Tobias Funk

XMCD experiments on paramagnetic biological systems and model compounds

Metallo proteins

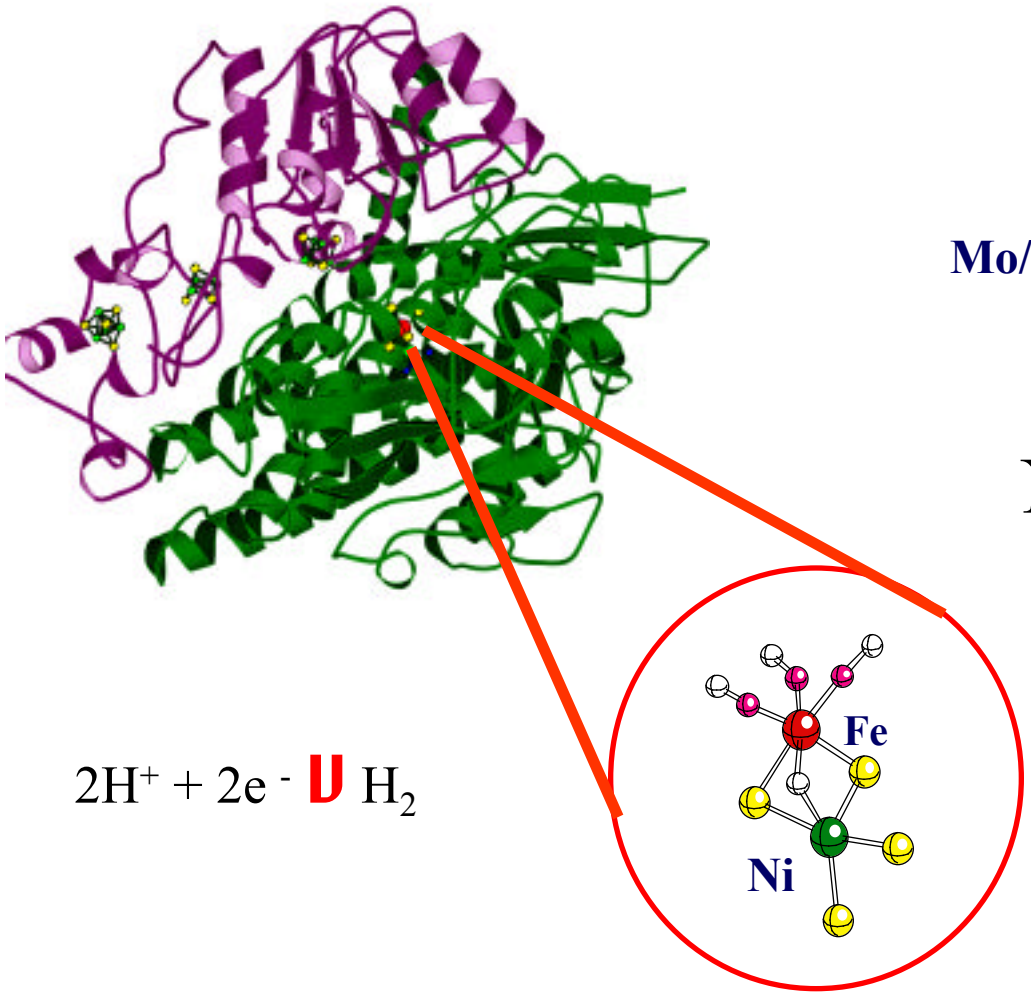
Magnetization of paramagnetic systems

Experimental realization

Results

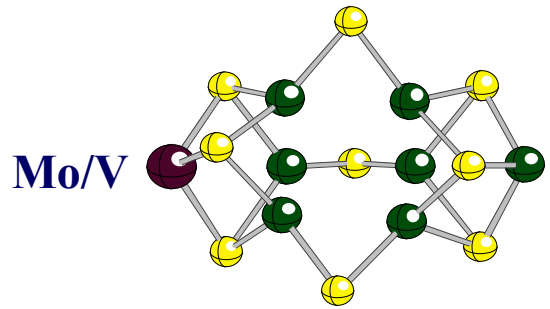
Goal: study paramagnetic proteins with XMCD

Hydrogenase (H_2ase)



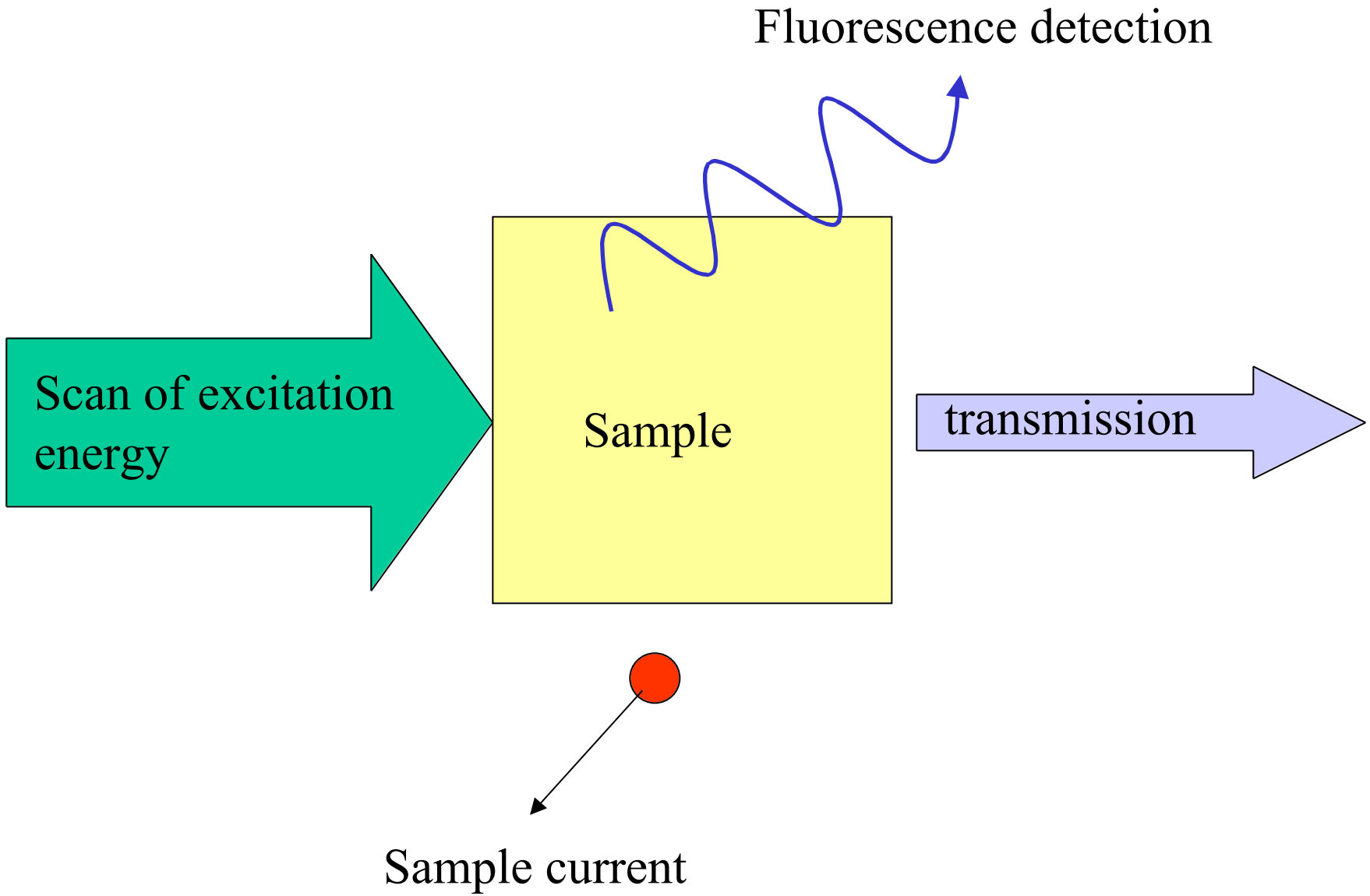
$2H^+ + 2e^- \cup H_2$

$2N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$



Nitrogenase (N_2ase)

Experiment

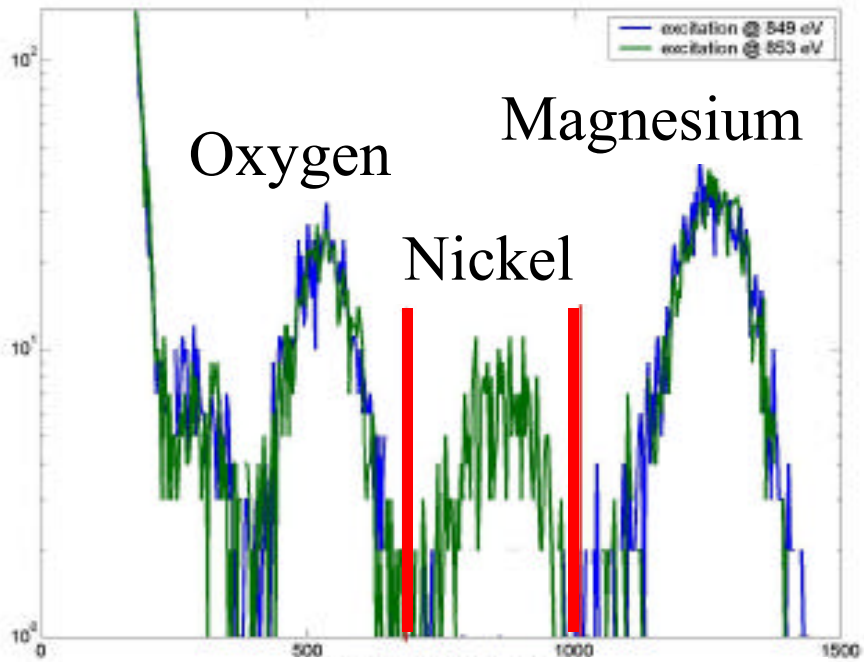

Fluorescence detection
Scan of excitation energy
Sample
transmission
Sample current

