# Angular and polarization dependence of 1s2p RIXS in probing magnetic properties of iron oxides

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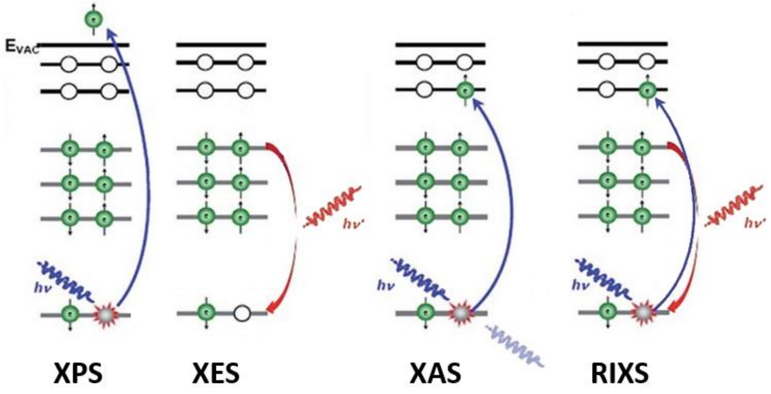
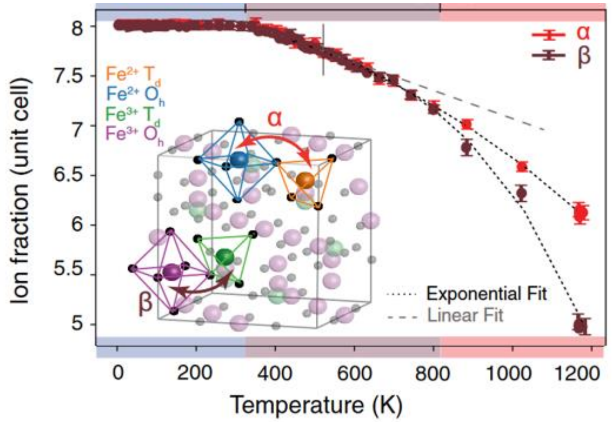
# Outlook

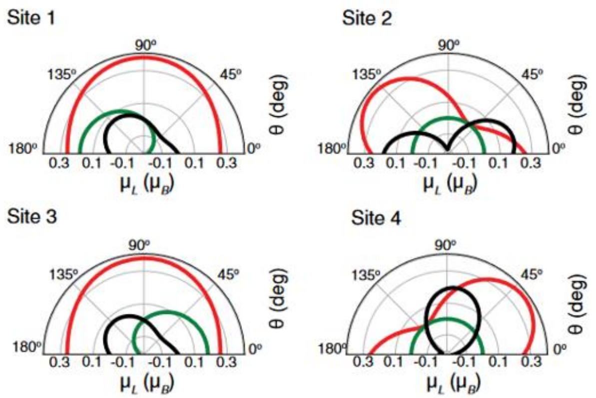
## 1s2p RIXS



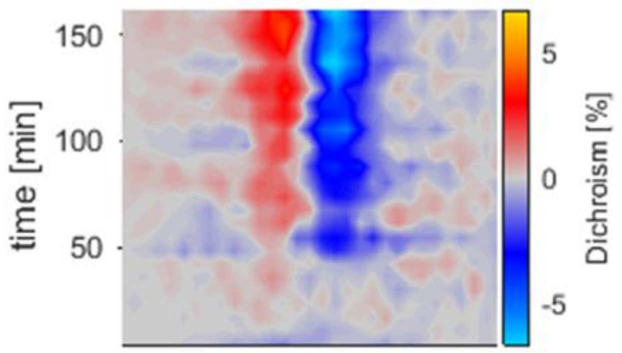

## $Fe_3O_4$: self-doping



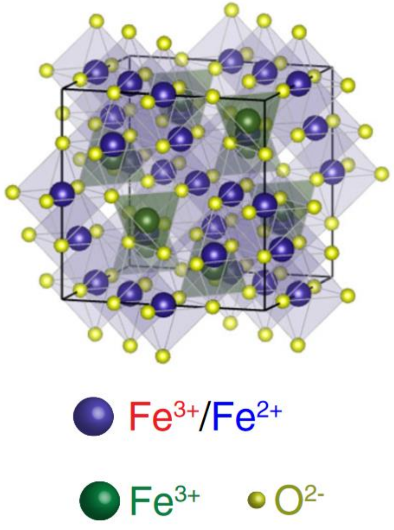

## $Fe_3O_4$: $\boldsymbol{L} \times \boldsymbol{S} \neq 0$



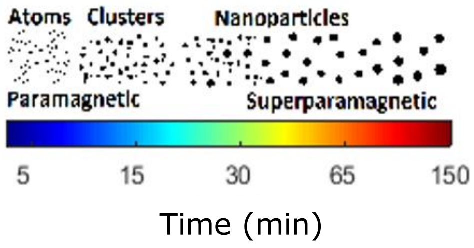

## Ferrite MNP: in-operando



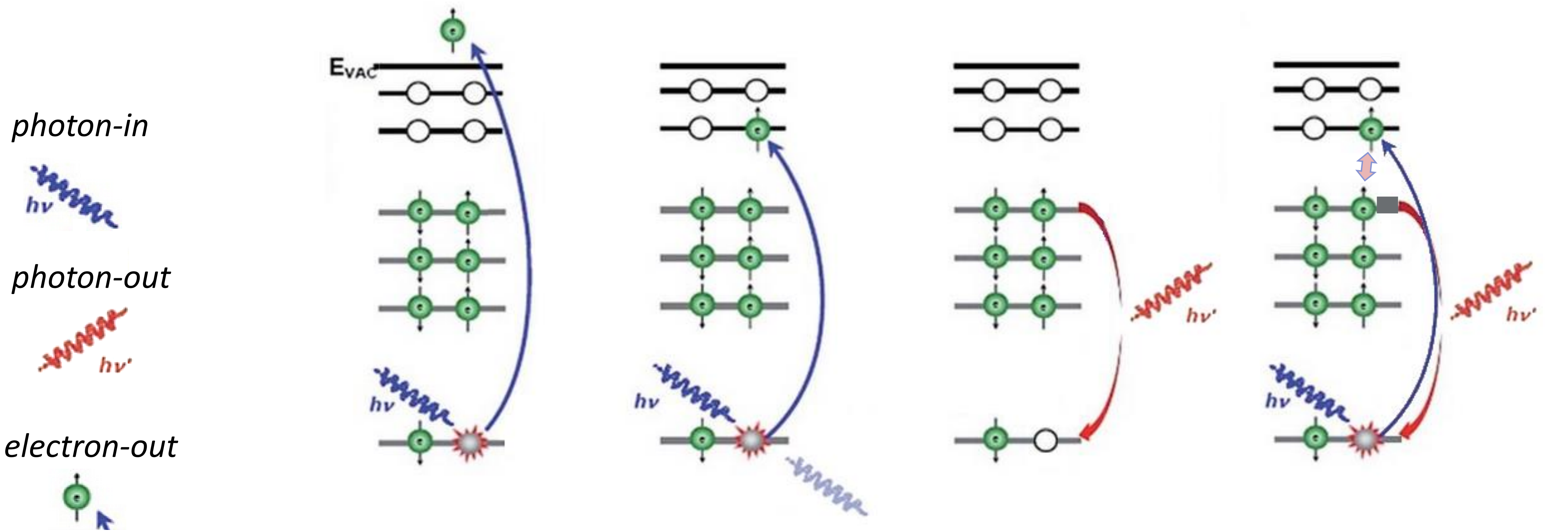

***Magnetite crystals***




***Particles in solution***

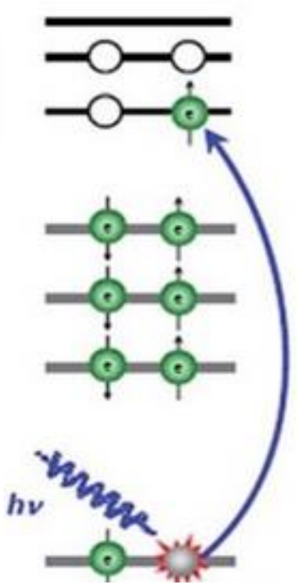


# X-ray spectroscopies




| XPS (RPES) | XAS | XES XRF | RIXS RXES |
| --- | --- | --- | --- |
| *(photon-in) electron-out* | *photon-in* | *photon-out* | *photon-in photon-out* |

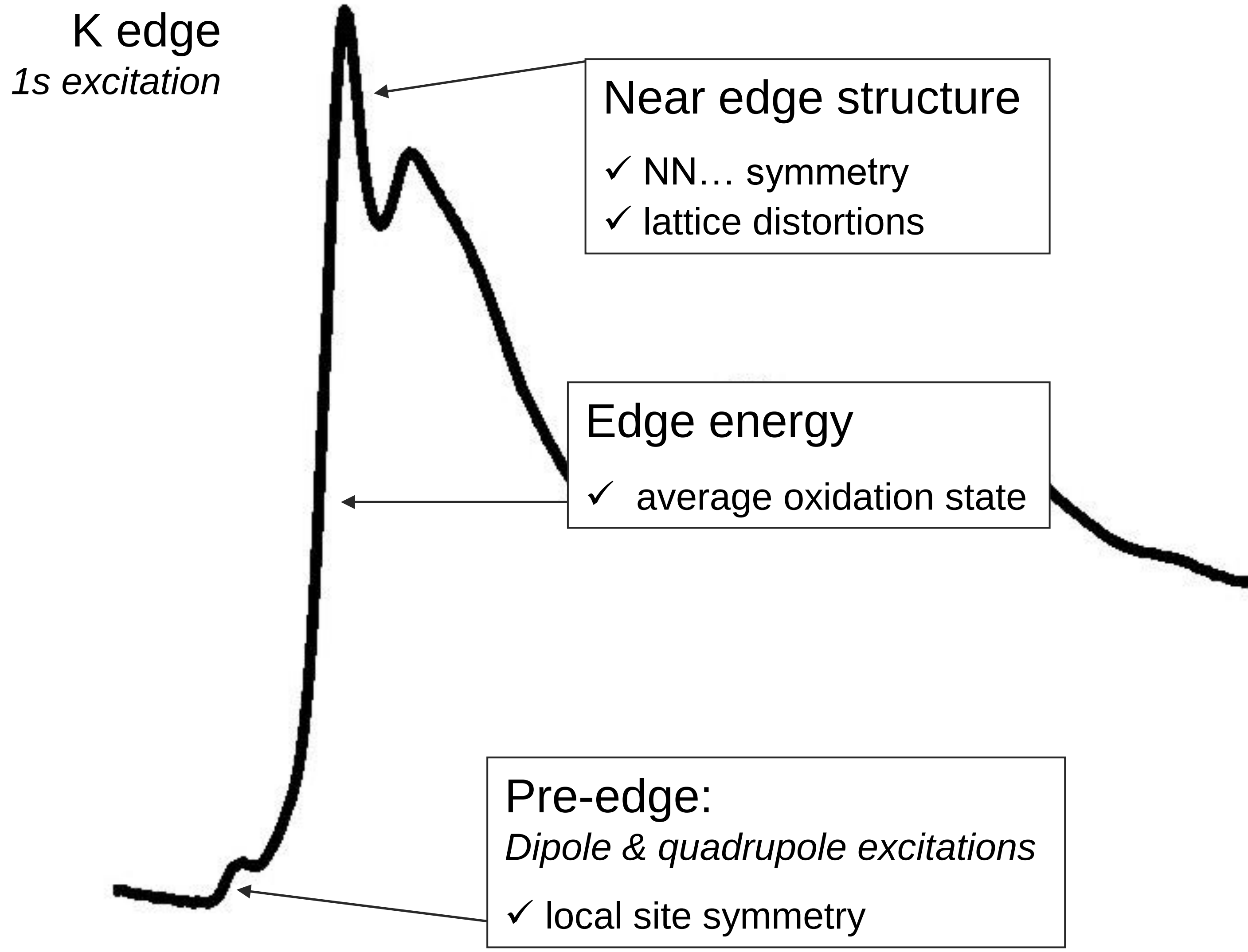
# X-ray Absorption Spectroscopy (XAS)



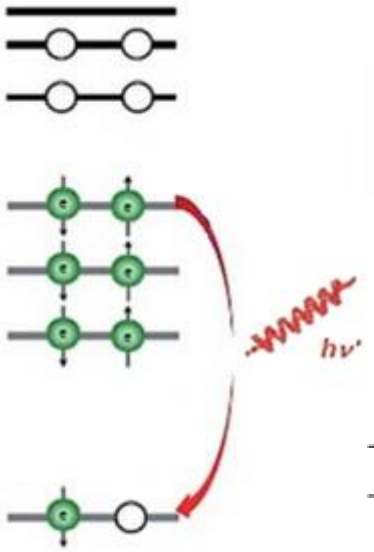

*Dipole transitions*
$\Delta l = \pm 1$
$\Delta j = \pm 1; 0$
$\Delta s = 0$

| Element | K 1s | $L_1$ 2s | $L_2$ $2p_{1/2}$ | $L_3$ $2p_{3/2}$ |
|---|---|---|---|---|
| 23 V | 5465 | 626.7† | 519.8† | 512.1† |
| 24 Cr | 5989 | 696.0† | 583.8† | 574.1† |
| 25 Mn | 6539 | 769.1† | 649.9† | 638.7† |
| 26 Fe | 7112 | 844.6† | 719.9† | 706.8† |
| 27 Co | 7709 | 925.1† | 793.2† | 778.1† |
| 28 Ni | 8333 | 1008.6† | 870.0† | 852.7† |
| 29 Cu | 8979 | 1096.7† | 952.3† | 932.7 |
| 30 Zn | 9659 | 1196.2* | 1044.9* | 1021.8* |

*Element & symmetry selective probe of* ***unoccupied electronic states***

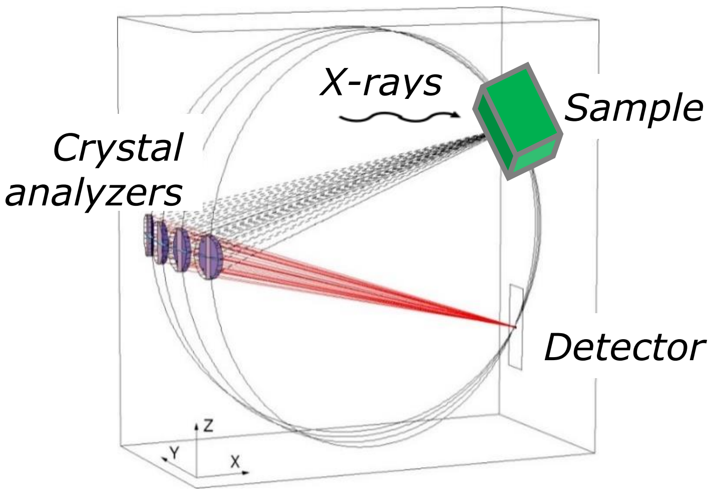


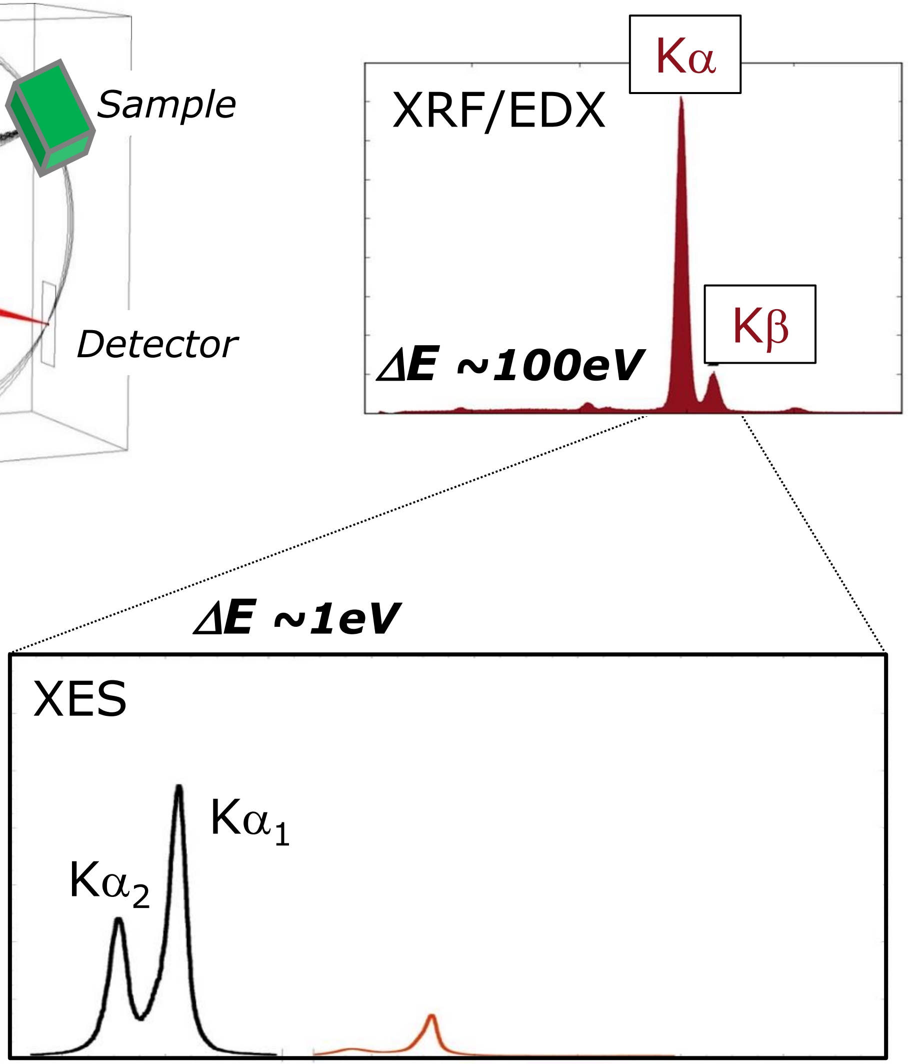
# X-ray Emission Spectroscopy (XES)




