

## X-ray emission calculations

In this section we discuss the X-ray emission spectra. X-ray emission spectra can be measured with any technique that excites a core electron. This includes X-rays, electrons, protons and nuclear decay. Popular X-ray emission techniques are Laboratory X-ray Fluorescence, Energy Dispersive X-ray emission (EDX) in electron microscopes, Proton induced X-ray Emission (PIXE), synchrotron non-resonant X-ray emission, K capture induced X-ray emission and Resonant Inelastic X-ray Scattering (RIXS). The description of RIXS will be rather different for soft x-ray L edges versus hard x-ray K edges and both will be described. The description of K edge RIXS also needs an accurate account of the pre-edge and edge in K edge XAS.

The main difference between XAS and XES is that in XAS one starts from the ground state, while in XES one starts from a core hole excited state. Initially, we will assume that the core hole state has no memory of its excitation and describe non-resonant X-ray emission spectra. If one excites the core electron with an x-ray, the core electron is excited in a photoemission experiment. This implies that one has to use a charge transfer approach, because the core hole is screened. However it turns out that in some cases one obtains a reasonable spectrum if one just adds the core hole state to the ground state. For example a ground state  $3d^5$  configuration can be described with a  $1s^1 3d^5$  core hole state.

### 1s3p x-ray emission in the Crystal Field Multiplet model

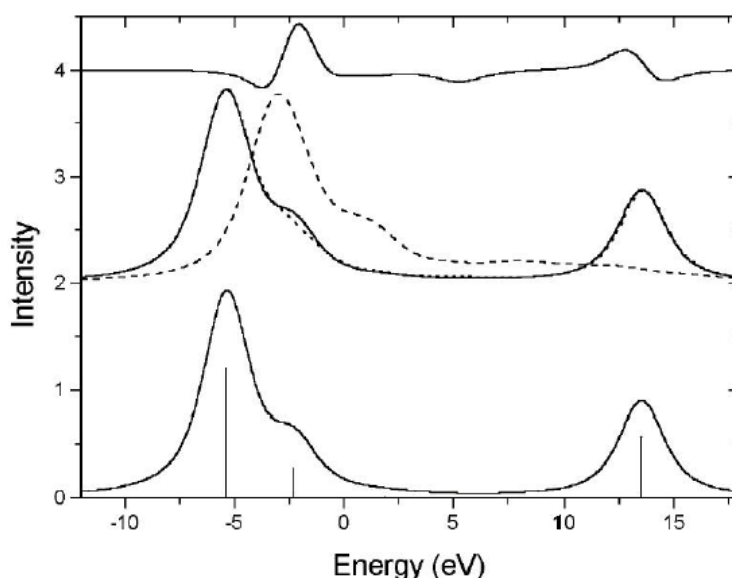
We will first discuss the 1s3p x-ray emission spectral shape, also known as K fluorescence. With divalent manganese as an example, we will step by step build up a scheme to interpret the experimental spectral shapes, using the multiplet models as described for x-ray absorption. The ground state of  $Mn^{II}$  has its five spin-up electrons filled. The five spin-down states are empty. We assume first that the core hole creation, for example by an above-resonance x-ray excitation, does not modify the valence electron situation. The intermediate state has a  $1s^1 3d^5$  configuration and after the 1s3p decay the final state is  $3p^5 3d^5$ .



The spectral shape consists of two structures, separated by the 3p3d exchange interaction. This assignment is essentially the original model as used by Tsutsumi. Starting from this model, we will step by step include the effects of the 3p and 3d spin-orbit coupling, the symmetry effects of the cubic crystal field. In section V.A. we extend the model to describe covalence effects as included with charge transfer and. we include the combined effects of off-resonance excitation and decay.

Assuming a  $Mn^{II}$  ion, the atomic ground state symmetry is  $^6S$ . In the  $1s^1 3d^5$  configuration the total symmetry can be found by multiplying the 1s electron with the  $^6S$  symmetry of the 3d electrons. This gives either a  $^5S$  state for anti-parallel alignment of the 1s and 3d electrons, or  $^7S$  for parallel alignment. The dipole selection rules imply that transitions are possible from  $^5S$  to  $^5P$  and from  $^7S$  to  $^7P$ , with the energy difference between  $^5P$  and  $^7P$  given by the 3p3d exchange interaction. Things are a bit more complex in reality because more than one  $^5P$  configuration can be made from a  $3p^5 3d^5$  configuration. Writing out all symmetry combinations one finds three  $^5P$  states and one  $^7P$  state.