Fluorescence detected absorption spectra

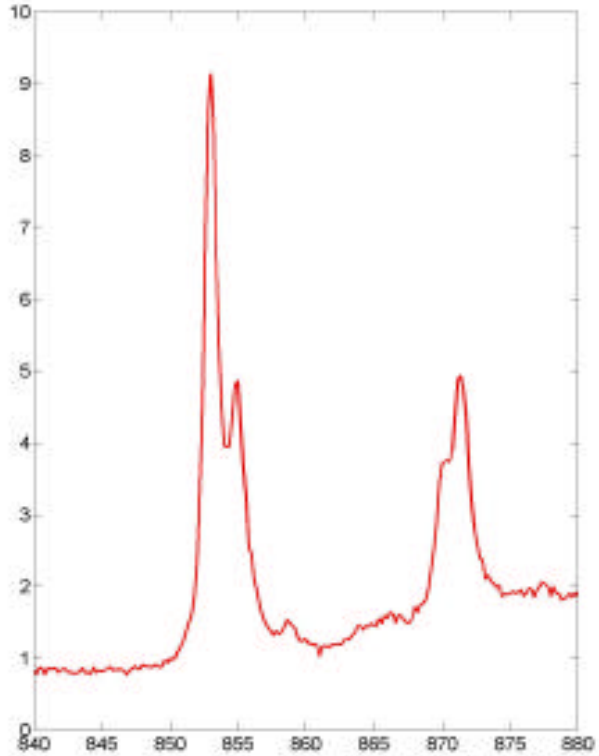
Excitation at

849eV

853eV

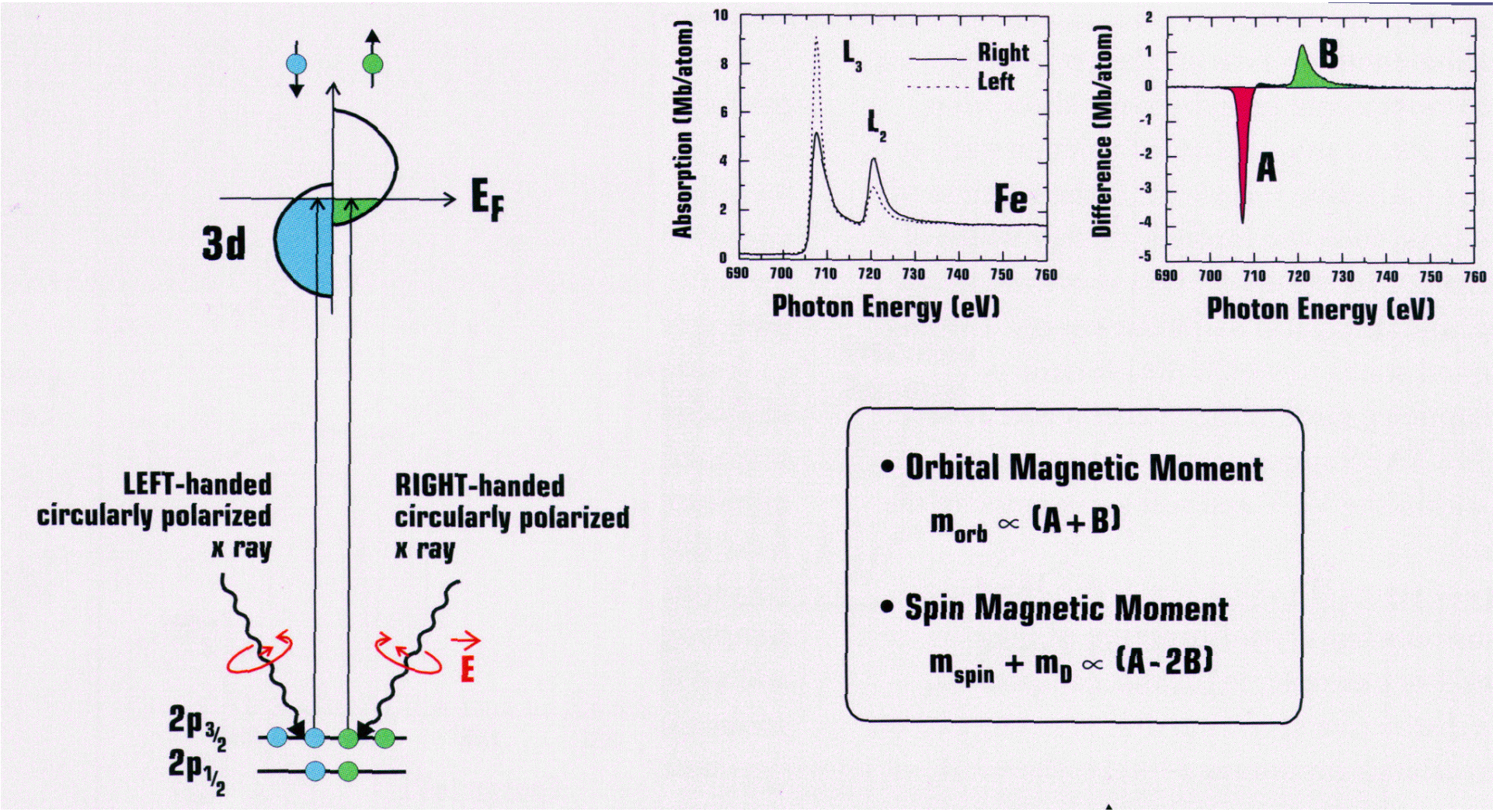


Fluorescence energy [eV]



excitation energy [eV]

X-ray Magnetic Circular Dichroism



Circular magnetic dichroism

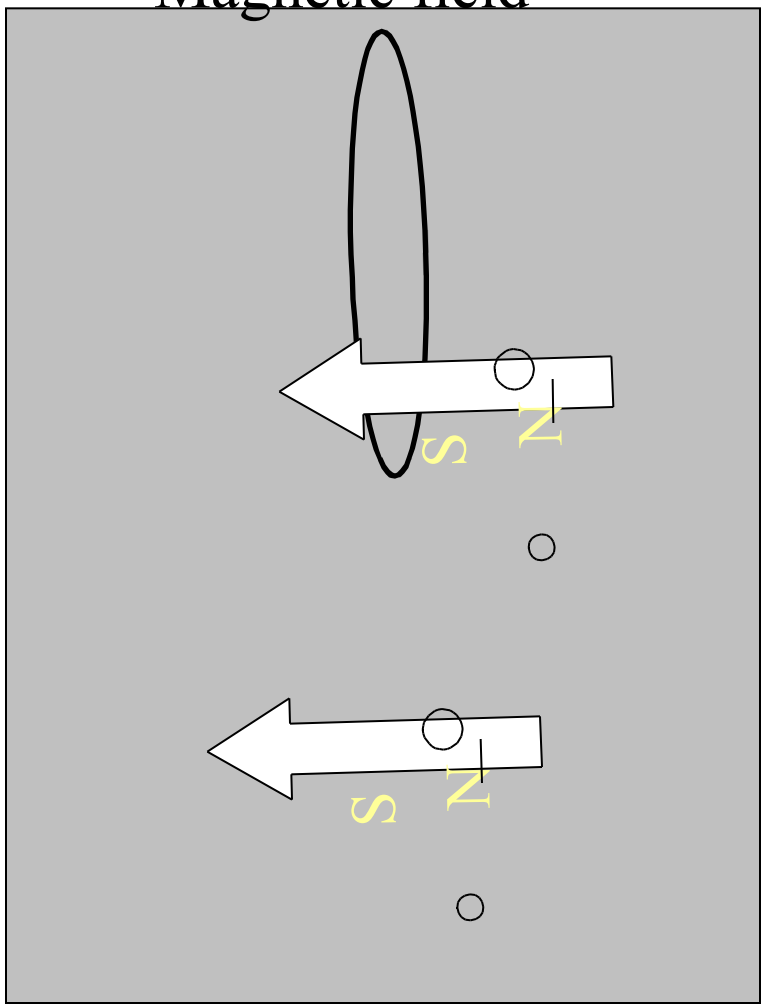
Circular polarized light

E-vector

left

right

Magnetic field

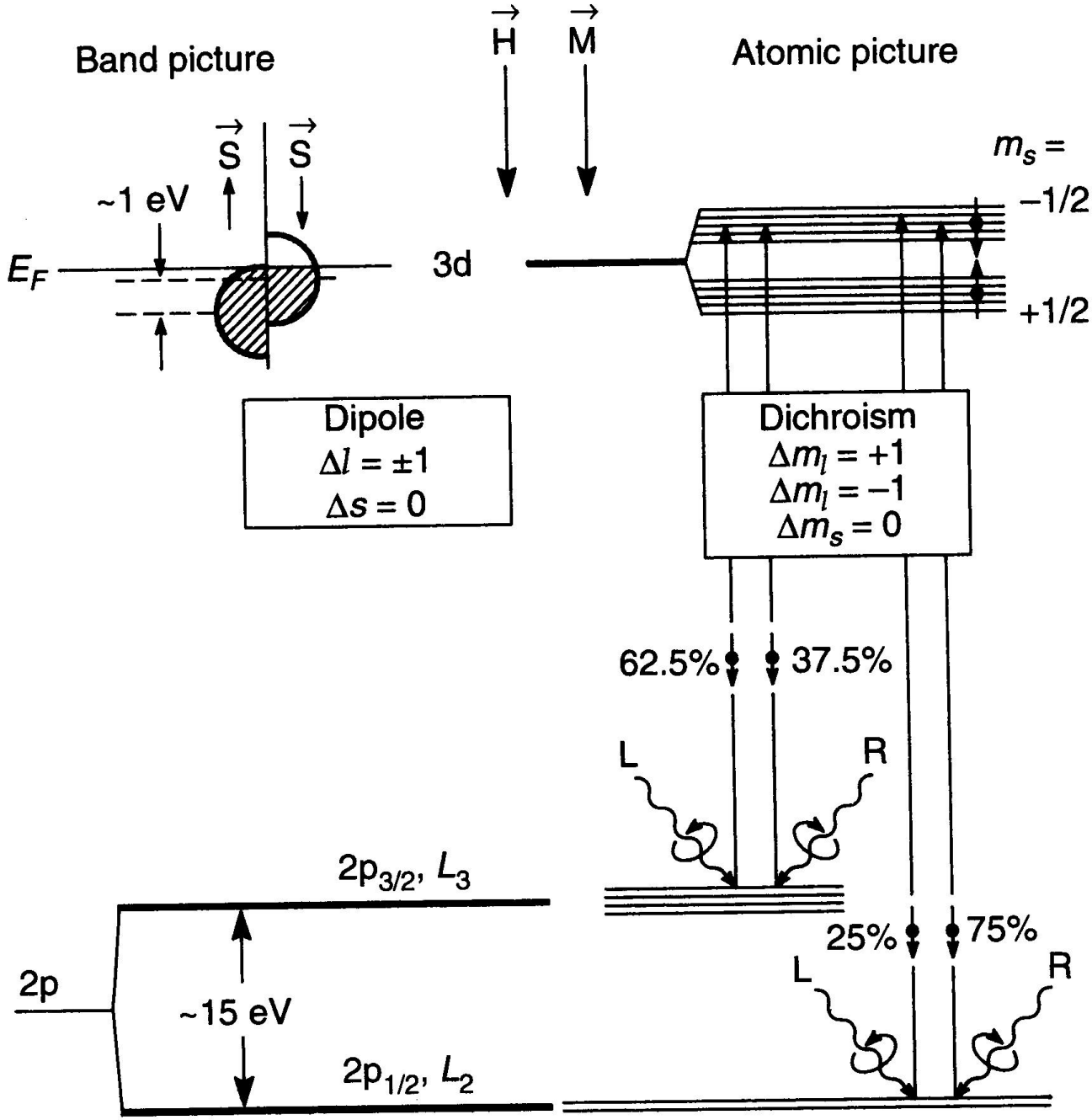


Dipole selection rules:

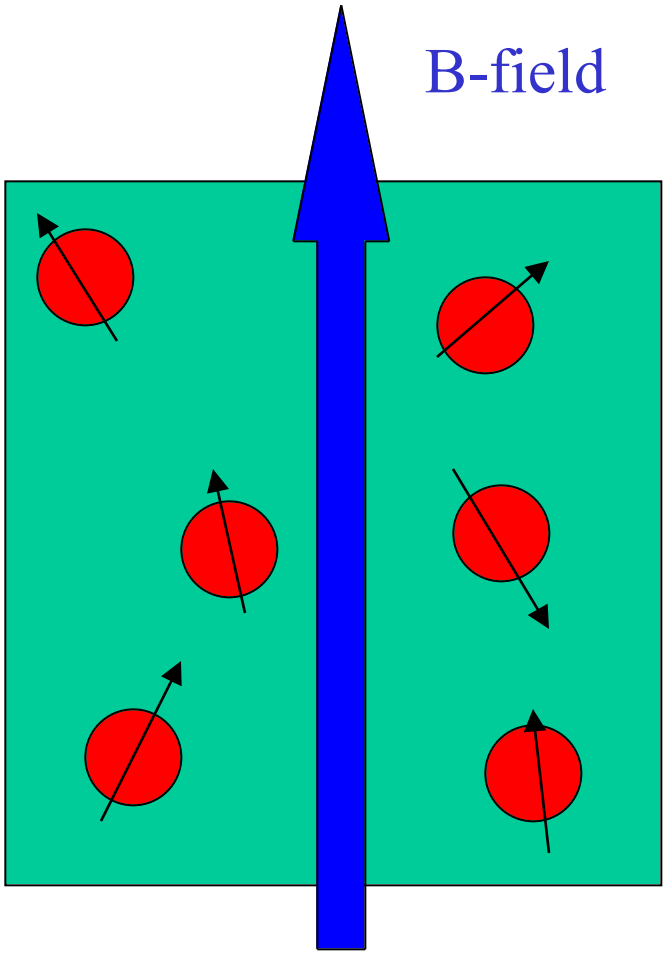
$\Delta l = -1, +1$

$\Delta m_l = 0, -1, +1$

$\Delta m_s = 0$


Band picture
Atomic picture
$\vec{H}$
$\vec{M}$
$\vec{S}$
$\vec{S}$
~1 eV
E_F
3d
$m_s =$
−1/2
+1/2
Dipole
$\Delta l = \pm 1$
$\Delta s = 0$
Dichroism
$\Delta m_l = +1$
$\Delta m_l = -1$
$\Delta m_s = 0$
62.5%
37.5%
L
R
$2p_{3/2}$, L_3
2p
~15 eV
$2p_{1/2}$, L_2
25%
75%
L
R

Magnetization of a paramagnetic system



$$M = \frac{N}{V} \cdot g_J \cdot \mu_B \cdot J \cdot B(x, J)$$

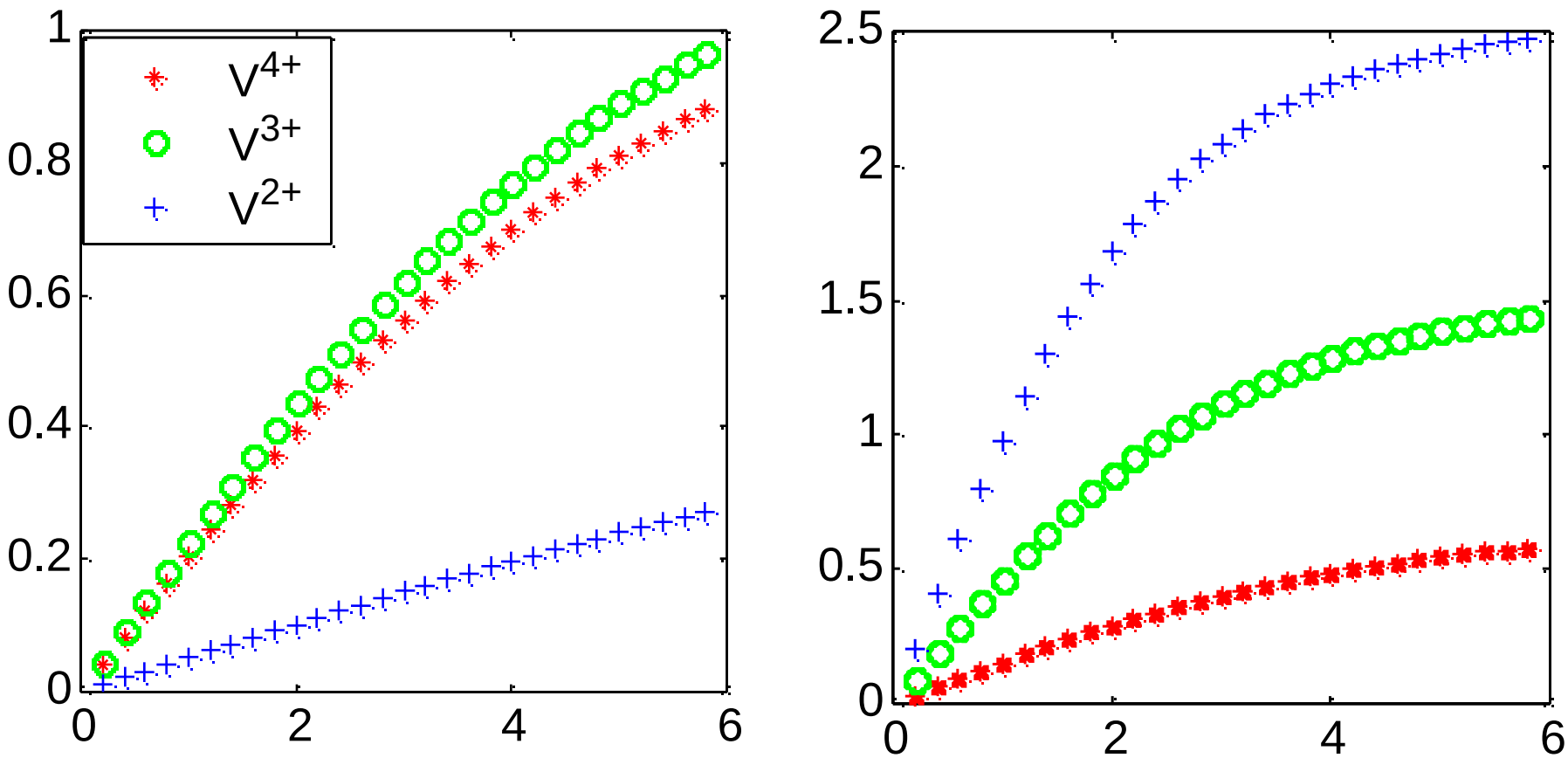
$$B(x, J) = \frac{(2J+1)}{2J} \coth\left(\frac{(2J+1)}{2J} x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J} x\right)$$

$$x = \frac{J g_J \mu_B H}{k_B T}$$

J calculated with Hund's rules

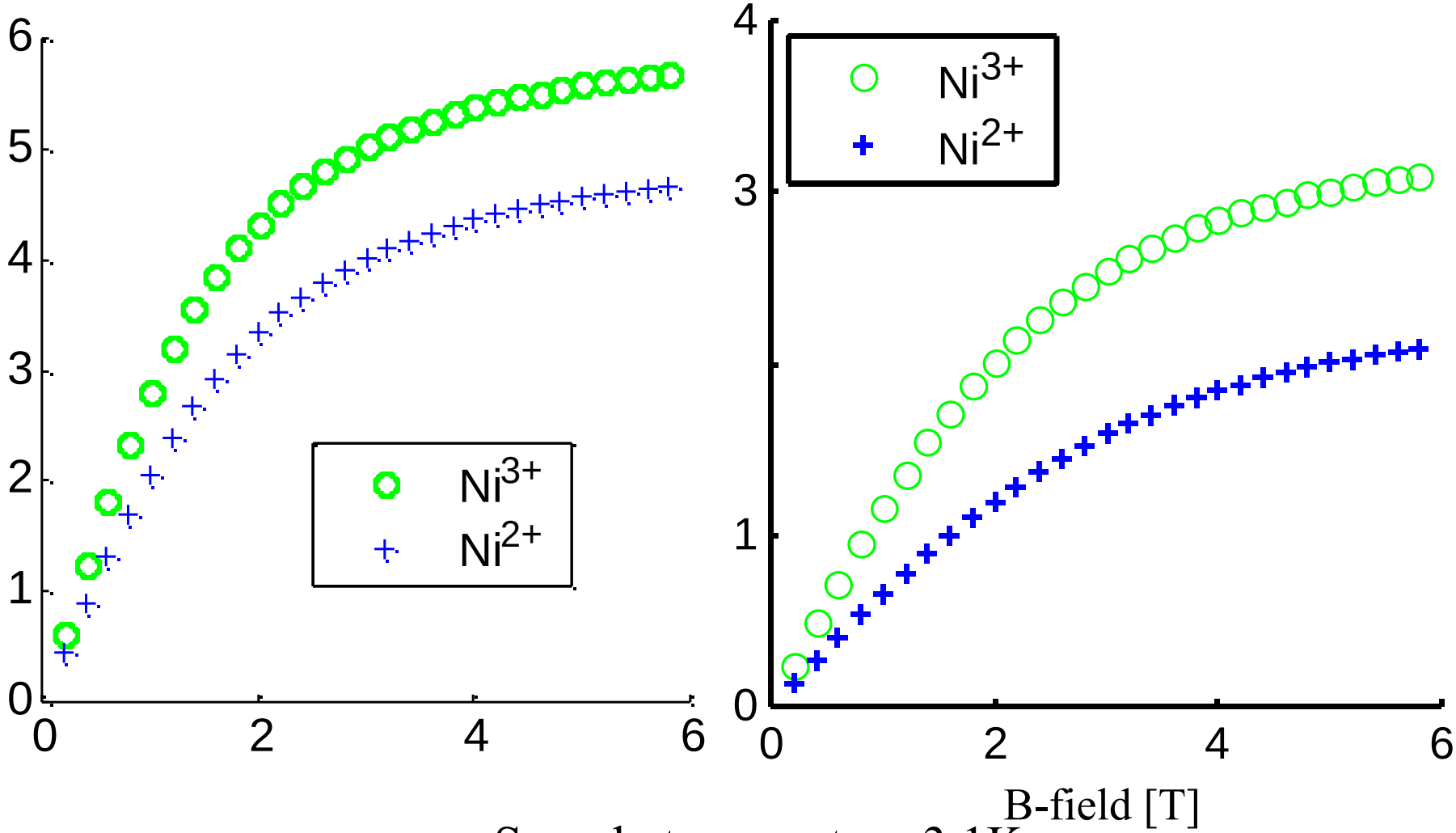
crystal field can lead to (full or partly) "quenching" of orbital momentum