Dipole transitions
$\Delta l = \pm 1$

| Element | $K\alpha_1$ | $K\alpha_2$ | $K\beta_1$ |
|---|---|---|---|
| 22 Ti | 4,510.84 | 4,504.86 | 4,931.81 |
| 23 V | 4,952.20 | 4,944.64 | 5,427.29 |
| 24 Cr | 5,414.72 | 5,405.509 | 5,946.71 |
| 25 Mn | 5,898.75 | 5,887.65 | 6,490.45 |
| 26 Fe | 6,403.84 | 6,390.84 | 7,057.98 |
| 27 Co | 6,930.32 | 6,915.30 | 7,649.43 |
| 28 Ni | 7,478.15 | 7,460.89 | 8,264.66 |
| 29 Cu | 8,047.78 | 8,027.83 | 8,905.29 |
| 30 Zn | 8,638.86 | 8,615.78 | 9,572.0 |



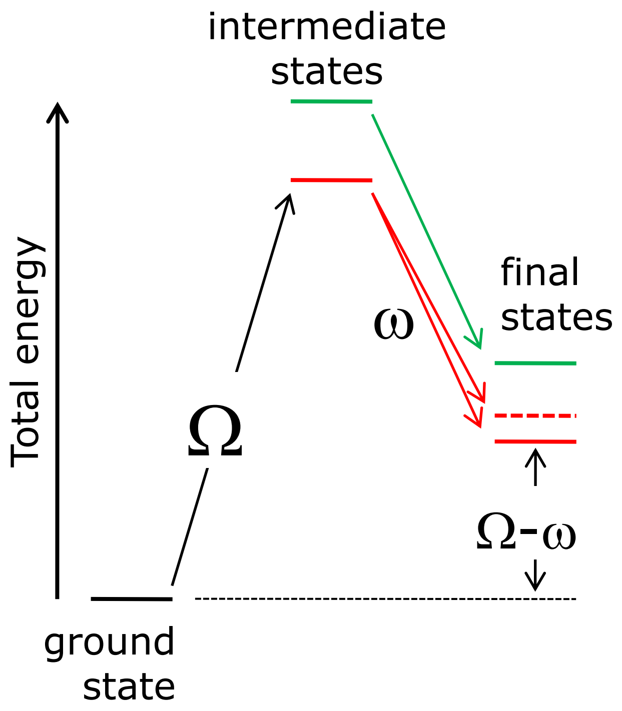



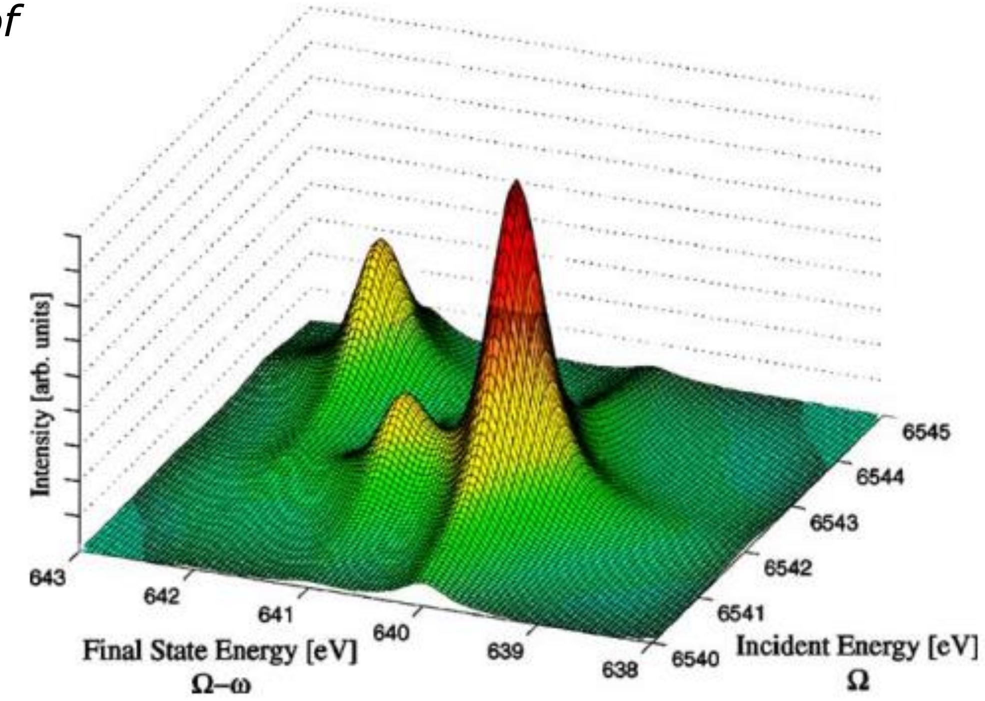

*Quantitative probe of* ***chemical composition***
***spin state***
***valence band structure***

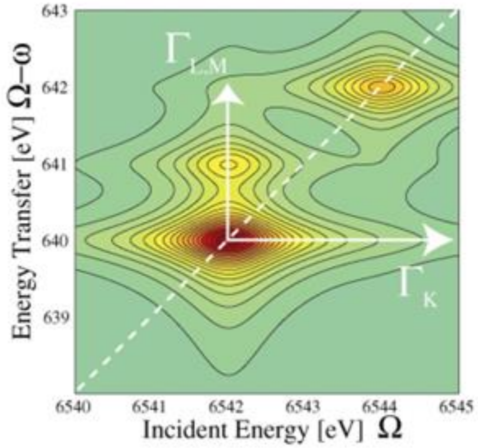
*Similar information content as XPS, using bulk sensitivity of hard X-rays*

# Resonant inelastic X-ray scattering (RIXS)

*Element & symmetry selective probe of* ***electronic correlations, electronic excitations, spin excitations****, etc.*



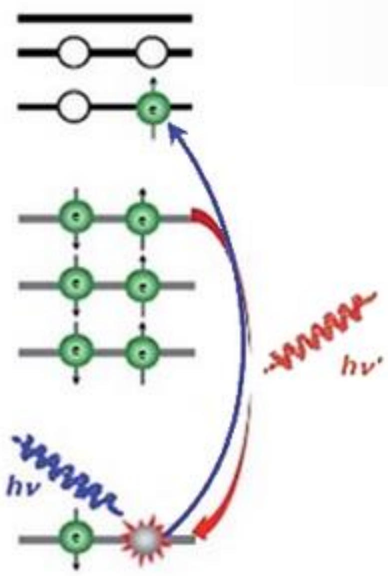




*Kramers – Heisenberg formula*

$$F(\Omega,\omega)=\sum_{\mathrm{f}}\left|\sum_n \frac{\langle f|T_2|n\rangle\langle n|T_1|g\rangle}{E_g-E_n+\Omega-i\,\Gamma_K/2}\right|^2\times\frac{\Gamma_{\mathrm{f}}/2\pi}{(E_g-E_f+\Omega-\omega)^2+\Gamma_{\mathrm{f}}^2/4}$$

*P.Glatzel & U. Bergmann, Coord. Chem. Rev. (2006)*

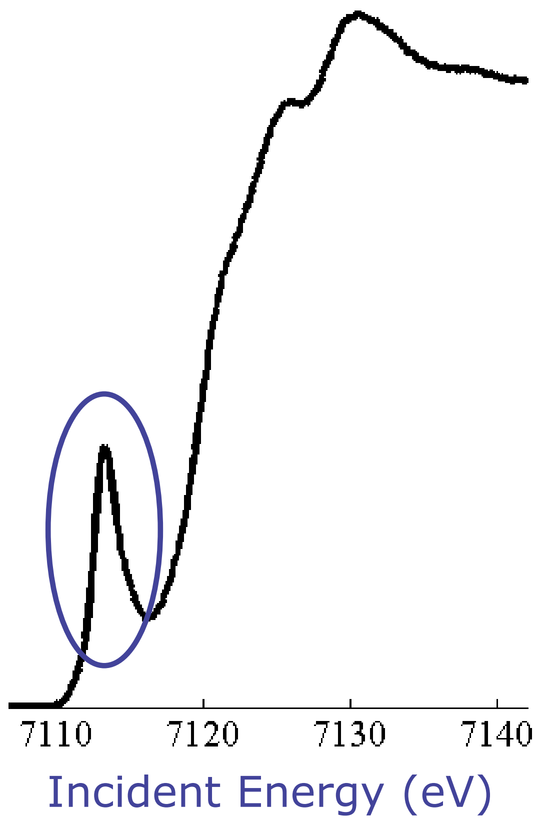
# 1s2p Resonant Inelastic X-ray Scattering (RIXS)



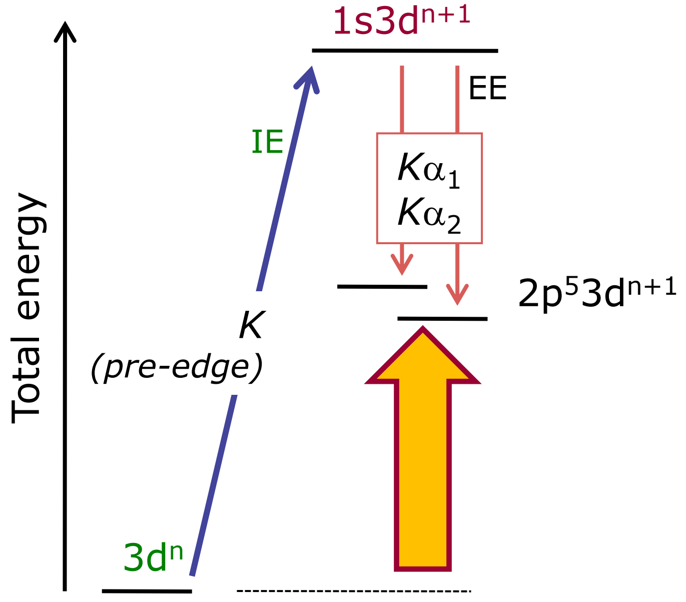

K pre-edge …

*Dipole transition*
*1s→ 4p(3d)*

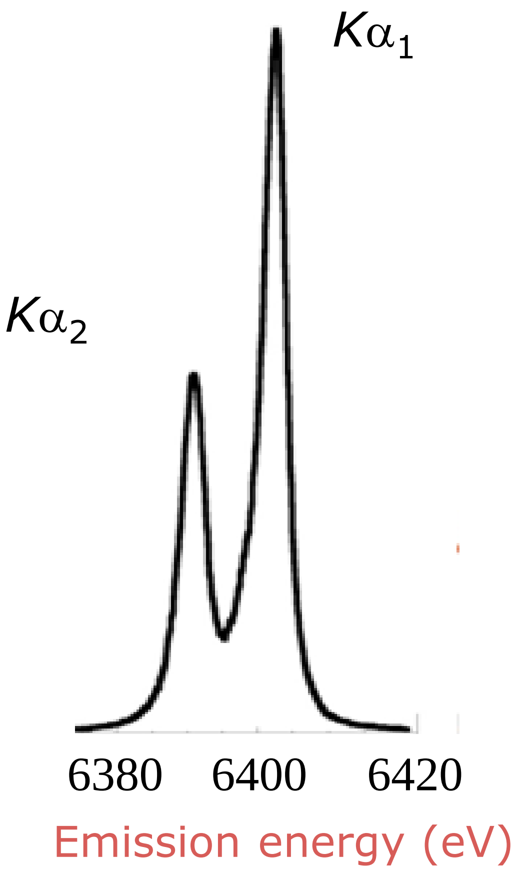
*Qudrupole tr.*
*1s→ 3d*




*… probed with high resolution emission detection*

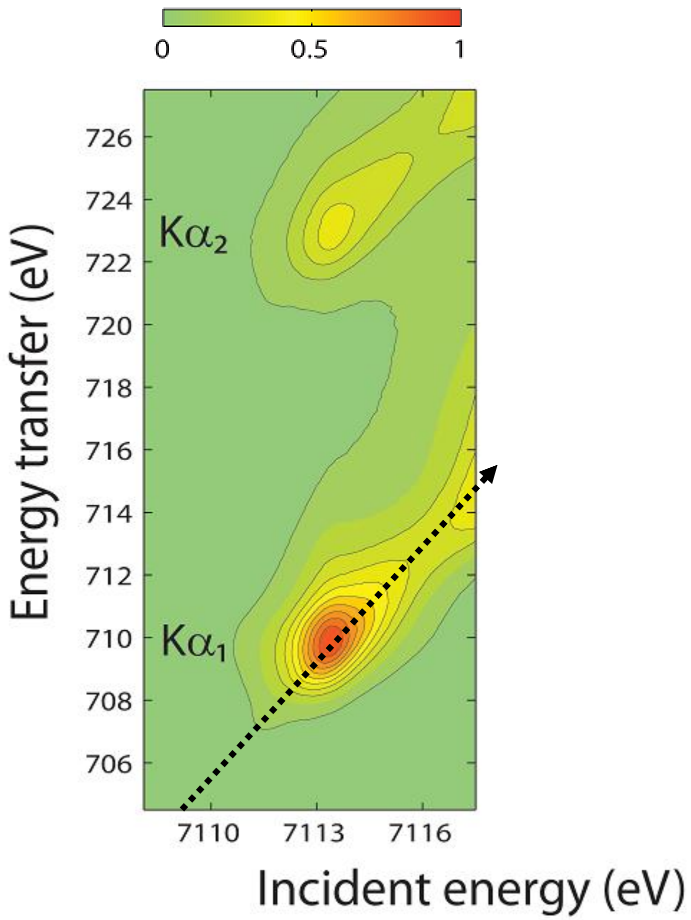



*The same final state as for $L_{2,3}$ edge probed using hard X-ray photon-in photon-out*

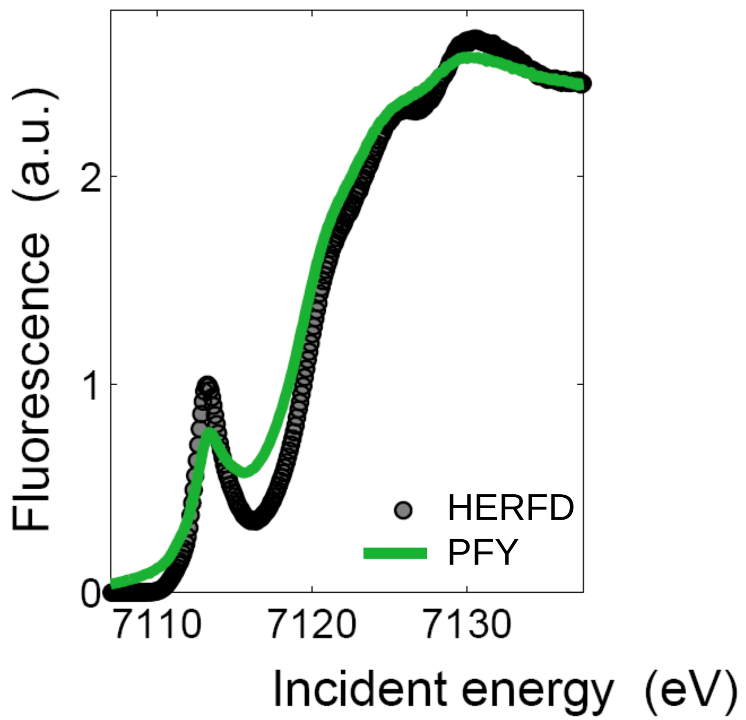



*W. A. Caliebe et al., Phys. Rev. B (1998)*

# 1s2p RIXS in magnetite ($Fe_3O_4$)

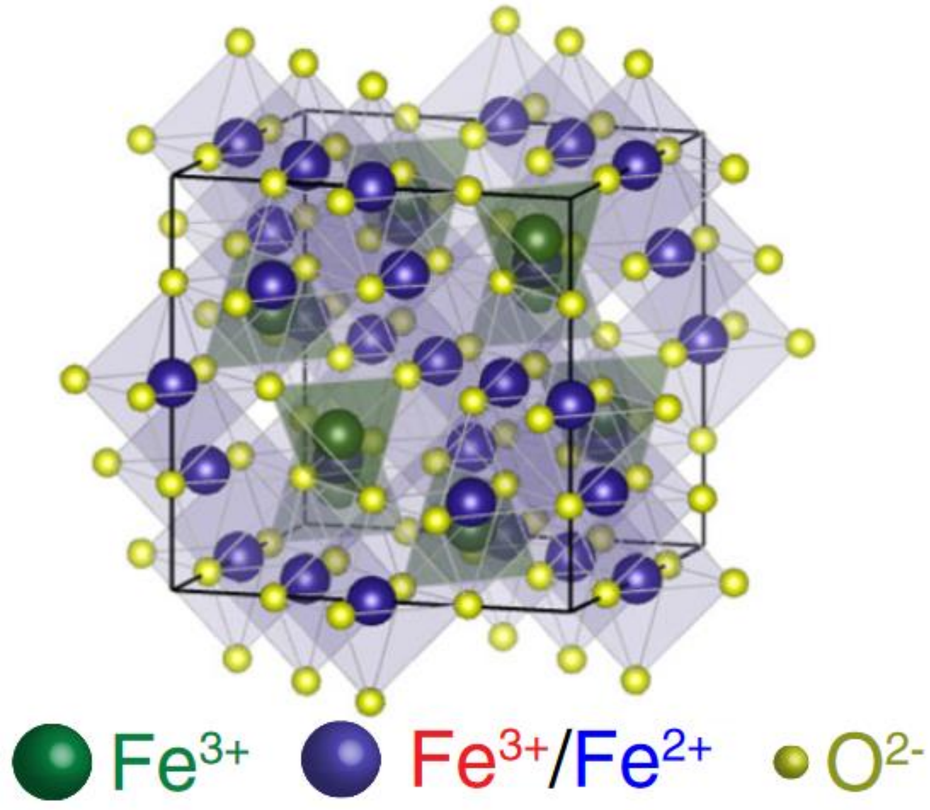



*Photon-in photon-out hard X-ray spectroscopy with negligible non-resonant background and reduced life-time broadening*