The bottom of this figure shows the atomic multiplet spectrum for which the 3d and 3p spin-orbit couplings have been set to zero. The overall intensities of the states are 7:5 for the  $^7P$  versus the  $^5P$  states. The main peak is the  $^7P$  state. The shoulder and the satellite are the  $^5P$  states and the small peak at about -6482 eV is the third  $^5P$  state. The satellite can be related to the anti-parallel aligned 3p and 3d electrons while the shoulder and low intensity state relate to orderings of the 3d-electrons different from the ground state. In fact the three  $^5P$  states are linear combinations of the three LS-like atomic states that are mixed by the strong 3p3d as well as 3d3d multiplet effects.



The middle spectrum (dashed) shows the effects of the addition of a cubic crystal field of 2.0 eV. This is already a relatively large crystal field and all oxides and halide systems have smaller crystal fields. It can be seen that compared to the atomic spectrum (solid) most peaks shift a little bit. In particular the  $^5P$  states are modified while the  $^7P$  states do still look very much like the atomic result. After broadening the sticks with the experimental and lifetime broadening, little changes are visible. This implies that 1s3p x-ray emission spectra are insensitive to the crystal field effects, much less sensitive than for example 2p x-ray absorption. The positive aspect of this is that one can assume that the 1s3p x-ray emission spectra are virtually the same for all high-spin divalent manganese atoms. The dashed spectrum from which the peak position has shifted is the low-spin  $Mn^{2+}$  spectrum. Low-spin 3d5 systems have a  $2T_2$  ground state, hence a very small exchange interaction.

For more details see [peng94a.pdf](#) and [degroot01cr.pdf](#)

We start with the Kbeta calculation of NiO using as a ground state  $1s^1 3d^8$ . The calculation involves the transition to  $3p^5 3d^8$ . This calculation is equivalent to an XAS calculation (with a few new features, see below).

The file ni2kb.rcn reads:

```
22 -9      2   10   1.0      5.E-06      1.E-09-2      130      1.0   0.65 99.0 0.50 0.0   0.70
      28      Ni2+ 1S01 3D08              1S01 3D08
      28      Ni2+ 3P05 3D08              3P05 3D08
      -1
```

Running this file yields ni2kb.rcf, which is modified to ni2kb.rcg:

```
      10      1      0      14      4      4      1      1 SHELL00300000 SPIN00000000 INTER8
      0                                80998080                                8065.47800      0000000
      1      3 1 13 1 10              00      9 00000000 0 8065.4790 .00      1
S 1  P 6  D 8
S 2  P 5  D 8
Ni2+ 1S01 3D08      5      .0000      13.9531      8.7121      .0002      .0804HR99999999
Ni2+ 3P05 3D08      8 8275.0040      13.3171      8.3201      1.3972      .0922HR99999999
      14.3333      17.7164      10.7984
Ni2+ 1S01 3D08      Ni2+ 3P05 3D08      .01256( 3P//R1// 1S)      .955HR 14 -99
      -99999999.
      -1
```

There are three shells involved in the transition: the 1s, 3p and 3d shell. This is different from 2p XAS where there are only two shells. The TTRCN program gives the 3d-shell as the third shell. One can reorder the shells (sometimes this is necessary, more later) or keep them as they are. If the 3d-shell is kept at the third position, one should add the crystal field also in the third position, i.e. use SHELL00300000. The 'excitation' energy is very large, 8275 eV, so one could better set this value to zero. Note that it is negative in the ni2kb.rcf file because the ground state energy is set to zero and has a lower energy as the transition involves the creation of an x-ray. ni2kb.rac is completely identical to any XAS rac-file.

Running rcg2 ni2kb and rac2 ni2kb gives the result. There is an important new feature, which involves the role of the 1s core hole. The 1s core hole has an exchange interaction with the 3d<sup>8</sup> shell. The value of the exchange interaction is small, its Slater integral is given as 0.08 eV in the ni2kb.rcg file above. But still this small value will split the lowest lying state into two parts, a 1s spin-up part and a 1s spin-down part. Both a 1s spin-down electron and a 1s spin-up electron will be excited, which implies that the 1s3p XES spectrum is the addition of these two states.