Magnetization without and with a partly quenched orbital momentum

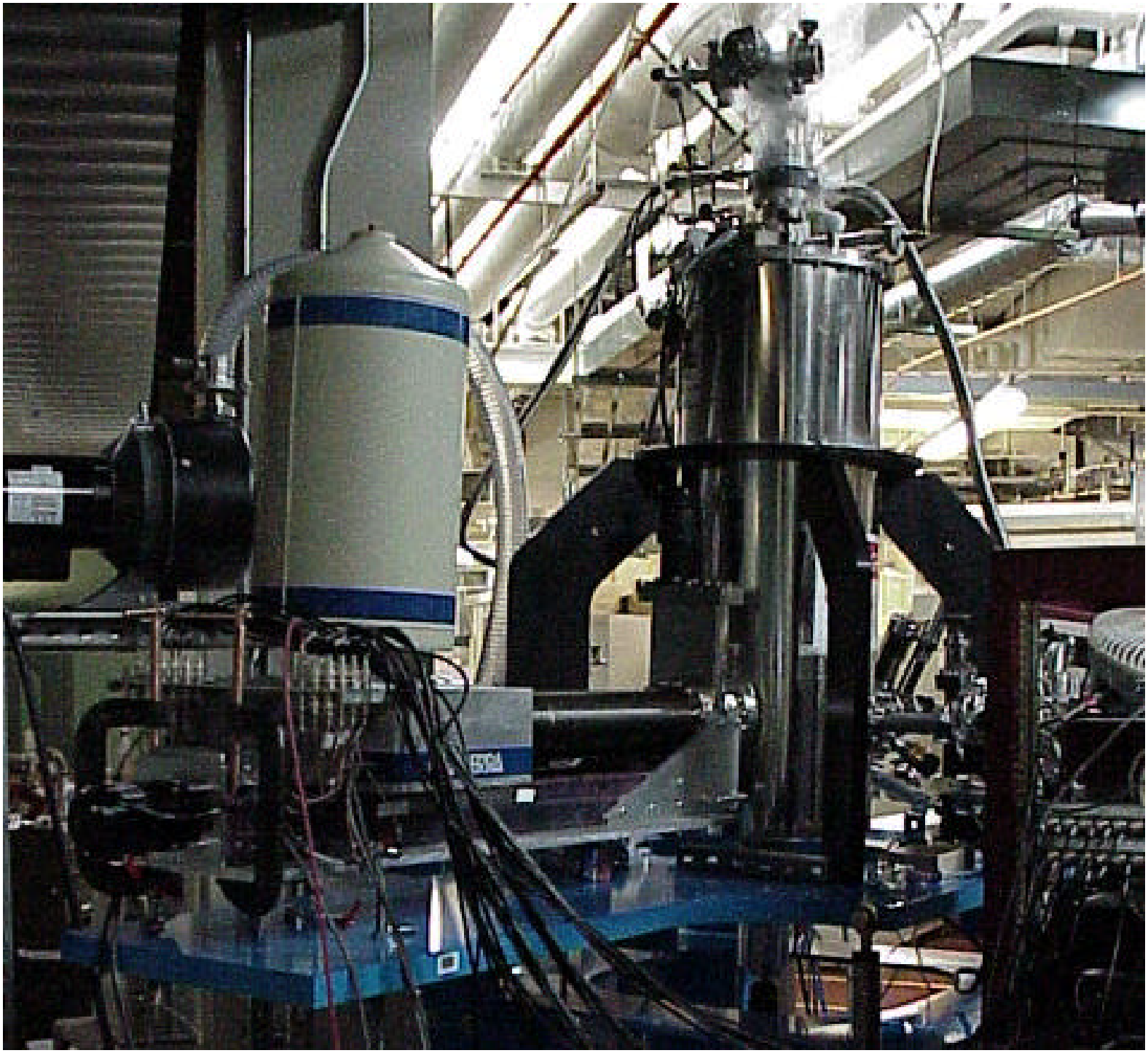


Sample temperature 2.6K

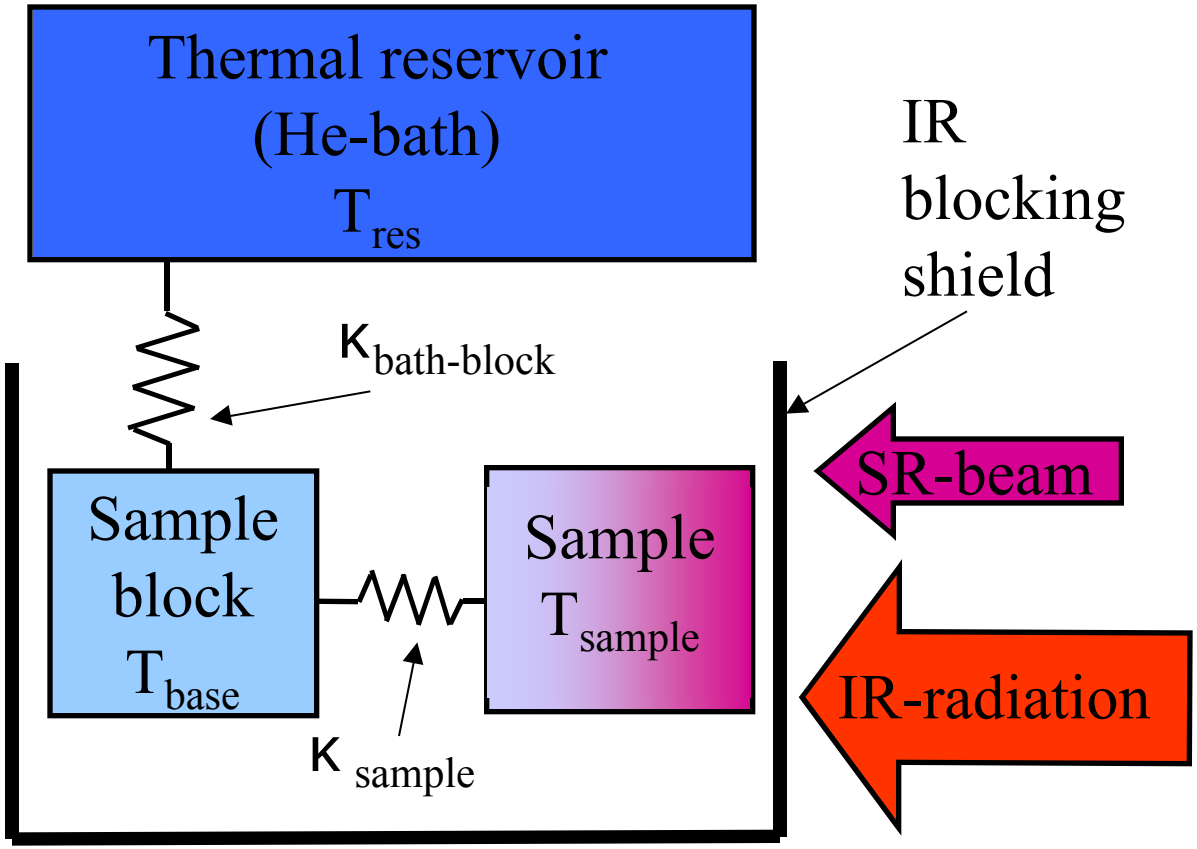
Magnetization without and with a partly quenched orbital momentum