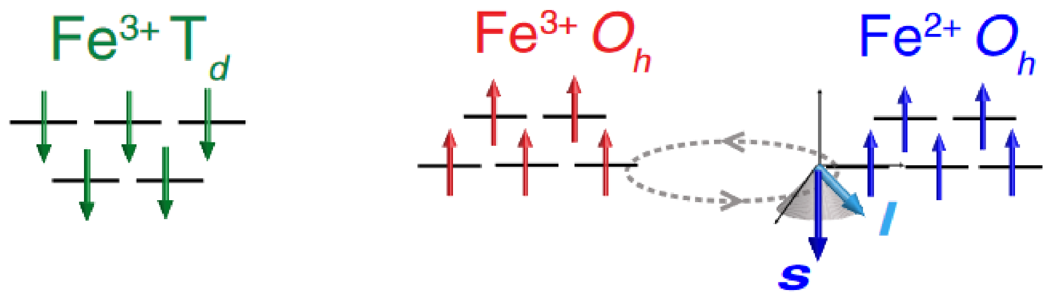



*M.Sikora, et al., Phys. Rev. Lett. (2010)*

# Magnetite and spinel ferrites



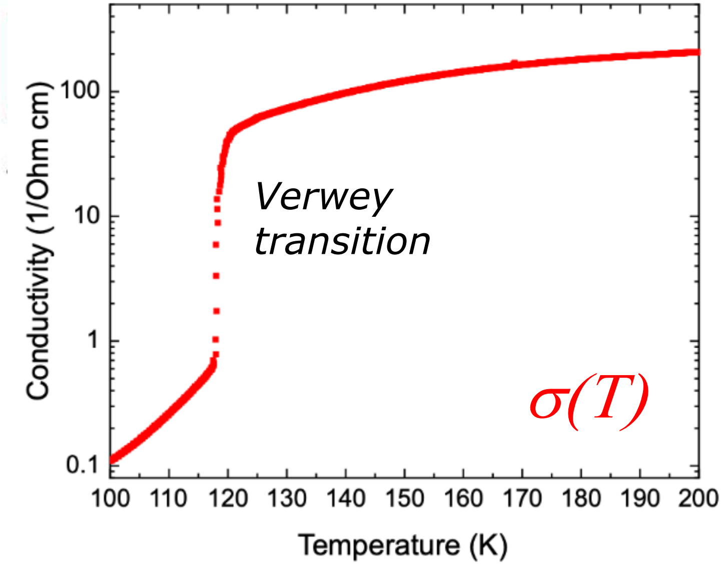

*Ferrimagnetic ground state*

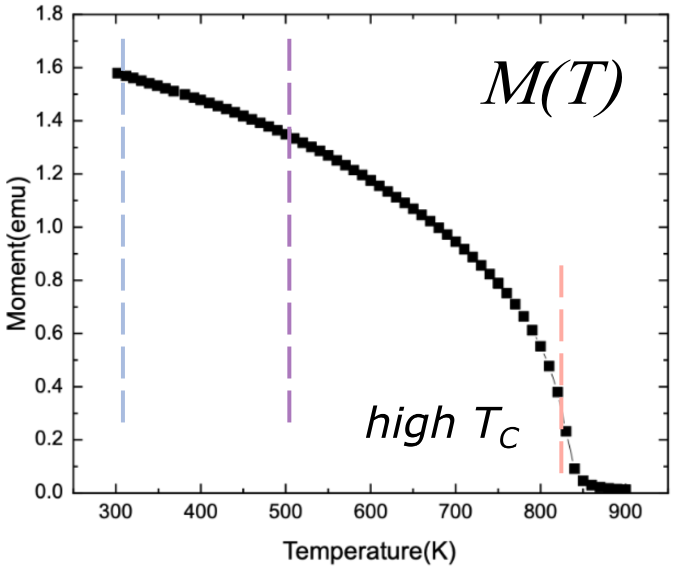


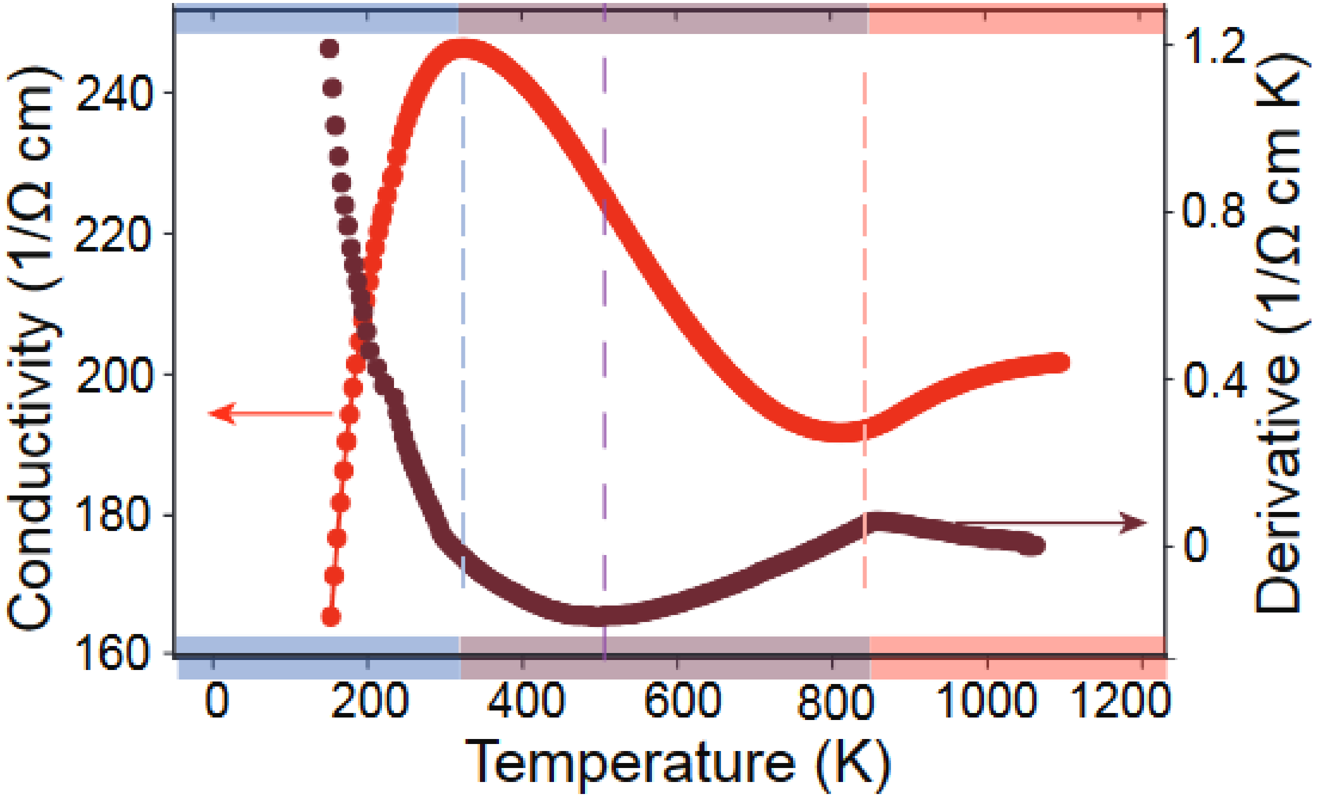

$[8Fe^{3+}]_{Td}\,[8Fe^{2+},8Fe^{3+}]_{Oh}\,O_{32} \rightarrow Fe_3O_4$ magnetite: $M_{sat} \approx 4\mu_B$ /f.u.

$M^{2+}O\cdot Fe^{3+}{}_2O_3 \rightarrow M^{2+}Fe_2O_4$ ferrites: $M_{sat} \approx \mu_S(M^{2+})$

# High T properties of magnetite

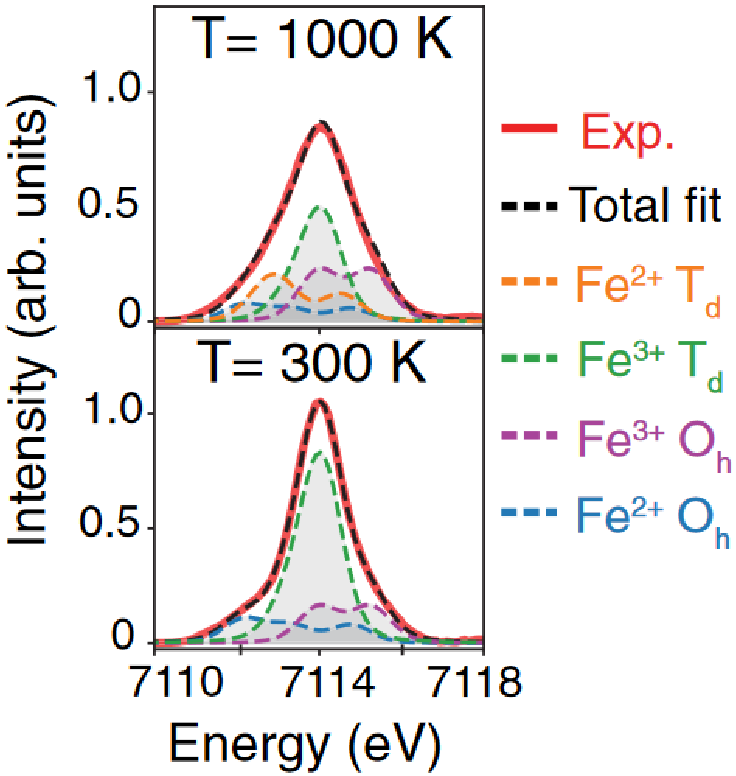


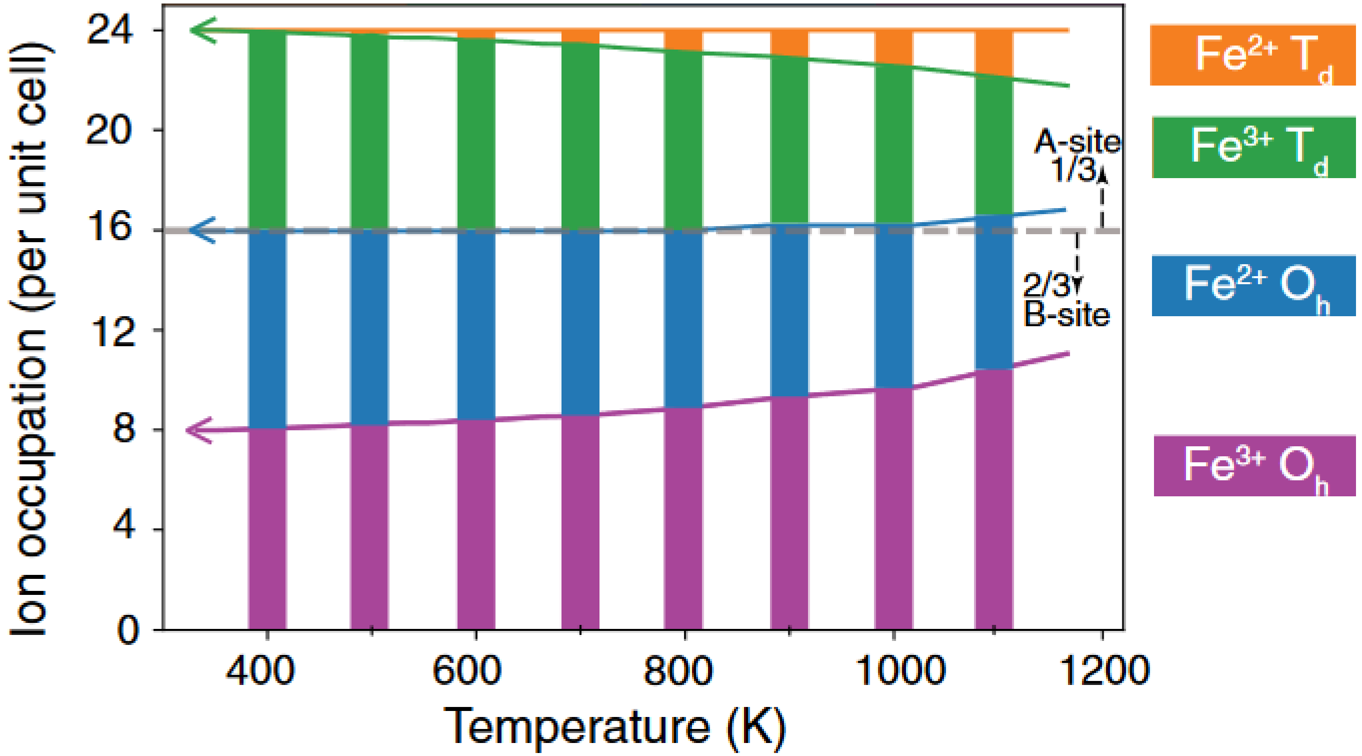




*H.Elnaggar, et al., Phys. Rev. Lett. (2021)*

# High temperature 1s2p HERFD-XAS of magnetite



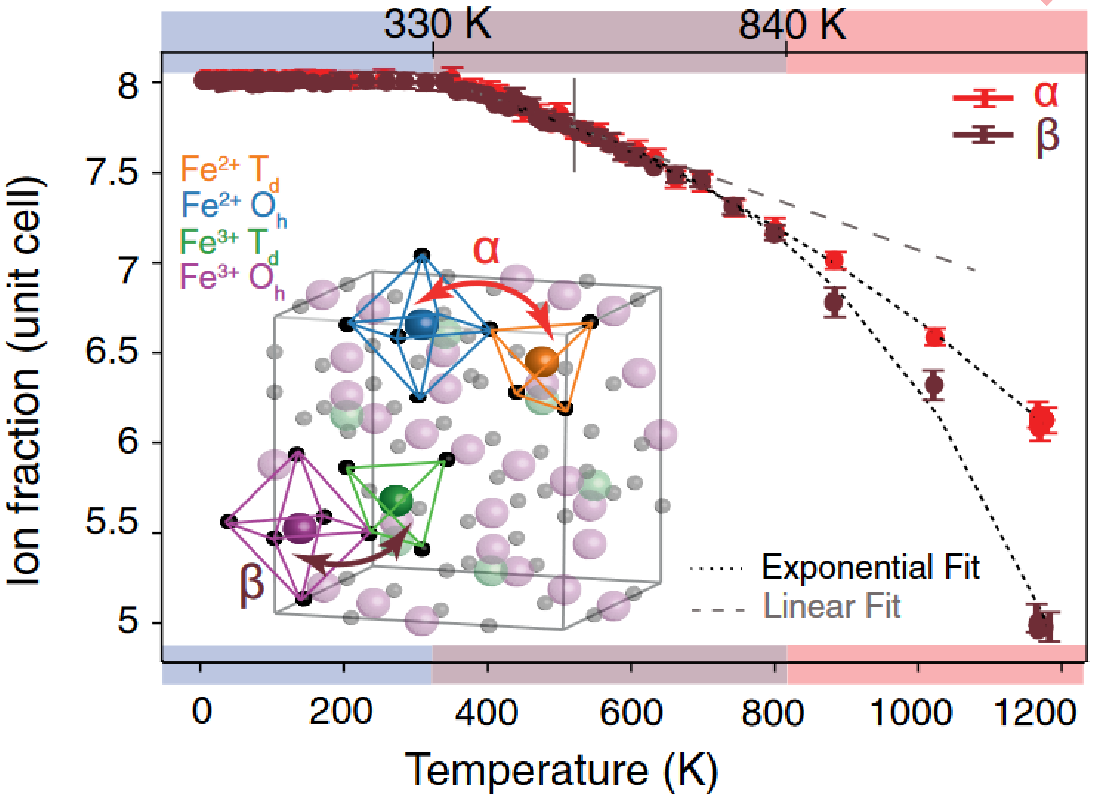

$$\alpha \mathrm{Fe}^{2+}_{O_h} + \beta \mathrm{Fe}^{3+}_{T_d} + (8-\alpha)\mathrm{Fe}^{2+}_{T_d} + (16-\beta)\mathrm{Fe}^{3+}_{O_h}$$

