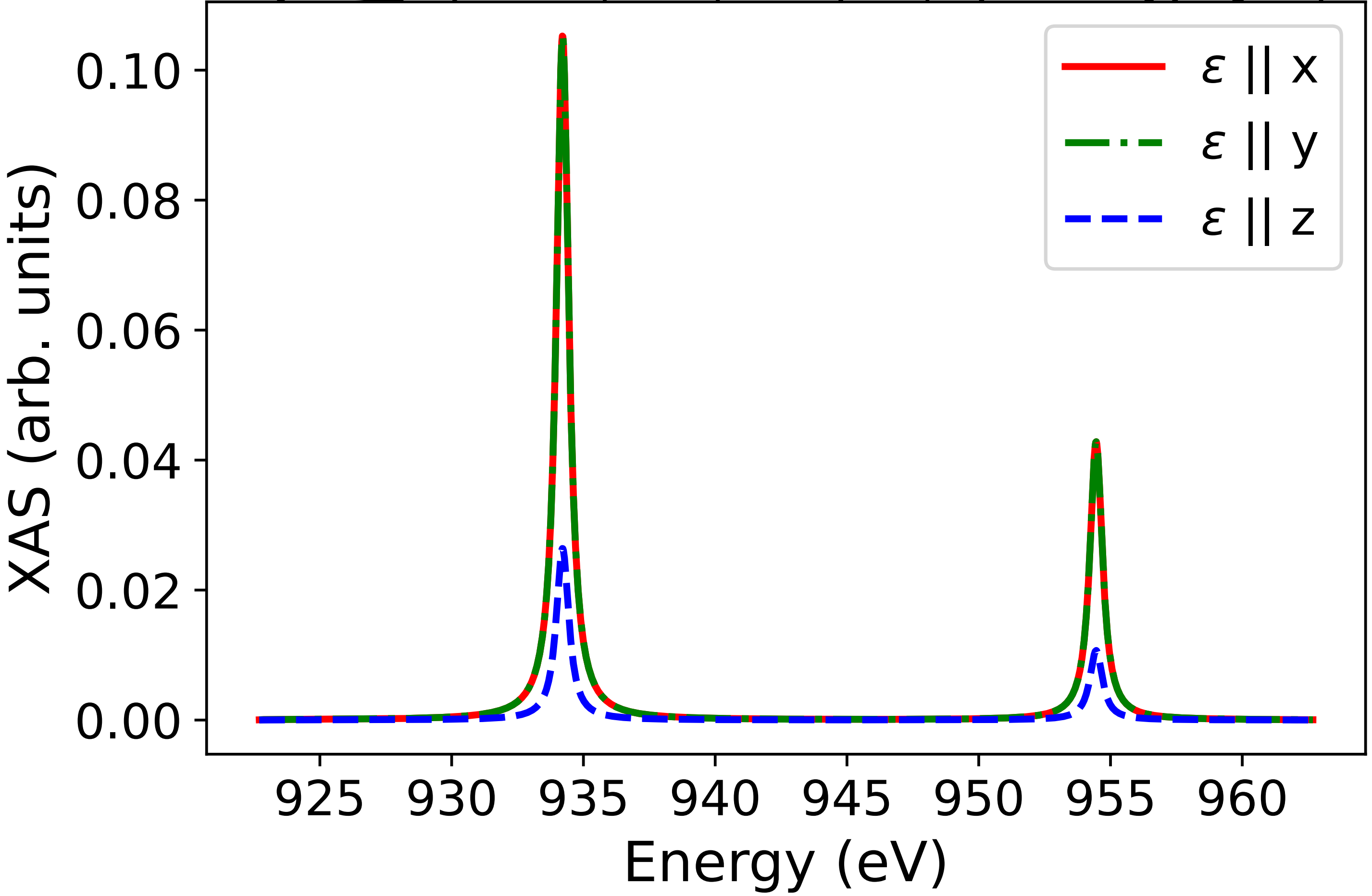
Cu d^9 L-edge: $\boldsymbol{\epsilon} || z$



X-ray Linear Dichroism

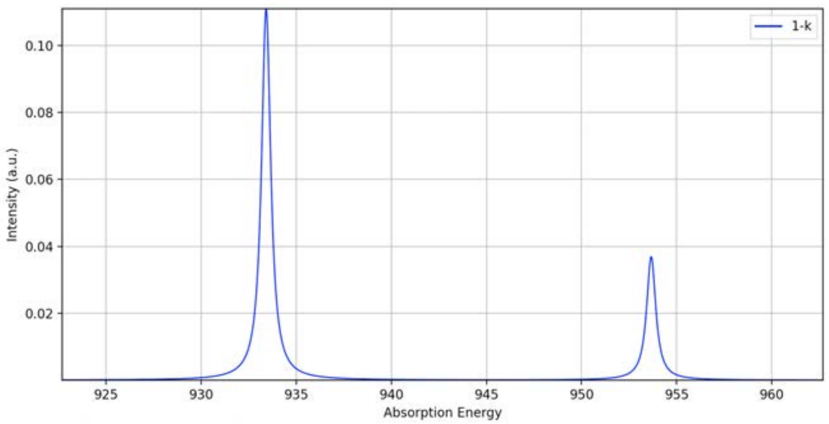
Cu^{2+} L_3-edge XAS

$$\sigma(\omega) = \sum \left|\langle f | T | i \rangle\right|^2 \frac{i/\pi}{\omega - E_f + i\Gamma/2}$$

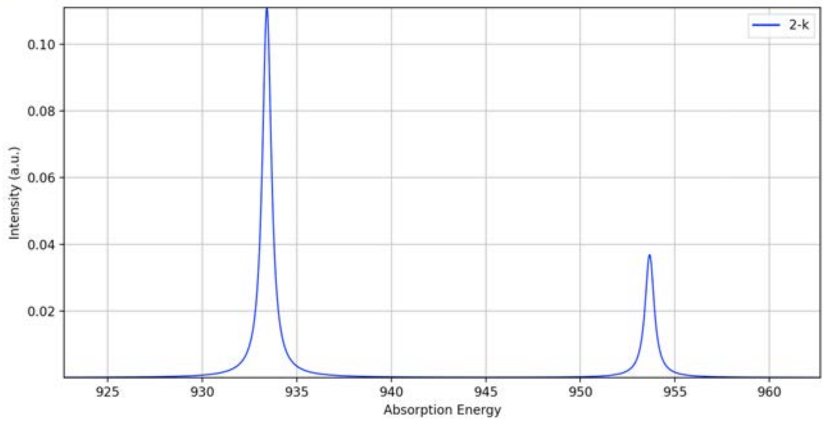


Let’s put things together

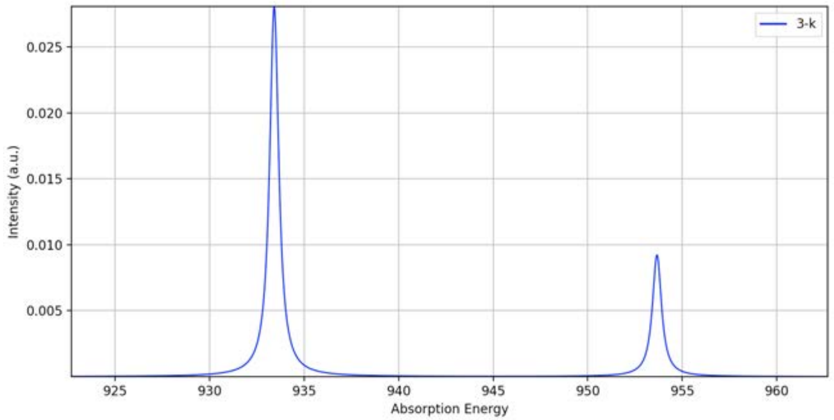
E_x



E_y



E_z



Qeustion:

How many measurements are required to fully describe all properties of dipole transitions ?

(think about the square)

Let's put things together

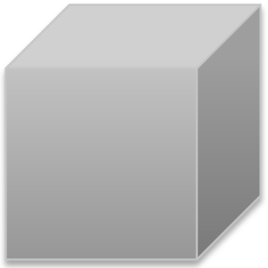
$$\sigma(\omega) = \sum_f \left| \langle f | T | i \rangle \right|^2 \frac{\imath/\pi}{\omega - E_f + \imath\Gamma/2}$$

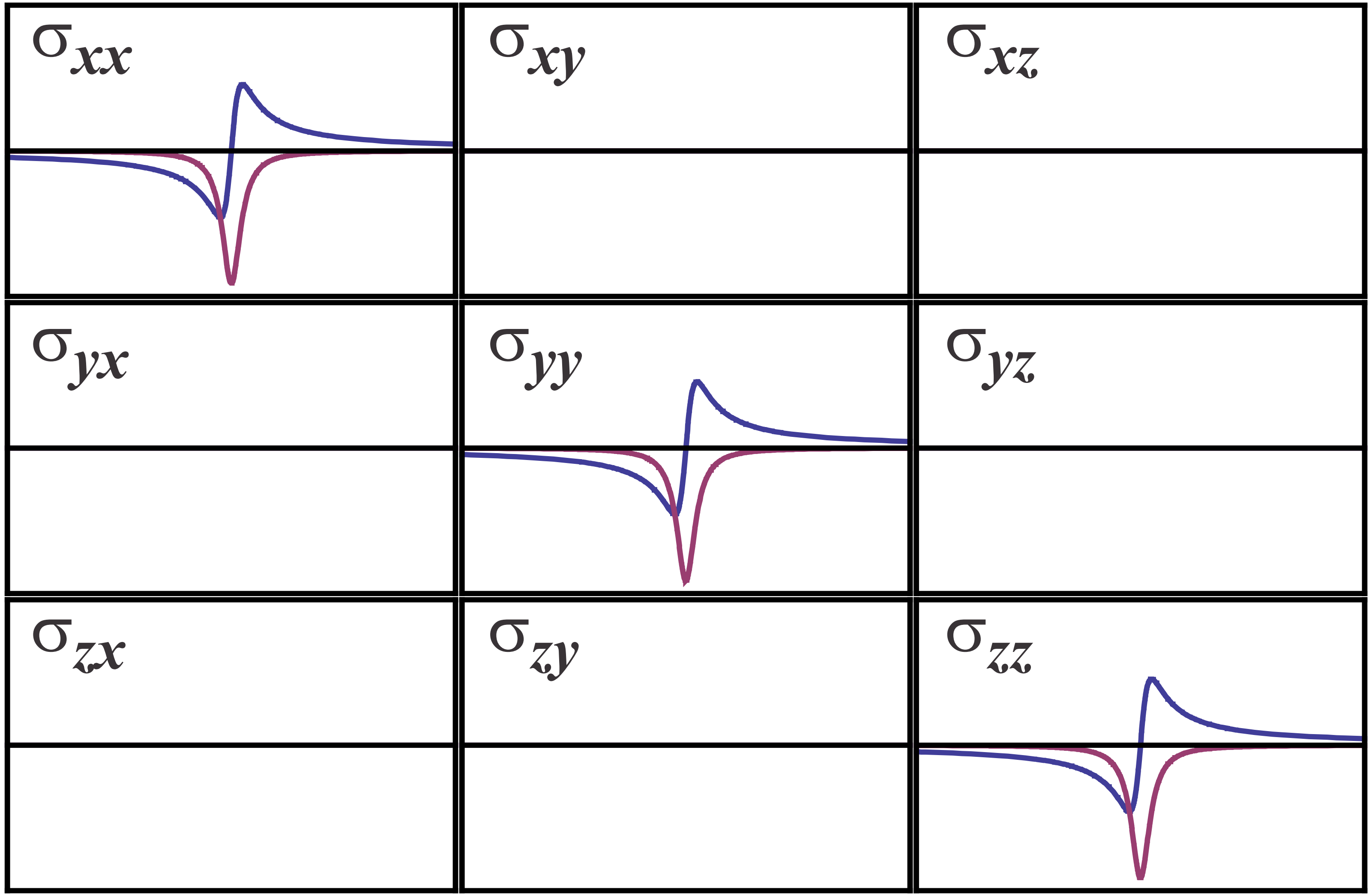
$$\sigma(\omega) = \sum_f \left| \langle i | T | f \rangle \langle f | T | i \rangle \right. \frac{\imath/\pi}{\omega - E_f + \imath\Gamma/2}$$

E_X - E_X	E_X - E_Y	E_X - E_Z
E_Y - E_X	E_Y - E_X	E_Y - E_Z
E_Z - E_X	E_Z - E_Y	E_Z - E_Z

Off-diagonal: -> y polarized light is changed by the system to an x polarized system: magnetism & chirality

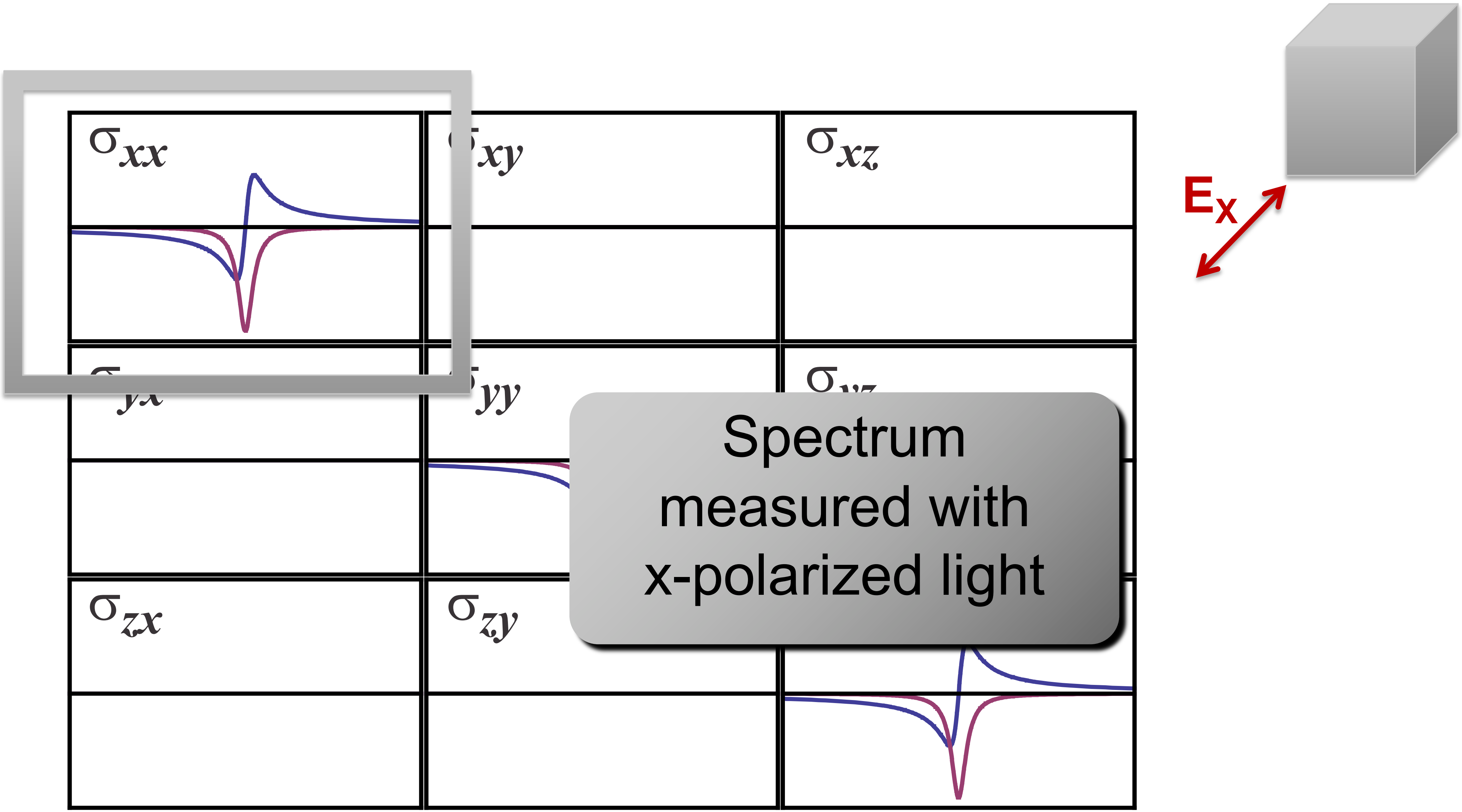
Building the conductivity Tensor: Cubic Symmetry