Sample temperature 3.1K



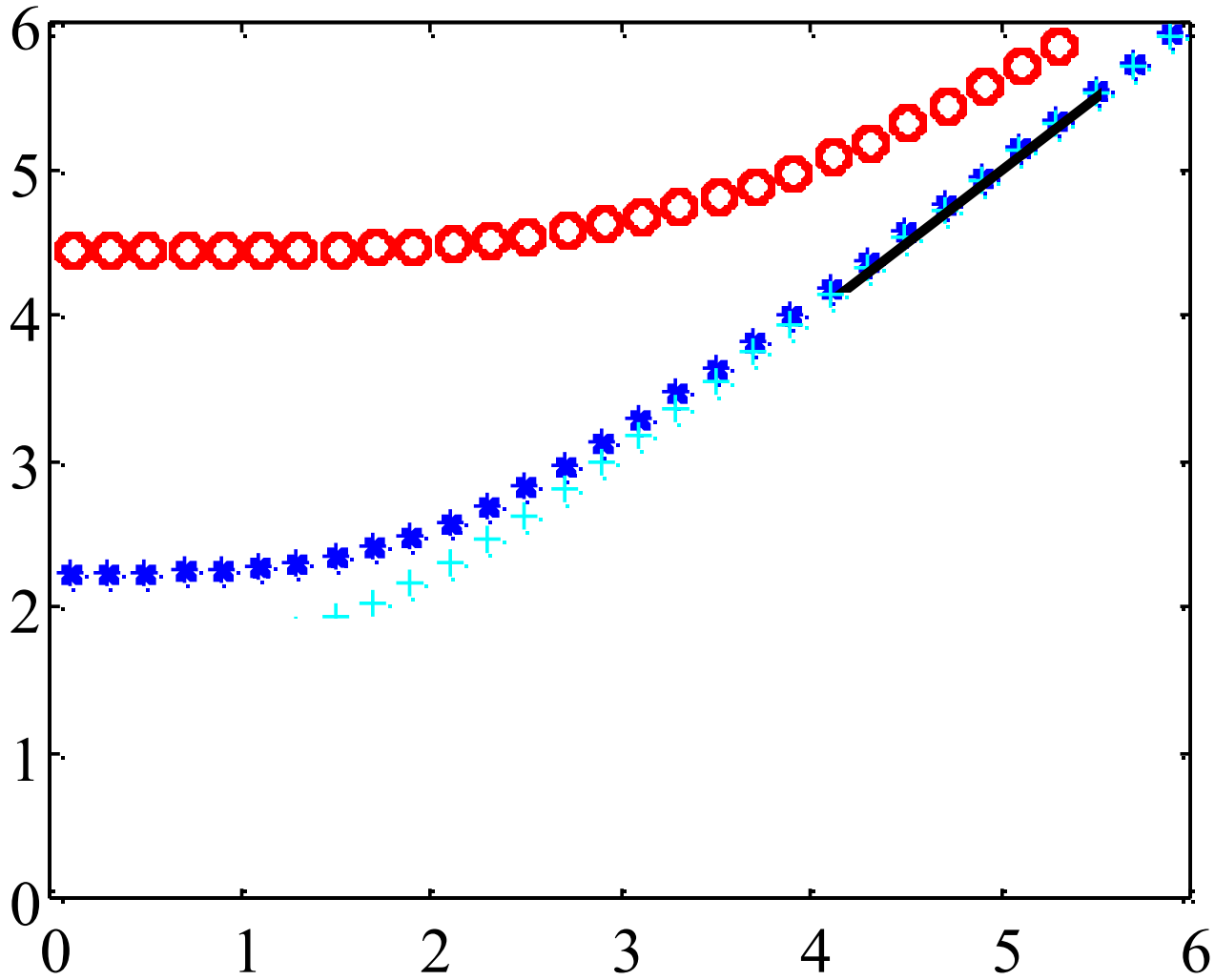
What is the sample temperature?



Heat flow equation: $$\dot{Q} = \frac{A}{L}\int_{T_{base}}^{T_{sample}} \kappa(T)\,dT$$

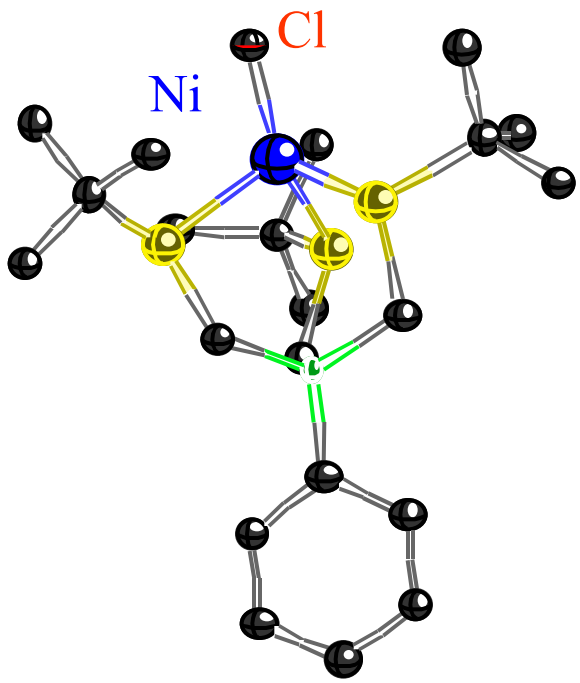
Sample temperature

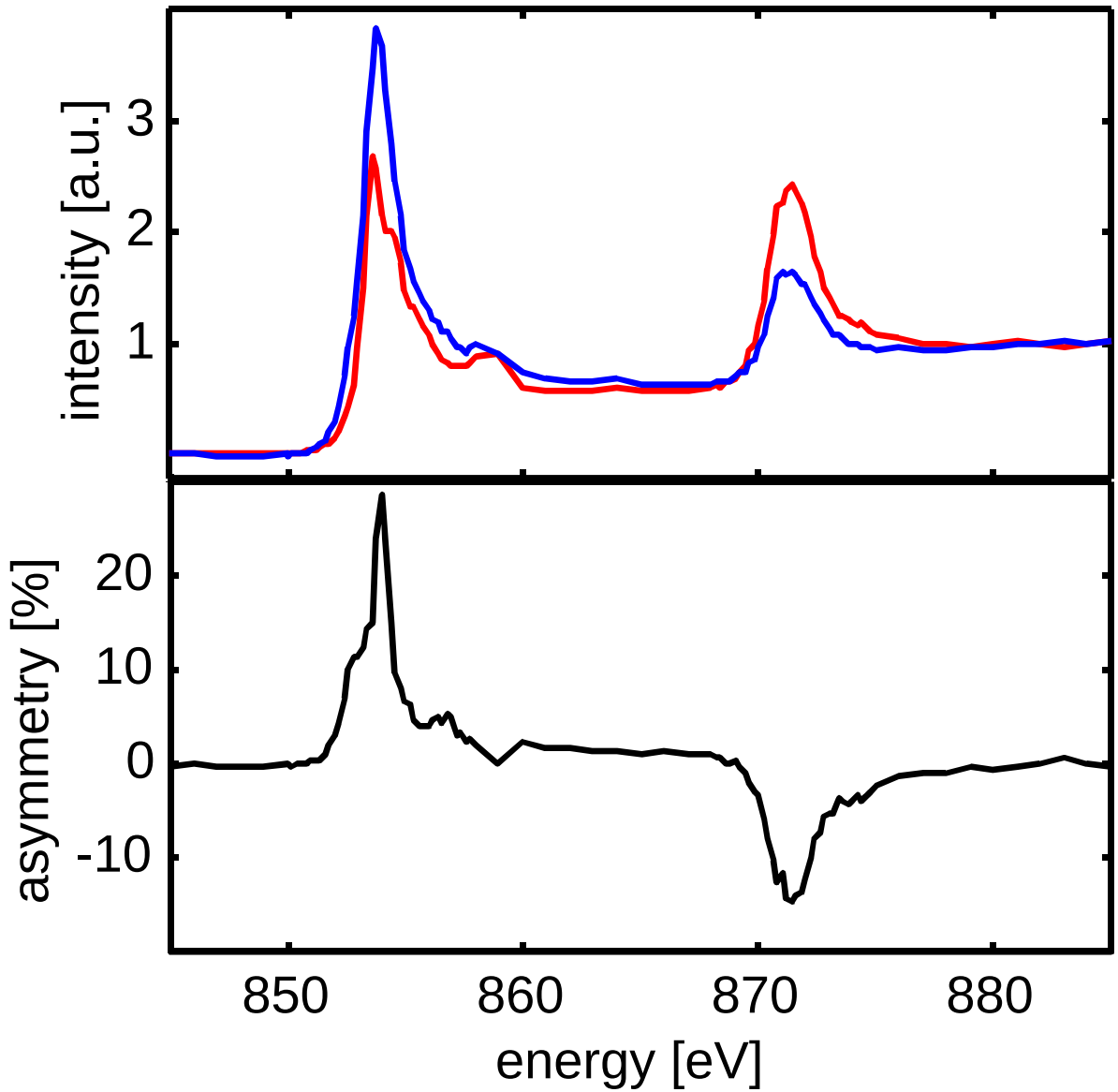
for a certain heat load and thermal conductivity κ(T)