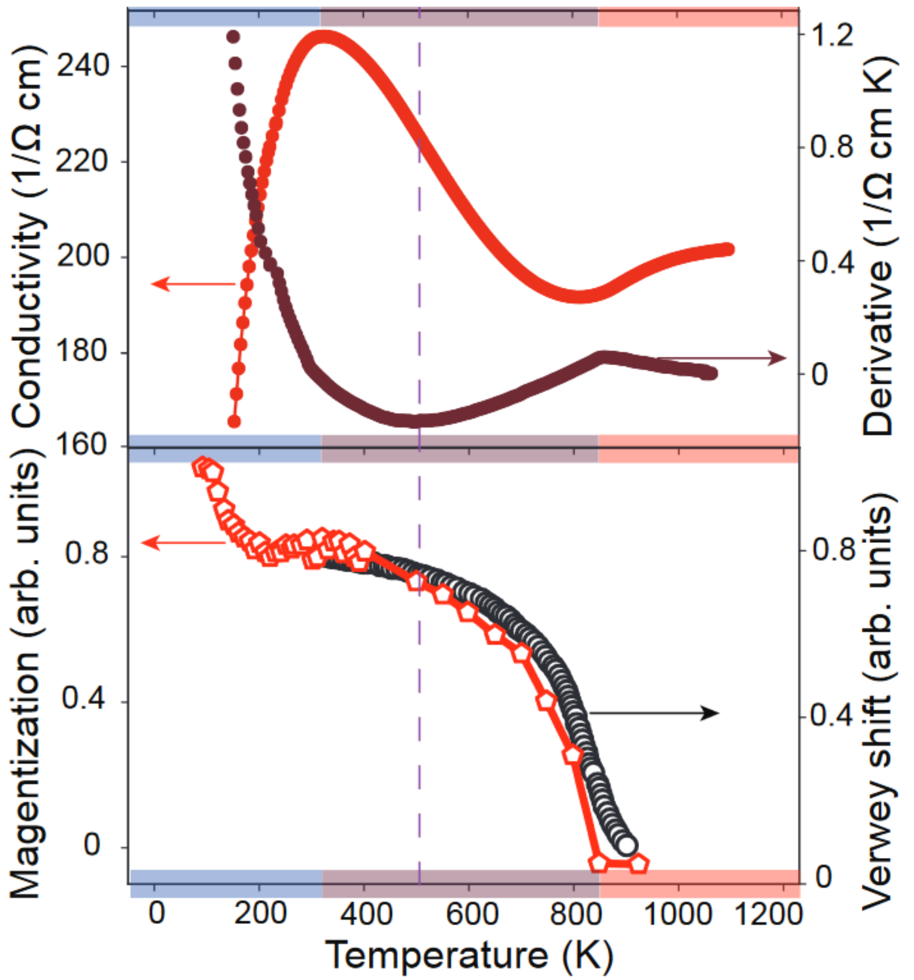
*H.Elnaggar, et al., Phys. Rev. Lett. (2021)*

# Self-doping in magnetite

*Charge transfer character from $T_d$ to $O_h$ sites reveals three distinct T ranges*

$[2Fe^{2+},5Fe^{3+}]_{Td}\,[6Fe^{2+},11Fe^{3+}]_{Oh}\,O_{32}$

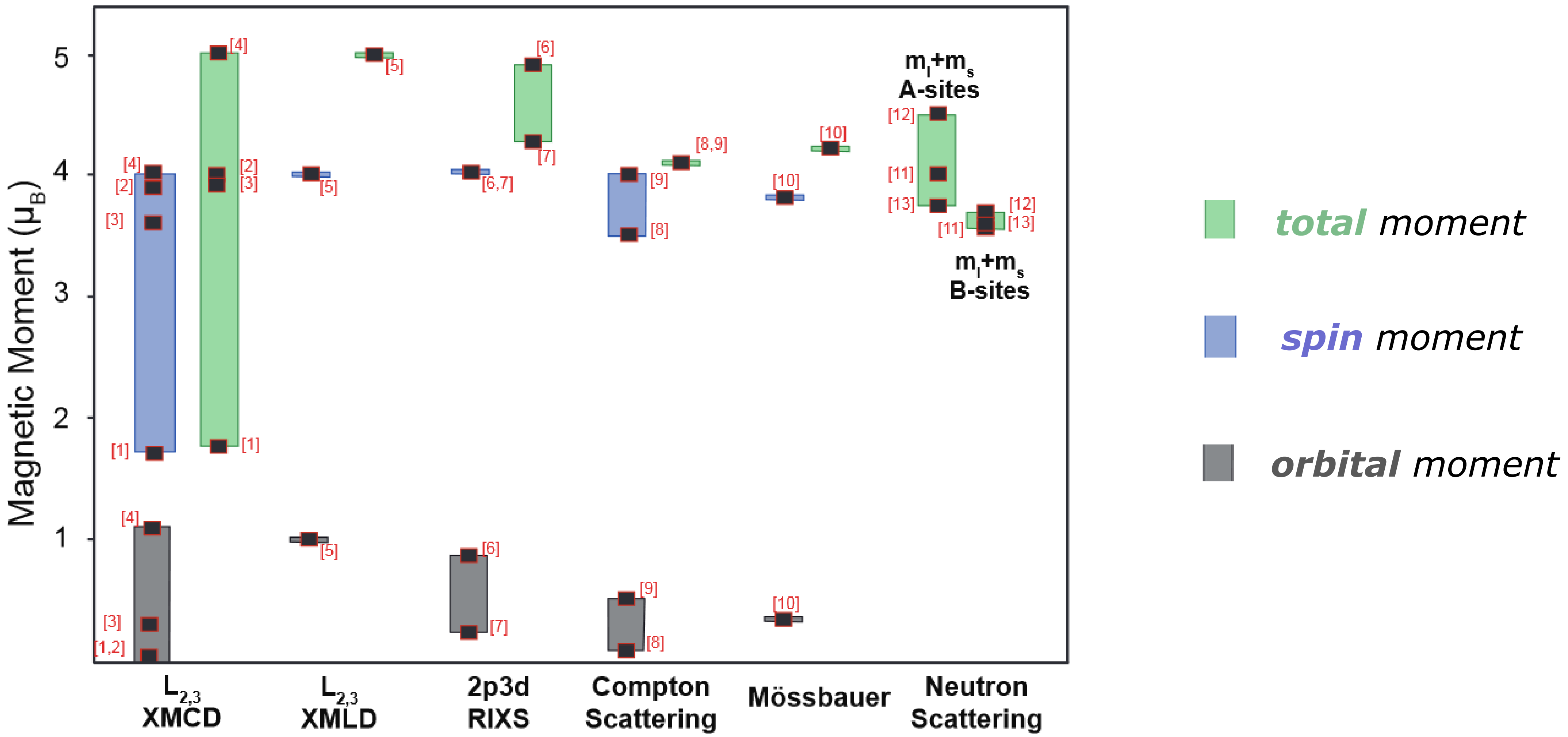



$$\alpha Fe^{2+}_{O_h} + \beta Fe^{3+}_{T_d} + (8-\alpha)Fe^{2+}_{T_d} + (16-\beta)Fe^{3+}_{O_h}$$

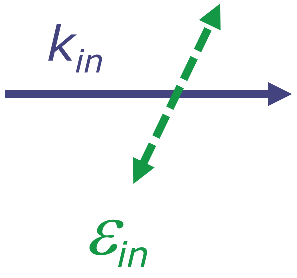
*H.Elnaggar, et al., Phys. Rev. Lett. (2021)*

# Orbital moment in magnetite

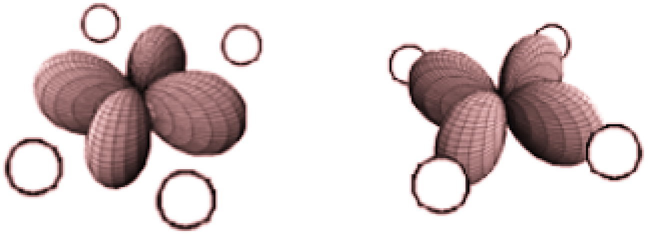



*H.Elnaggar, et al., Phys. Rev. Lett. (2019)*

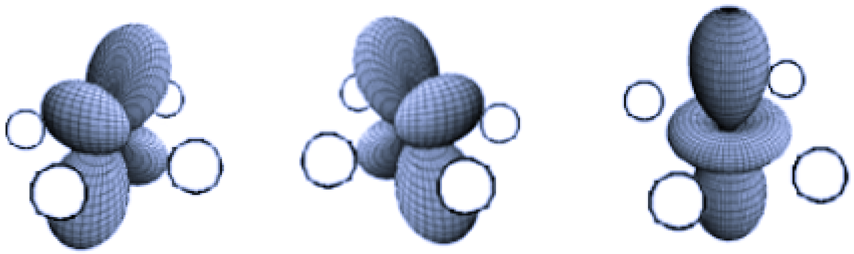
# X-ray linear dichroism




*high absorption*



*low absorption*

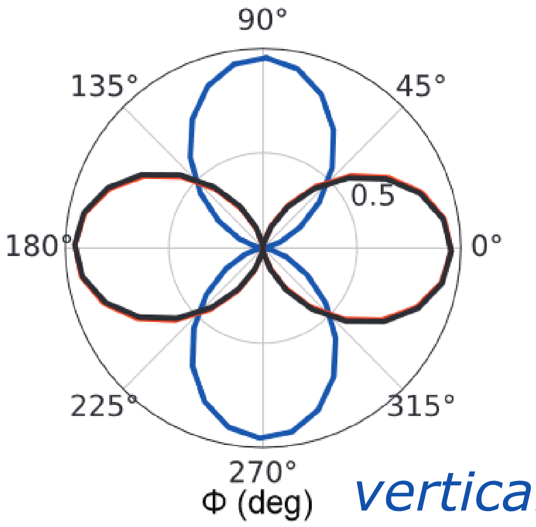


*The difference in spectral shape observed at distinct orientation of photon polarization with respect to crystal/molecule/orbital orientation*