Note that the spin of the 1s core electron is maintained during its excitation step. This implies that a 1s spin-up electron is excited to a spin-up empty state. If one would be able to detect specifically the 1s3p decay of the spin-up electron, one can derive the spin-polarised density of empty states. More later.

The ni2kb.plo file reads:

```
postscript ni2kb.ps
landscape
rows_per_page 2
columns_per_page 2
horizontal_order
energy_range 8260 8300
lorentzian 1.0 1e20
gaussian 0.50
old_racah ni2kb.ora
```

```

frame_title SPIN-UP
spectrum energy -2.56114
frame_title SPIN-DOWN
spectrum
frame_title TOTAL
addlines energy -2.56114
spectrum
frame_title DIFFERENCE
addlines energy -2.56114 scale -1
spectrum
end

```

A new command is the line `spectrum energy -2.56114`. This line searches the energy -2.56114 in the ni2kb.ora file and plots its spectrum. The initial state energies as given in ni2kb.ora read:

```

EIGVAL -1.601465 -0.895388 -0.856988  0.906233  0.922287  0.960687
EIGVAL -2.599537 -1.601465 -1.601465 -1.563065 -0.895388 -0.895388 -
EIGVAL -2.561137 -1.601465 -1.563065 -0.895388  0.510307  0.922287

```

The initial state at -2.599537 eV is the spin-down excited electron, leaving behind a spin-down 1s core hole that interacts with the two spin-down 3d-holes. The state at -2.561137 eV is the spin-up excited electron. If one would like to plot its spectrum, one has to add the command energy -2.56114. Note that the value of the energy has been rounded in the plo-file. The reason is that the dipole transition matrices in the ni2kb.ora file are rounded after 5 decimals, for example:

```

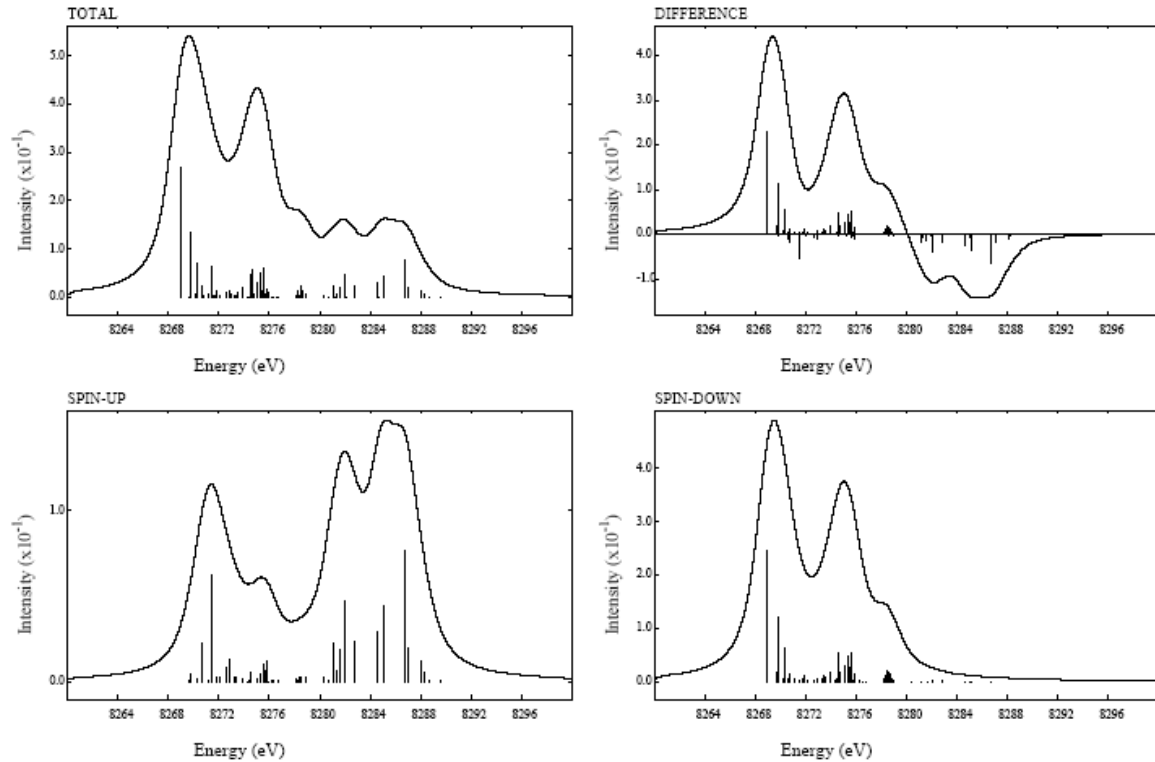
TRANSFORMED MATRIX for TRIAD 31 (^S0+ 1- S1- 0) (7*45) DIM :2:3:4 ACTOR
LEFT

      ---- MATRIX ----      PRINTTRANS

BRA/KET :   8266.38   8267.11   8267.20   8267.69   8268.08   8268.54   8268.92
8269.48   8270.05   8270.33   8270.84   8271.29
-----
-----
-2.56114:  0.000002  0.001663  0.017063  0.000084  0.041320  0.001037  0.171345
0.010649  0.032435  0.048425  0.007387  0.006736