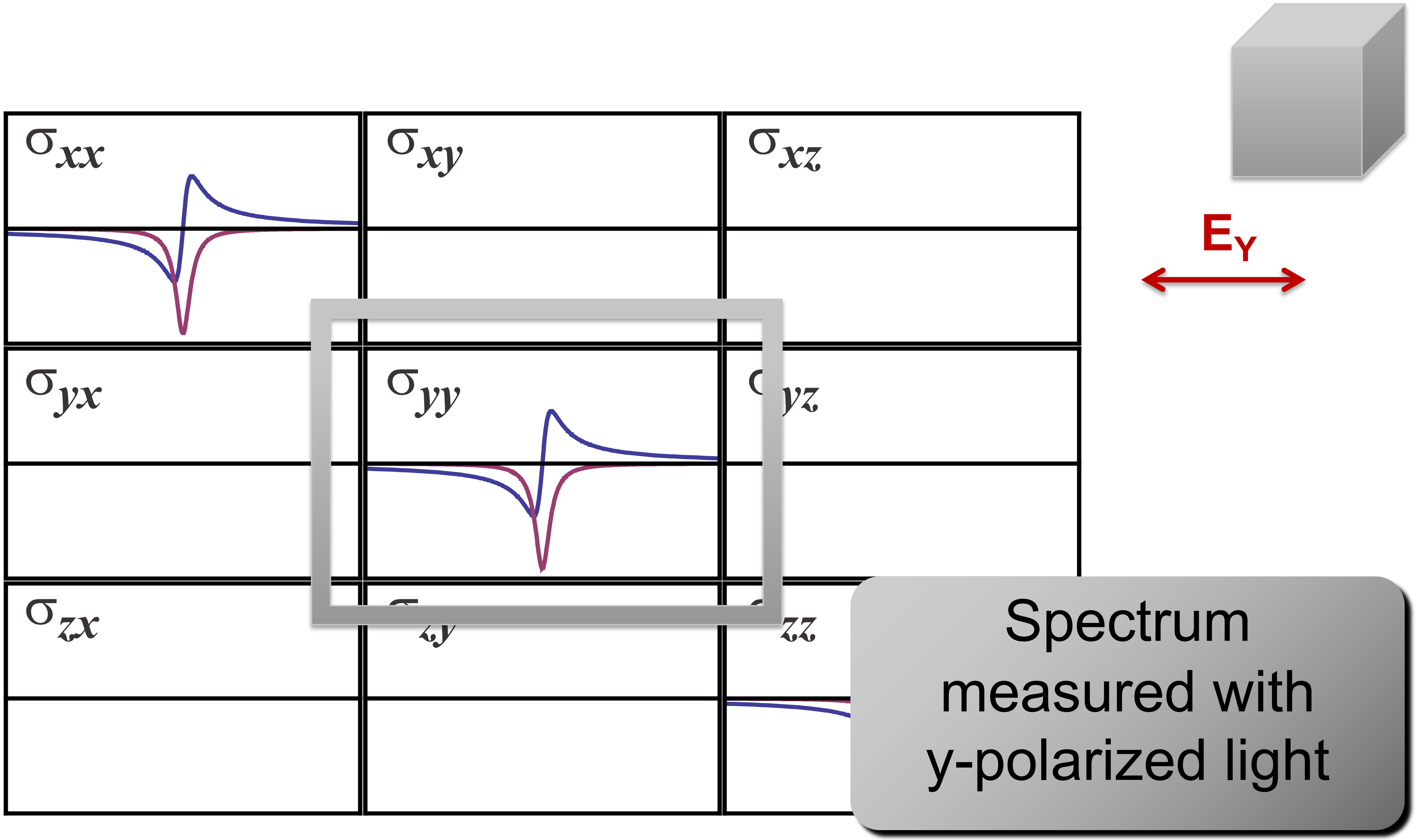
M. W. Haverkort

Building the conductivity Tensor: Cubic Symmetry



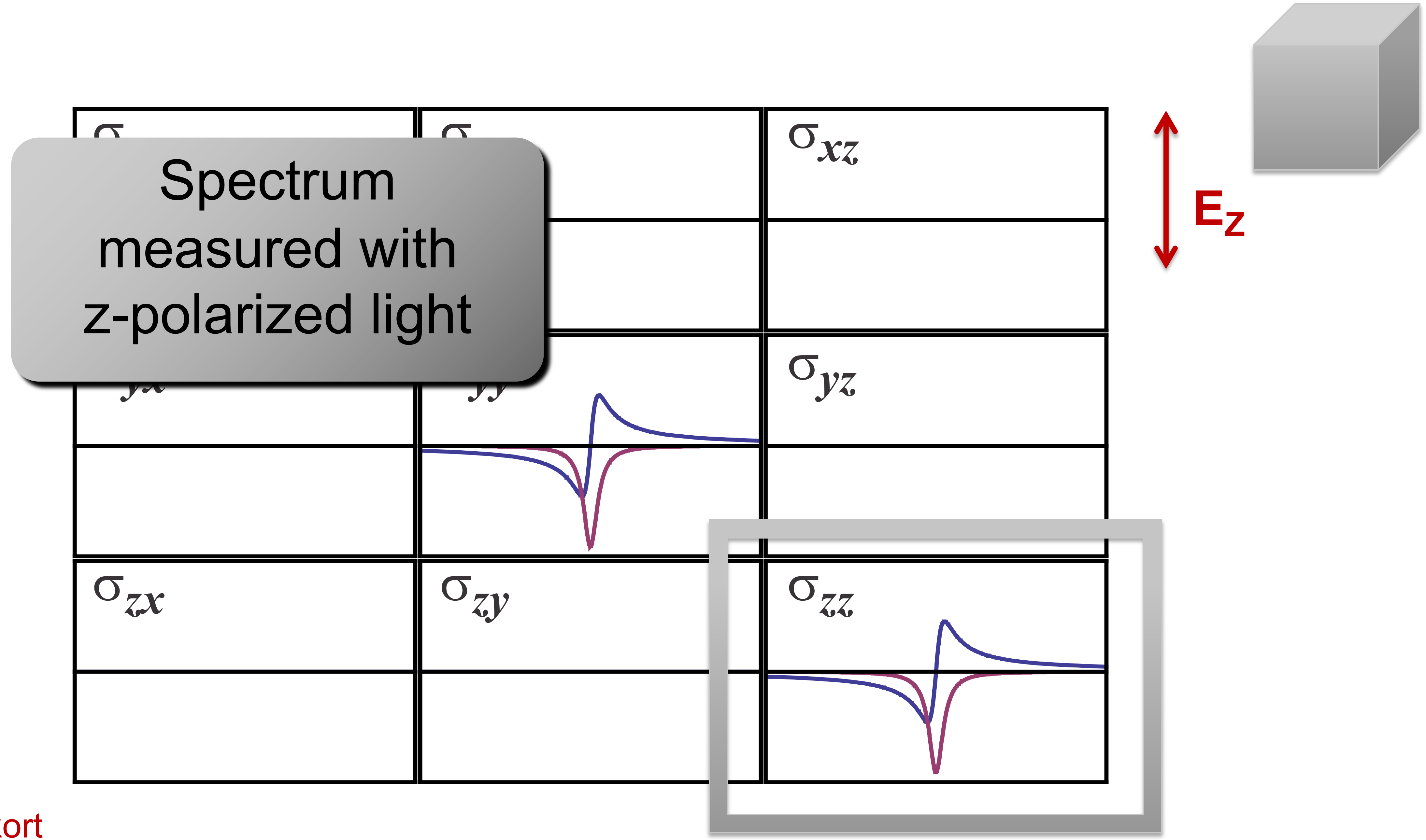
M. W. Haverkort

Building the conductivity Tensor: Cubic Symmetry

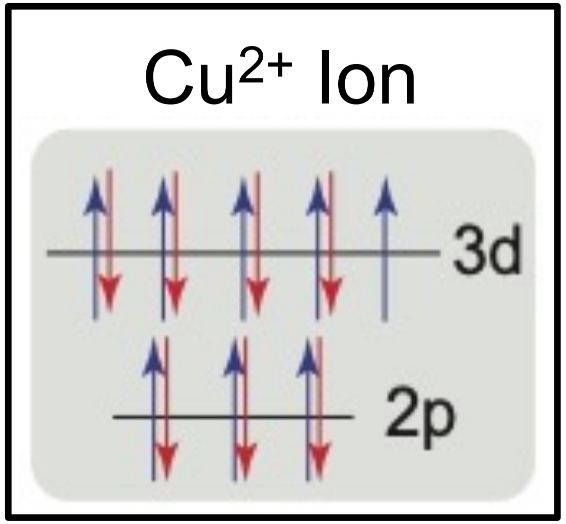


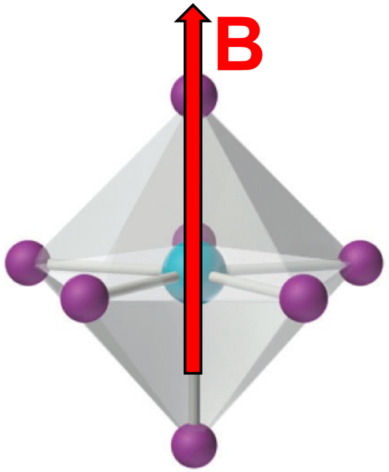
M. W. Haverkort

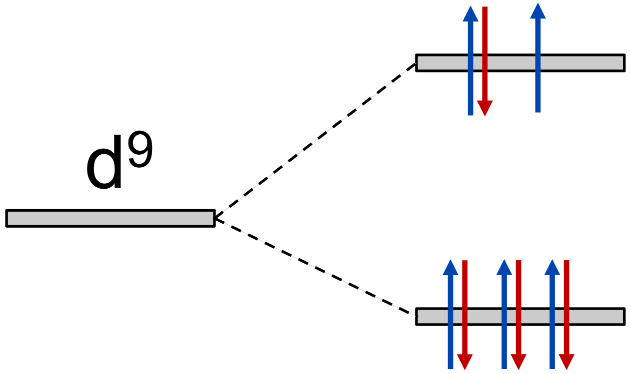
Building the conductivity Tensor: Cubic Symmetry



XAS: Calculating Cu d^9 L-edge in Oh symmetry + magnetic field







e_g:($d_{x^2-y^2}$, d_{z^2})

t_{2g}:(d_{xy}, d_{zy}, d_{zx})

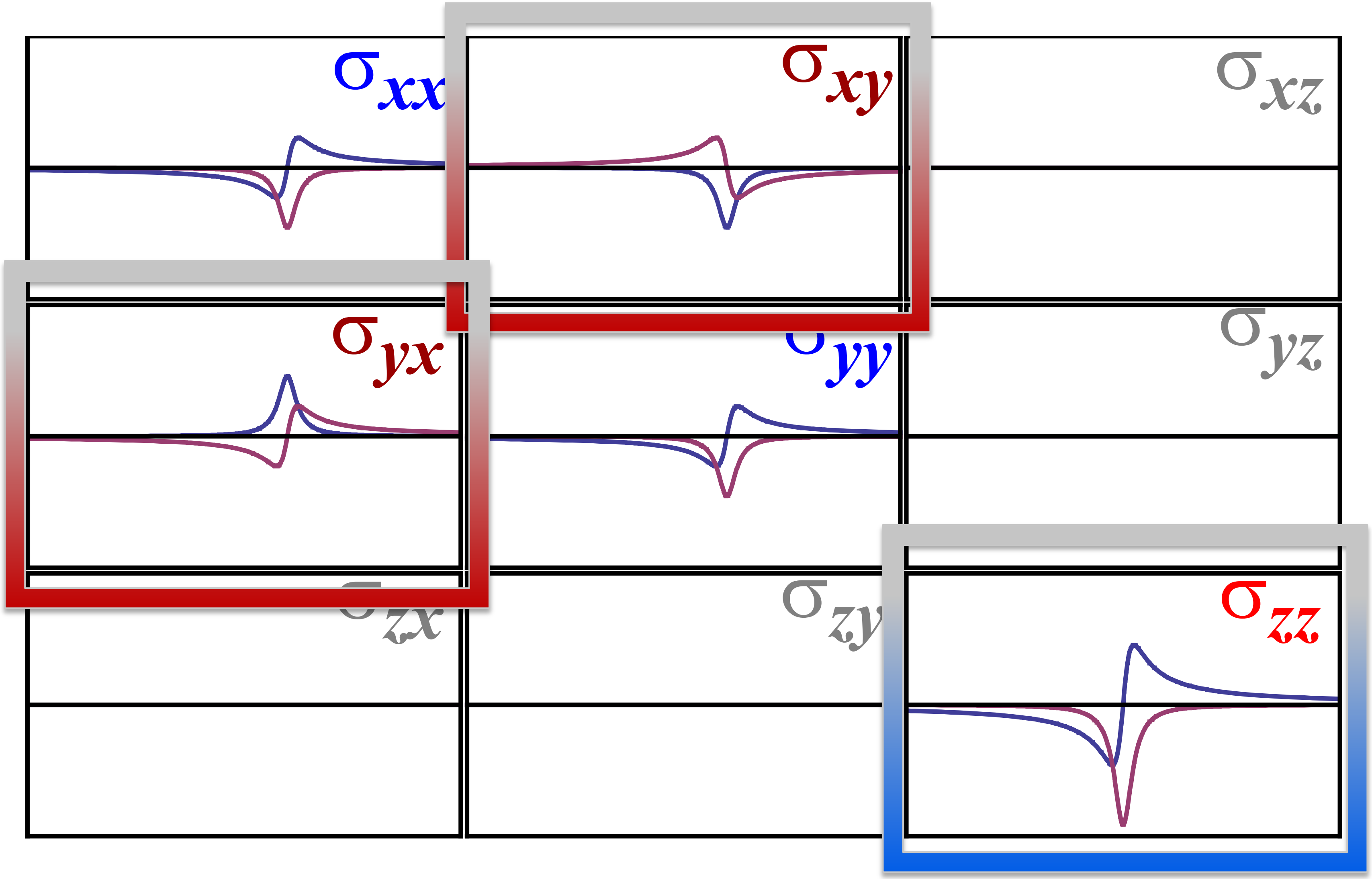
HOLE:

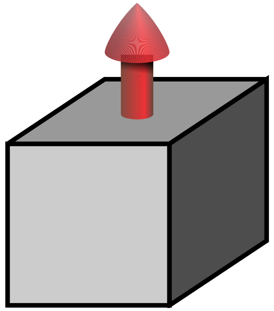
Spin-orbit coupling dictates an orientation of the hole

Dichroism?

Building the conductivity Tensor with a Magnetic Field

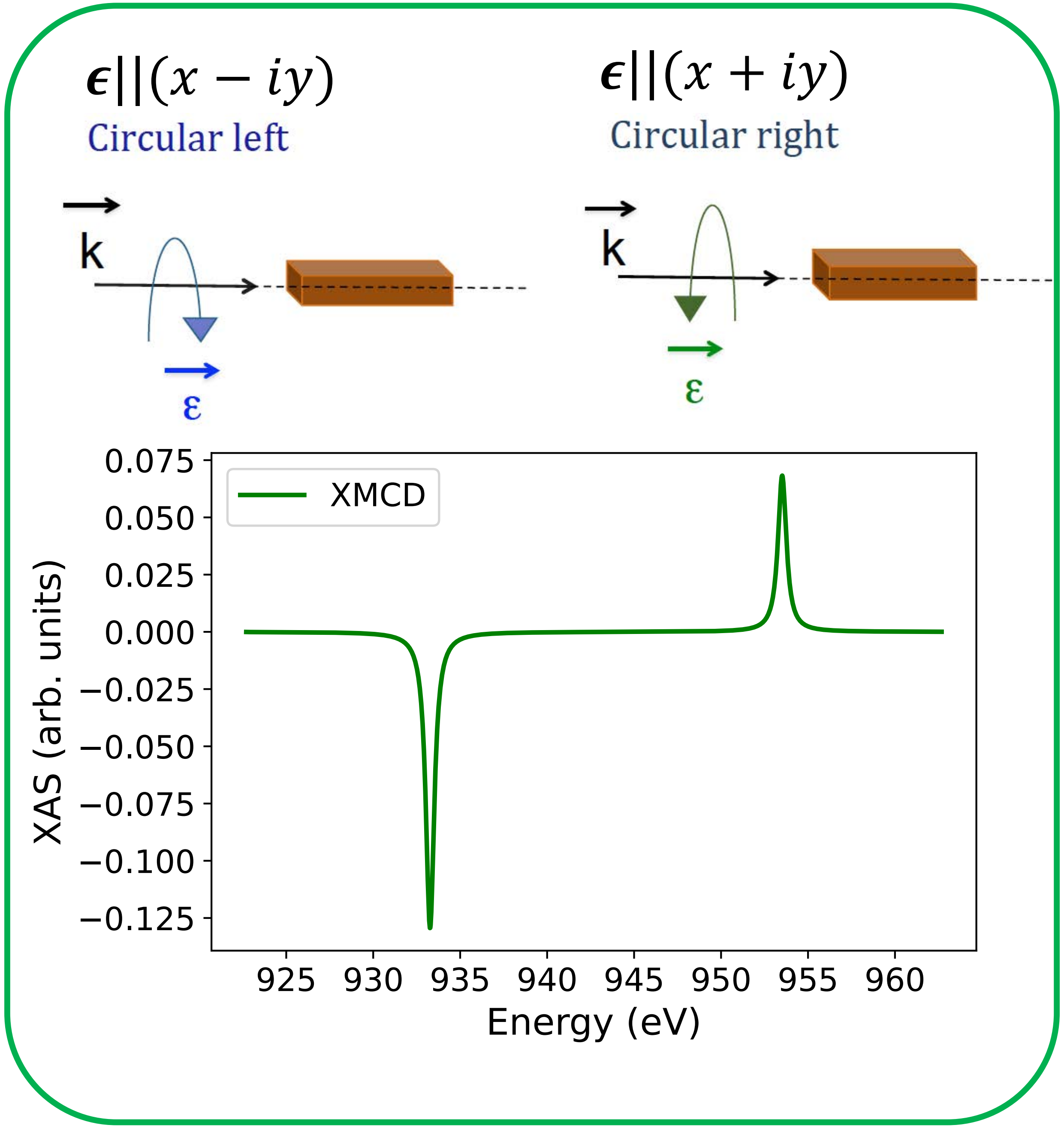
Antisymmetric off-diagonals -> gives XMCD





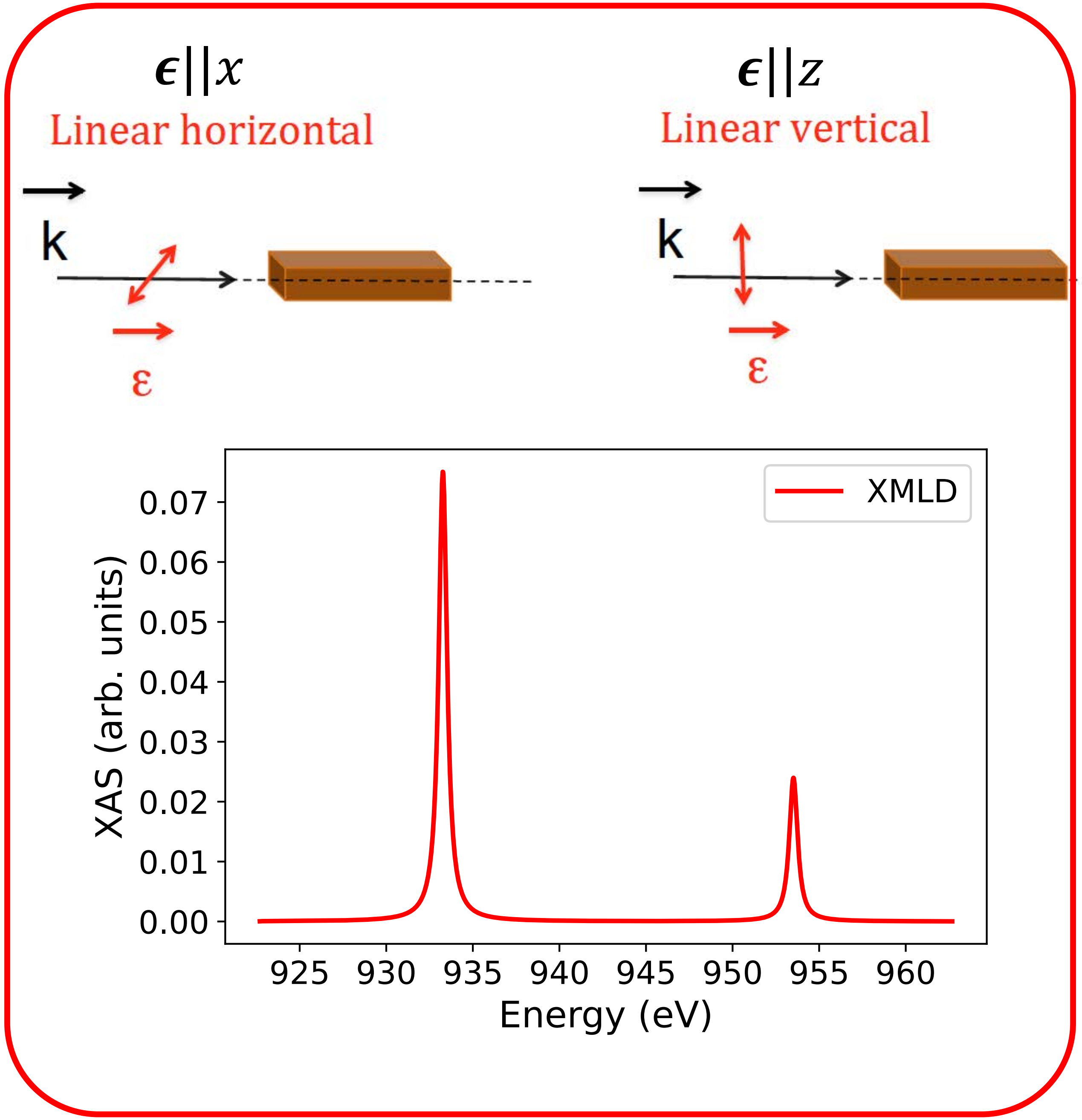
Diagonal-> gives XMLD

XMCD



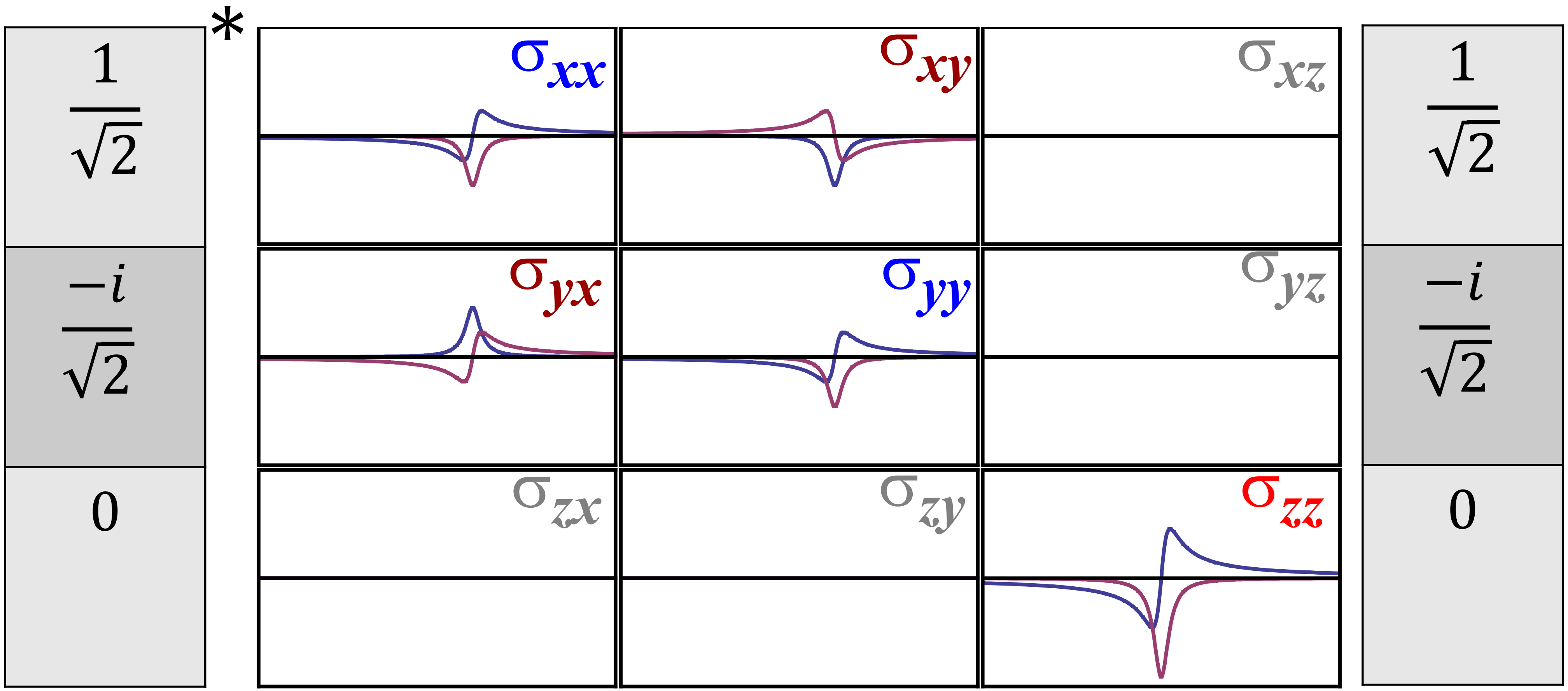
$\epsilon||(x - iy)$
Circular left
$\epsilon||(x + iy)$
Circular right
k
ε
XMCD
XAS (arb. units)
Energy (eV)
0.075
0.050
0.025
0.000
−0.025
−0.050
−0.075
−0.100
−0.125
925
930
935
940
945
950
955
960

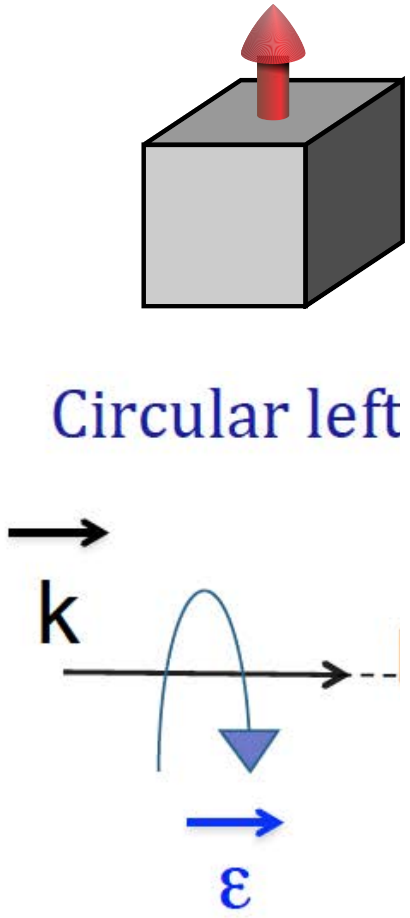
XMLD



$\epsilon||x$
Linear horizontal
$\epsilon||z$
Linear vertical
k
ε
XMLD
XAS (arb. units)
Energy (eV)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
925
930
935
940
945
950
955
960