*Selective probe of **structural anisotropy** and **orbital order***

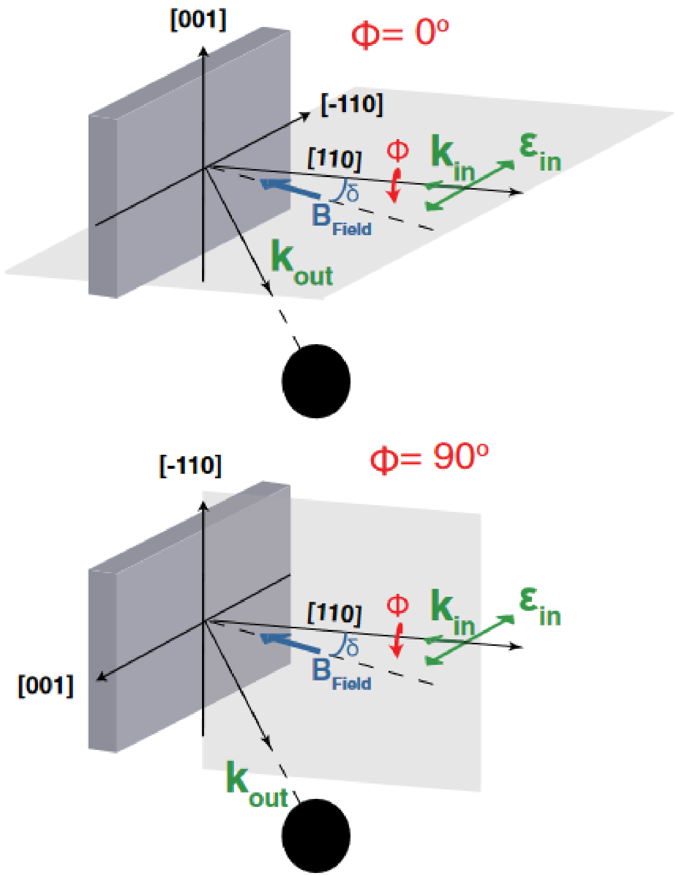
**Angular dependence**

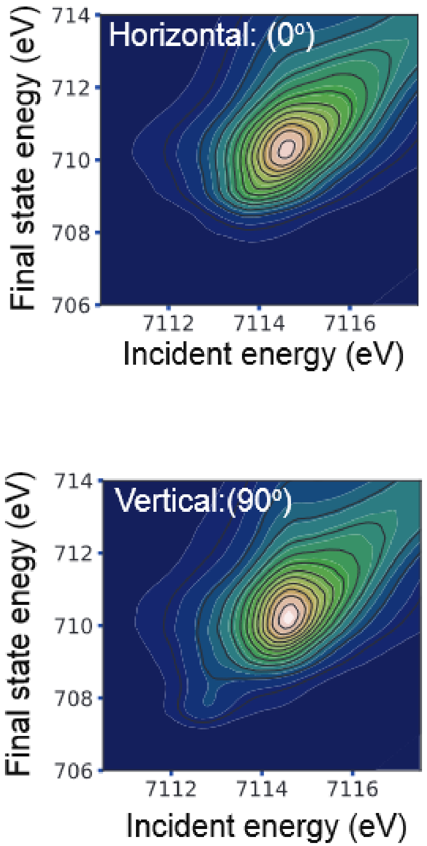
*horizontal $E_{in}$*



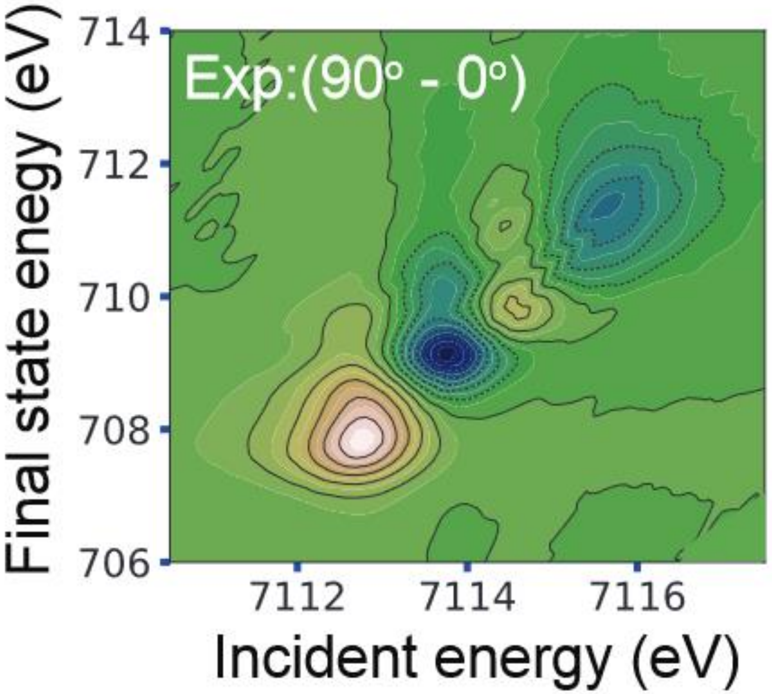

*vertical $E_{in}$*

# 1s2p RIXS XLD in magnetite



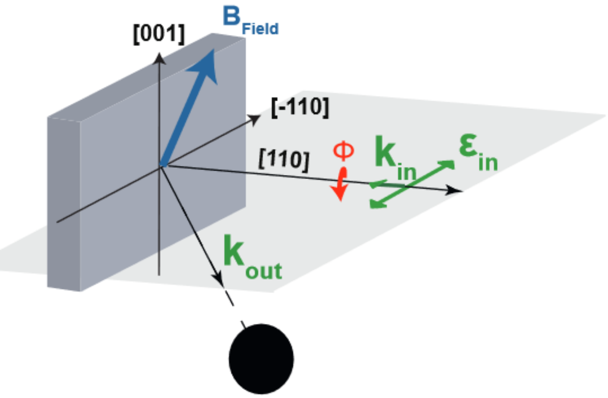



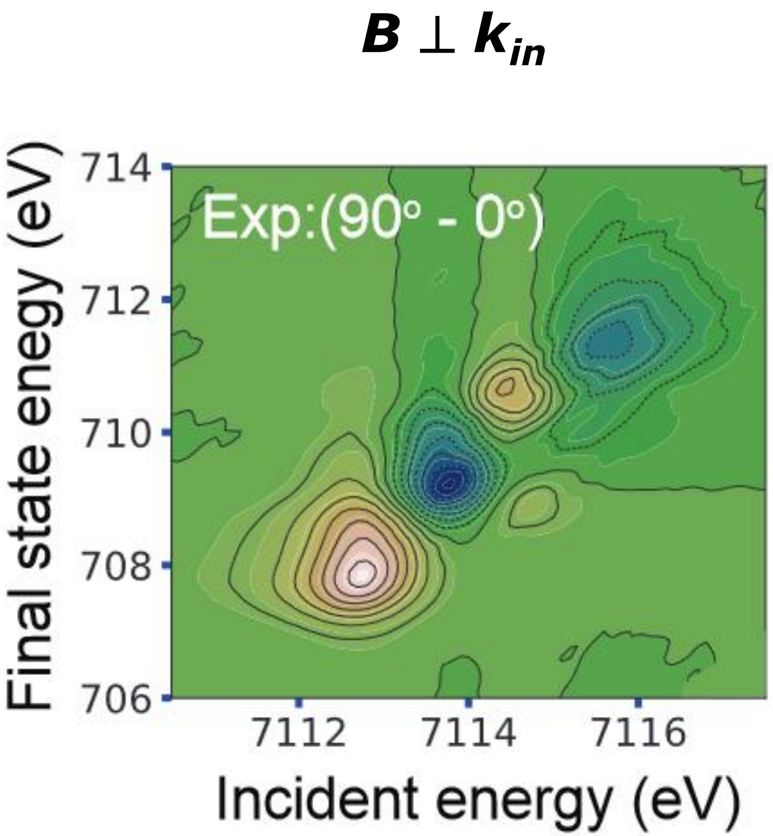

***B* || *k*$_{in}$**

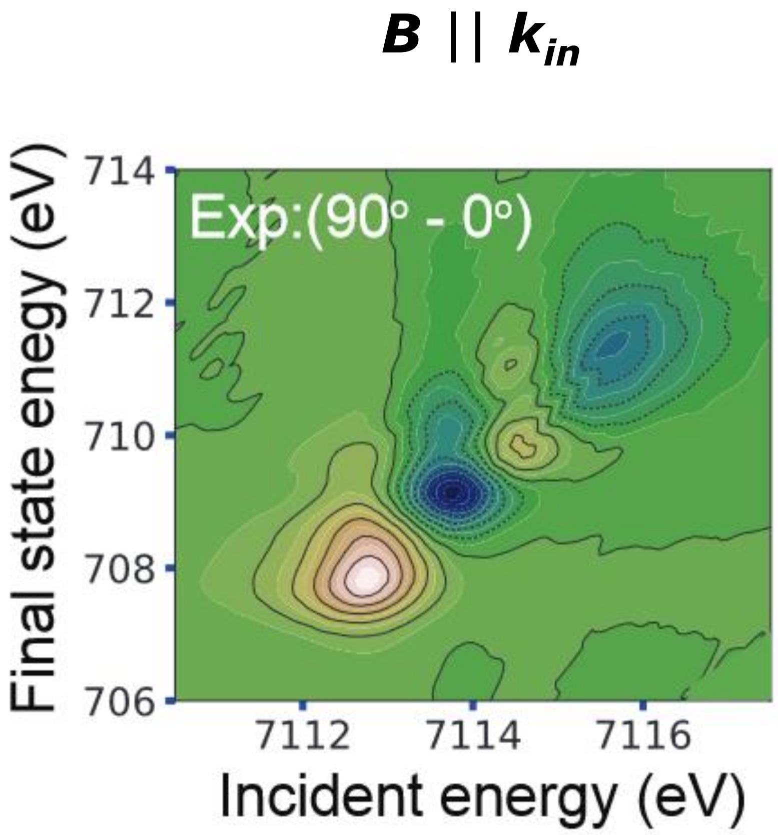



*H.Elnaggar, et al., Phys. Rev. Lett. (2019)*

# 1s2p RIXS XLD in magnetite



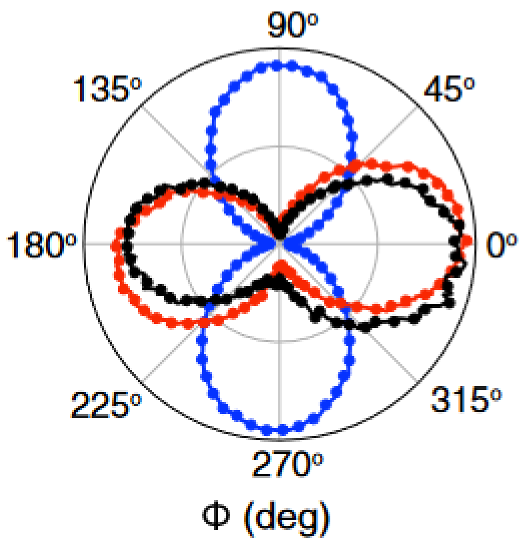



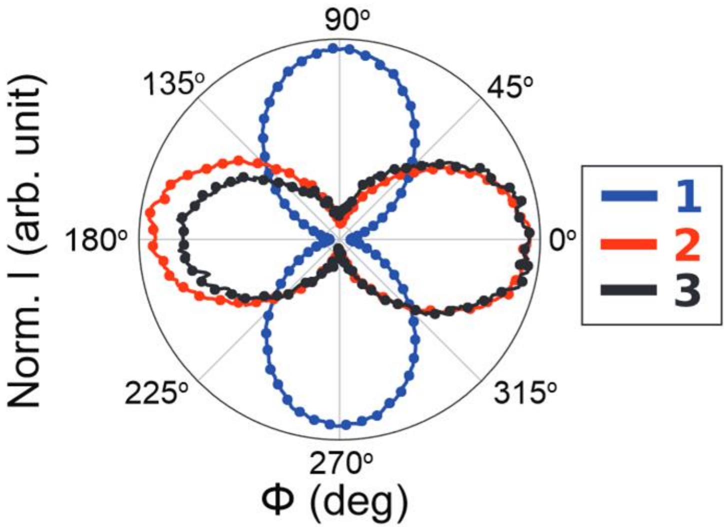




*H.Elnaggar, et al., Phys. Rev. Lett. (2019)*

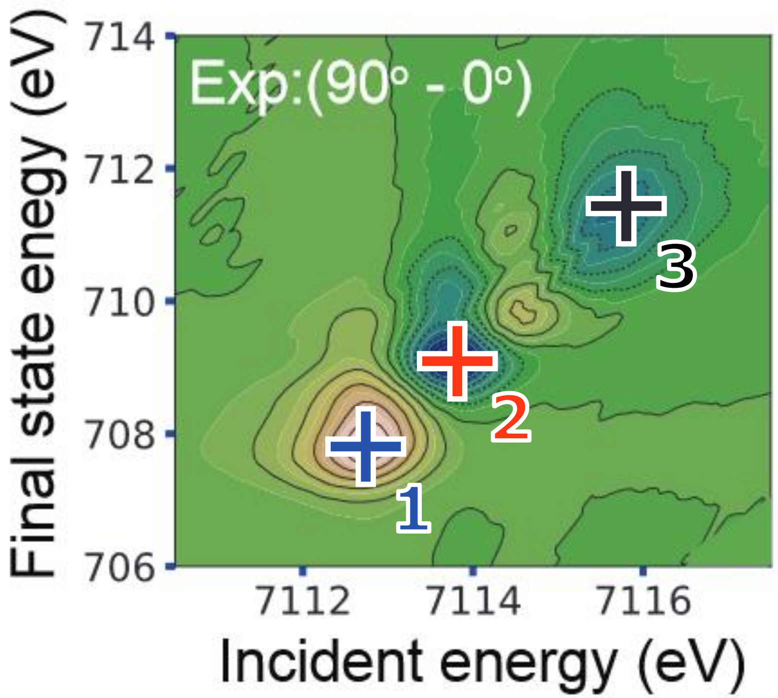
# 1s2p RIXS angular dependence

$\boldsymbol{B} \perp \boldsymbol{k}_{in}$




$\boldsymbol{B} \parallel \boldsymbol{k}_{in}$




*H.Elnaggar, et al., Phys. Rev. Lett. (2019)*

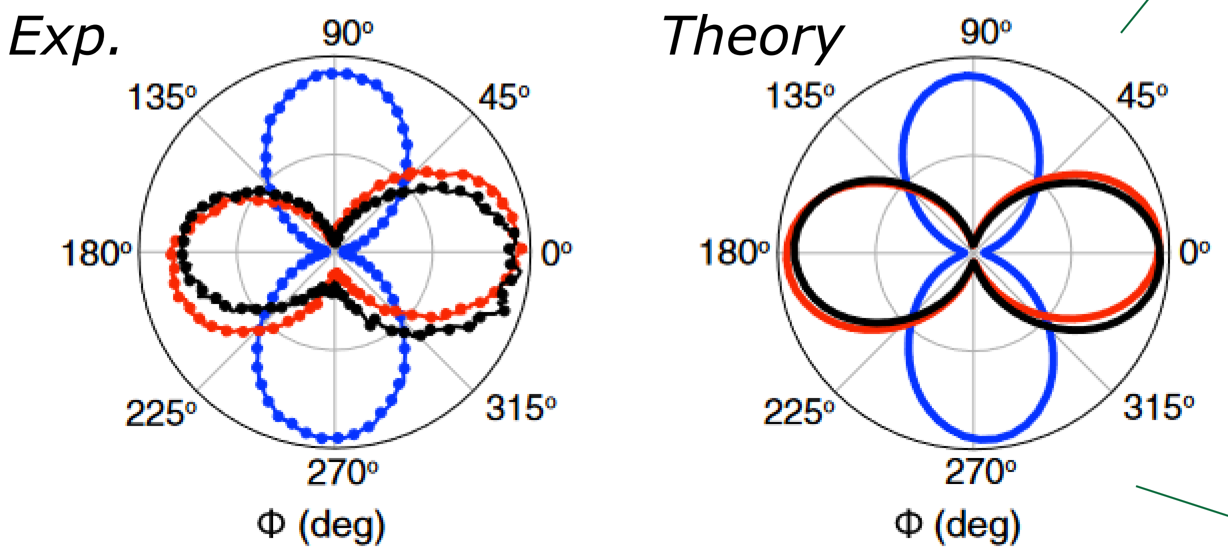
# Theoretical simulations

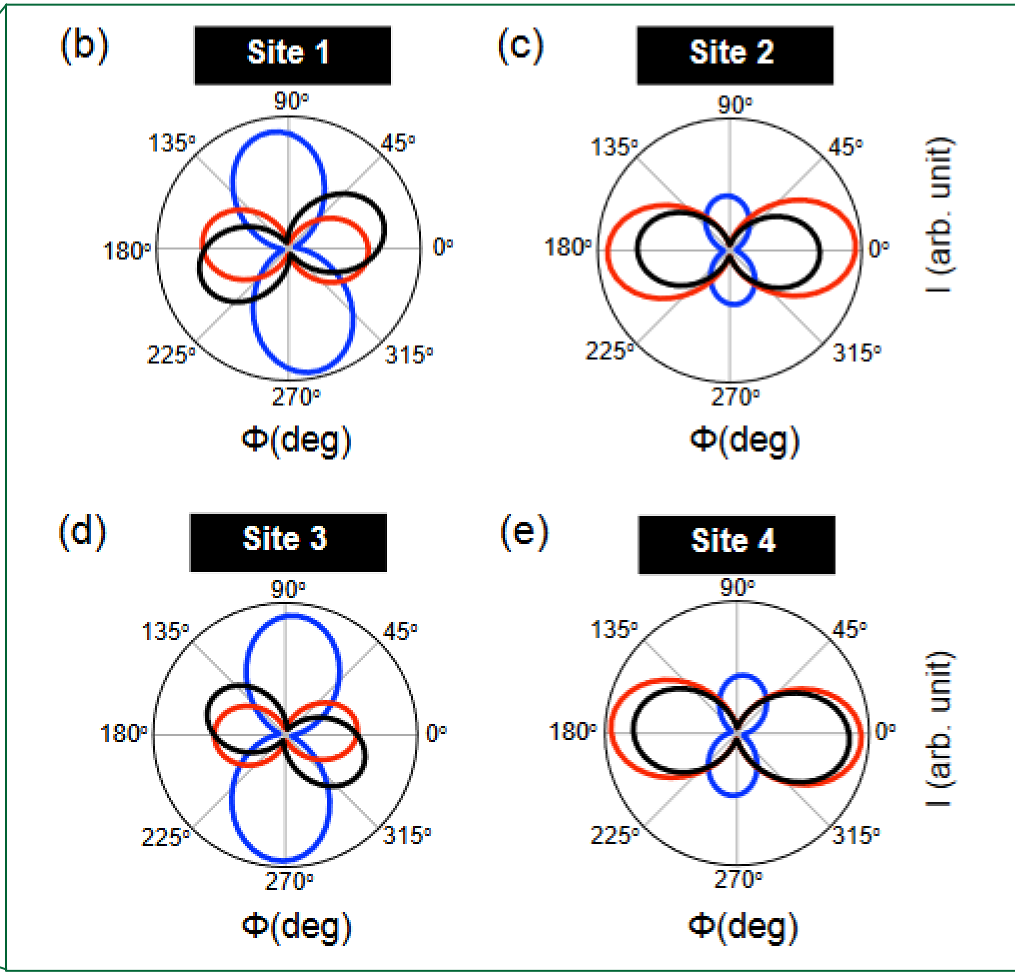
*Configuration interaction calculations using QUANTY code, taking into account:*

- *intra-atomic Coulomb interaction*
- *crystal field*
- *spin-orbit coupling*
- *exchange interactions*

***XLD origins predominantly in $Fe^{2+}$ $O_h$ sites***

$\boldsymbol{B \perp k_{in}}$

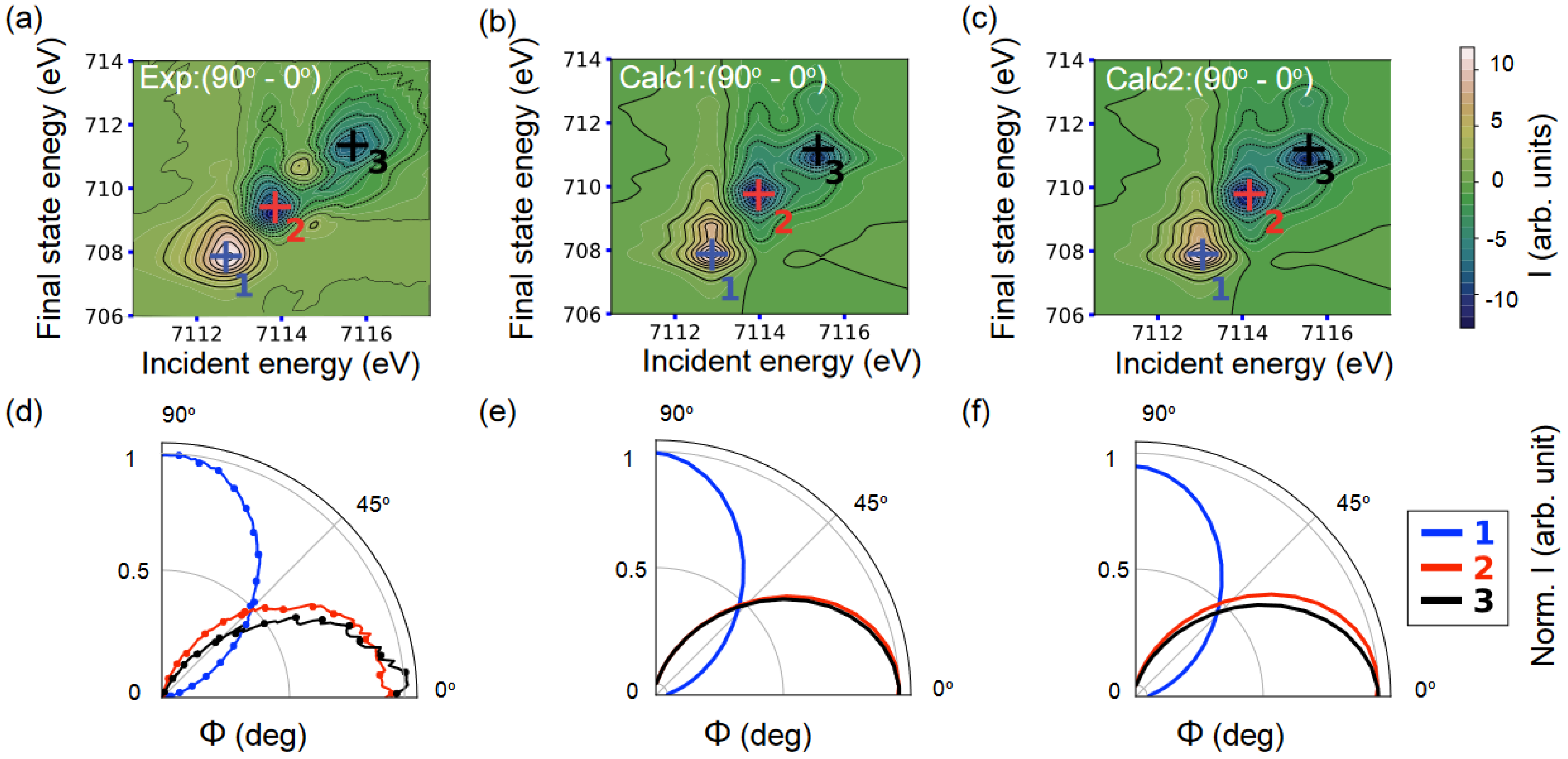



*H.Elnaggar, et al., Phys. Rev. Lett. (2019)*

# Theoretical simulations (2)

$B \perp k_{in}$



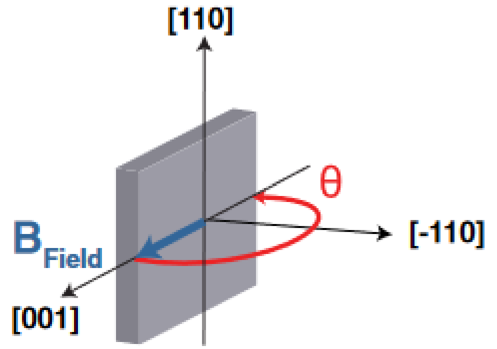

*Experiment*

*Theory with static (trigonal) distortion*

*Theory with dynamic distortion mimicking $X_3$ phonon modes*

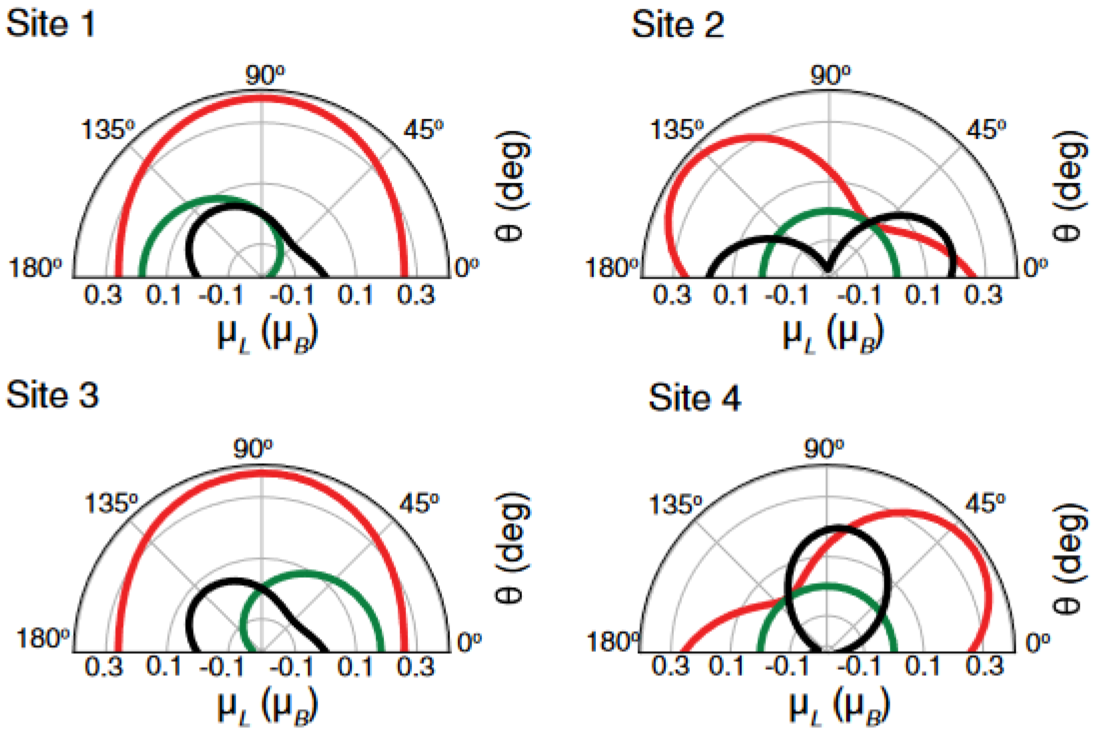
*H.Elnaggar, et al., Phys. Rev. Lett. (2019)*