```

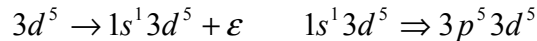
One should give exactly this energy value of **-2.56114**.



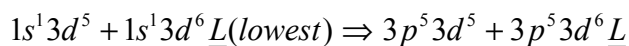
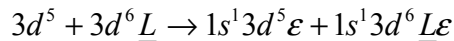
The figure above gives the result of the ni2kb calculation of the 1s3p transition in Ni2+. The top-left gives the total 1s3p XES spectral shape, given with positive energies. The two spectra at the bottom give the spin-up and spin-down spectra and the spectrum at the top-right gives the difference between spin-up and spin-down. Note that the peaks between 8280 eV and 8290 eV are pure spin-up. This implies that if one detects the x-rays at this energy, say with a 10 eV bandwidth fluorescence detector, one can measure the spin-up density of empty states. The complete series 1s3p and 1s2p spin-polarised calculations of 3d-systems have been published in [wang97a.pdf](#).

### 1s3p x-ray emission in the Charge Transfer Multiplet model

In the previous sections we used the approximation that one can calculate the 1s3p x-ray emission spectral shape from a model using the following two transitions, where the excitation step is not used explicitly in the results:



In case Mn<sup>II</sup> this model gives a good account of the spectral shape. If one looks at other systems though, less good agreement is found. The main reason for this is that in the 1s excitation step major screening or charge transfer effects occur. Essentially one is removing a core electron implying a core charge that has increased by one. This pulls down the valence 3d electrons by the core hole potential. Because the 3d electrons are pulled down in a larger energy than the 4s and 4p electrons, the intermediate state configurations will be different from the ground state configurations. Essentially one has to subtract the core hole potential  $Q$  from the ground state energy positions as used in the charge transfer model. Below the transitions are given for two configurations:



The lowest two intermediate states are selected and the 1s3p x-ray emission spectrum is calculated for these states, which implies that one assumed the intermediate states to relax to their lowest configuration(s). Two states are used, because the lowest state is split by the 1s3d exchange interaction. This 'relaxed' model has been used in the calculations of the 1s3p x-ray emission spectra of divalent nickel compounds<sup>36</sup>. Using an intermediate state configuration  $1s^1 3d^8 + 1s^1 3d^9 \underline{L} + 1s^1 3d^{10} \underline{L}\underline{L}'$ . The charge transfer values for NiBr<sub>2</sub> and NiF<sub>2</sub> are respectively 4.3 and 0.3 eV and with a core hole potential of 7.5 eV and a correlation energy U of 7.3 eV this gives that the lowest energy is the  $1s^1 3d^9 \underline{L}$  configuration. For NiF<sub>2</sub> the  $1s^1 3d^8$  configuration has an energy of 3.2 eV and the  $1s^1 3d^{10} \underline{L}\underline{L}'$  configuration of 4.1 eV. In case of NiBr<sub>2</sub> these values are respectively 7.2 eV and 0.1 eV<sup>36</sup>.