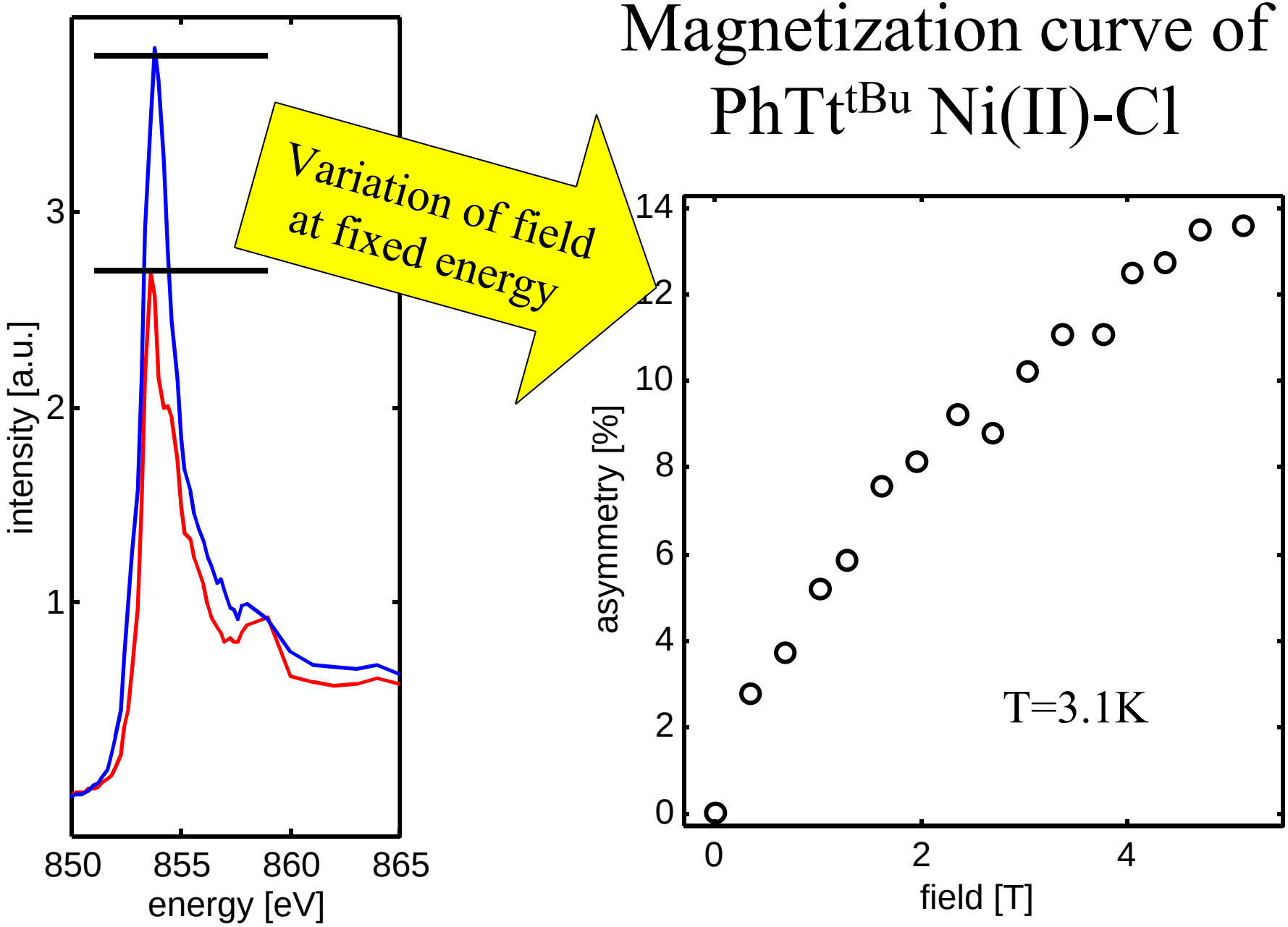
XMCD on PhTt^{tBu} Ni(II)-Cl

B-field =5.1T
Temperature=3.1K

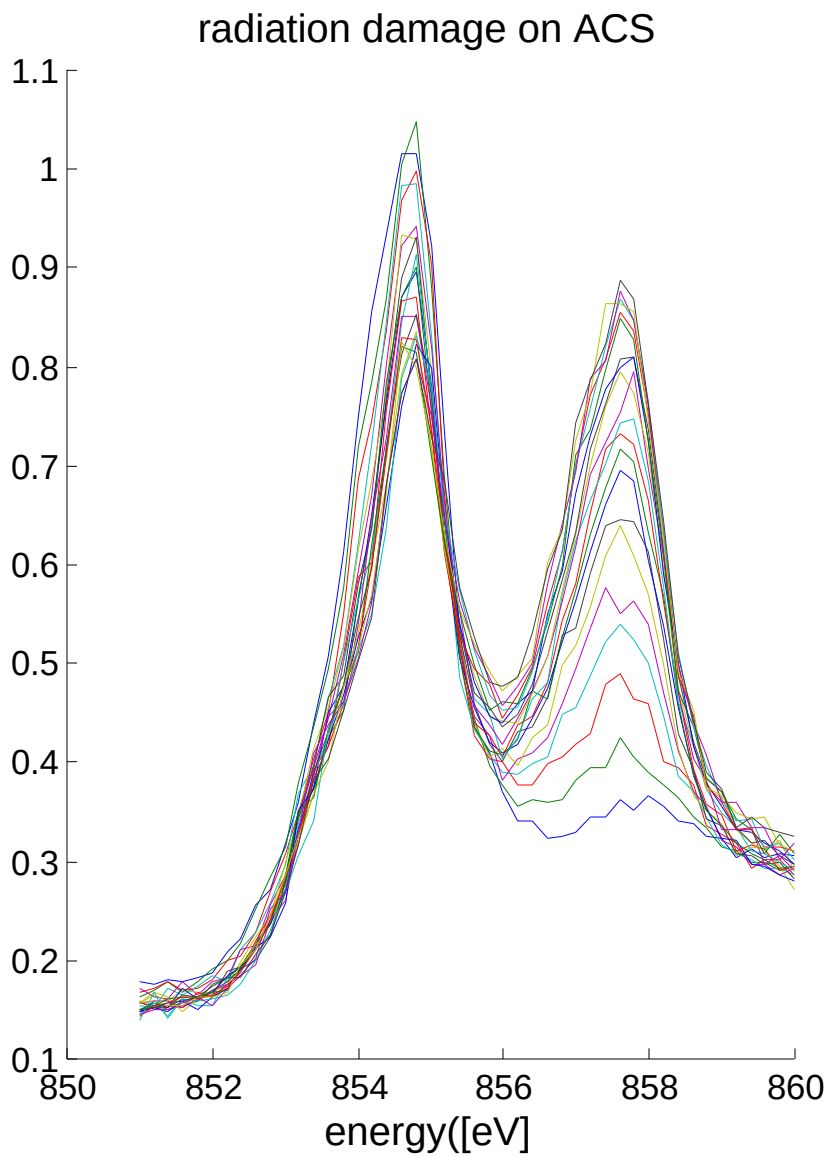


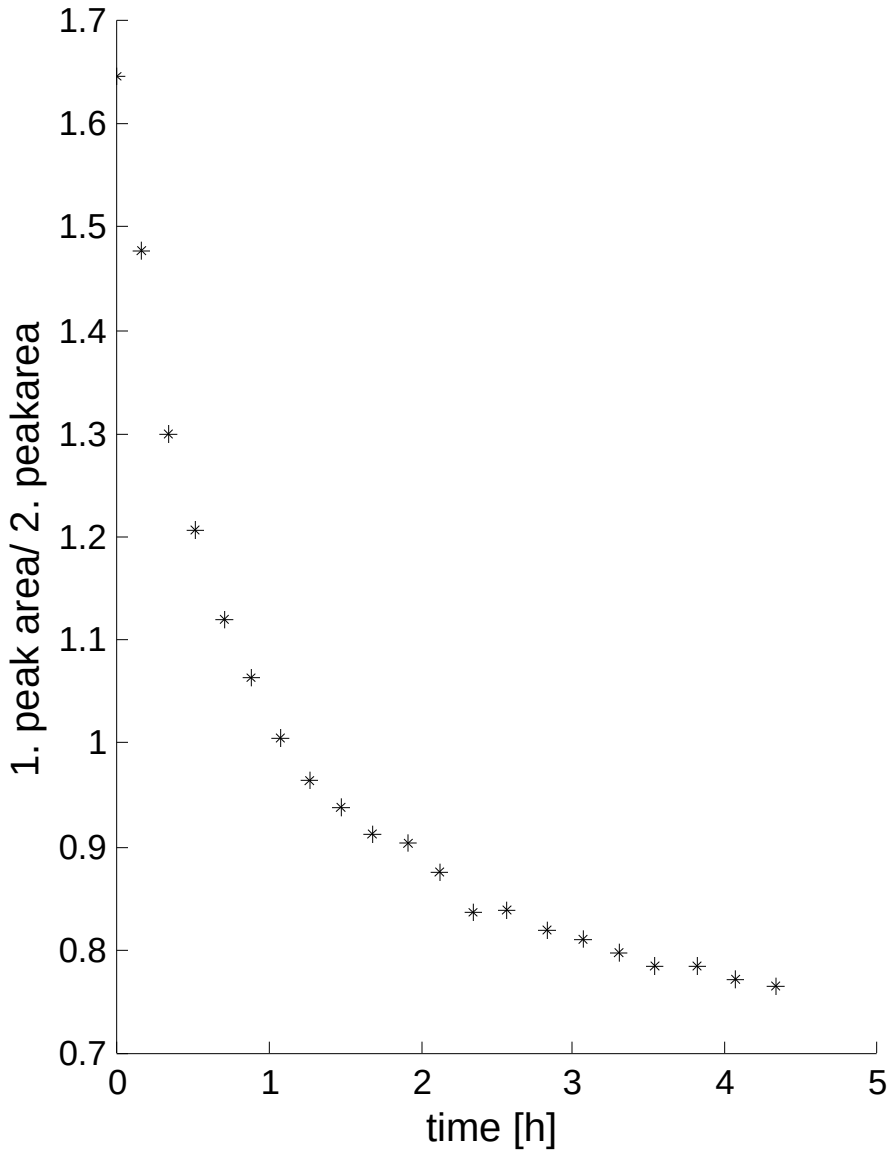


Magnetization curve of PhTt^{tBu} Ni(II)-Cl

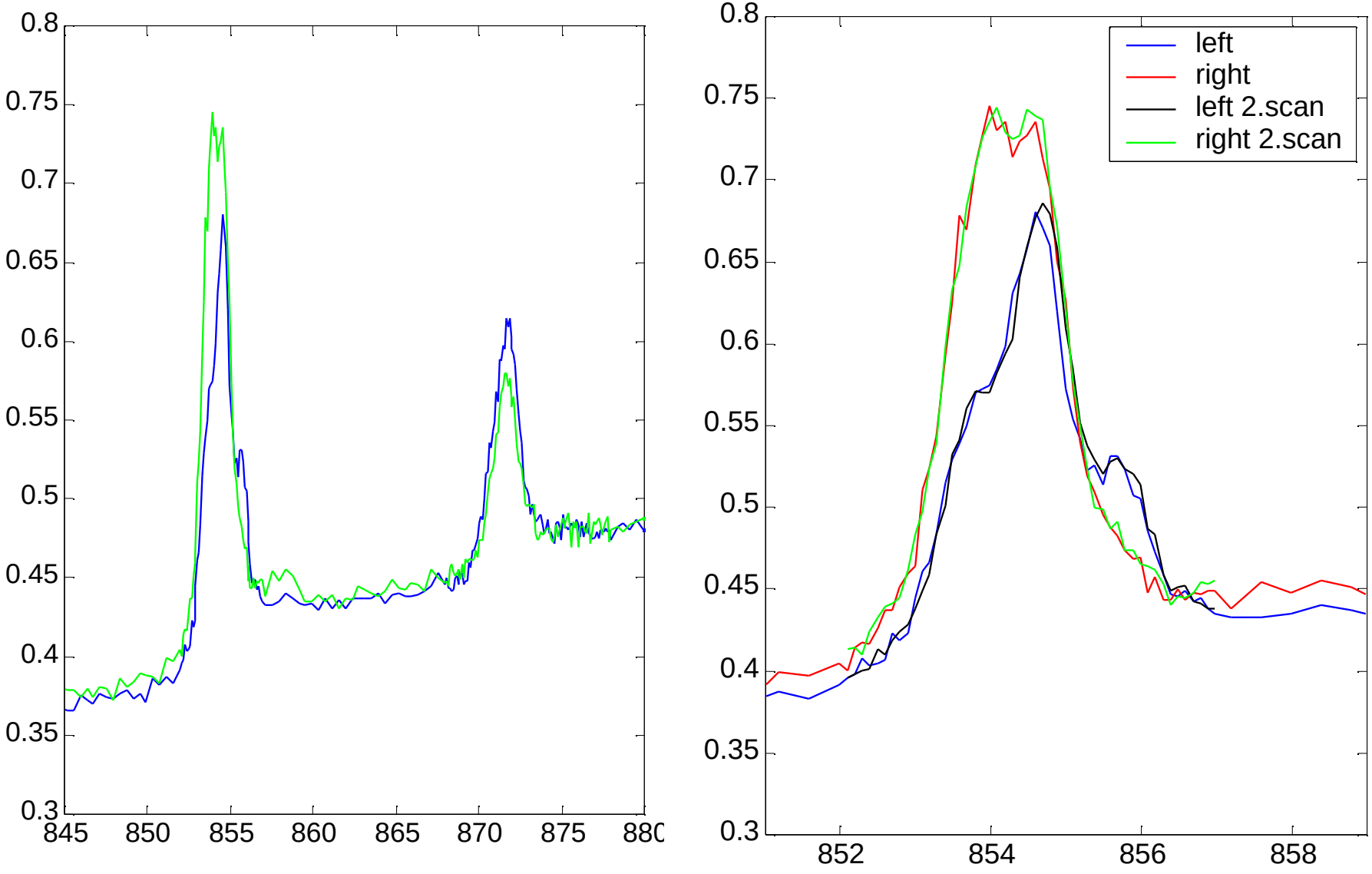


Radiation damage?!