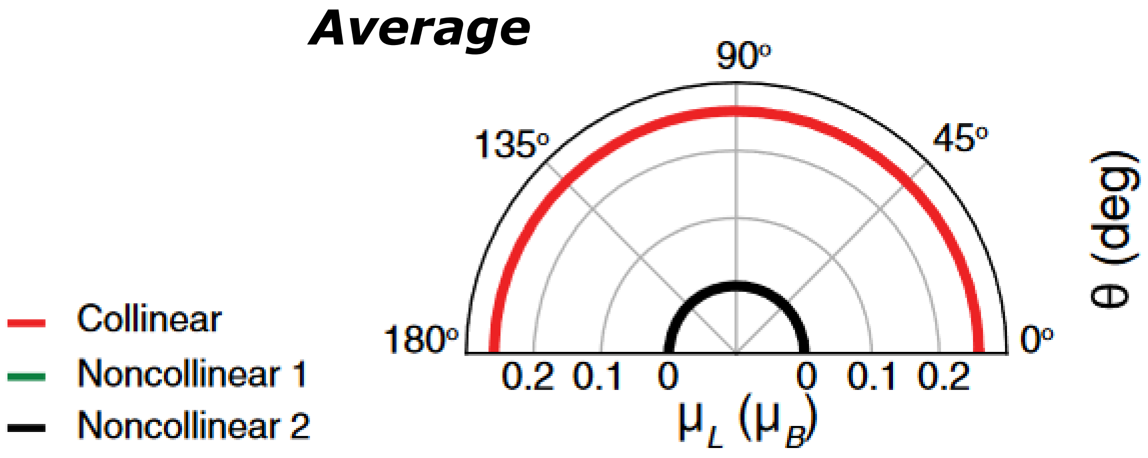
# Predictions of the theoretical model




- ***Average orbital magnetic moment*** *deduced by RIXS-AD is 0.26 ± 0.03 $\mu_B$ / f.u.*

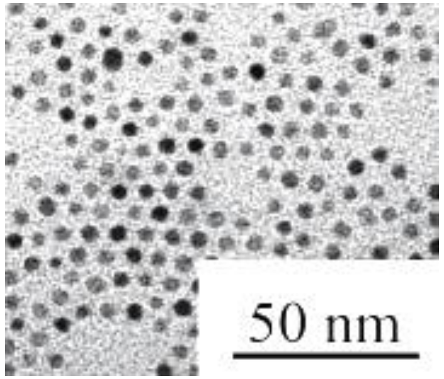
- *Noncollinear orbital contributions may tilt as much as 82° away from the orientation of magnetic spin moment (external field)*

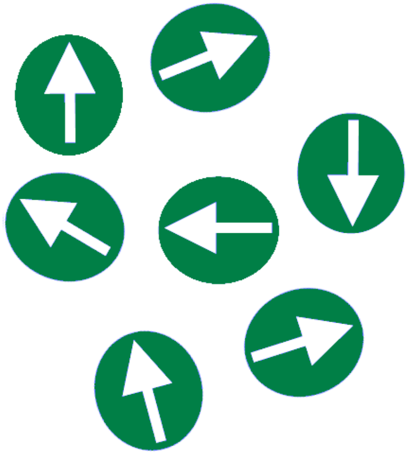


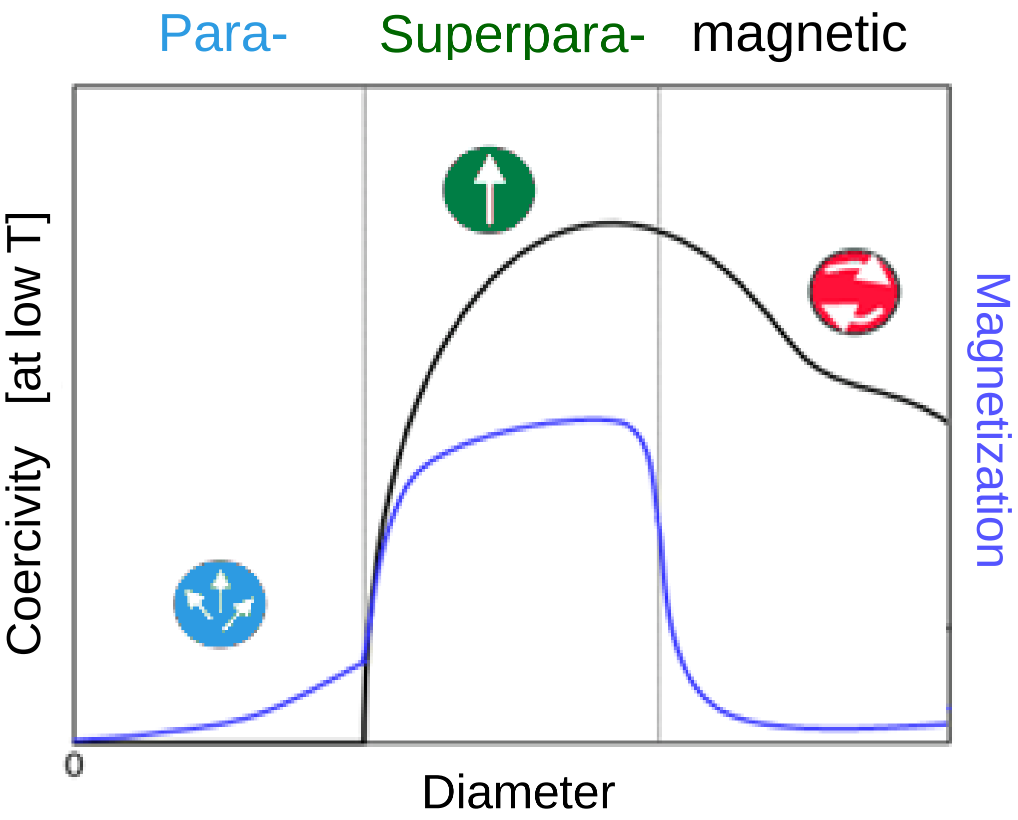



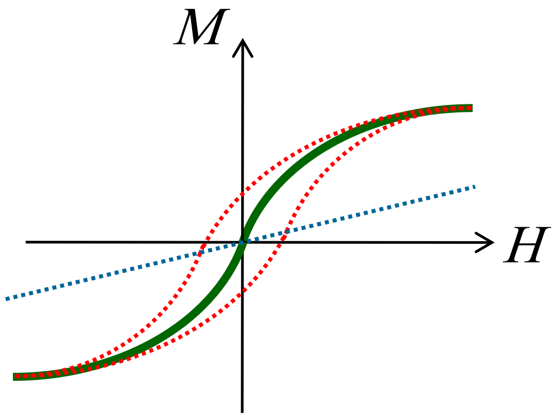

*H.Elnaggar, et al., Phys. Rev. Lett. (2019)*

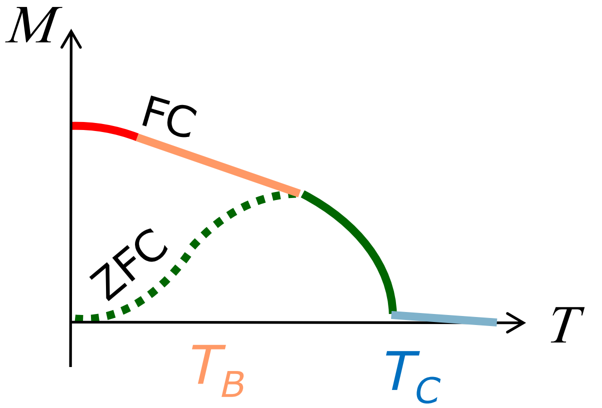
# Magnetic nanoparticles (MNP)



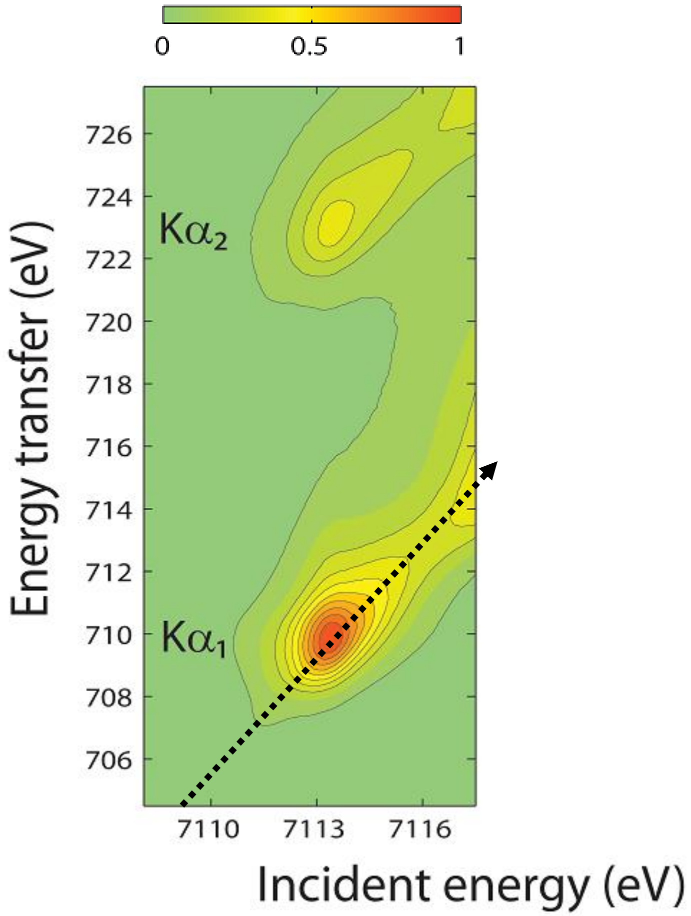


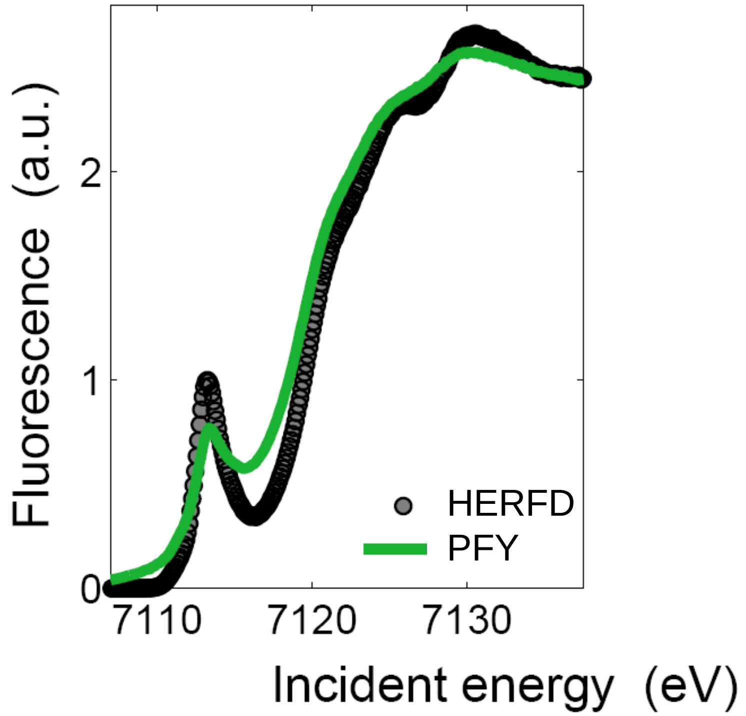




*Magnetic response of MNP depends on temperature and distribution of magnetic moments (diameters) of particles' ensemble*

# 1s2p RIXS and RIXS-MCD in magnetite ($Fe_3O_4$)



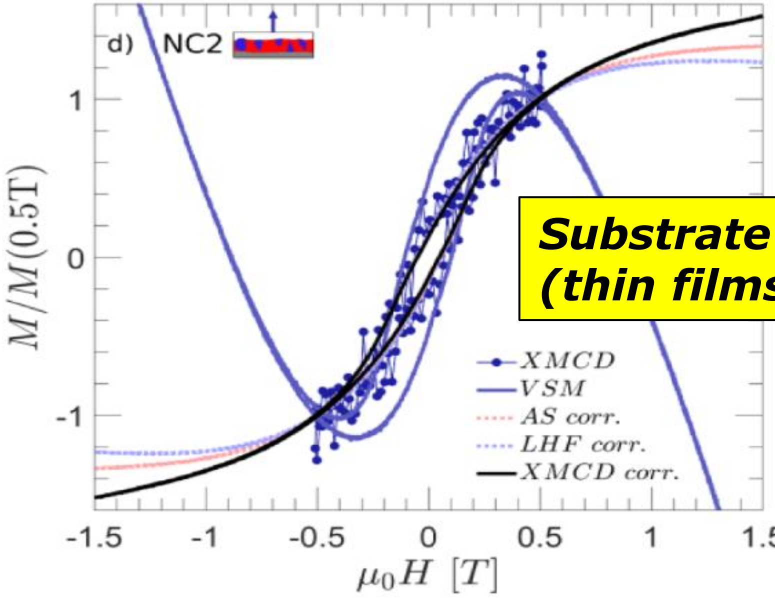

*Photon-in photon-out hard X-ray spectroscopy with negligible non-resonant background and reduced life-time broadening*