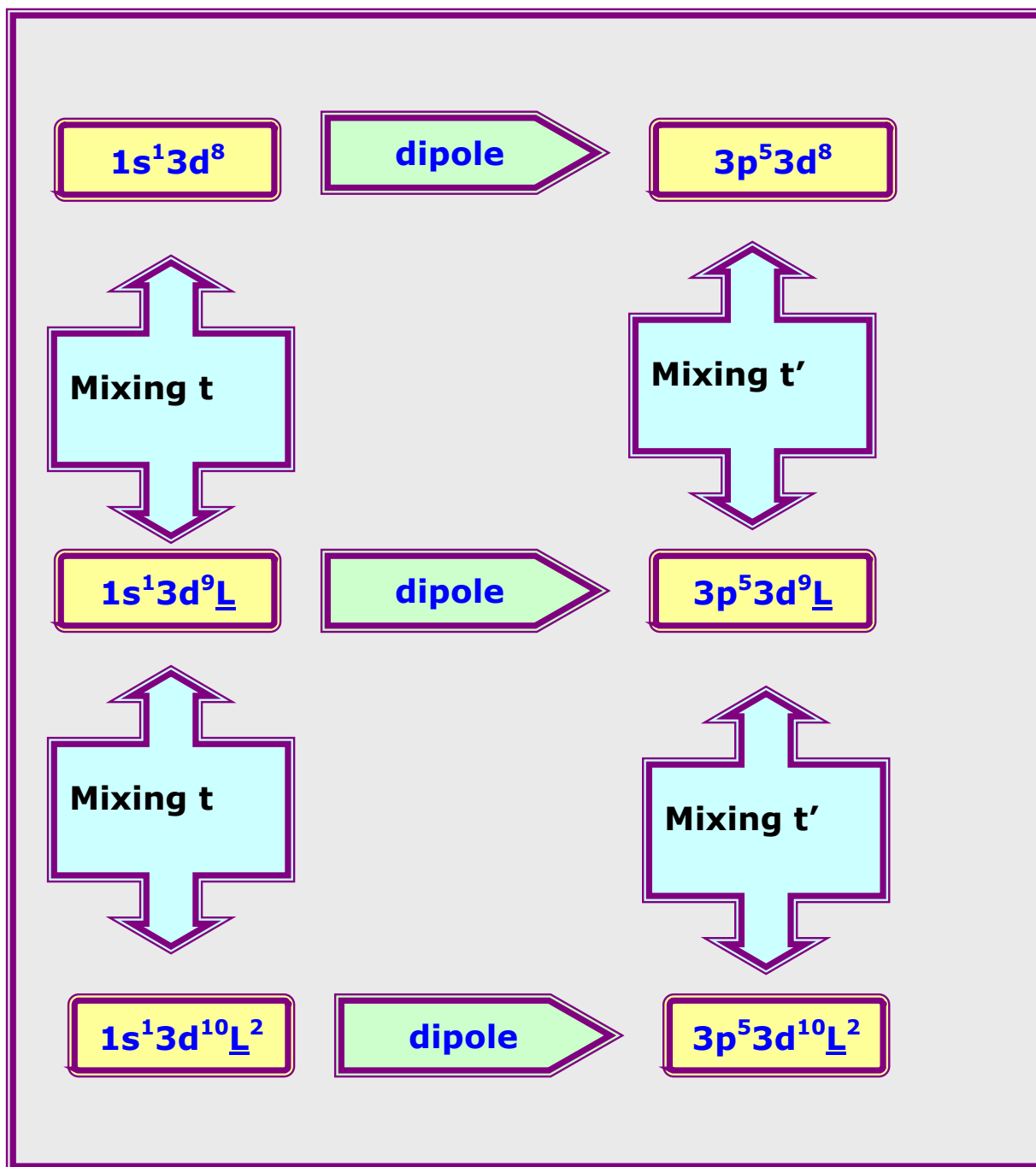
The 'relaxed' charge transfer model used is not necessarily the correct model. Another approach is to assume that the intermediate states do not relax at all. In this section we will follow this approximation. The model is the same as in the previous section:

$$3d^5 + 3d^6 \underline{L} \rightarrow 1s^1 3d^5 \epsilon + 1s^1 3d^6 \underline{L}\epsilon$$

$$1s^1 3d^5 + 1s^1 3d^6 \underline{L} (XPS \text{ spectrum}) \Rightarrow 3p^5 3d^5 + 3p^5 3d^6 \underline{L}$$