XMCD

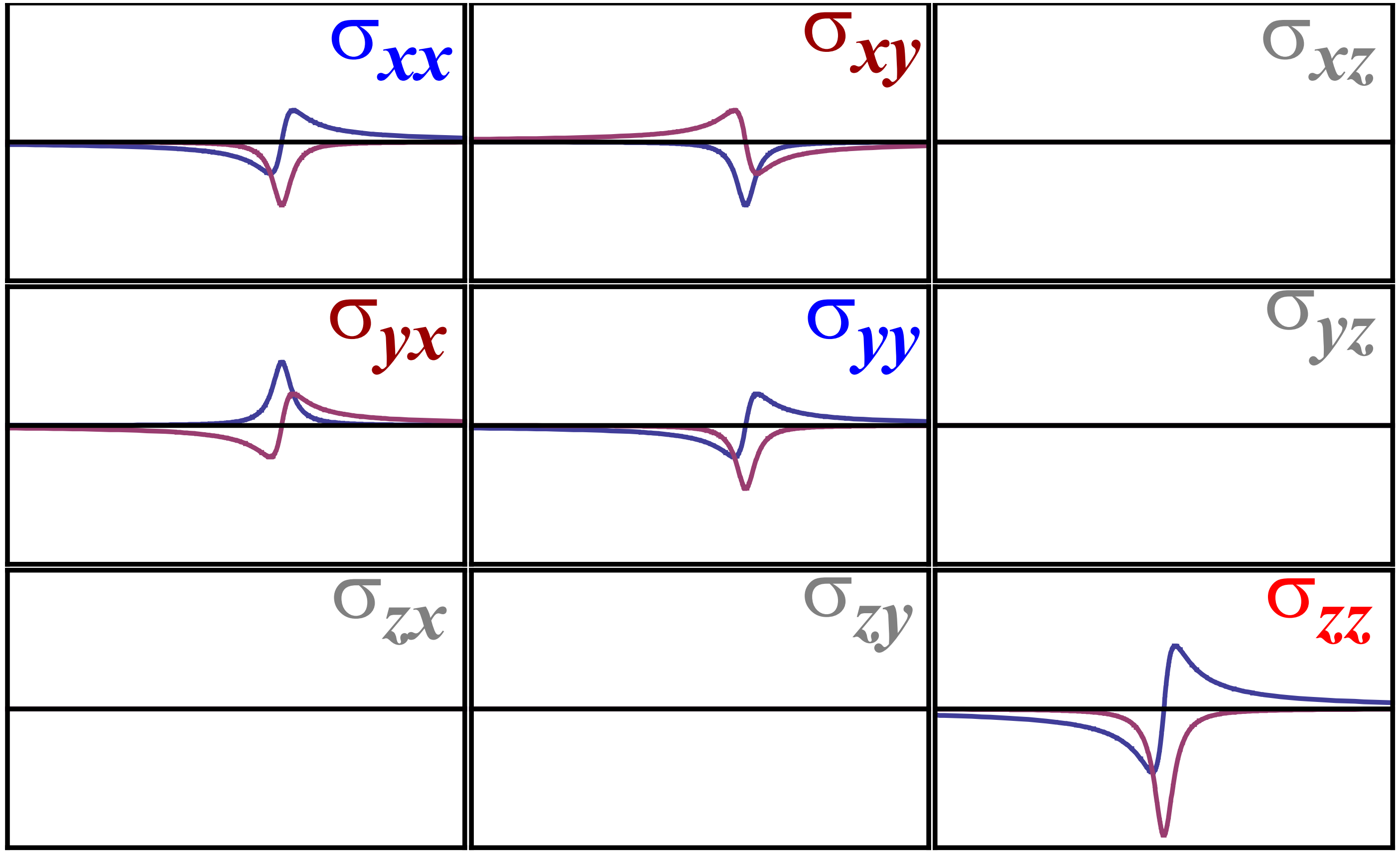




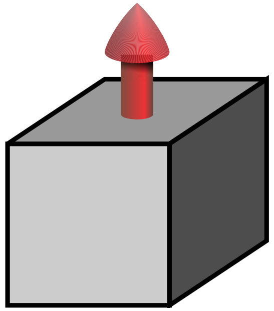
$$\frac{\sigma_{xx}}{2} + \frac{\sigma_{yy}}{2} + i\left(\frac{\sigma_{yx}}{2} - \frac{\sigma_{xy}}{2}\right)$$

XMCD

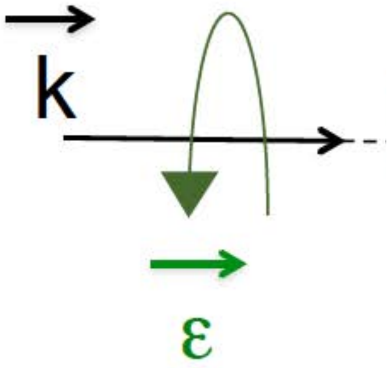
$$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} \\ 0 \end{pmatrix}^{*}$$



$$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} \\ 0 \end{pmatrix}$$



Circular right

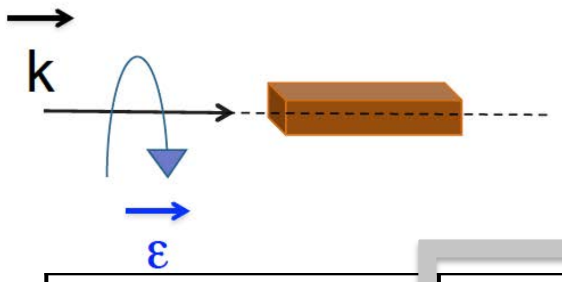


$$\frac{\sigma_{xx}}{2}+\frac{\sigma_{yy}}{2}-i\left(\frac{\sigma_{yx}}{2}-\frac{\sigma_{xy}}{2}\right)$$

XMCD

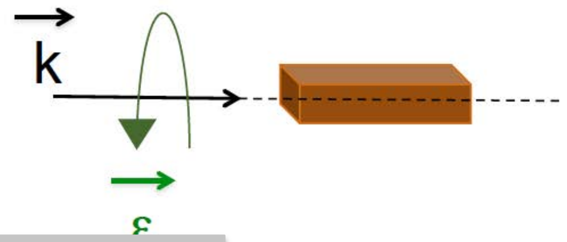
$\epsilon || (x - iy)$

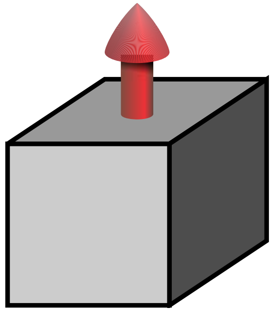
Circular left

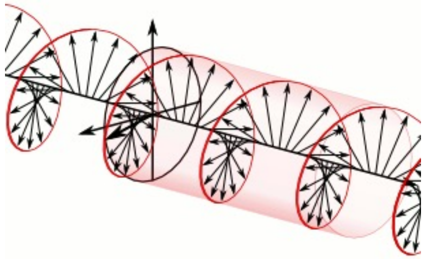


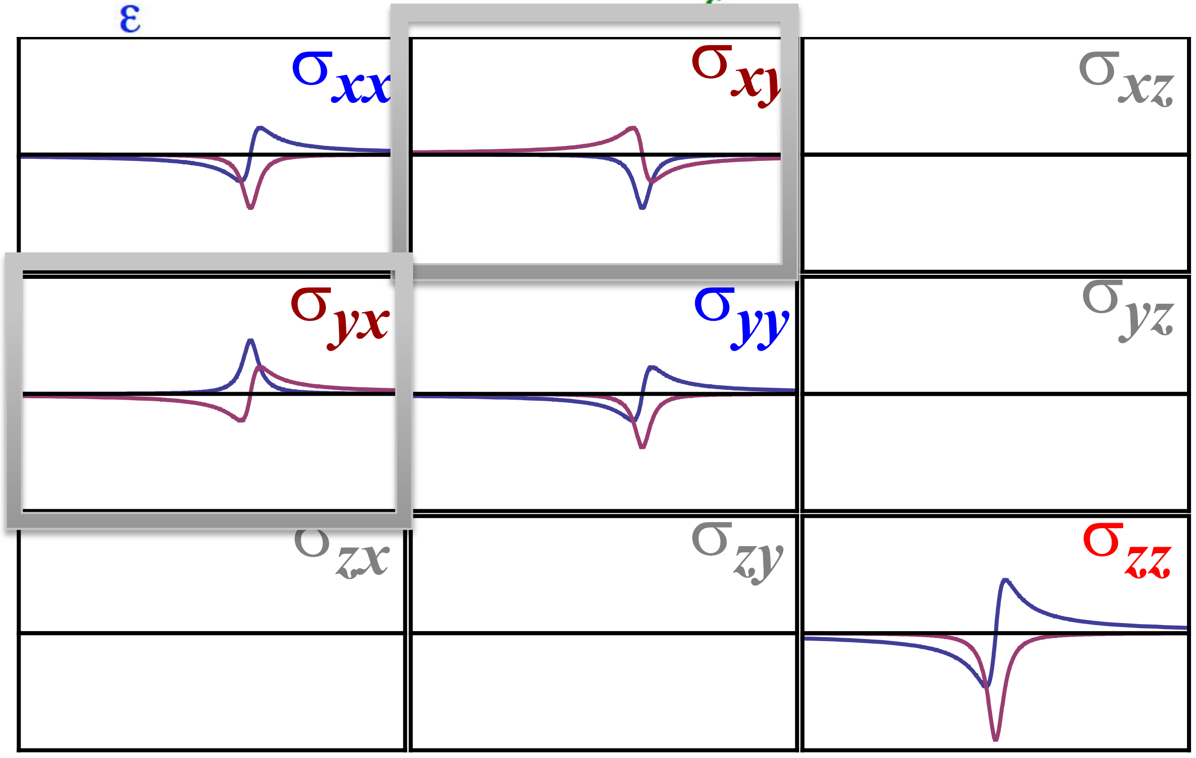
$\epsilon || (x + iy)$

Circular right



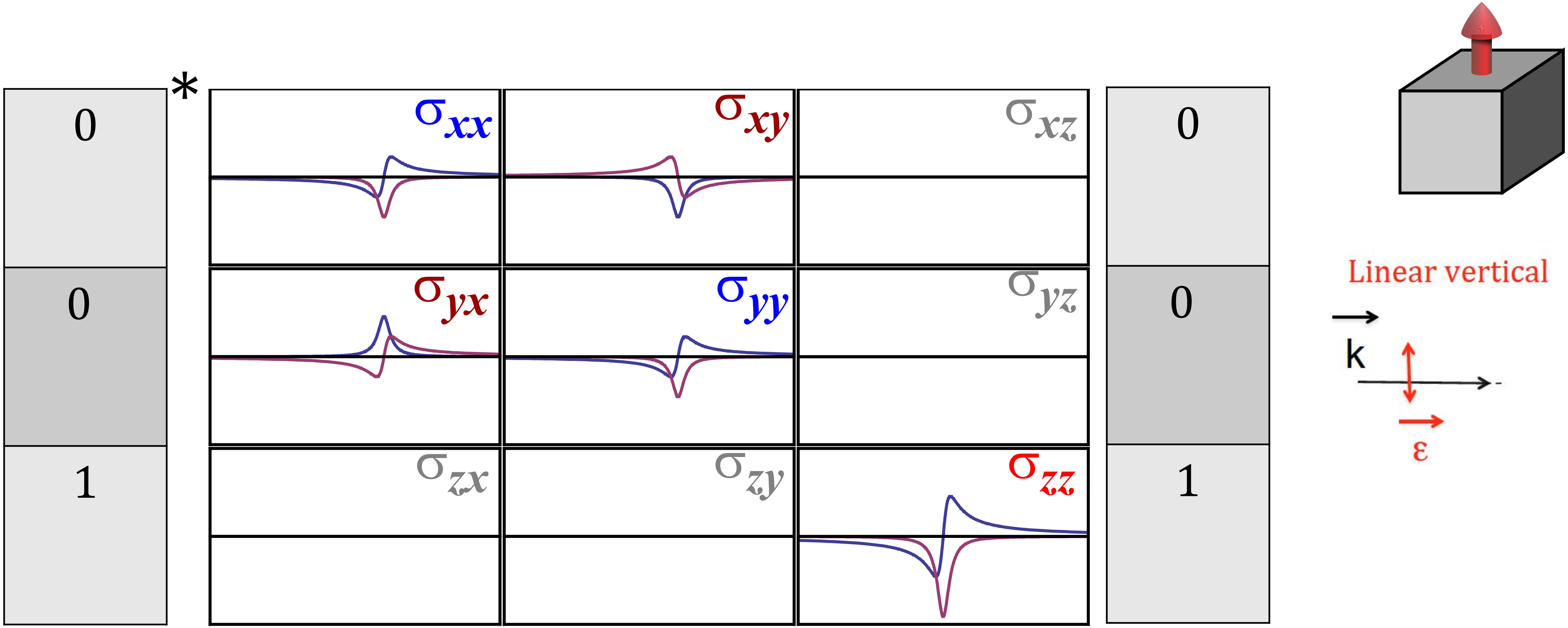






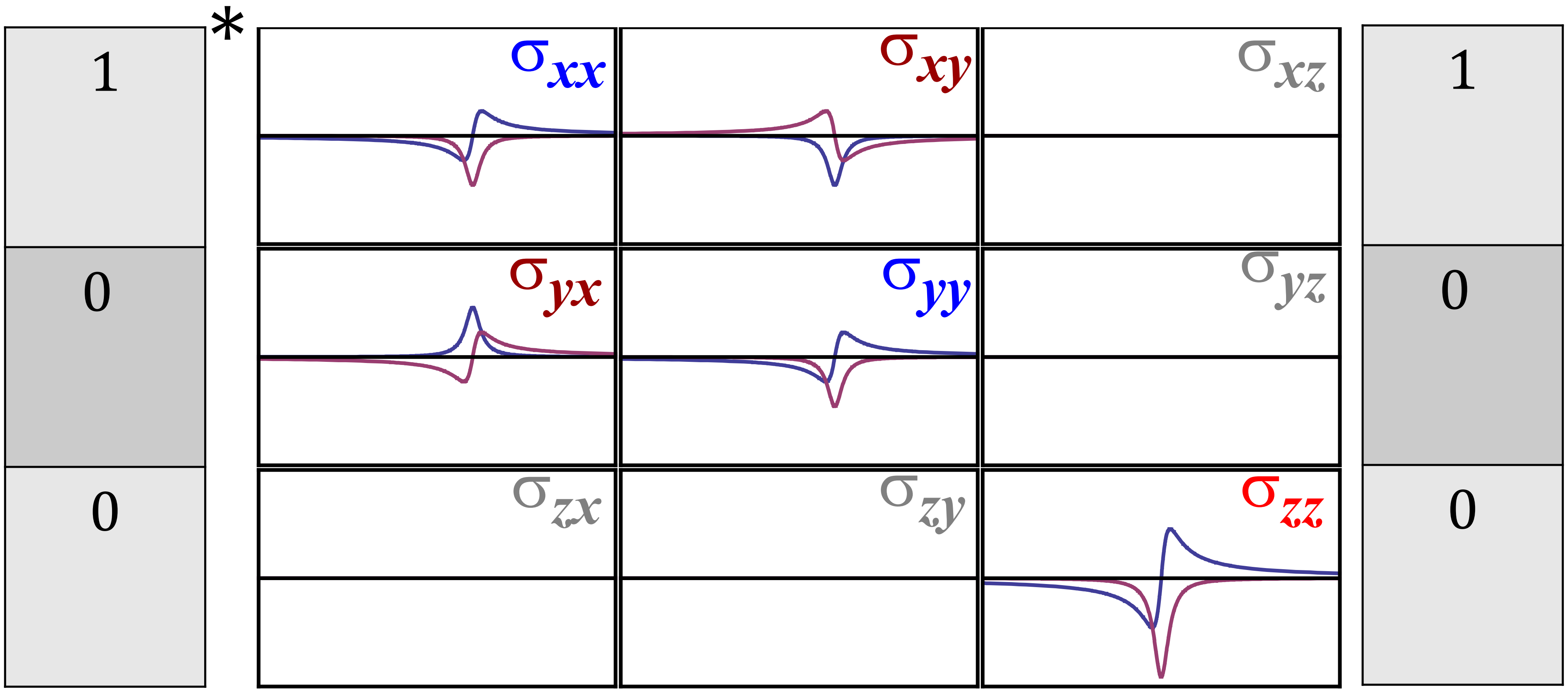
$$i(\sigma_{yx} - \sigma_{xy})$$

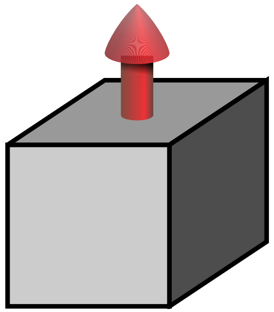
XMLD

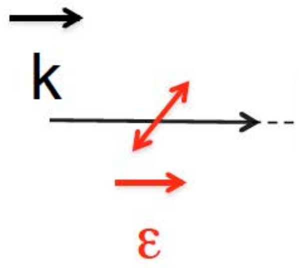


σ_{zz}

XMLD





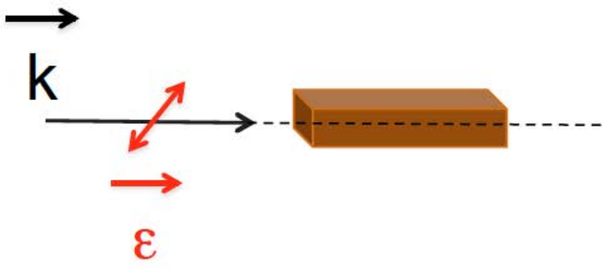


$$\sigma_{xx}$$

XMLD

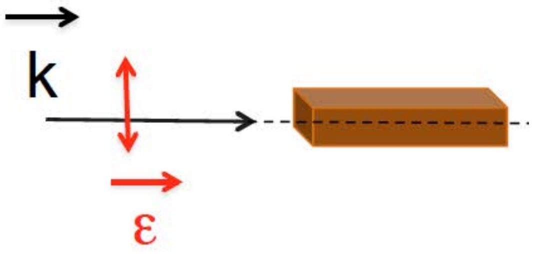
$\epsilon || x$

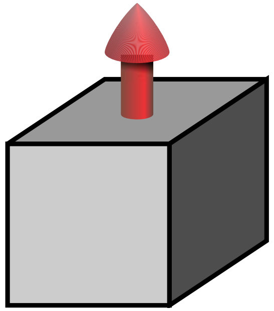
Linear horizontal

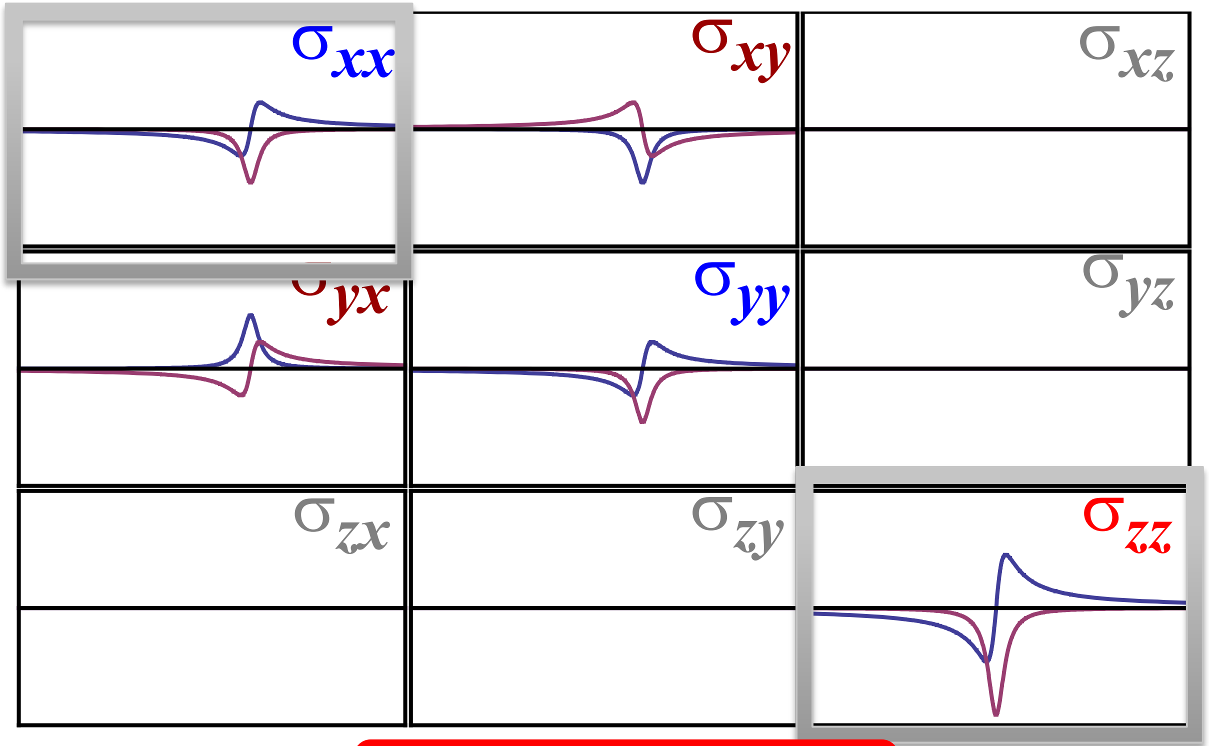


$\epsilon || z$

Linear vertical

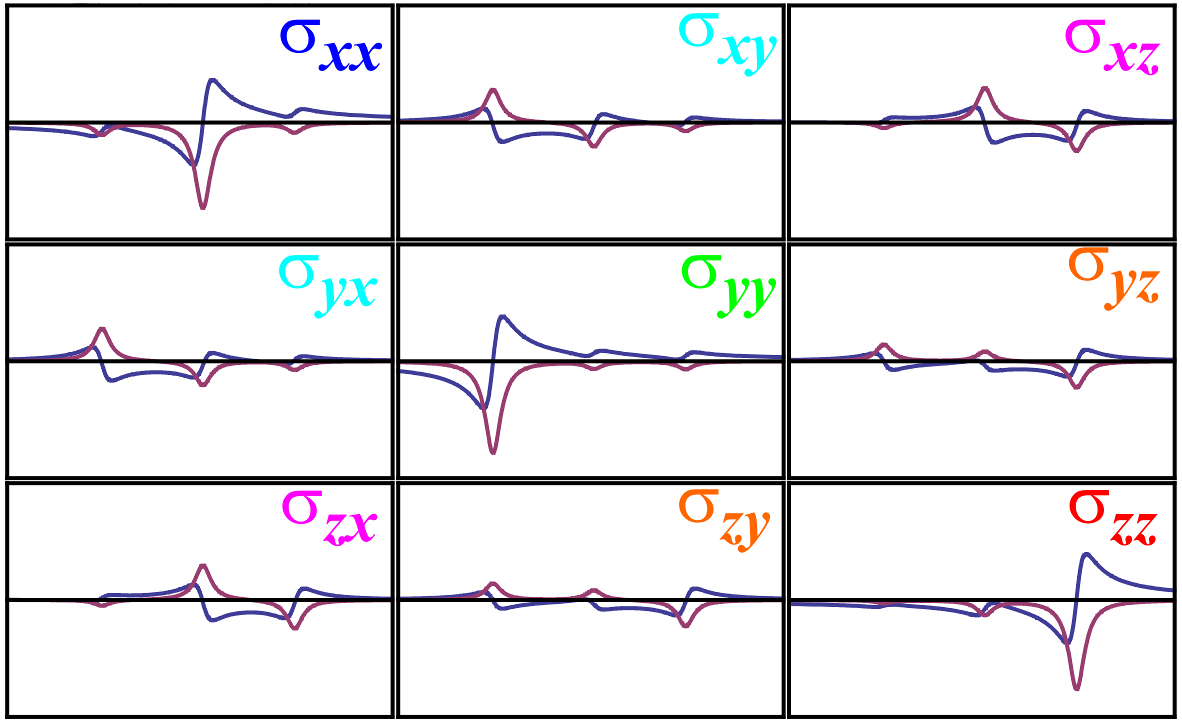






$$(\sigma_{xx} - \sigma_{zz})$$

We can compute all possible dichroisms from the conductivity tensor!