*M.Sikora, et al., Phys. Rev. Lett. (2010)*

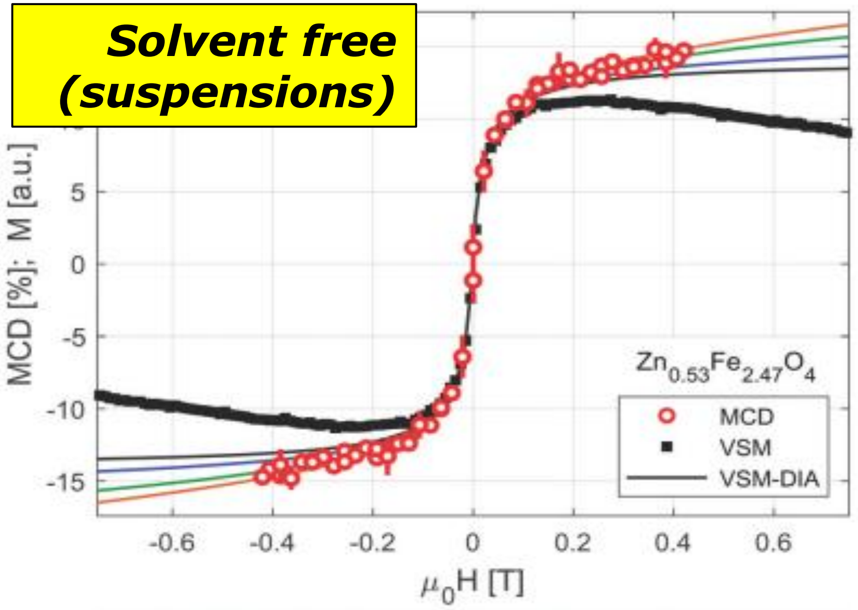
# Magnetometry with RIXS-MCD

K. Pitala et al., JMMM (2022)



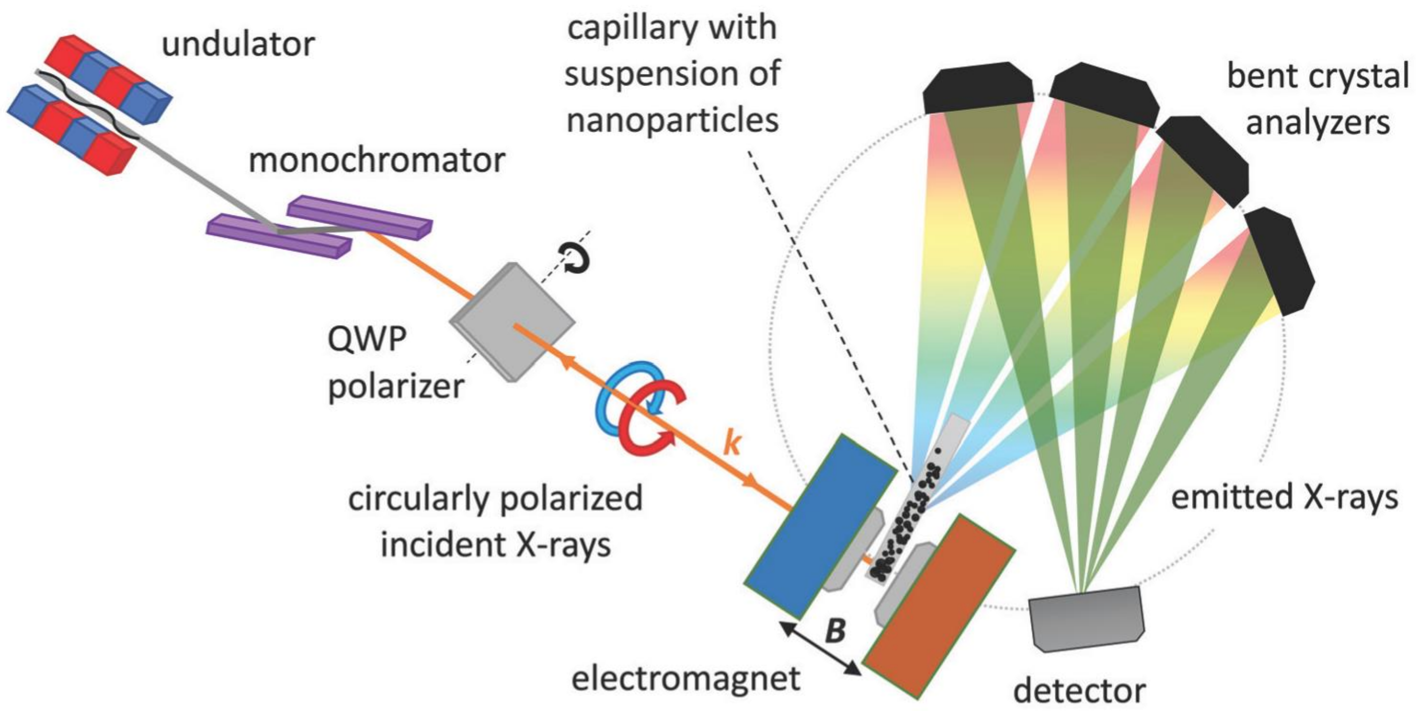

**Substrate free (thin films)**

**Solvent free (suspensions)**

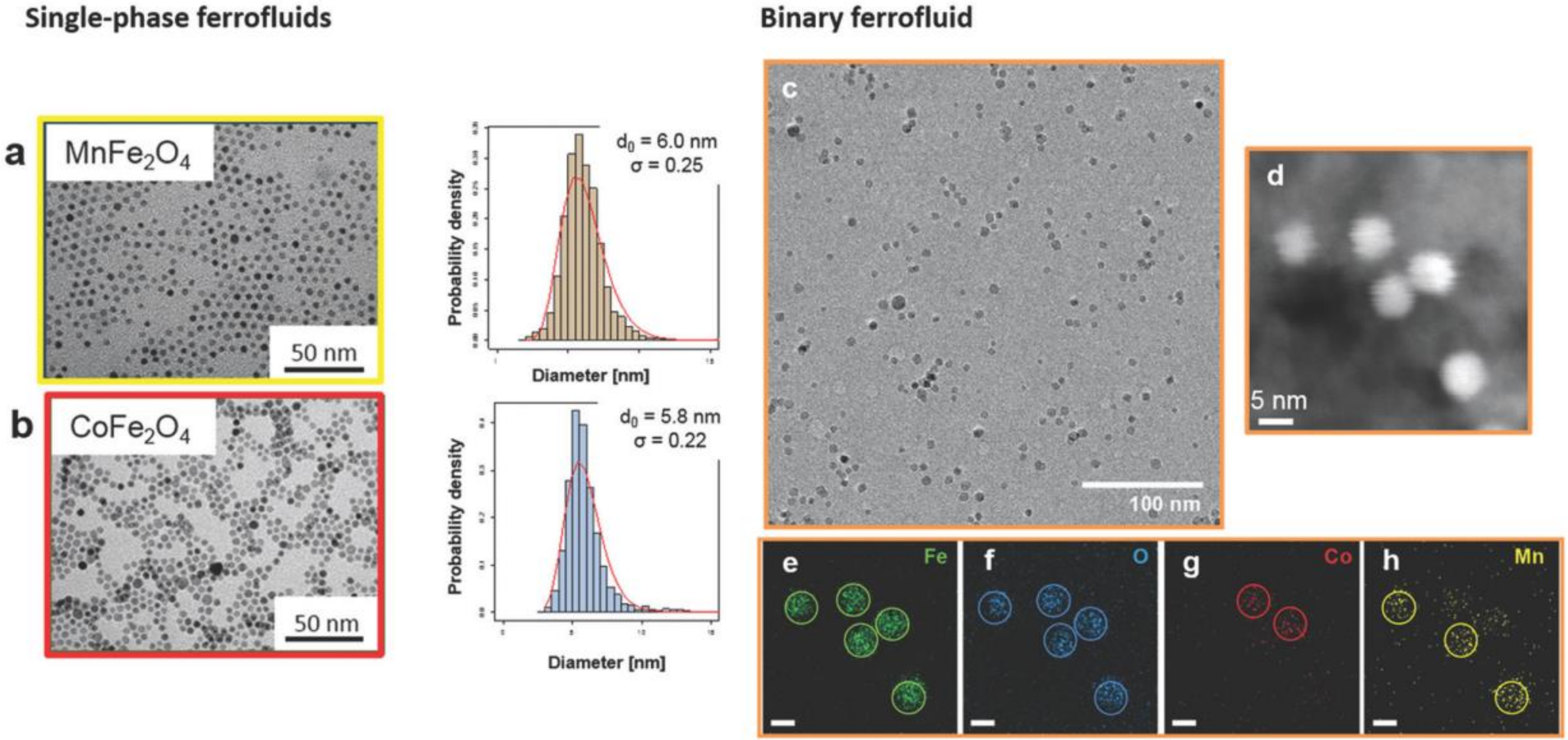



J. Kuciakowski et al., Nanoscale (2020)

***Element selective (volume) magnetization***



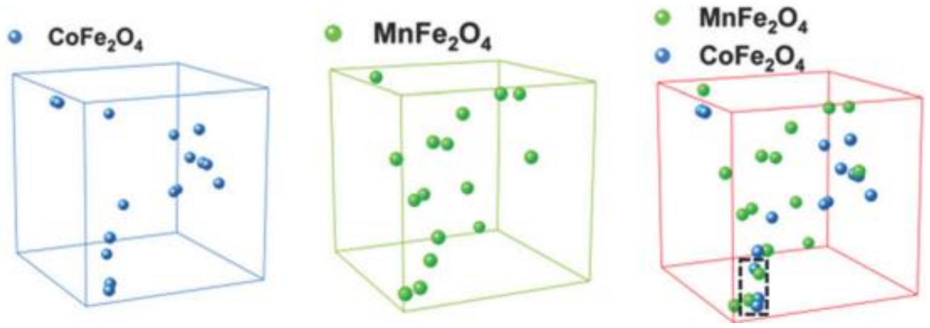

*Available at ID26 at ESRF and Galaxies at Soleil*
*Proposal for Heroes at Solaris (submitted)*

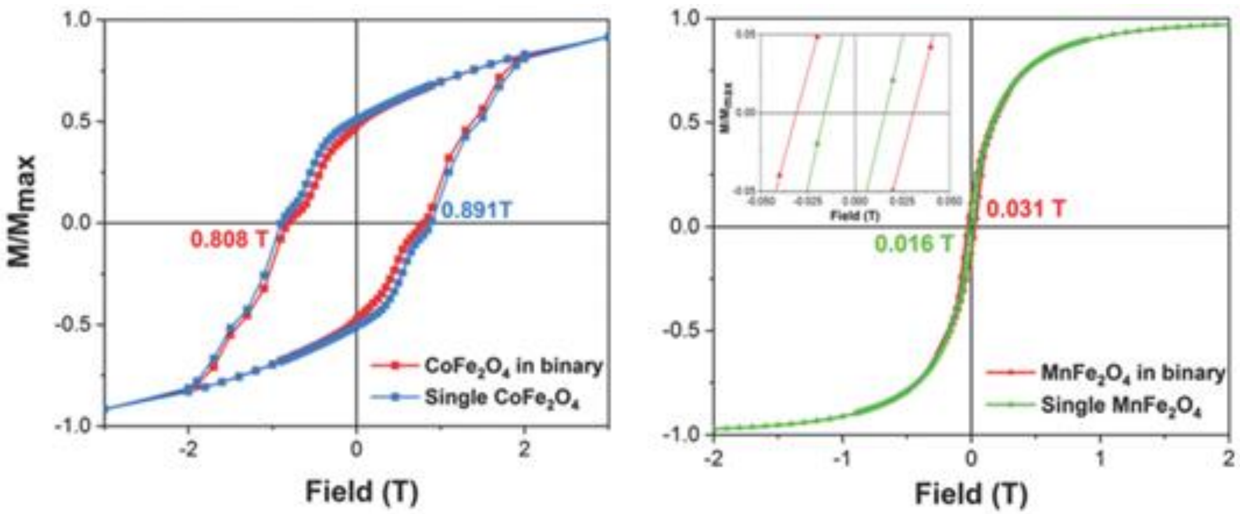



*Magnetization profiles of nanoparticles in suspensions are shaped by interaction with external field, but are also prone to local dipole fields of neighbors (interparticle interactions)*

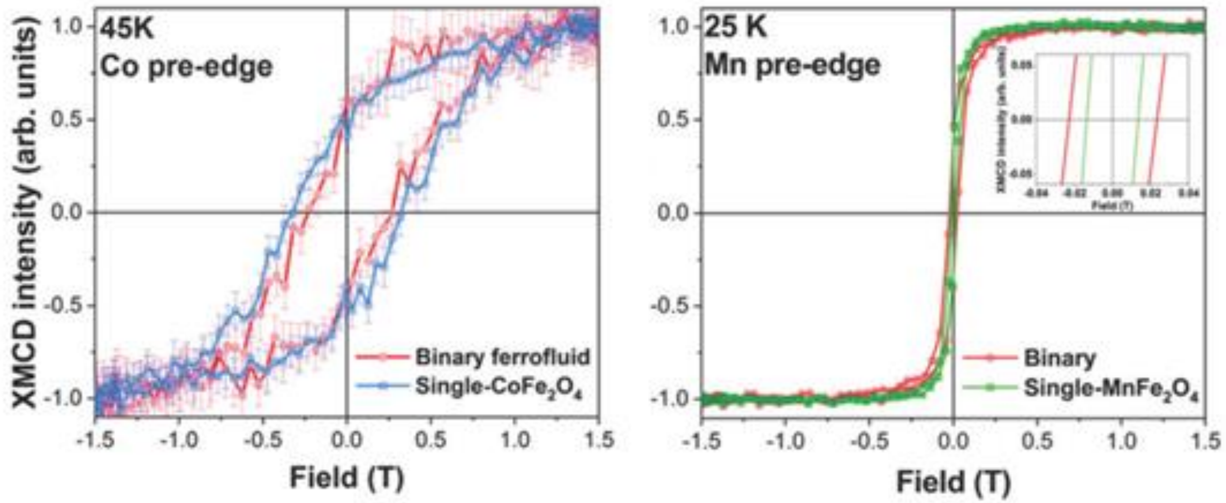
*N.Daffe, et al., Nanoscale (2020)*

# Interparticle interactions



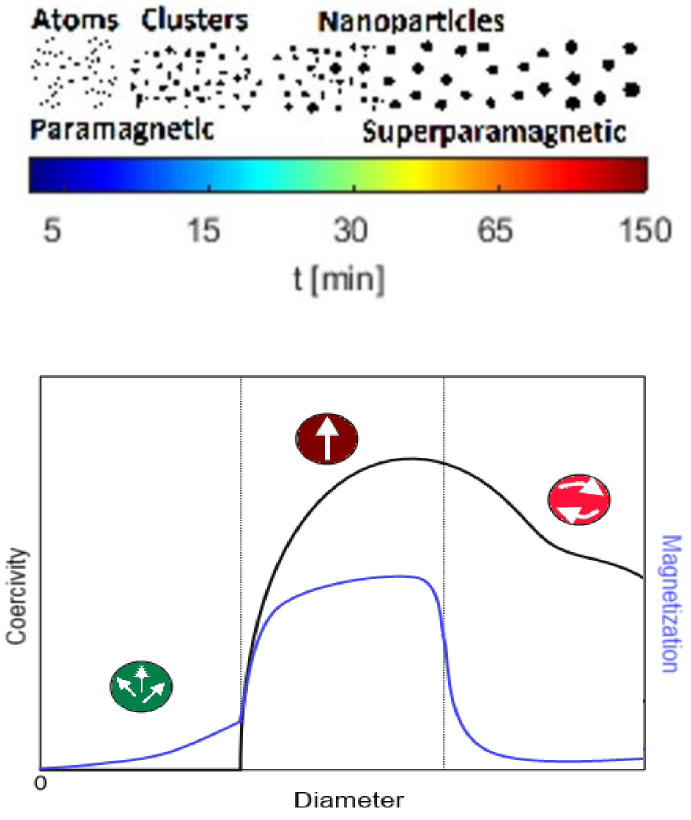

*Magnetization profiles obtained from micromagnetic calculations of the binary clusters observed in Cryo-TEM*



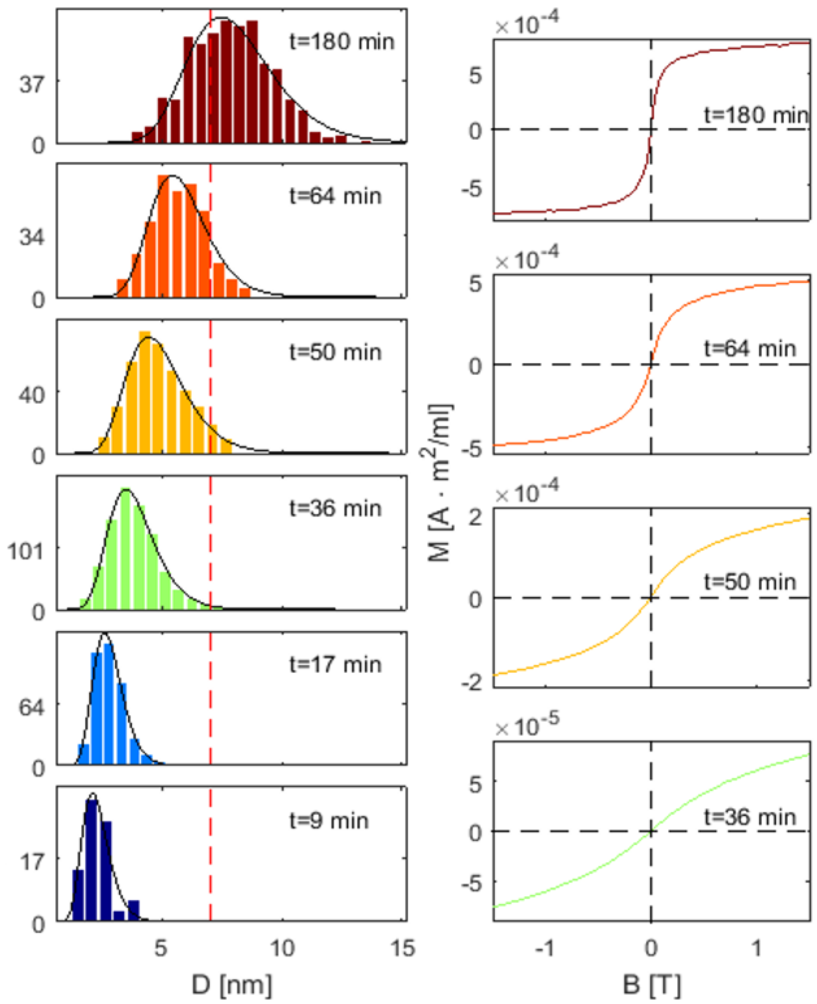

*XMCD magnetometry in zero field cooled frozen binary ferrofluid confirms widening of hysteresis profiles for soft magnetic particles and narrowing of hysteresis for the hard ones*