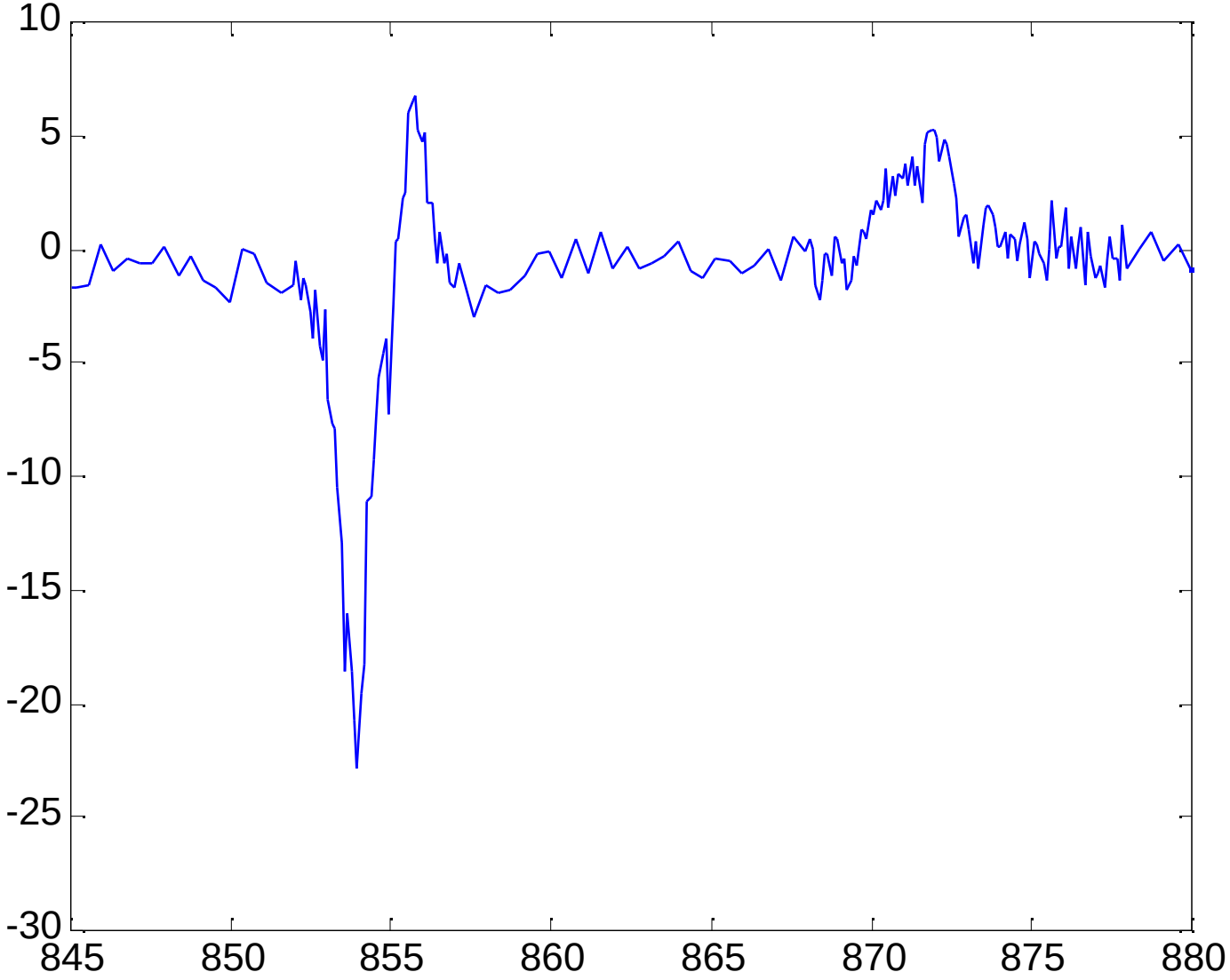


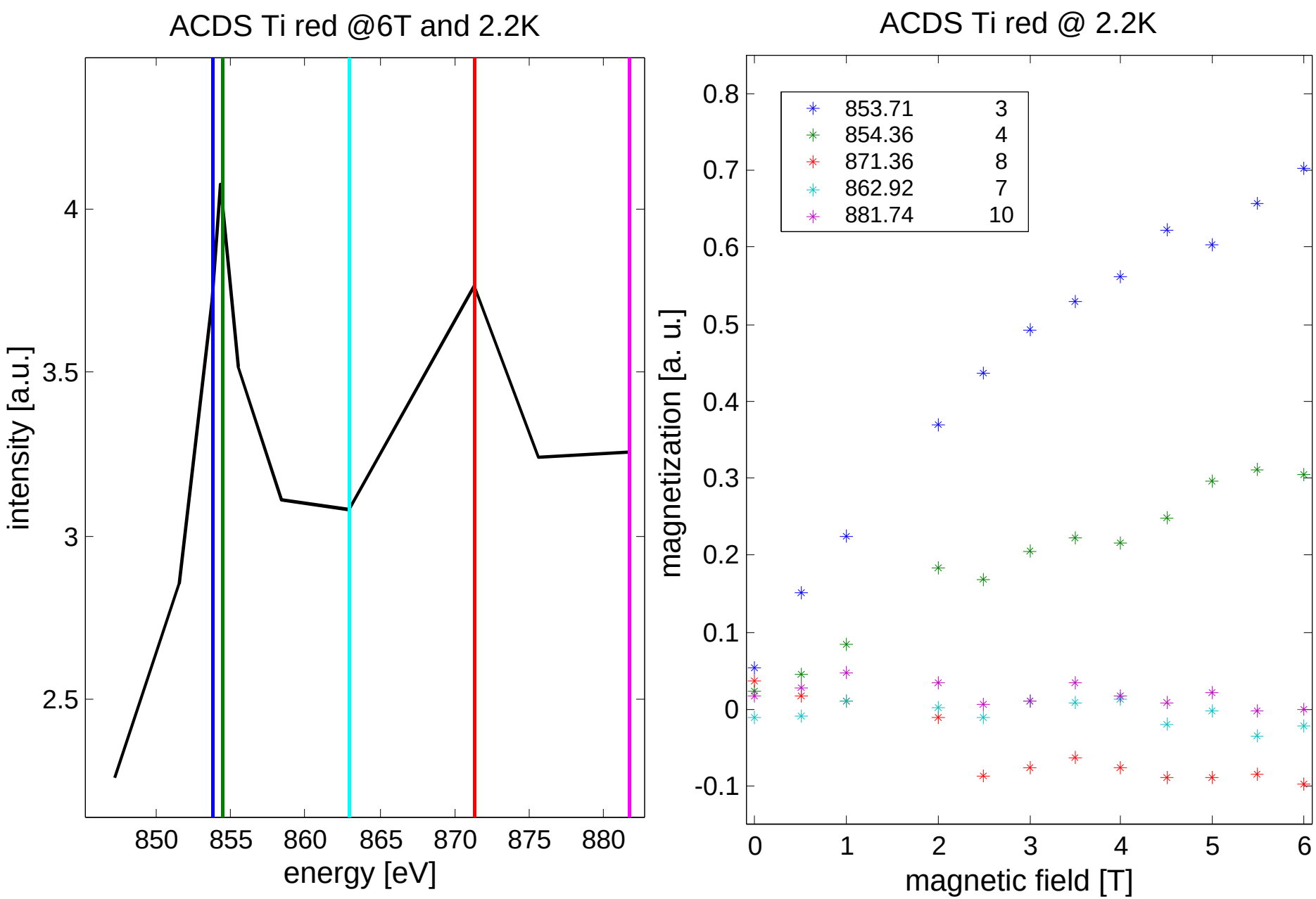


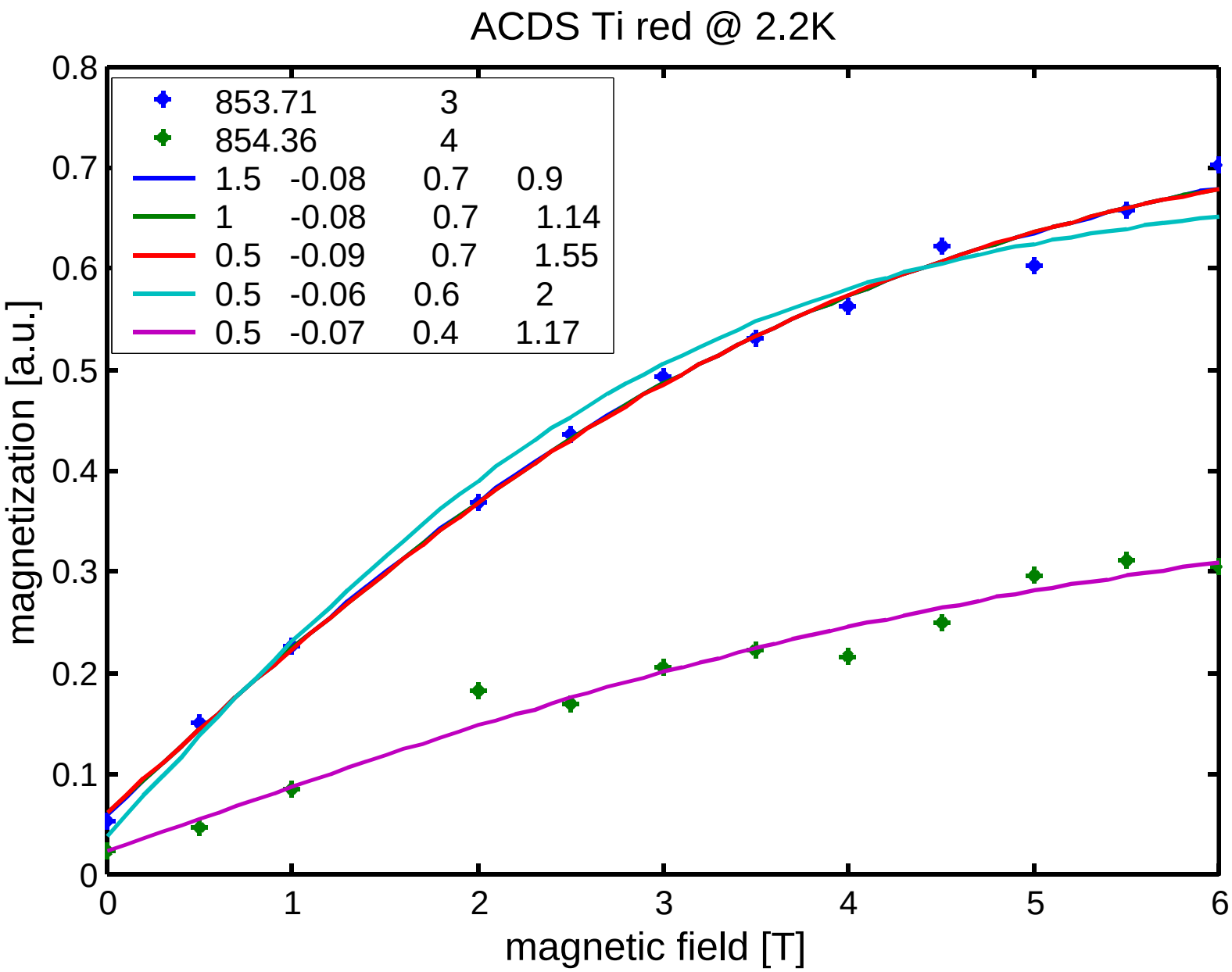
ACS Ti reduced at 6T and 2.2K (Ni-edge)

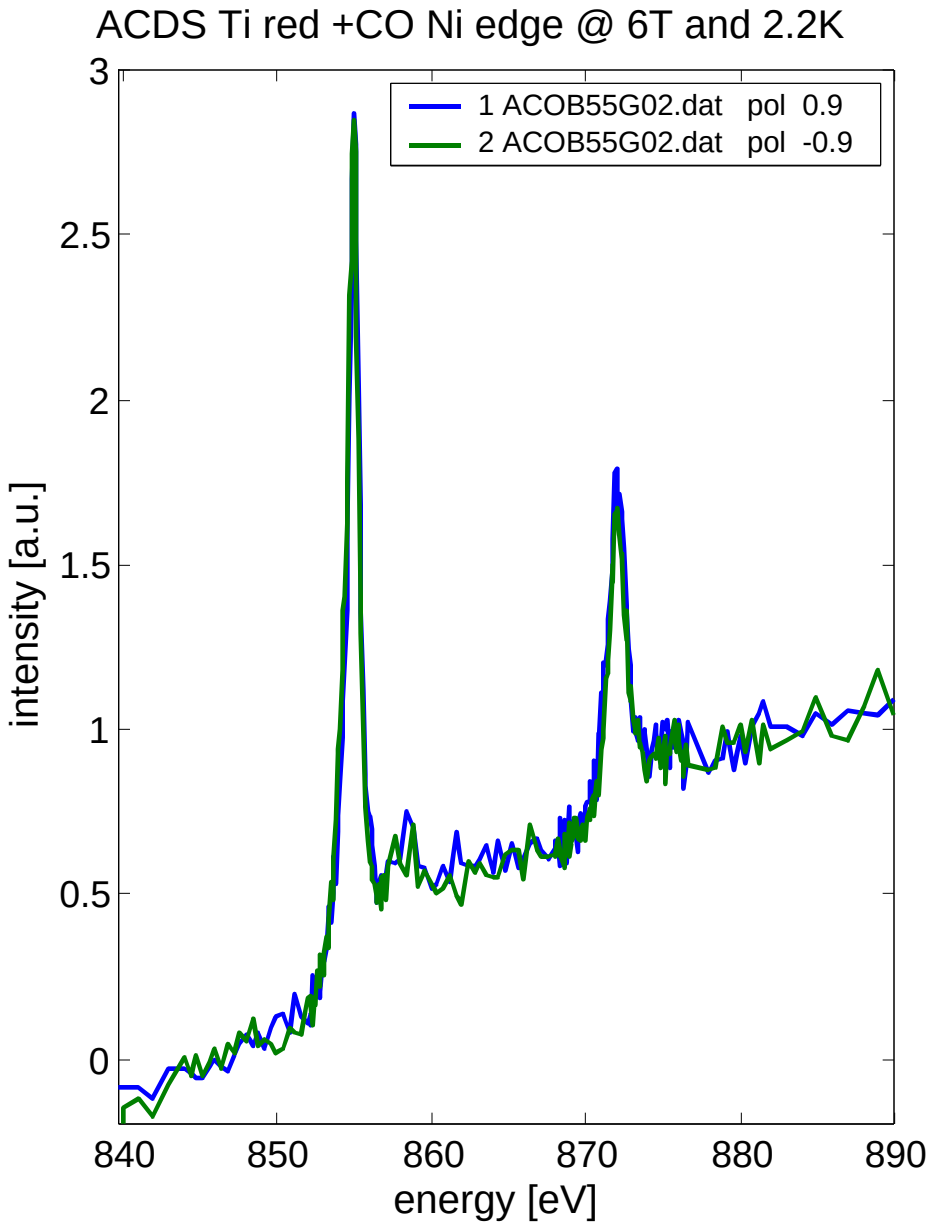


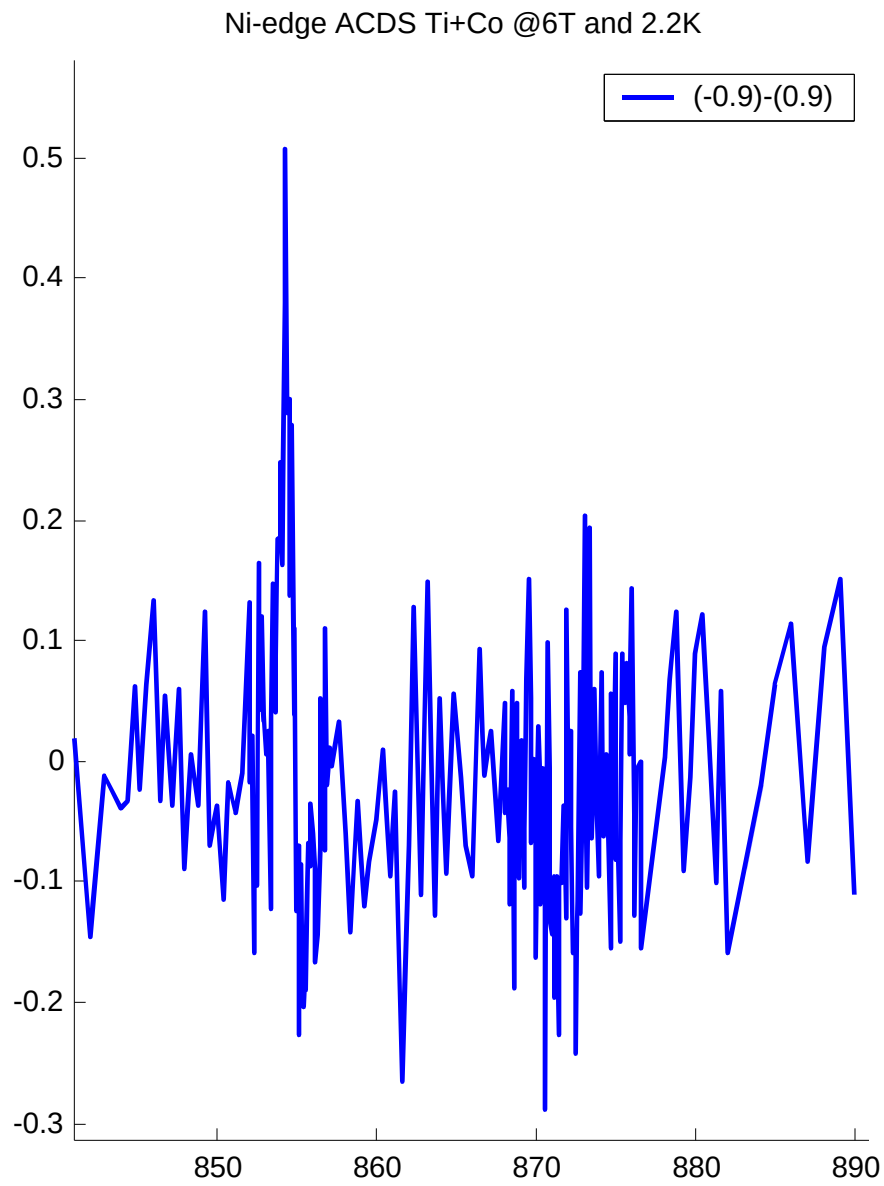
ACS Ti reduced at 6T and 2.2K, (Ni-edge)




ACDS Ti red @6T and 2.2K
intensity [a.u.]
energy [eV]
4
3.5
3
2.5
850
855
860
865
870
875
880
ACDS Ti red @ 2.2K
magnetization [a. u.]
magnetic field [T]
853.71 3
854.36 4
871.36 8
862.92 7
881.74 10
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
1
2
3
4
5
6


ACDS Ti red @ 2.2K
853.71 3
854.36 4
1.5 -0.08 0.7 0.9
1 -0.08 0.7 1.14
0.5 -0.09 0.7 1.55
0.5 -0.06 0.6 2
0.5 -0.07 0.4 1.17
magnetization [a.u.]
magnetic field [T]
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
1
2
3
4
5
6


ACDS Ti red +CO Ni edge @ 6T and 2.2K
1 ACOB55G02.dat pol 0.9
2 ACOB55G02.dat pol -0.9
intensity [a.u.]
energy [eV]
3
2.5
2
1.5
1
0.5
0
840
850
860
870
880
890


Ni-edge ACDS Ti+Co @6T and 2.2K
(-0.9)-(0.9)
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
850
860
870
880
890

Summary

XMCD on paramagnetic 3d transition metals require:

B-fields ≥ 4T and temperatures ≤ 4K

Biological samples have limited thermal conductivity

Heat shielding necessary to obtain low sample temperatures

Ni-Azurin shows XMCD signal on the Ni site