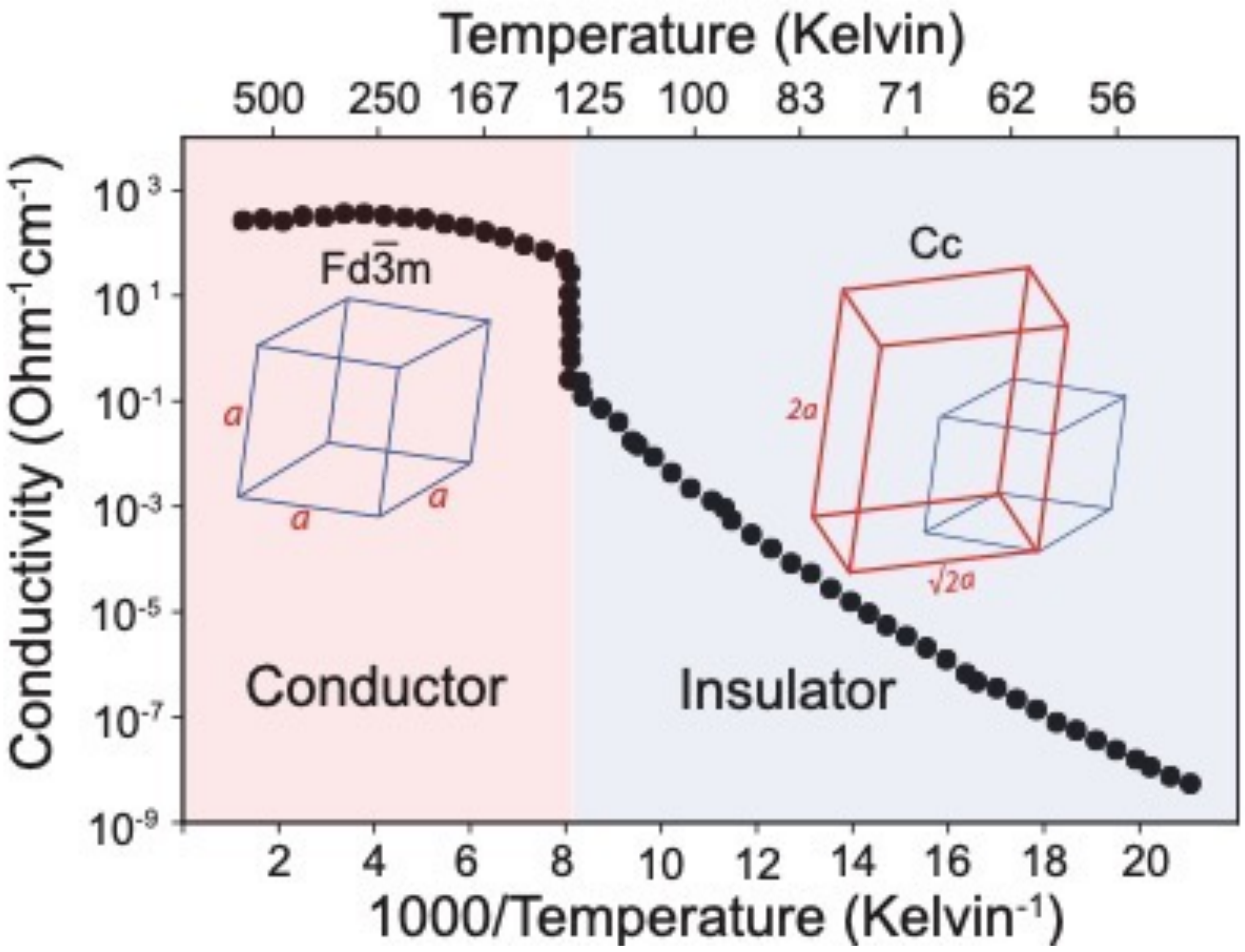


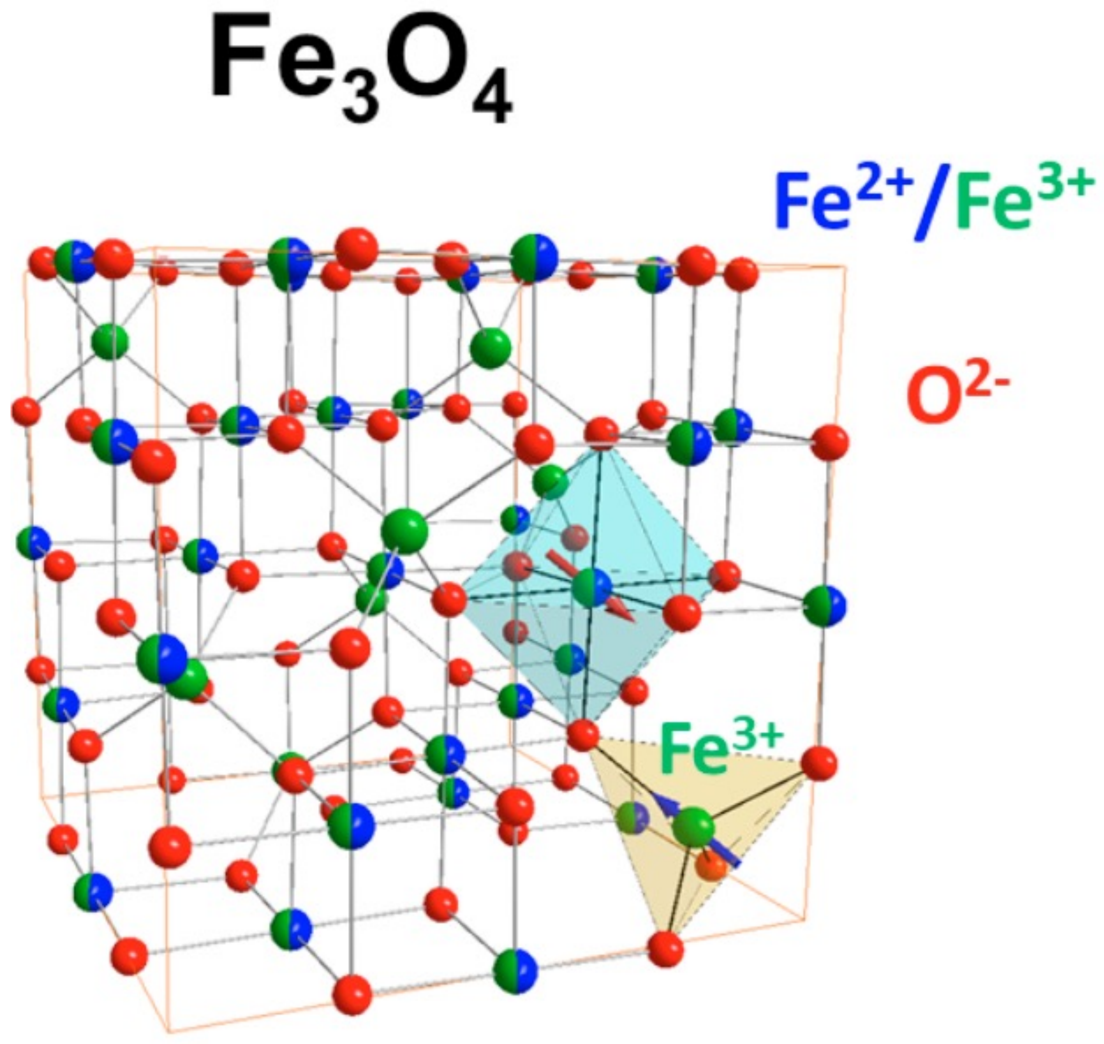
Maximum of **nine** spectra required in the most general case

M. W. Haverkort

We can also measure all this: Fe_3O_4

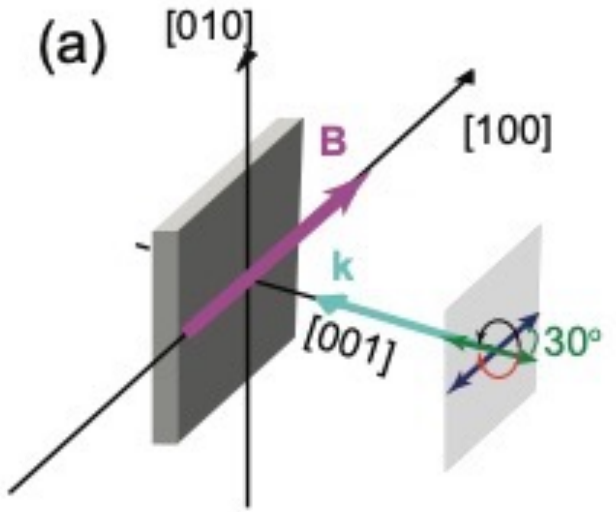
Magnetite: $[Fe^{3+}]_{Td}\ [Fe^{2+}\ ,\ Fe^{3+}]_{Oh}O_4$

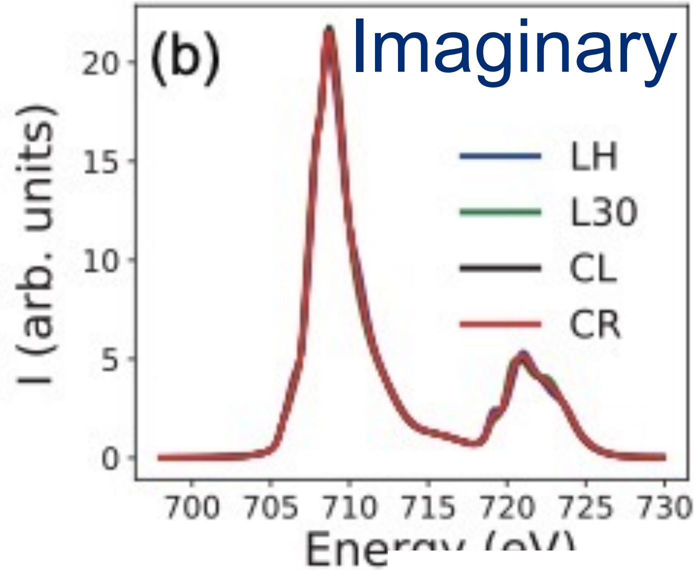




Fe_3O_4 : Fe $L_{3,2}$-edge XAS

Magnetite: $[Fe^{3+}]_{Td}\,[Fe^{2+}, Fe^{3+}]_{Oh}O_4$





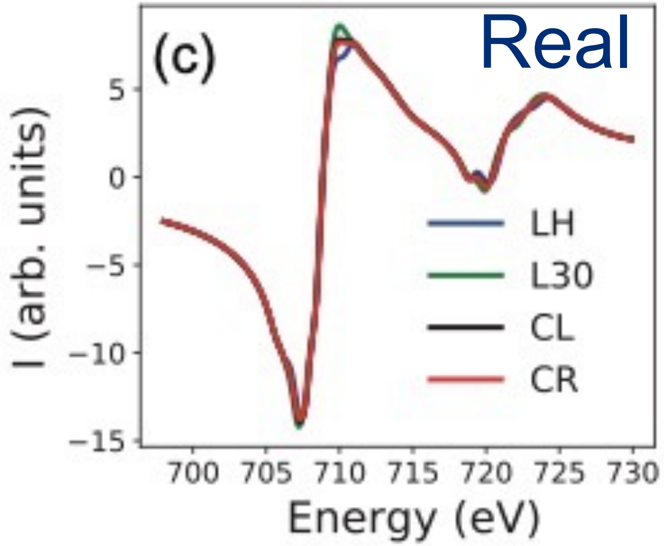
To get all elements

- Circular
- Linear

$$\chi_1(\omega) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\chi_2(\omega')}{\omega' - \omega}\, d\omega'$$

Kramers-Kronig

Transformation

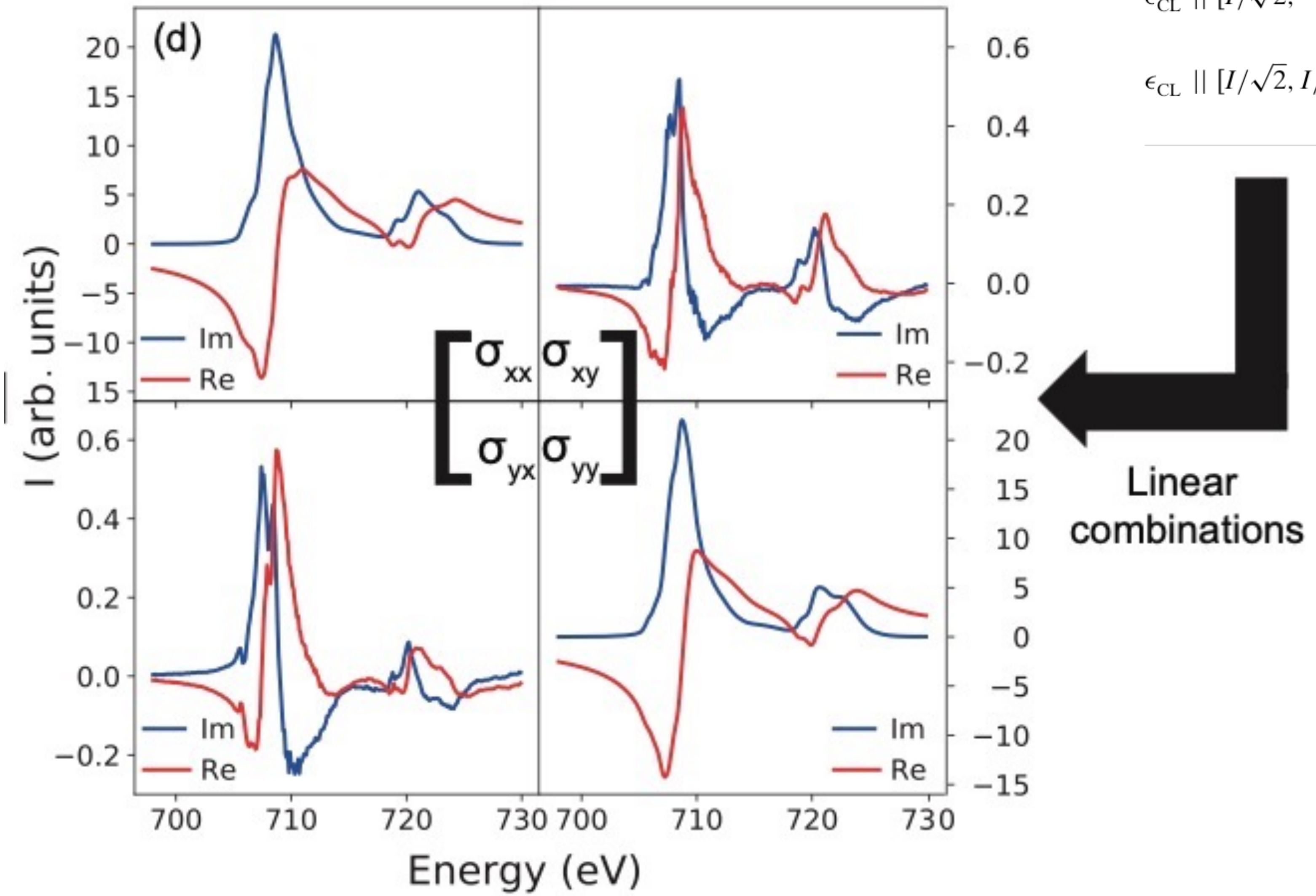


Elnaggar et. al., J. Synchrotron Rad. (2021). 28, 247–258

Fe_3O_4 : Fe $L_{3,2}$-edge XAS

Magnetite: $[Fe^{3+}]_{Td}$ $[Fe^{2+}$, $Fe^{3+}]_{Oh}O_4$

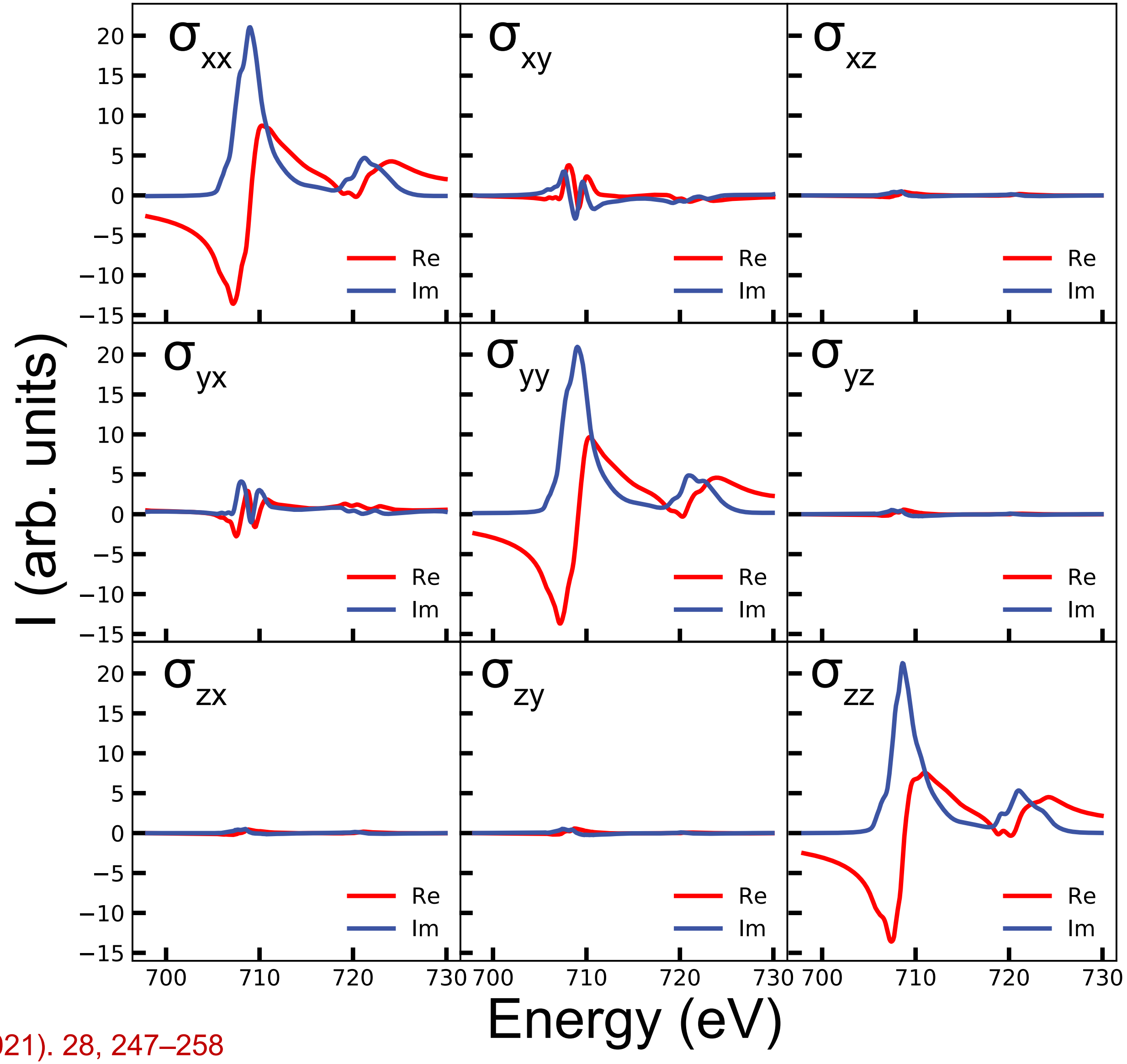
Measured	Constructed
$\epsilon_{LH} \parallel [1, 0, 0]$	$\sigma_{xx} = \mathrm{XAS}_{LH}$
$\epsilon_{L30} \parallel [\sqrt{3}/2, -1/2, 0]$	$\sigma_{yy} = \mathrm{XAS}_{CL} + \mathrm{XAS}_{CR} - \mathrm{XAS}_{LH}$
$\epsilon_{CL} \parallel [I/\sqrt{2}, -I/\sqrt{2}, 0]$	$\sigma_{xy} = \frac{1}{6}[2\sqrt{3}\,\mathrm{XAS}_{LH} - 4\sqrt{3}\,\mathrm{XAS}_{L30} + (\sqrt{3} - 3I)\,\mathrm{XAS}_{CR} + (\sqrt{3} + 3I)\,\mathrm{XAS}_{CL}]$
$\epsilon_{CL} \parallel [I/\sqrt{2}, I/\sqrt{2}, 0]$	$\sigma_{yx} = \frac{1}{6}[2\sqrt{3}\,\mathrm{XAS}_{LH} - 4\sqrt{3}\,\mathrm{XAS}_{L30} + (\sqrt{3} + 3I)\,\mathrm{XAS}_{CR} + (\sqrt{3} - 3I)\,\mathrm{XAS}_{CL}]$