*N.Daffe, et al., Nanoscale (2020)*

# Nucleation and growth of magnetic nanoparticles

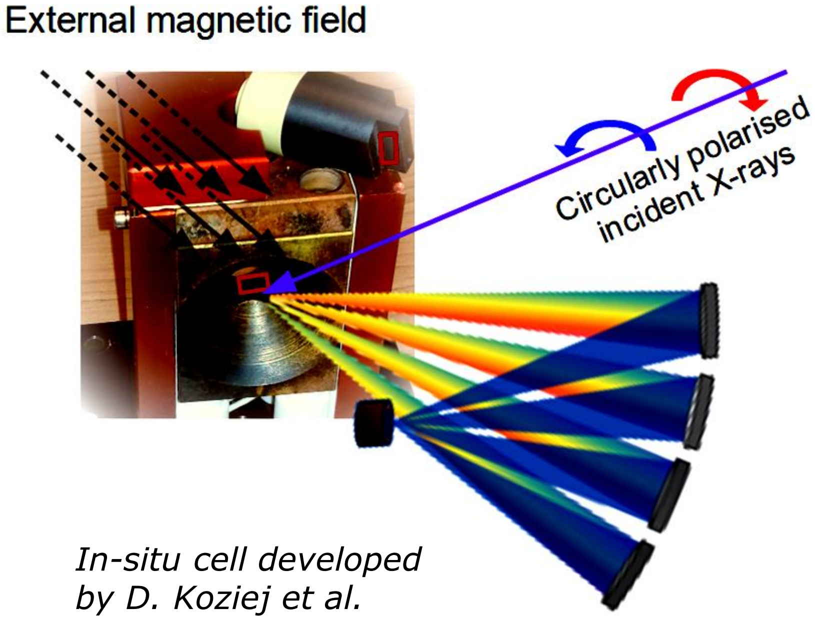



*Goal: to determine critical radius between* ***paramagnetic*** *&* ***superparamagnetic*** *state*

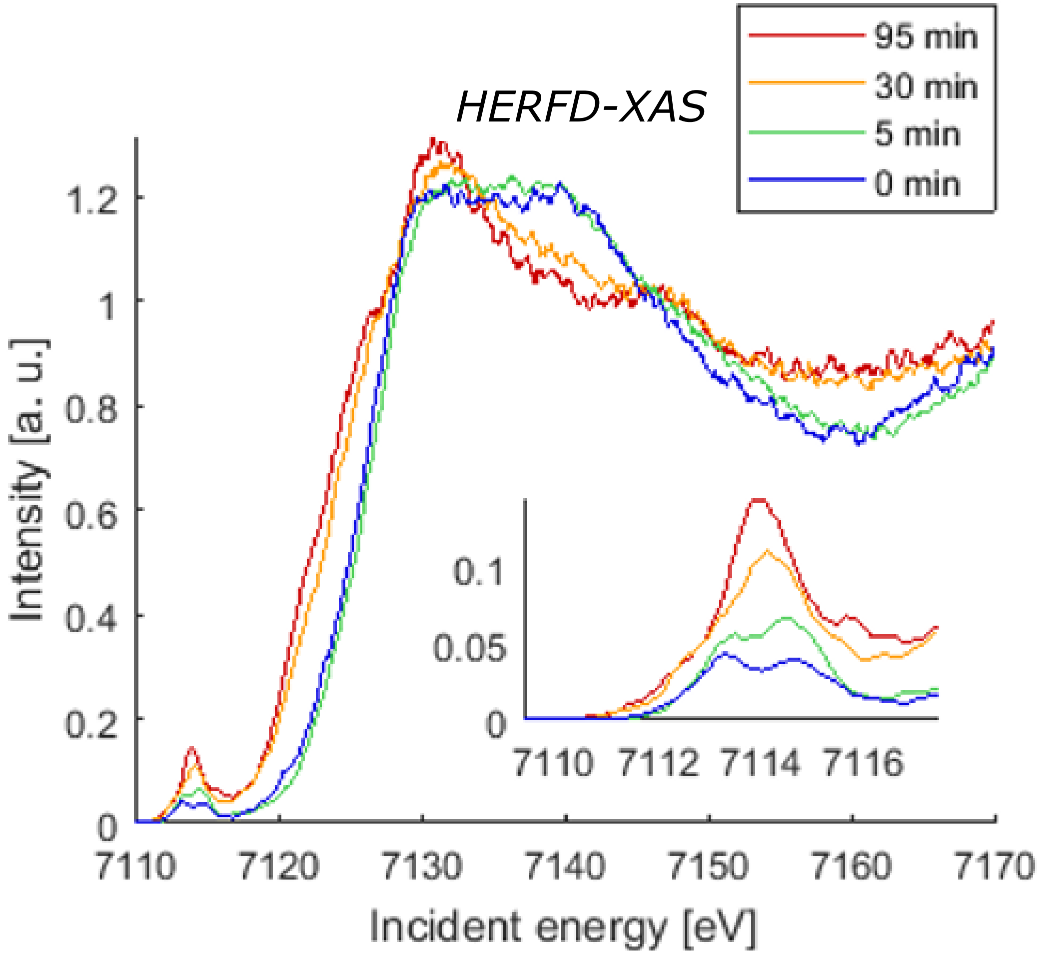



*Fe(acac)$_3$ thermal decomposition*

# In-situ SPION growth



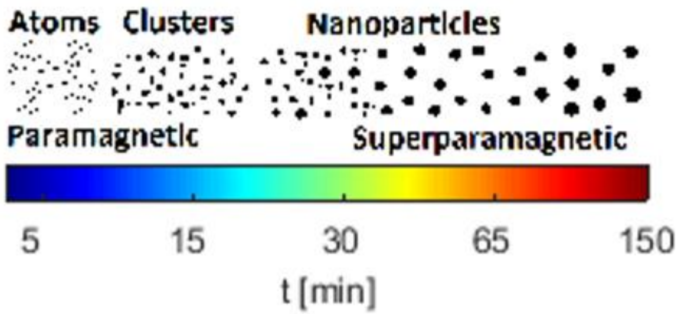

*In-situ cell developed by D. Koziej et al. (ETH & UHH)*




*Evolution from pure octahedral to mixed (octahedral & tetrahedral) local structure during transition from Fe(acac)$_3$ to spinel ferrite*

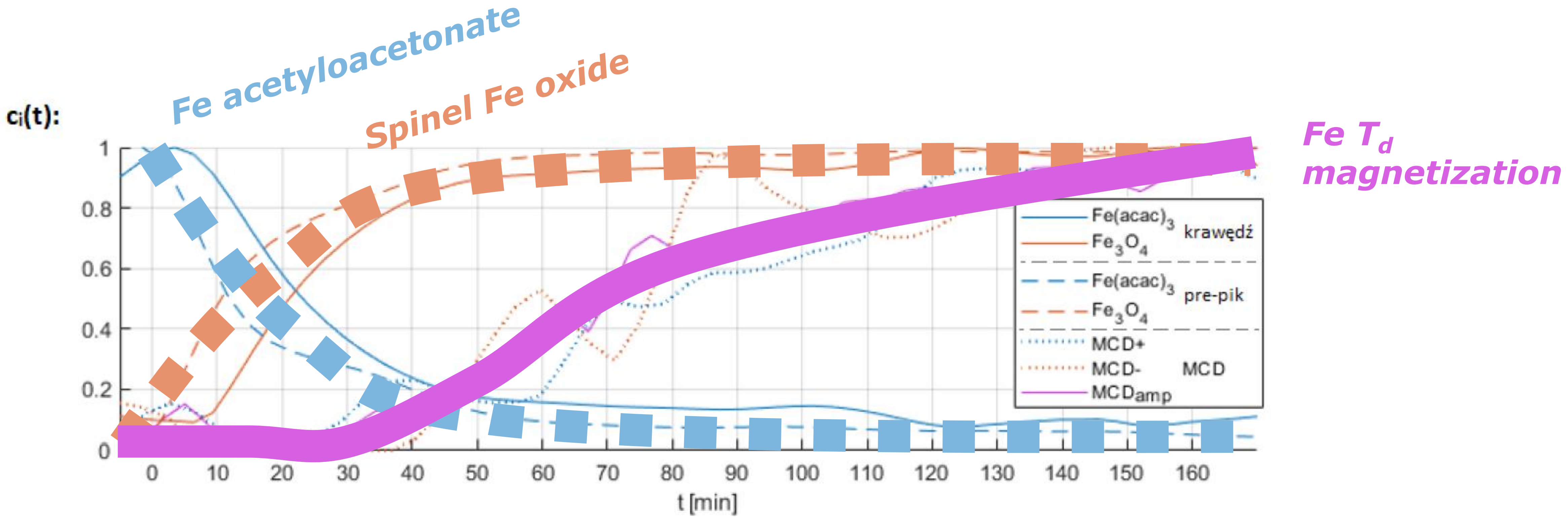
*Further spectral evolution during particle growth is remarkable*

# Reaction (and magnetization) kinetics




*Burst of superparamagnetism is delayed*
*with respect to appearance of spinel phase in $Fe_3O_4$*
*(but not in $CoFe_2O_4$)*

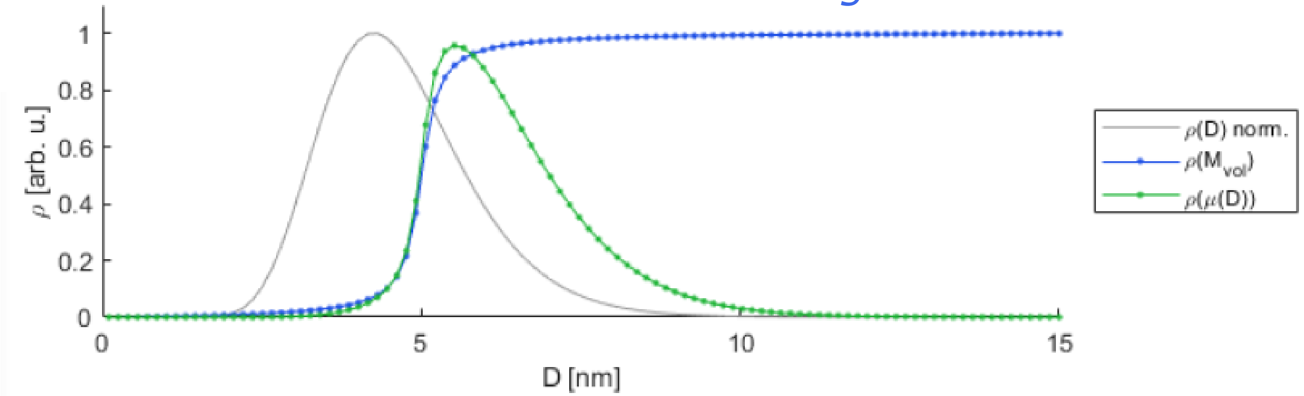
*Burst of superparamagnetism coincides*
*with rapid increase in occupation of tetrahedral sites*



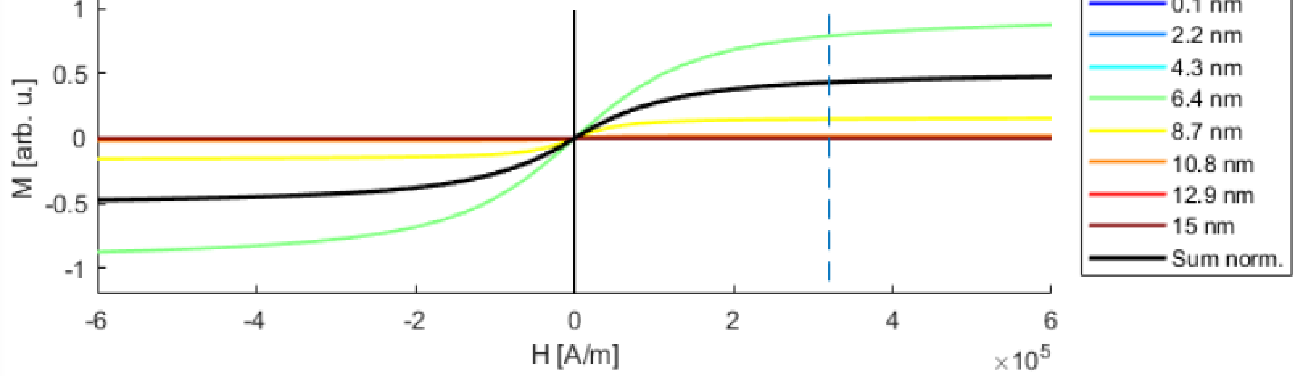

*J.Kuciakowski, PhD thesis*

# Critical radius

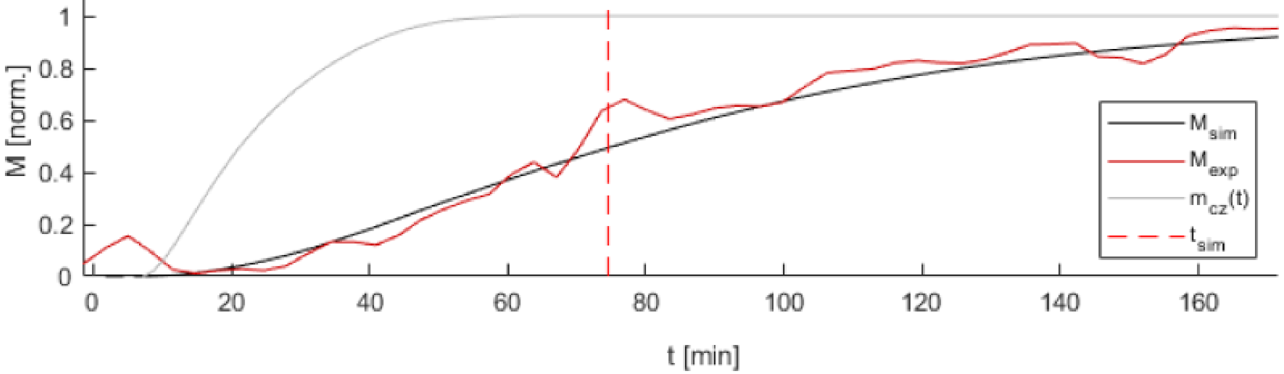
*Distribution of size and magnetic order*



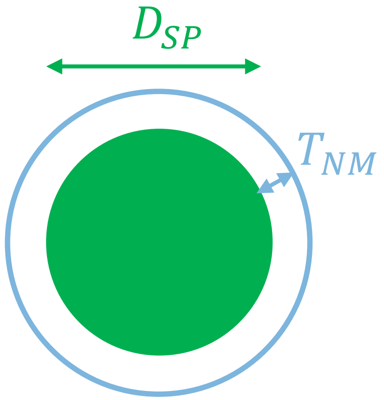

*Effective magnetization profiles*




*Magnetization of the ensemble of MNP at $3.2 \times 10^5$ A/m*




*XMCD(t) evolution can be fitted properly only if a non-magnetic fraction of spinel phase (likely as a shell of MNP) is included*




*Best fit values for synthesis at T = 180°C*

| *Stoichiometry* | $D_{SP}$ [nm] | $T_{NM}$ [nm] |
|---|---|---|
| $Fe_3O_4$ | 4.5 | 0.2 |
| $CoFe_2O_4$ | 0.1 | 0.1 |

*J.Kuciakowski, PhD thesis*

# Acknowledgements

NAWA

UCZELNIA BADAWCZA
INICJATYWA DOSKONAŁOŚCI

*Utrecht University*
- Hebatalla Elnaggar
- Frank de Groot

*UPMC, Paris*
- Claire Carvallo
- Nieli Daffe
- Amélie Juhin
- Philippe Sainctavit

*ESRF, Grenoble*
- Pieter Glatzel
- Sara Lafuerza
- Mauro Rovezzi

*SOLEIL, St. Aubin*
- James Ablett

*Hamburg University*
- Philip Jeaker
- Dorota Koziej

*AGH, Krakow*
- Katarzyna Berent
- Marta Gajewska
- Mateusz Gala
- Zbigniew Kąkol
- Andrzej Kozłowski
- Angelika Kmita
- Juliusz Kuciakowski
- Dorota Lachowicz
- Krzysztof Maćkosz
- Krzysztof Pitala
- Joanna Stępień
- Aleksandra Szkudlarek
- Wojciech Szczerba
- Wojciech Tabiś
- Elżbieta Trynkiewicz
- Magdalena Wytrwał
- Szczepan Zapotoczny
- Jan Żukrowski

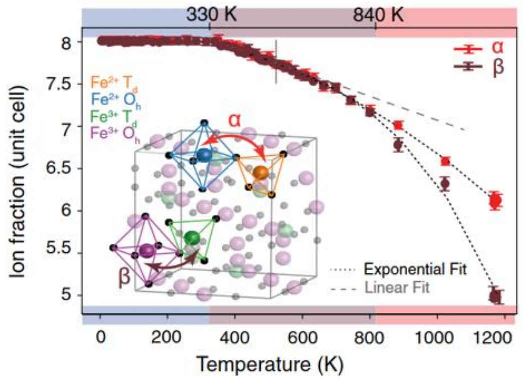
# Conclusions

## 1s2p RIXS

*Hard X-ray photon-in photon-out probe with negligible non-resonant background, reduced lifetime broadening & enhanced dichroism*

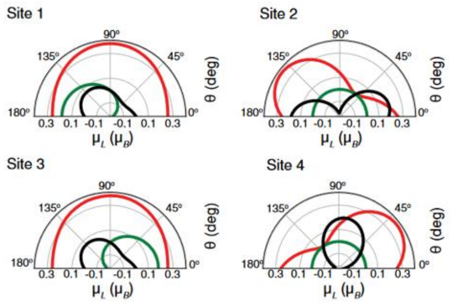
## $Fe_3O_4$: self-doping

*Charge transfer from $T_d$ to (interstitial) $O_h$ sites reveals three distinct T ranges, which coincides with anomalies in conductivity and magnetic order temperature*




## $Fe_3O_4$: $\boldsymbol{L} \times \boldsymbol{S} \neq 0$

*Noncollinear contributions to $Fe^{2+}$ orbital moment may tilt as much as 82° away from the orientation of magnetic spin moment*




## Ferrite MNP: in-operando

*1s2p RIXS-MCD opens up possibility for selective (solvent free) study of magnetic (oxide) nanoparticles in solutions, including in-situ & operando*