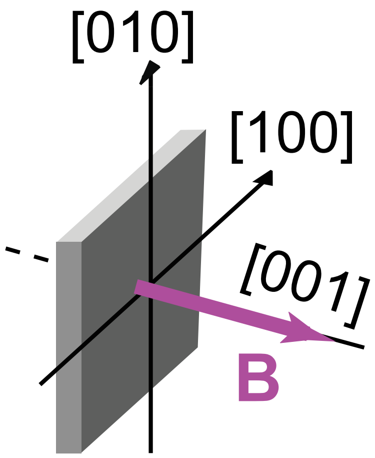


Elnaggar et. al., J. Synchrotron Rad. (2021). 28, 247–258

Fe_3O_4 : Fe $L_{3,2}$-edge Conductivity Tensor

Magnetite: $[Fe^{3+}]_{Td}\ [Fe^{2+}, Fe^{3+}]_{Oh} O_4$

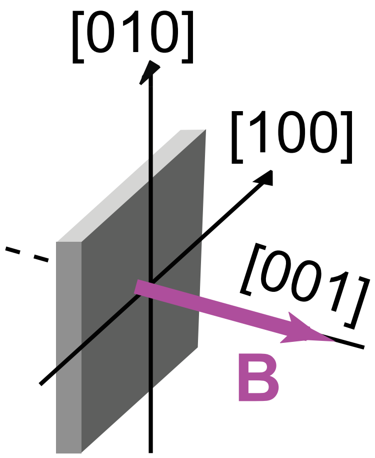




Elnaggar et. al., J. Synchrotron Rad. (2021). 28, 247–258

Fe_3O_4 : Fe $L_{3,2}$-edge Diagonal Elements

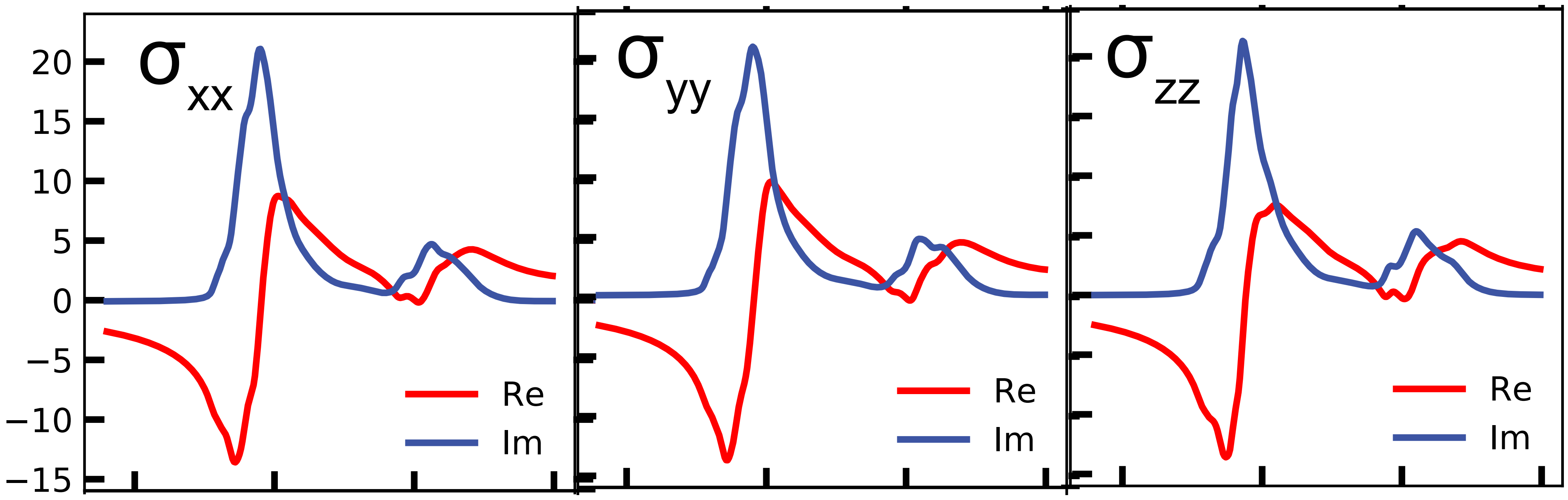
Magnetite: $[Fe^{3+}]_{Td}$ $[Fe^{2+}, Fe^{3+}]_{Oh}O_4$



Diagonal Elements:

- $\sigma_{xx} = \sigma_{yy}$
- σ_{zz} is different

→ XMLD in cubic symmetry



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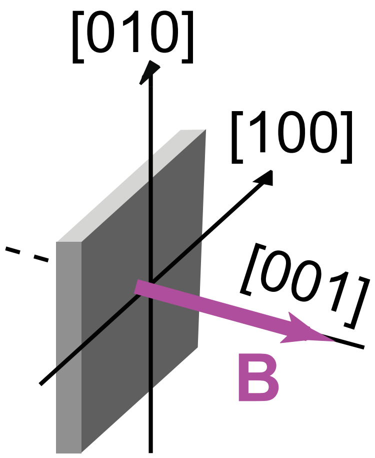
Fe_3O_4 : Fe $L_{3,2}$-edge Non-diagonal Elements

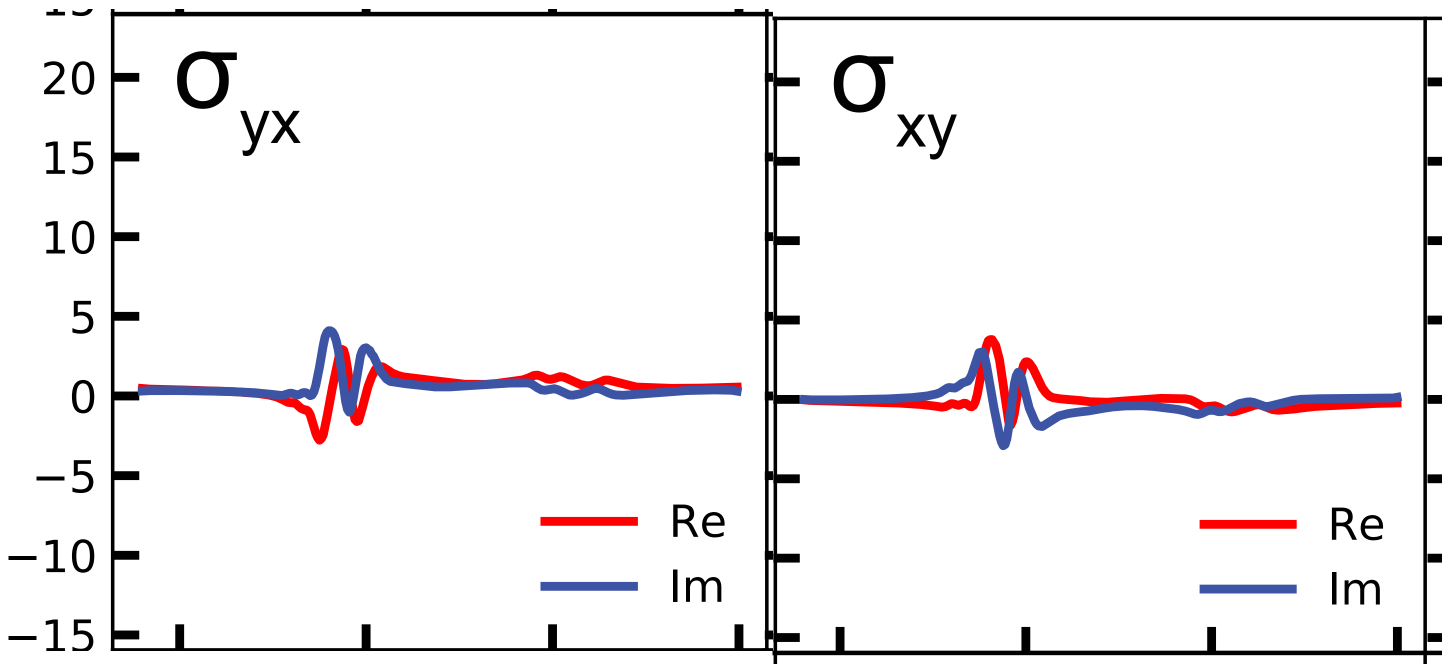
Magnetite: $[Fe^{3+}]_{Td}$ $[Fe^{2+}$, $Fe^{3+}]_{Oh}O_4$

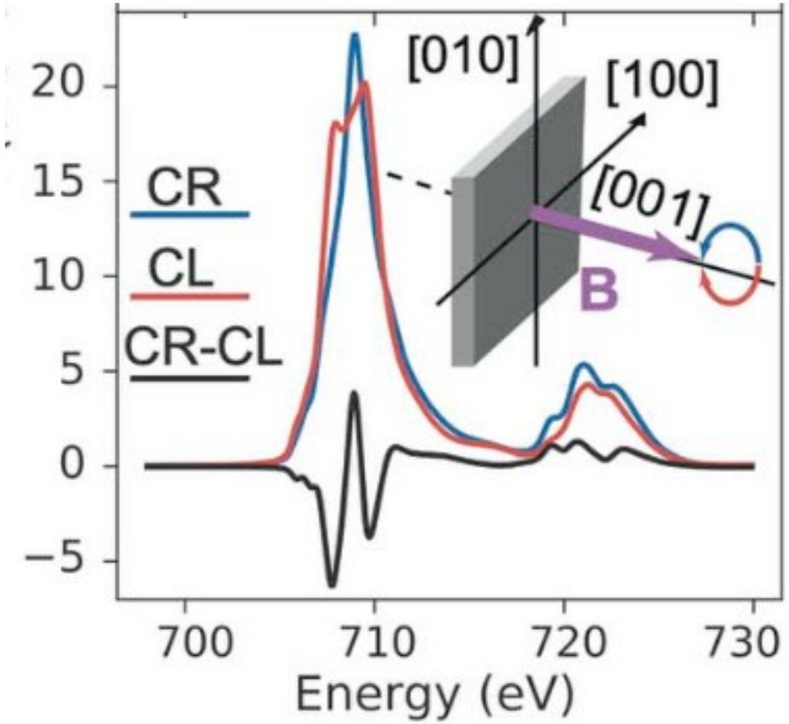


Off-diagonal Elements:

- $\sigma_{xy} = -\sigma_{yx}$
- gives XMCD

XMCD in cubic symmetry

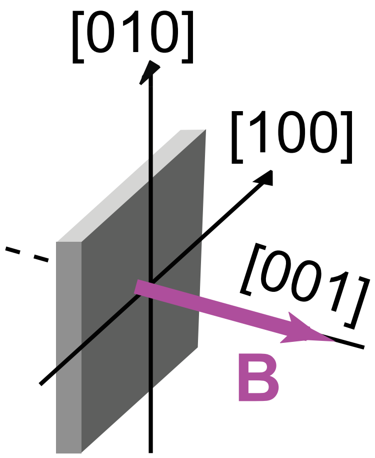




Elnaggar et. al., J. Synchrotron Rad. (2021). 28, 247–258

Fe_3O_4 : Fe $L_{3,2}$-edge Non-diagonal Elements

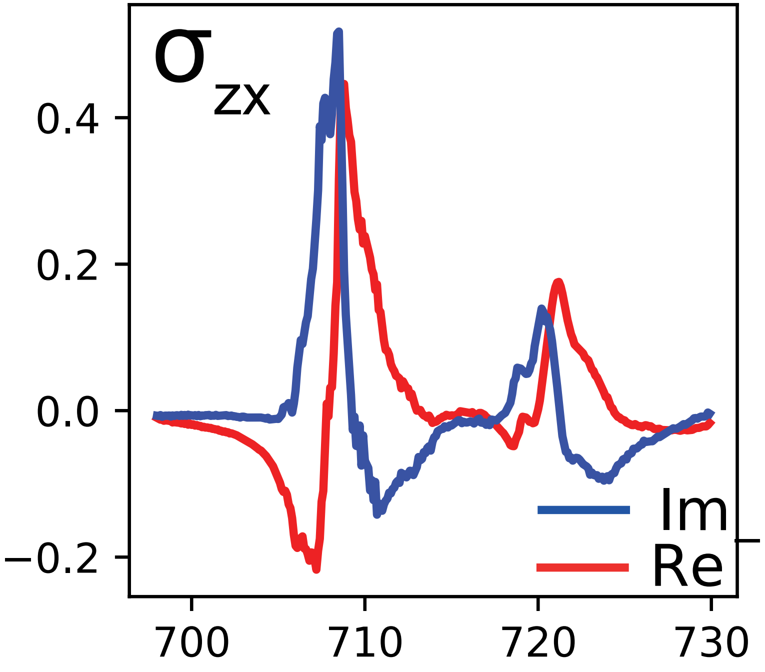
Magnetite: $[Fe^{3+}]_{Td}$ $[Fe^{2+}$, $Fe^{3+}]_{Oh}O_4$

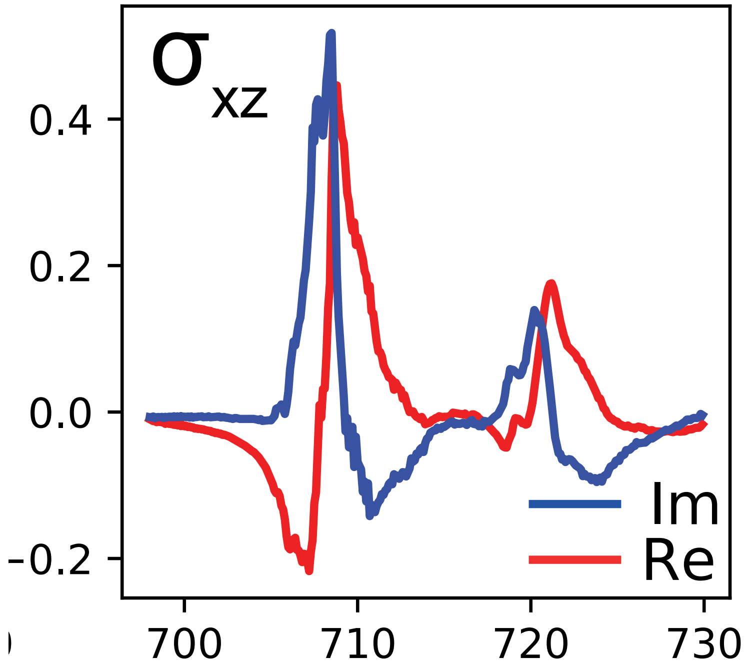


Off-diagonal Elements:

- $\sigma_{xz} = \sigma_{zx}$
- 10x less

→ XMLD signature of small non-cubic distortion

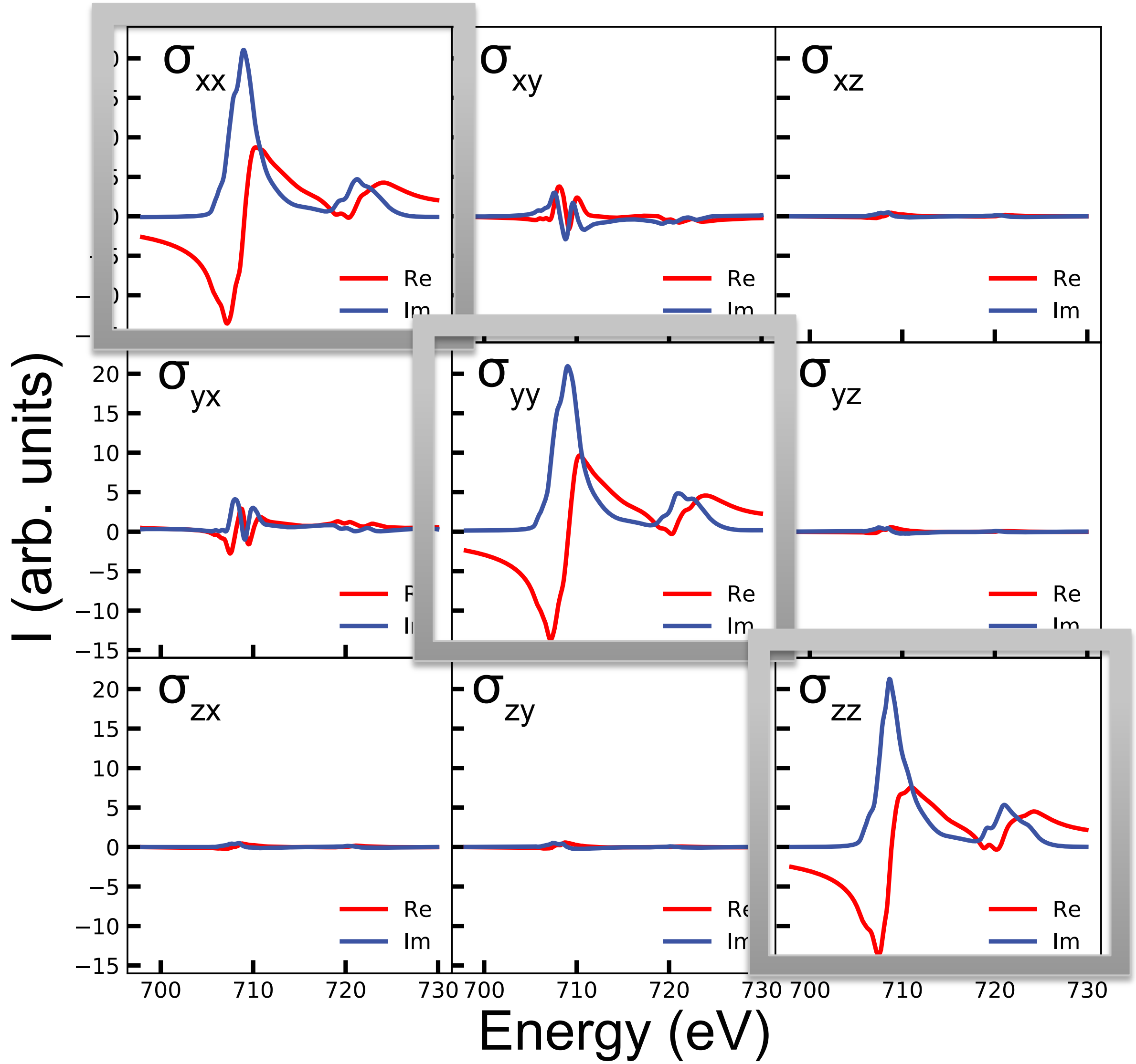




Elnaggar et. al., J. Synchrotron Rad. (2021). 28, 247–258

Fe_3O_4 : Creating a Spherical Tensor (rank 2)

Create linear combination based on spherical symmetry

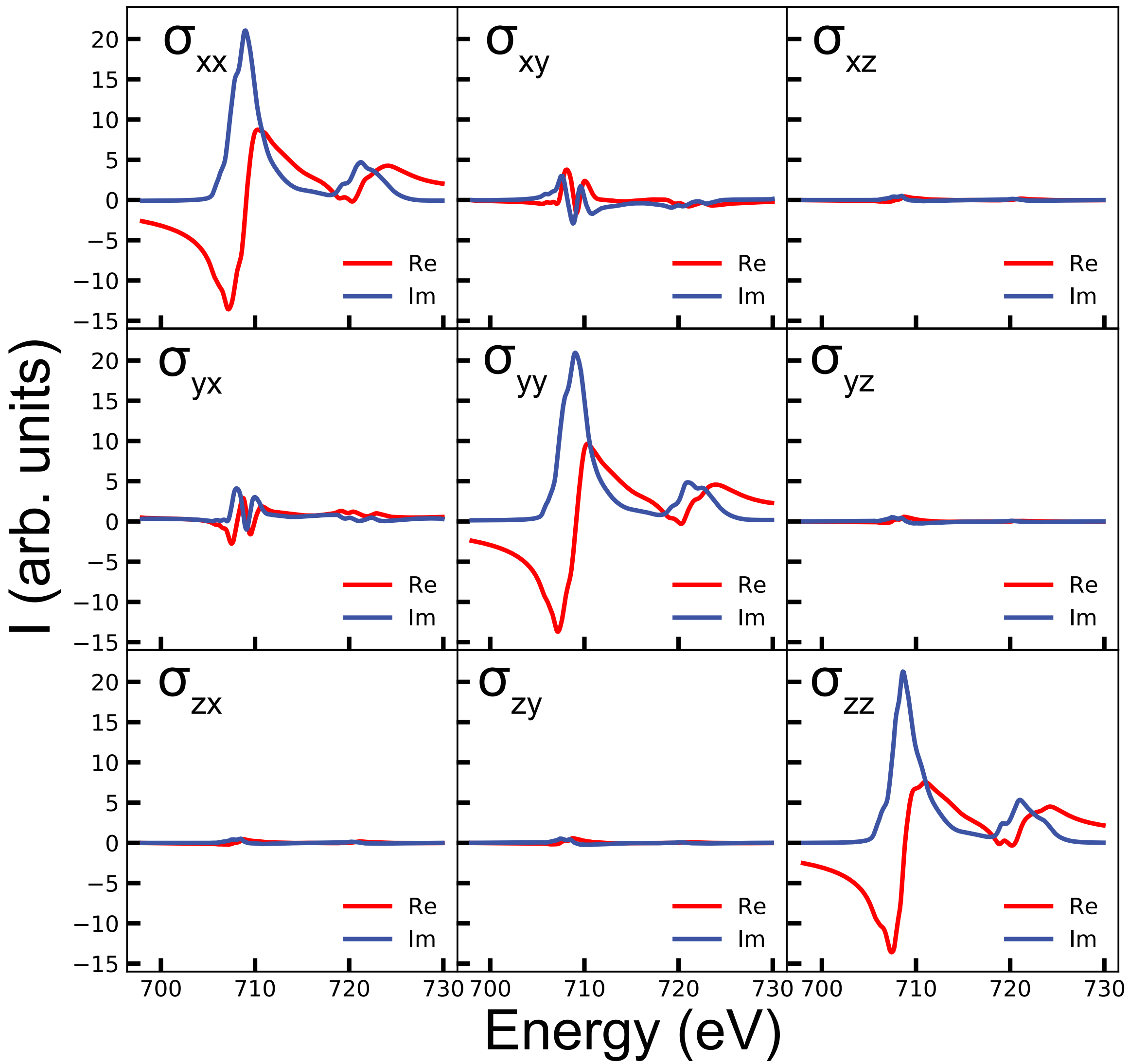


Rank 0 --> Isotropic

$$XAS_{iso} = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$$

Fe_3O_4 : Creating a Spherical Tensor (rank 2)

Create linear combination based on spherical symmetry



Rank 1 --> circular dichroism, 3 terms

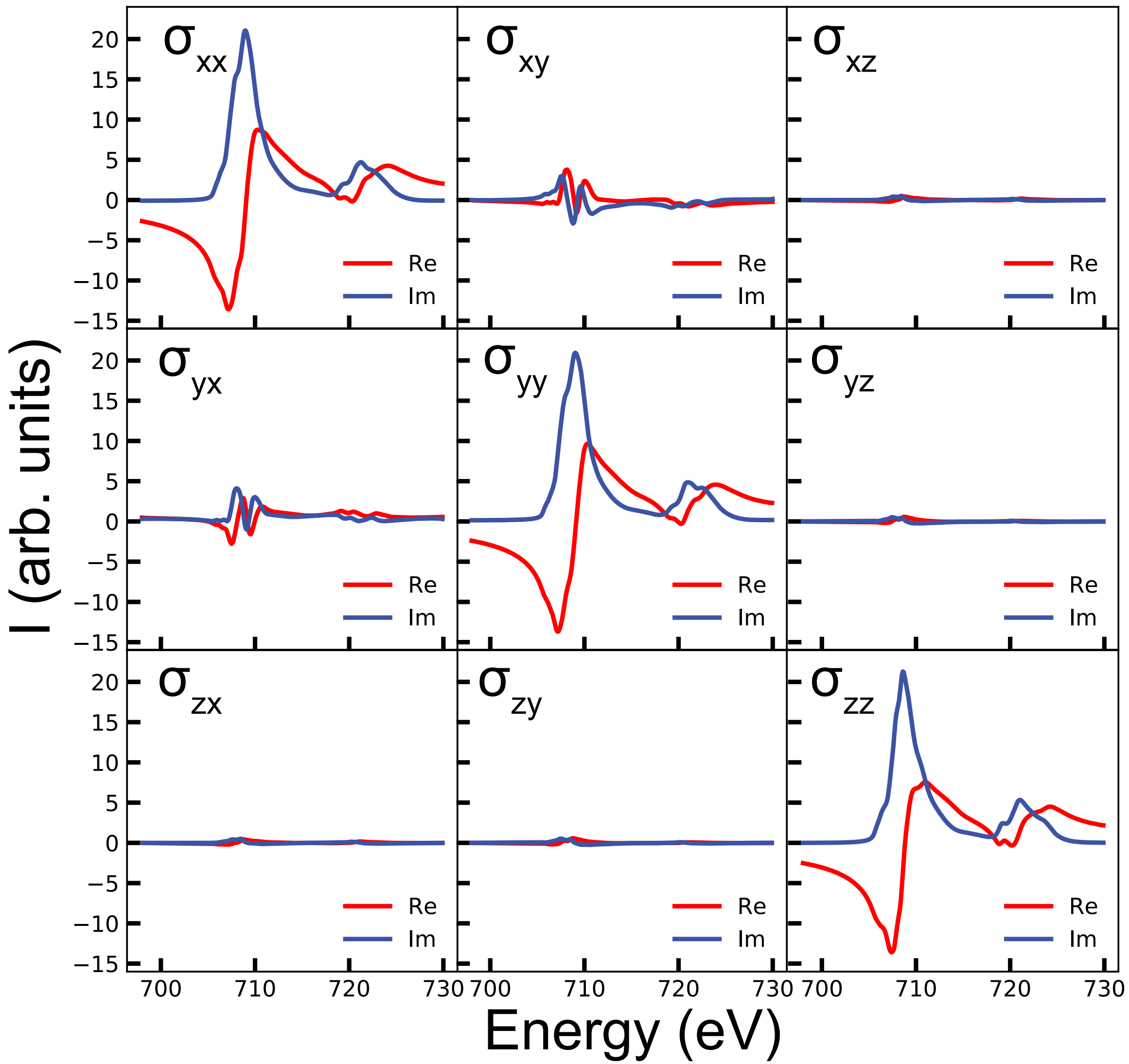
$$\sigma(1,0) = -4\pi\alpha\hbar\omega\ \mathbf{Im}\ [(-1)^0\{\boldsymbol{\epsilon}^{1*}\otimes\boldsymbol{\epsilon}^1\}^1_0\{< I|\boldsymbol{r}^1 G^+\boldsymbol{r}^1|I >\}^1_0]$$
$$= -4\pi\alpha\hbar\omega\mathbf{Im}[\ \frac{1}{2}\left(i\epsilon^*_x\epsilon_y - i\epsilon_x\epsilon^*_y\right)\left(< I|rY^*_{1,1}G^+rY_{1,1}|I > - < I|rY^*_{1,-1}G^+rY_{1,-1}|I >\right)\ ] \quad (30)$$

$$\sigma(1,1) = -4\pi\alpha\hbar\omega\ \mathbf{Im}\ [(-1)^1\{\boldsymbol{\epsilon}^{1*}\otimes\boldsymbol{\epsilon}^1\}^1_{-1}\{< I|\boldsymbol{r}^1 G^+\boldsymbol{r}^1|I >\}^1_1]$$
$$-4\pi\alpha\hbar\omega\mathbf{Im}[\ \frac{-1}{2\sqrt{2}}\left(\epsilon^*_x\epsilon_z - \epsilon_x\epsilon^*_z + i\epsilon_y\epsilon^*_z - i\epsilon^*_y\epsilon_z\right)\left(< I|rY^*_{1,0}G^+rY_{1,1}|I > + < I|rY^*_{1,-1}G^+rY_{1,0}|I >\right)\ ] \quad (31)$$

$$\sigma(1,-1) = -4\pi\alpha\hbar\omega\ \mathbf{Im}\ [(-1)^{-1}\{\boldsymbol{\epsilon}^{1*}\otimes\boldsymbol{\epsilon}^1\}^1_1\{< I|\boldsymbol{r}^1 G^+\boldsymbol{r}^1|I >\}^1_{-1}]$$
$$-4\pi\alpha\hbar\omega\mathbf{Im}[\ \frac{1}{2\sqrt{2}}\left(\epsilon^*_x\epsilon_z - \epsilon_x\epsilon^*_z + i\epsilon^*_y\epsilon_z - i\epsilon_y\epsilon^*_z\right)\left(< I|rY^*_{1,0}G^+rY_{1,-1}|I > + < I|rY^*_{1,1}G^+rY_{1,0}|I >\right)\ ] \quad (32)$$

Fe_3O_4 : Creating a Spherical Tensor (rank 2)

Create linear combination based on spherical symmetry



Rank 2 --> Linear dichroism, 5 terms

$$\sigma(2,0) = -4\pi\alpha\hbar\omega\ \mathbf{Im}\ [(-1)^0\{\boldsymbol{\epsilon}^{1*}\otimes\boldsymbol{\epsilon}^1\}^2_0.\{< I|\boldsymbol{r}^1 G^+\boldsymbol{r}^1|I>\}^2_0]$$
$$= -4\pi\alpha\hbar\omega\mathbf{Im}[\ \frac{1}{6}(2|\epsilon_z|^2-|\epsilon_x|^2-|\epsilon_y|^2)$$
$$(2< I|rY^*_{1,0}G^+rY_{1,0}|I> - < I|rY^*_{1,-1}G^+rY_{1,-1}|I> - < I|rY^*_{1,1}G^+rY_{1,1}|I>)\ ] \quad (33)$$

$$\sigma(2,1) = -4\pi\alpha\hbar\omega\ \mathbf{Im}\ [(-1)^1\{\boldsymbol{\epsilon}^{1*}\otimes\boldsymbol{\epsilon}^1\}^2_{-1}.\{< I|\boldsymbol{r}^1 G^+\boldsymbol{r}^1|I>\}^2_1]$$
$$= -4\pi\alpha\hbar\omega\ \mathbf{Im}[\ \frac{1}{2\sqrt{2}}\left(\epsilon_x\epsilon_z^*+\epsilon_x^*\epsilon_z-i\epsilon_y\epsilon_z^*-i\epsilon_y^*\epsilon_z\right)$$
$$(< I|rY^*_{1,-1}G^+rY_{1,0}|I> - < I|rY^*_{1,0}G^+rY_{1,1}|I>)\ ] \quad (34)$$

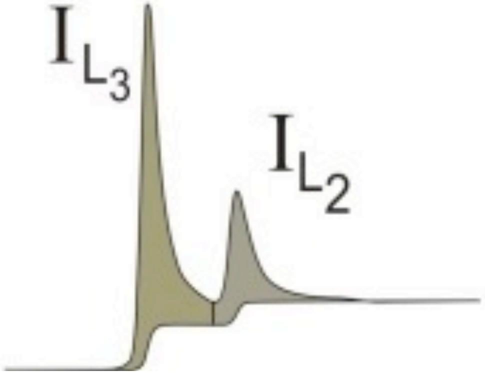
$$\sigma(2,-1) = -4\pi\alpha\hbar\omega\ \mathbf{Im}\ [(-1)^{-1}\{\boldsymbol{\epsilon}^{1*}\otimes\boldsymbol{\epsilon}^1\}^2_1.\{< I|\boldsymbol{r}^1 G^+\boldsymbol{r}^1|I>\}^2_{-1}]$$
$$= -4\pi\alpha\hbar\omega\mathbf{Im}[\ \frac{1}{2\sqrt{2}}\left(\epsilon_x\epsilon_z^*+\epsilon_x^*\epsilon_z+i\epsilon_y^*\epsilon_z+i\epsilon_y\epsilon_z^*\right)$$
$$(< I|rY^*_{1,0}G^+rY_{1,-1}|I> - < I|rY^*_{1,1}G^+rY_{1,0}|I>)\ ] \quad (35)$$

$$\sigma(2,2) = -4\pi\alpha\hbar\omega\ \mathbf{Im}\ [(-1)^2\{\boldsymbol{\epsilon}^{1*}\otimes\boldsymbol{\epsilon}^1\}^2_{-2}.\{< I|\boldsymbol{r}^1 G^+\boldsymbol{r}^1|I>\}^2_2]$$
$$= -4\pi\alpha\hbar\omega\mathbf{Im}\left[\frac{-1}{2}\left((\epsilon_x-i\epsilon_y)(\epsilon_x^*-i\epsilon_y^*)\right)(< I|rY^*_{1,-1}G^+rY_{1,1}|I>)\right] \quad (36)$$

$$\sigma(2,-2) - 4\pi\alpha\hbar\omega\ \mathbf{Im}\ [(-1)^{-2}\{\boldsymbol{\epsilon}^{1*}\otimes\boldsymbol{\epsilon}^1\}^2_2.\{< I|\boldsymbol{r}^1 G^+\boldsymbol{r}^1|I>\}^2_{-2}]$$
$$= -4\pi\alpha\hbar\omega\mathbf{Im}\left[\frac{1}{2}\left((\epsilon_x+i\epsilon_y)(\epsilon_x^*+i\epsilon_y^*)\right)(< I|rY^*_{1,1}G^+rY_{1,-1}|I>)\right] \quad (37)$$

Can we learn more from dichroism: Sum Rules for Circular Dichroism

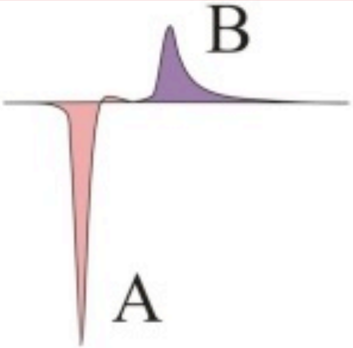
XAS



Isotropic ~ number of holes

$$\int \mu = \int (\mu_1 + \mu_0 + \mu_{-1}) = \frac{C}{5}\langle N_h \rangle.$$

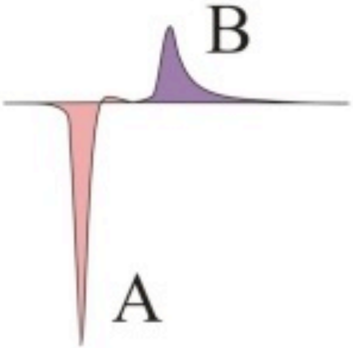
XMCD



XMCD ~ orbital moment

$$\langle L_z \rangle = -\frac{\int (\mu_+ - \mu_-)}{\int \mu} \cdot 2\langle N_h \rangle.$$

XMCD



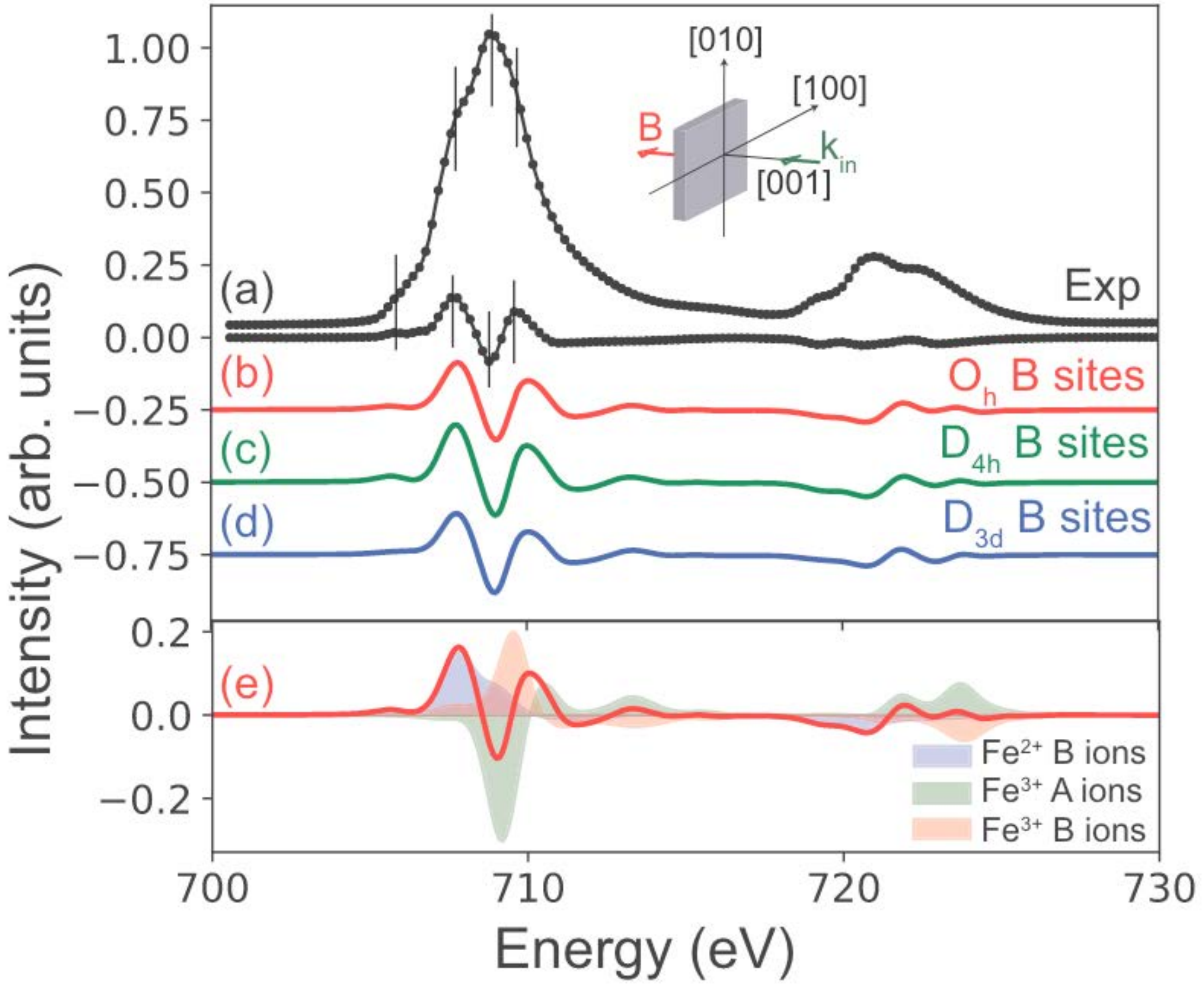
XMCD ~ spin moment

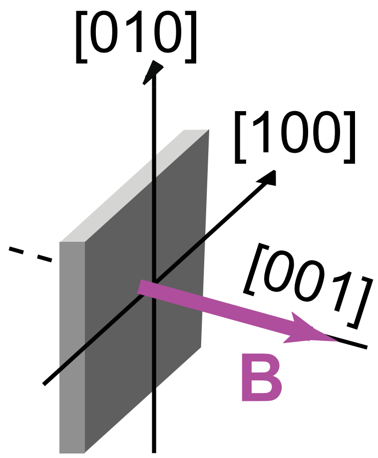
$$\left(\mathcal{I}_{-1}^{c+\frac{1}{2}} - \mathcal{I}_{1}^{c+\frac{1}{2}}\right) = \frac{2}{3\underline{n}}\mathbf{S}_z + \frac{2(2l+3)}{3l\underline{n}}\mathbf{T}_z$$

Thole et. al., Phys. Rev. lett. (1992). 68

Fe_3O_4: Quantifying Magnetic Moments from XMCD

Magnetite: $[Fe^{3+}]_{Td}$ $[Fe^{2+}, Fe^{3+}]_{Oh}O_4$





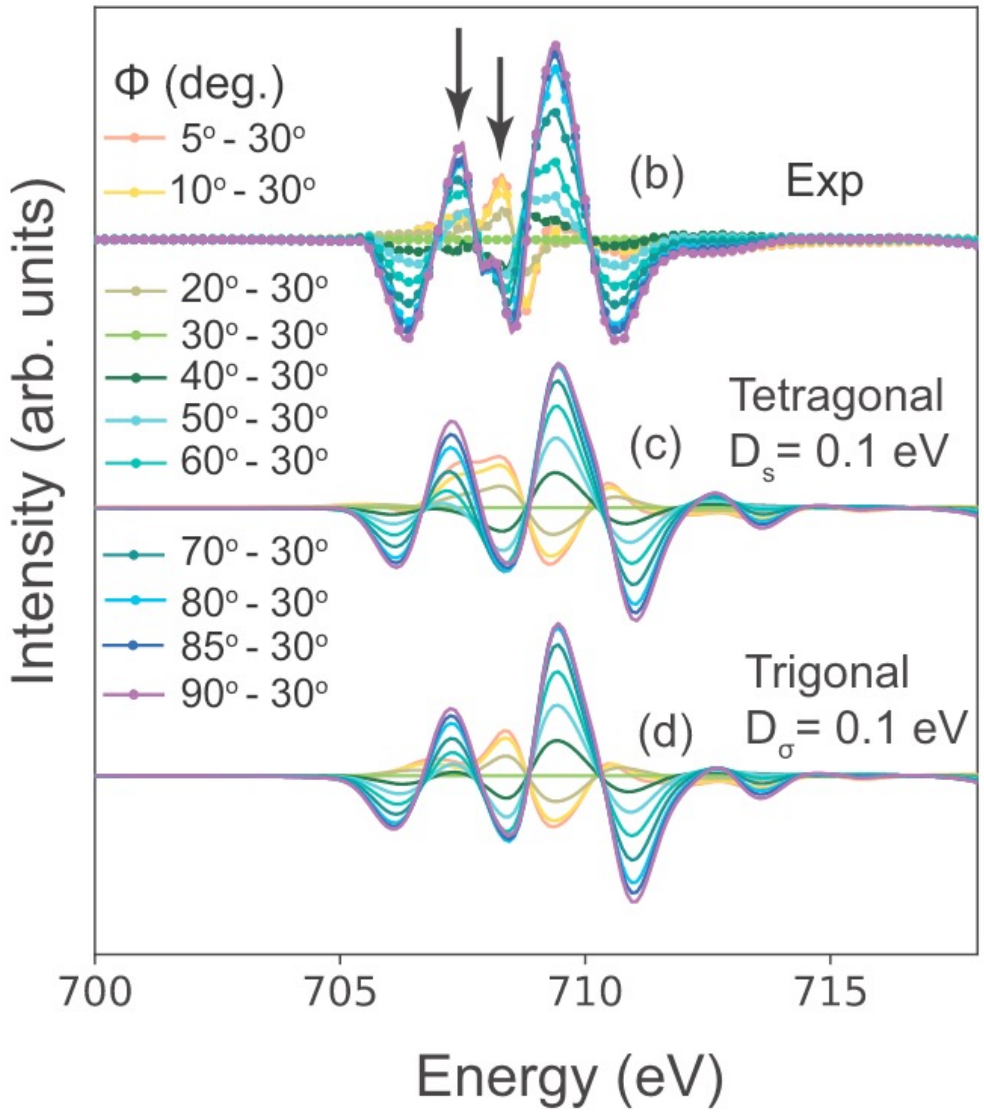
Sum Rules

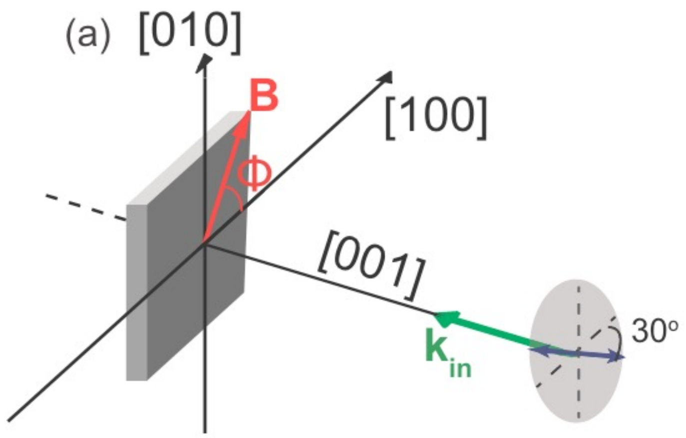
Magnetic moment (μ_B)	
Spin	Orbital
-3.983 ± 0.004	-0.22 ± 0.02

Elnaggar et. al., Phys. Rev. Mat. (2020). 4, 024415

Fe_3O_4: Quantifying Small Distortion from XMLD

Magnetite: $[Fe^{3+}]_{Td}\ [Fe^{2+}, Fe^{3+}]_{Oh}O_4$





Trigonal distortion

D_σ = 0.1 eV

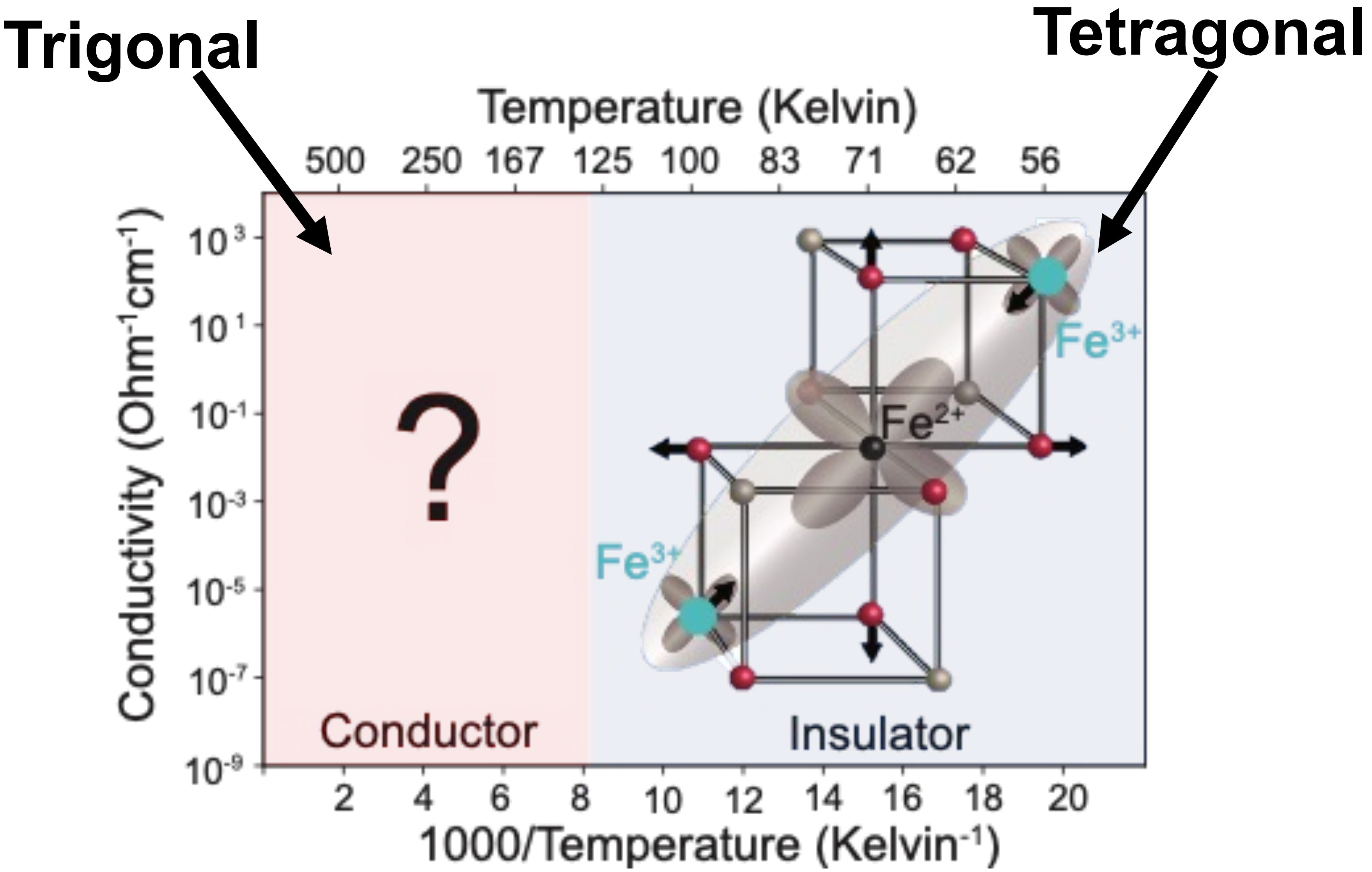
XMLD has two effects:

- Structure
- Magnetic

Elnaggar et. al., Phys. Rev. Mat. (2020). 4, 024415

Fe_3O_4: Quantifying Small Distortion from XMLD

Magnetite: $[Fe^{3+}]_{Td}$ $[Fe^{2+}, Fe^{3+}]_{Oh}O_4$

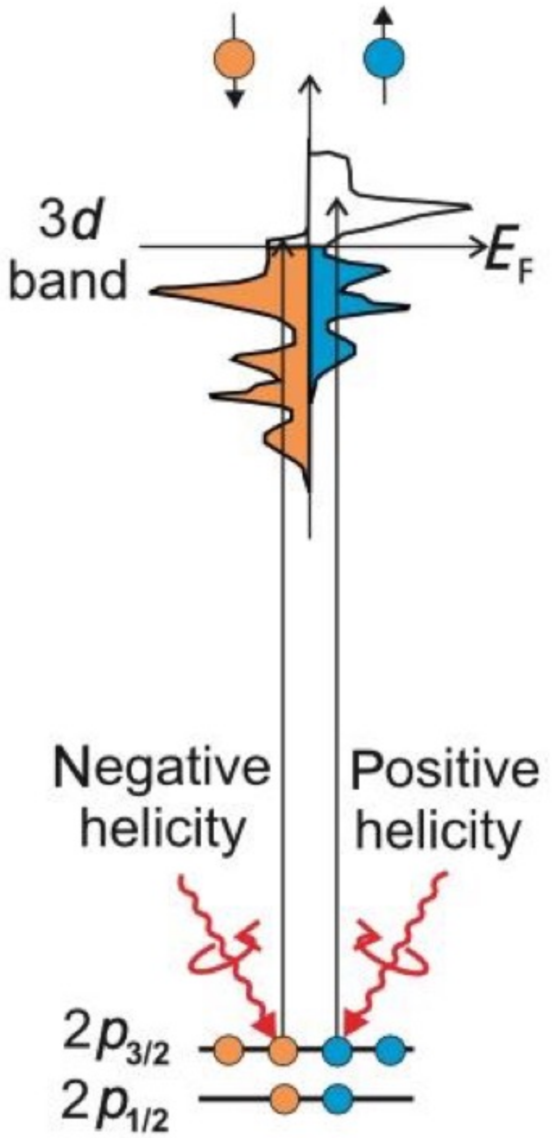


Elnaggar et. al., Phys. Rev. Mat. (2020). 4, 024415

Concluding Remarks

- Dichroism gives more information
- There are many dichroism signals (e.g., magnetic, structural, chiral, linear, circular,…)
- We can deduce which dichroisms arise from symmetry (e.g., Oh vs D4h
- Sum rules relate the spectra to ground state properties (e.g., spin and orbital moments)
- The structure of X(M)LD can help pinpoint small distortions

Sum Rules for Circular Dichroism



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X-Ray Circular Dichroism as a Probe of Orbital Magnetization

B. T. Thole,[1] Paolo Carra,[2] F. Sette,[2] and G. van der Laan[3]

VOLUME 70, NUMBER 5 PHYSICAL REVIEW LETTERS 1 FEBRUARY 1993

X-Ray Circular Dichroism and Local Magnetic Fields

Paolo Carra,[1] B. T. Thole,[1),(2] Massimo Altarelli,[1] and Xindong Wang[3]

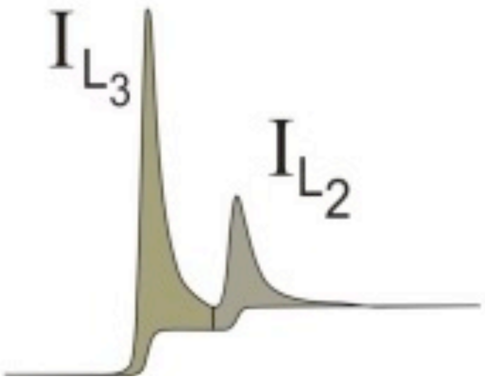
$$(\mathcal{I}_{-1}^{c+\frac{1}{2}}-\mathcal{I}_{1}^{c+\frac{1}{2}})-\frac{l}{l-1}(\mathcal{I}_{-1}^{c-\frac{1}{2}}-\mathcal{I}_{1}^{c-\frac{1}{2}})=\frac{2}{3\underline{n}}\mathbf{S}_z+\frac{2(2l+3)}{3l\underline{n}}\mathbf{T}_z$$

$$\mathcal{I}_{-1}-\mathcal{I}_1=\frac{1}{\underline{n}}\sum_{m,\sigma}\underline{n}_{m\sigma}\frac{-m}{l}=\frac{\mathbf{L_z}}{l\underline{n}}$$

Thole et. al., Phys. Rev. lett. (1992). 68

Sum Rules for Circular Dichroism

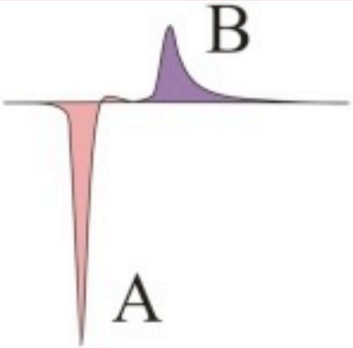
XAS



Isotropic ~ number of holes

$$\int \mu = \int (\mu_1 + \mu_0 + \mu_{-1}) = \frac{C}{5} \langle N_h \rangle.$$

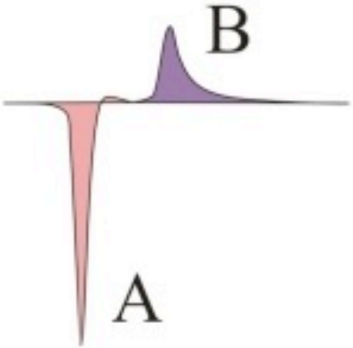
XMCD



XMCD ~ orbital moment

$$\langle L_z \rangle = -\frac{\int (\mu_+ - \mu_-)}{\int \mu} \cdot 2\langle N_h \rangle.$$

XMCD

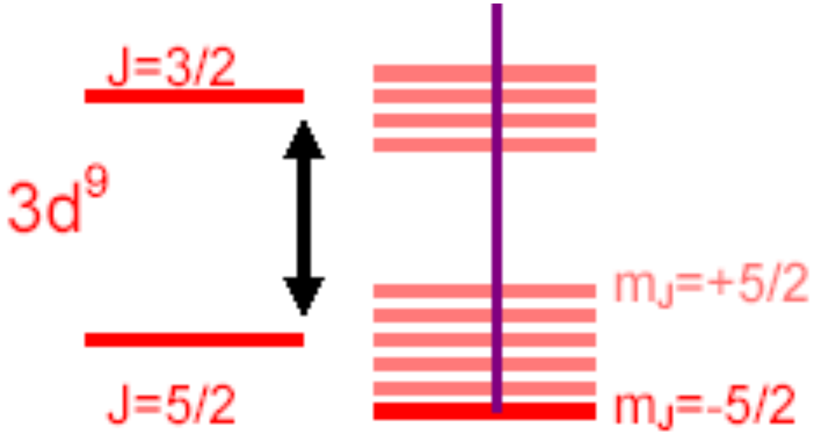


XMCD ~ spin momeny

$$(\mathcal{I}_{-1}^{c+\frac{1}{2}} - \mathcal{I}_{1}^{c+\frac{1}{2}}) = \frac{2}{3\underline{n}} \mathbf{S}_z + \frac{2(2l+3)}{3l\underline{n}} \mathbf{T}_z$$

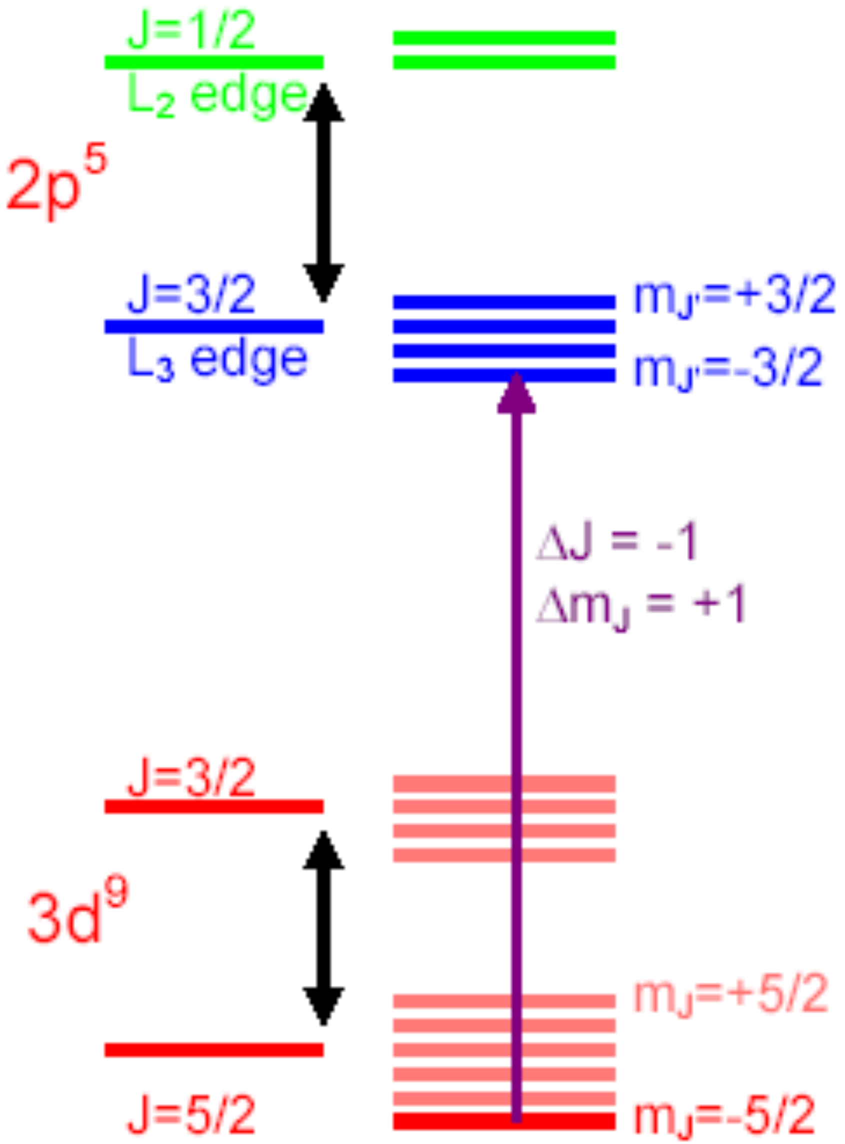
Sum Rules for Circular Dichroism: Cu^{2+}

Cu^{2+}: $3d^9$

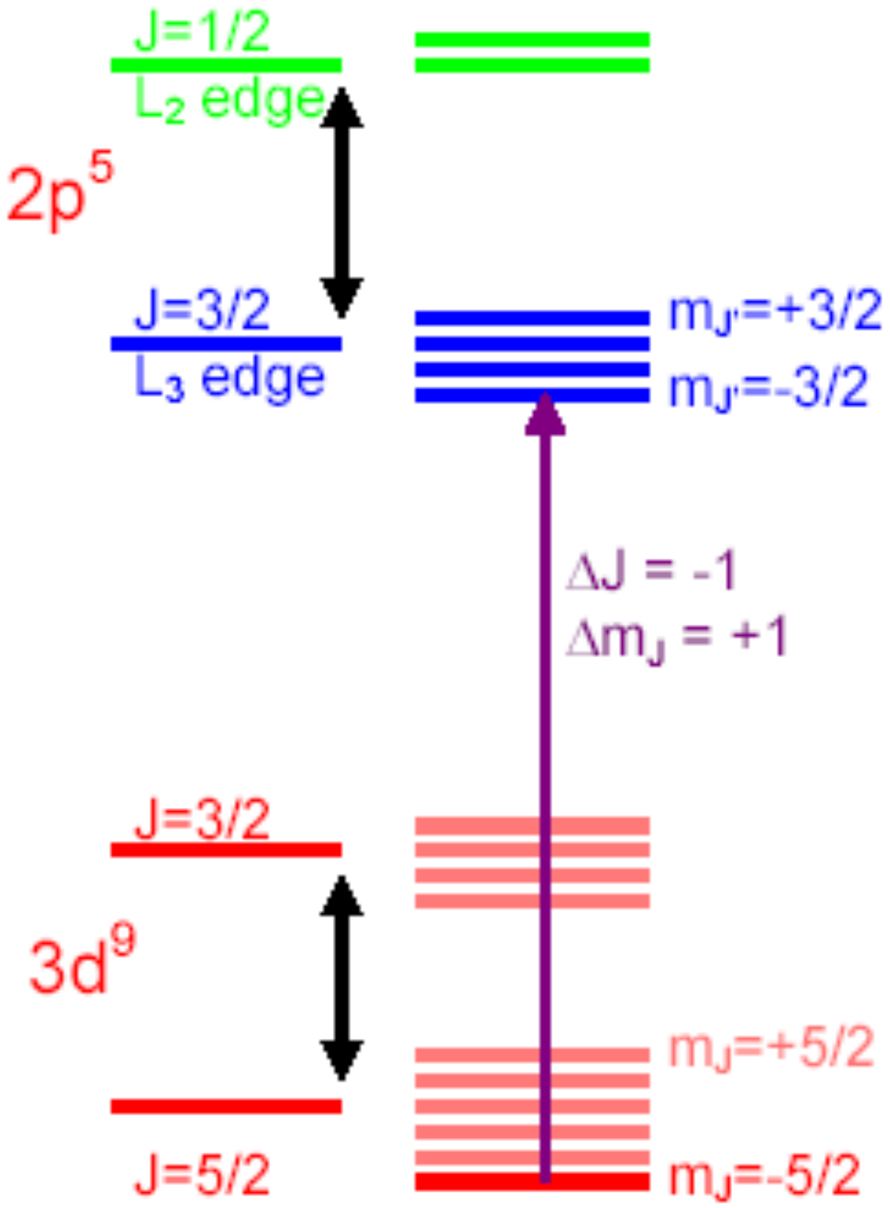


Sum Rules for Circular Dichroism: Cu^{2+}

Cu^{2+}: $3d^9$



Sum Rules for Circular Dichroism: Cu^{2+}



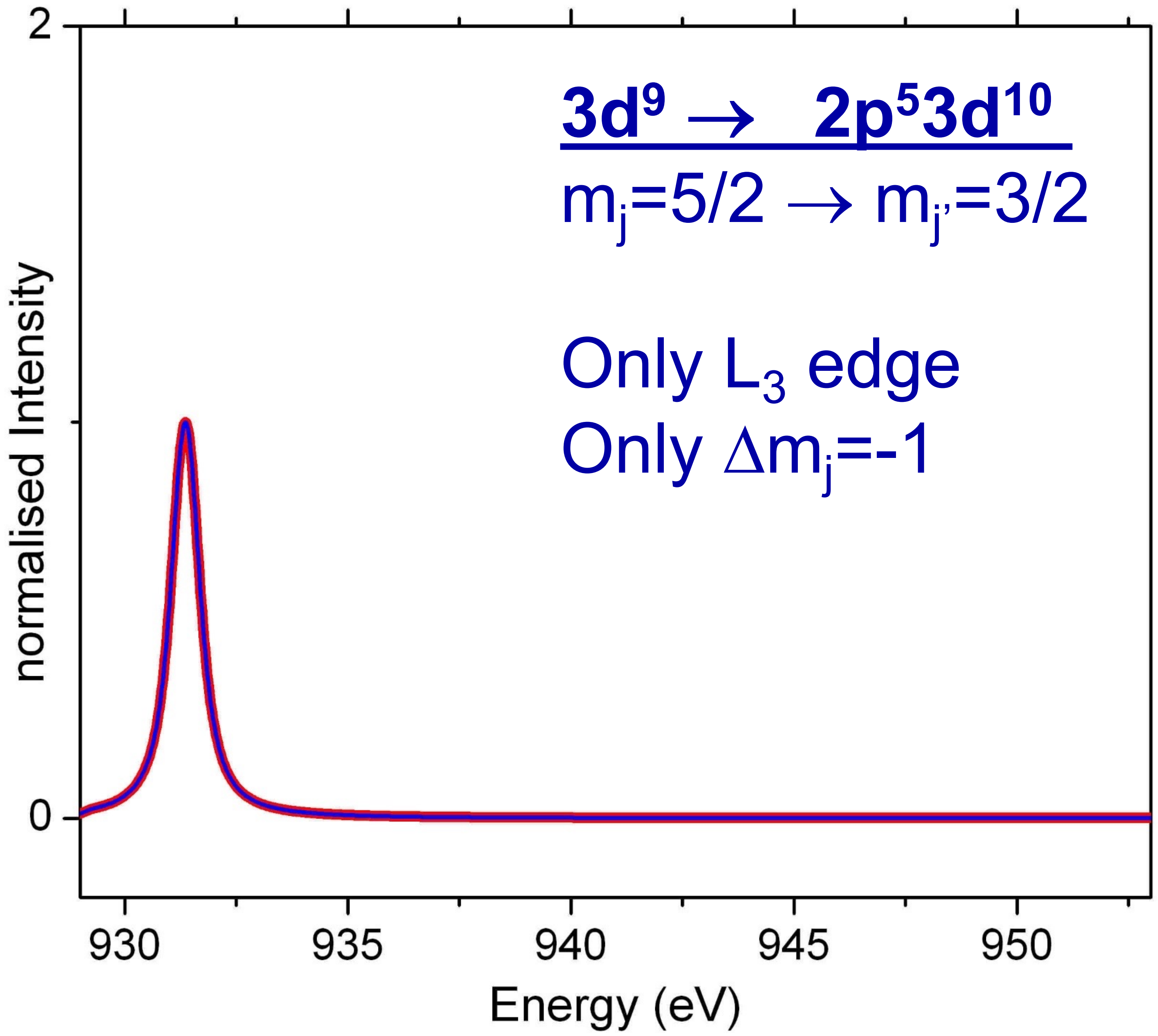
$3d^9 \rightarrow\ 2p^5 3d^{10}$

m_j=-5/2 → $m_{j'}$=-3/2

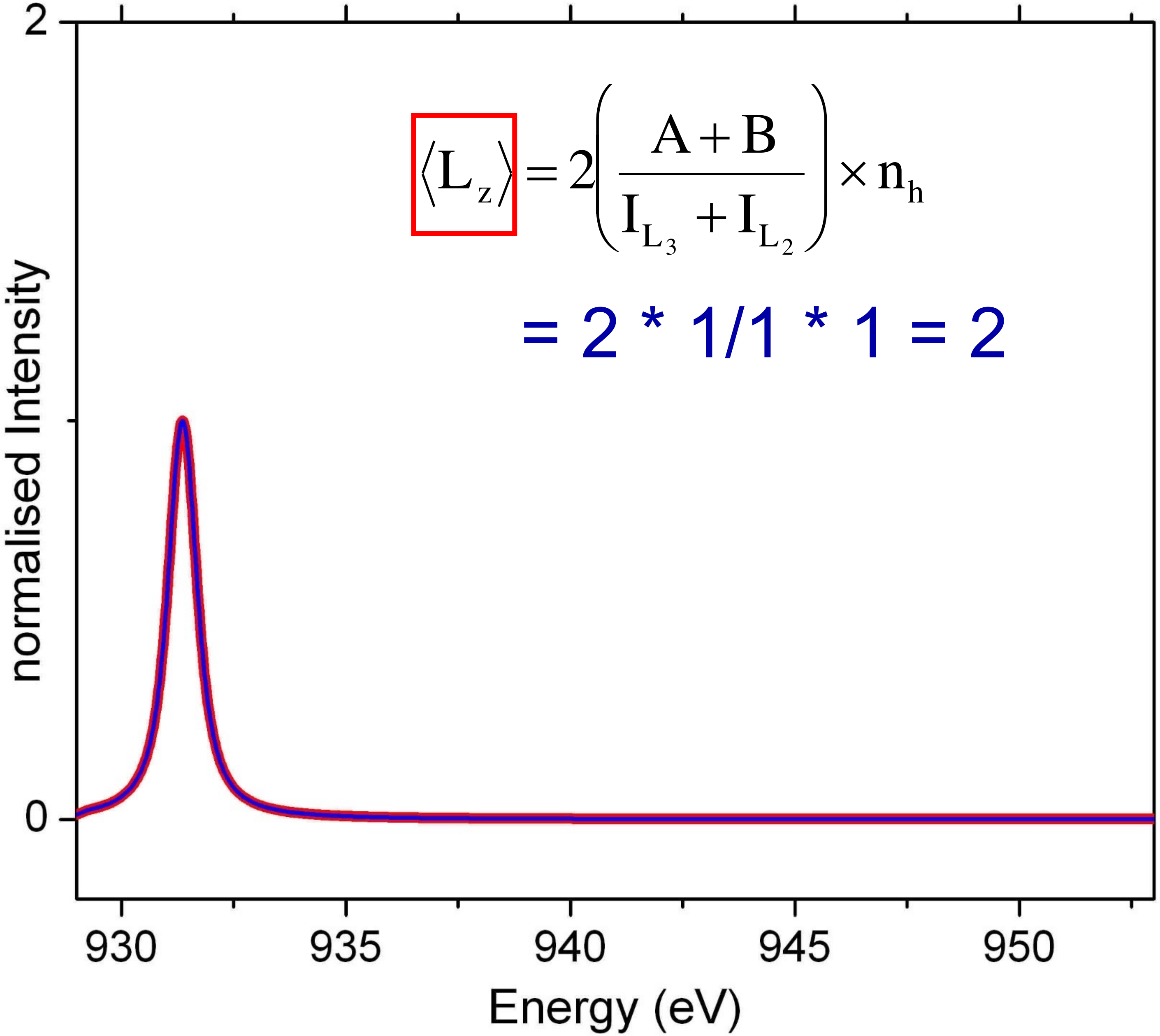
Only L_3 edge

Only Δm_j=+1

Sum Rules for Circular Dichroism: Cu^{2+}



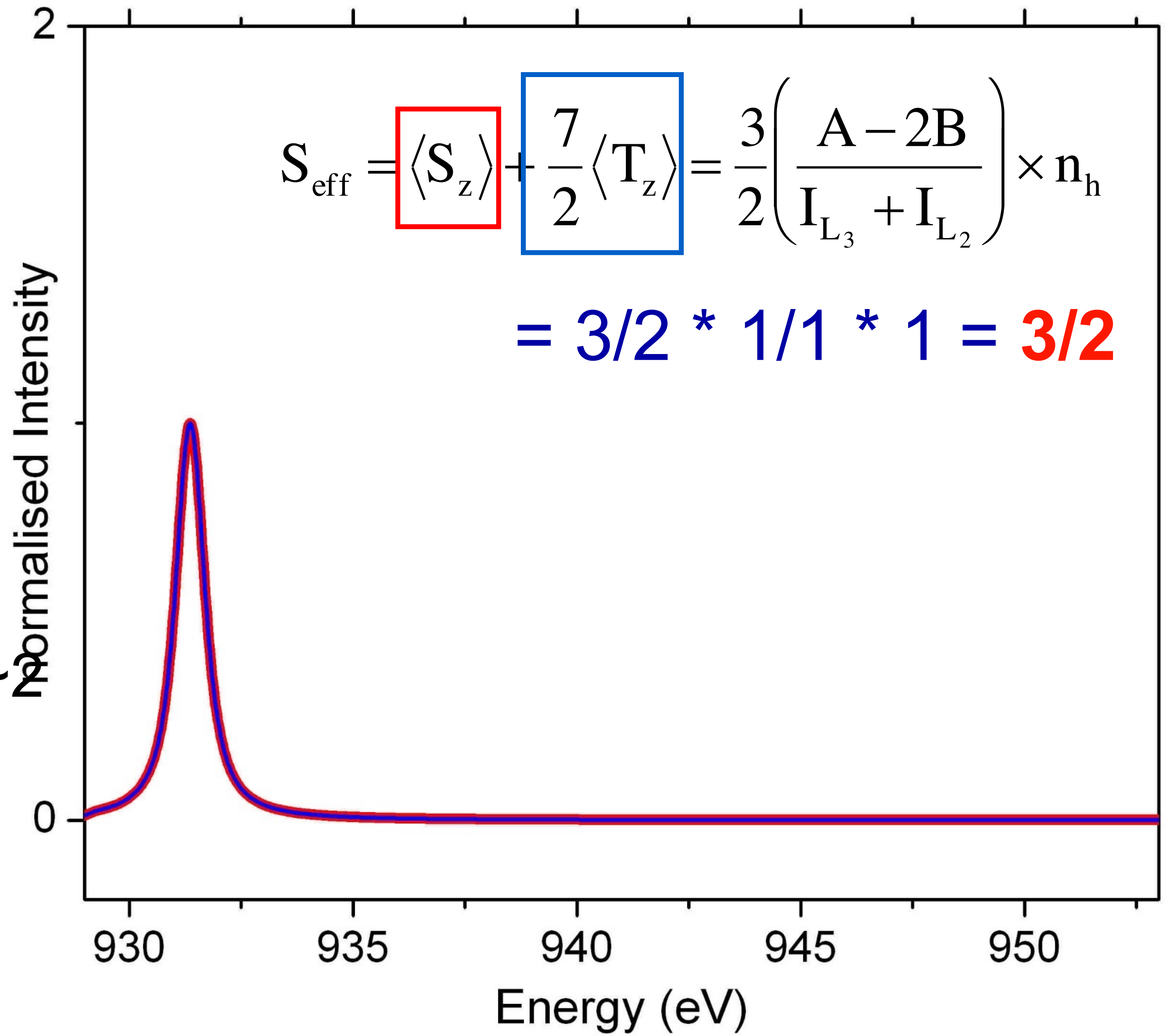
Sum Rules for Circular Dichroism: Cu^{2+}



$$\langle L_z \rangle = 2\left(\frac{A+B}{I_{L_3}+I_{L_2}}\right)\times n_h$$

= 2 * 1/1 * 1 = 2

Sum Rules for Circular Dichroism: Cu^{2+}

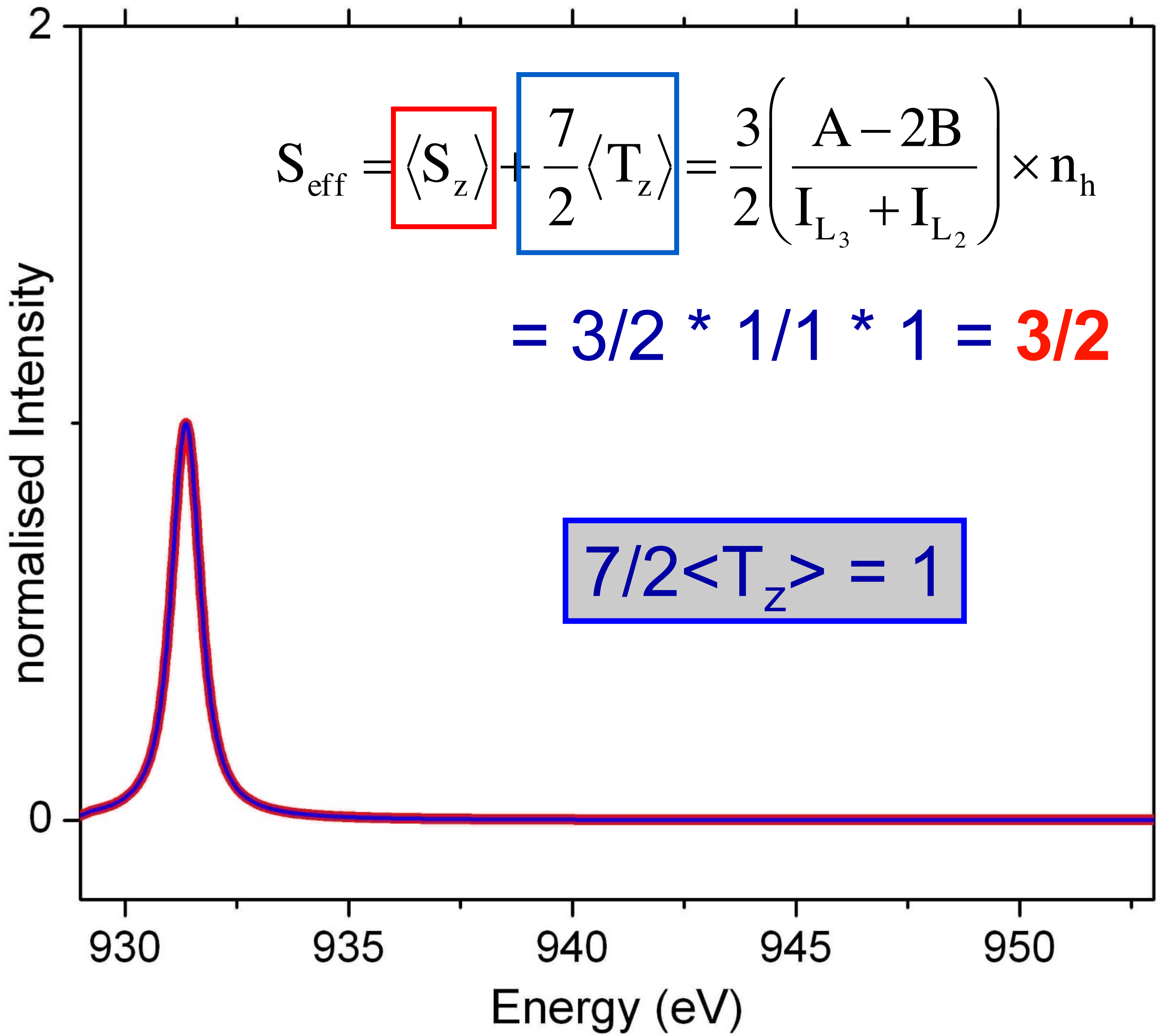


$$S_{eff} = \langle S_z \rangle + \frac{7}{2}\langle T_z \rangle = \frac{3}{2}\left(\frac{A - 2B}{I_{L_3} + I_{L_2}}\right) \times n_h$$

= 3/2 * 1/1 * 1 = **3/2**

a`7e\8V#1S~2

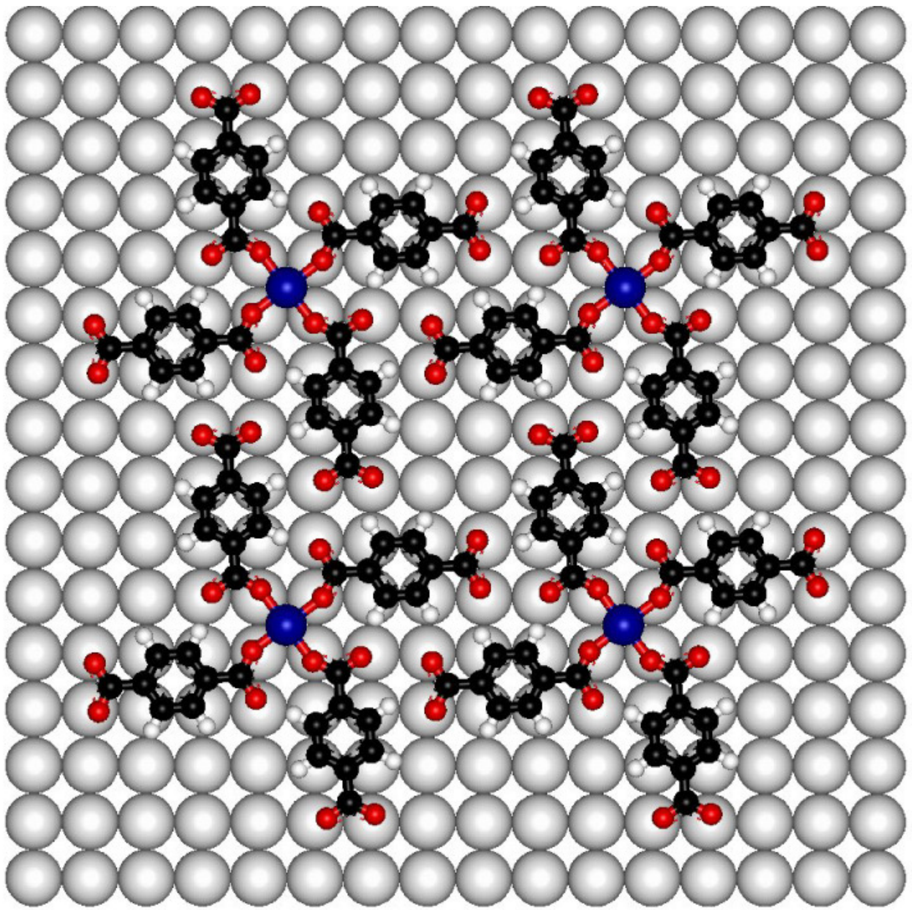
Sum Rules for Circular Dichroism: Cu^{2+}

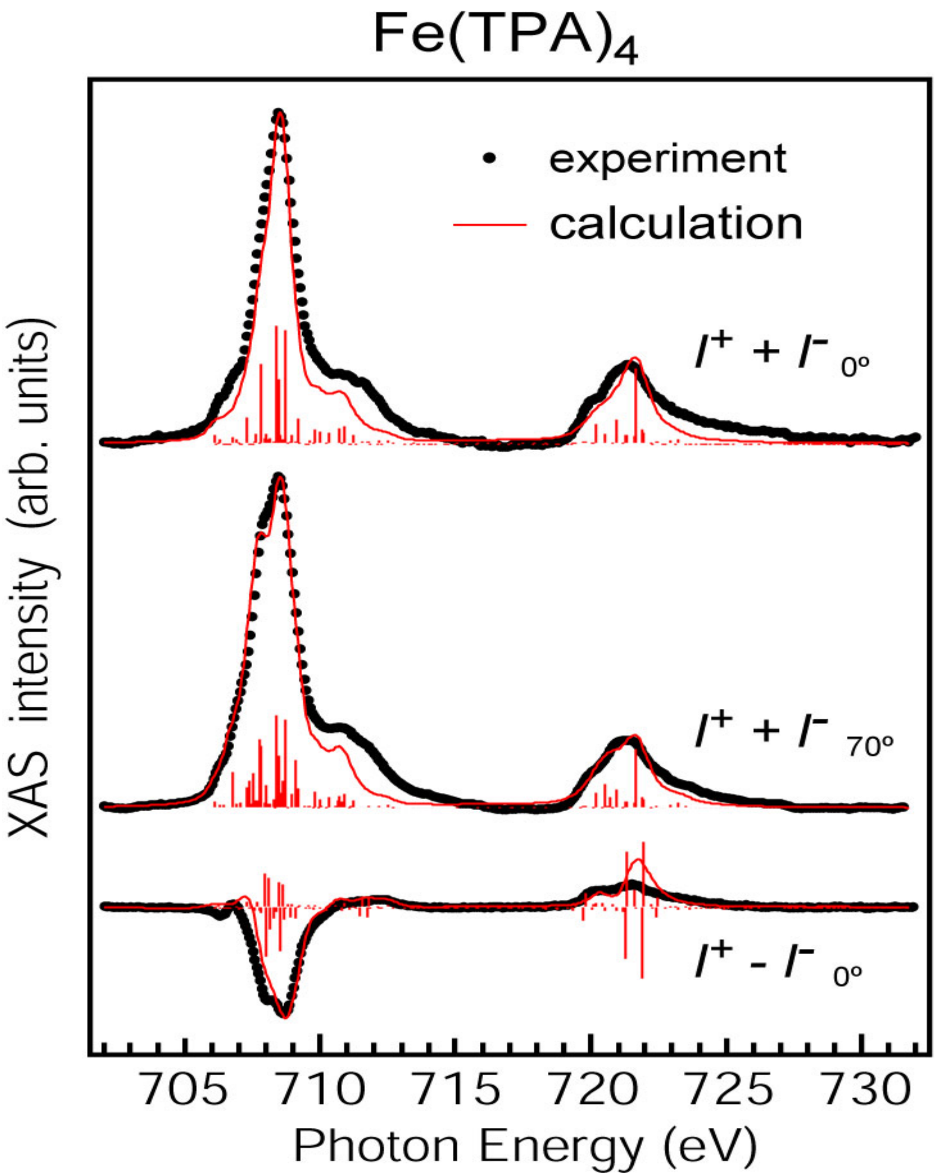


Phys. Rev. B. 80, 184410 (2009)

XMCD to probe the orbital moment of magnetic molecules

Fe(TPA)$_4$ on Cu(100)





Lz=0.55 +-0.07

Nature Materials 8, 189 (2009)

XMCD to probe the orbital moment of magnetic molecules

What if the system is antiferromagnetic?

X-ray Magnetic Linear Dichroism