One calculates the 1s XPS spectral shape and then for all these intermediate states the 1s3p x-ray emission spectral shape is calculated. One then adds the 1s3p spectra with the intensities from the 1s XPS calculation. In principle one should use the Kramers-Heisenberg formula to account for interference effects, but in case of 1s core levels interference effects are absent. In section V we will explicitly use the Kramers-Heisenberg formula for 2p3s and 2p3d resonant x-ray emission spectral shapes.

We will use a 3 configuration charge transfer description to simulate the Ni 1s3p XES spectral shape. The configurations are  $1s^13d^8 + 1s^13d^9\bar{L} + 1s^13d^{10}\bar{L}\bar{L}'$ . The complete



mixing scheme is given below.

## Chapter 6

## X\_RAY EMISSION AND RIXS

The files nikbct.rcg and nikbct.rac are equivalent to the charge transfer XAS calculations. nikbct.rcg reads:

```

10          14      0      0      1      1  INTER0
0          80998080          8065.47800      0000000
1      3 1 13 1 10          00      9 00000000      8065.4780 .00      0 1
S01  P06  D08
S02  P05  D08
NI2+ 1S01 3D08      5          HR99999999
NI3+ 1S01 3D09      3          HR99999999
-999999999.
10          14      0      0      1      1  INTER0
0          80998080          8065.47800      0000000
1      4 1 14 1 10          00      9 00000000      8065.4780 .00      0 1
S01  P06  D09  D09
S02  P05  D09  D09
NI2+ 1S01 3D08      5          HR99999999
NI3+ 1S01 3D09      3          HR99999999
-999999999.
10          14      0      0      1      1  INTER0
0          80998080          8065.47800      0000000
1      4 1 14 1 10          00      9 00000000      8065.4780 .00      0 1
S01  P06  D10  D08
S02  P05  D10  D08
NI2+ 1S01 3D08      5          HR99999999
NI3+ 1S01 3D09      3          HR99999999
-999999999.
10          14      0      4      0      4  INTER2 shell103000000
0          80998080          8065.47800      0000000
1      3 1 13 1 10          00      9 00000000      8065.4780 .00      0 1
S01  D08  D10
S01  D09  D09
NI2+ 1S01 3D08      5      0.0000      13.9531      8.7121      0.1142      0.0794HR99999999
NI3+ 1S01 3D09      3      0.0000      0.1042      0.0724          HR99999999
-999999999.
10          14      0      4      0      4  INTER2 shell103000000
0          80998080          8065.47800      0000000
1      3 1 13 1 10          00      9 00000000      8065.4780 .00      0 1
S01  D09  D09
S01  D10  D08
NI2+ 1S01 3D09      3      0.0000      0.1042      0.0724          HR99999999
NI3+ 1S01 3D10      1      0.0000          HR99999999
-999999999.
10          14      0      4      0      4  INTER2 shell103000000
0          80998080          8065.47800      0000000
1      3 1 13 1 10          00      9 00000000      8065.4780 .00      0 1
P05  D08  D10
P05  D09  D09
NI2+ 3P05 3D08      8      -50.0          13.3171      8.3201      1.3972      0.0922HR99999999
      14.3333      17.7164      10.7984
NI3+ 3P05 3D09      6      -50.0          1.3662      0.0842      12.0323      15.0004HR99999999
      9.0274
-999999999.

```



```

10          14    0    4    0    4  INTER2 shell03000000
0          80998080          8065.47800    0000000
1      3 1 13 1 10          00      9 00000000    8065.4780 .00    0 1
P05  D09  D09
P05  D10  D08
NI3+ 3P05 3D09    6  -50.0          1.3662    0.0842    12.0323    15.0004HR99999999
      9.0274
NI1+ 3P05 3D10    2  -50.0          1.3332
      -99999999.
-1

```

The final states have been set to the arbitrary value of -50 eV.

The file nikbct.ban reads:

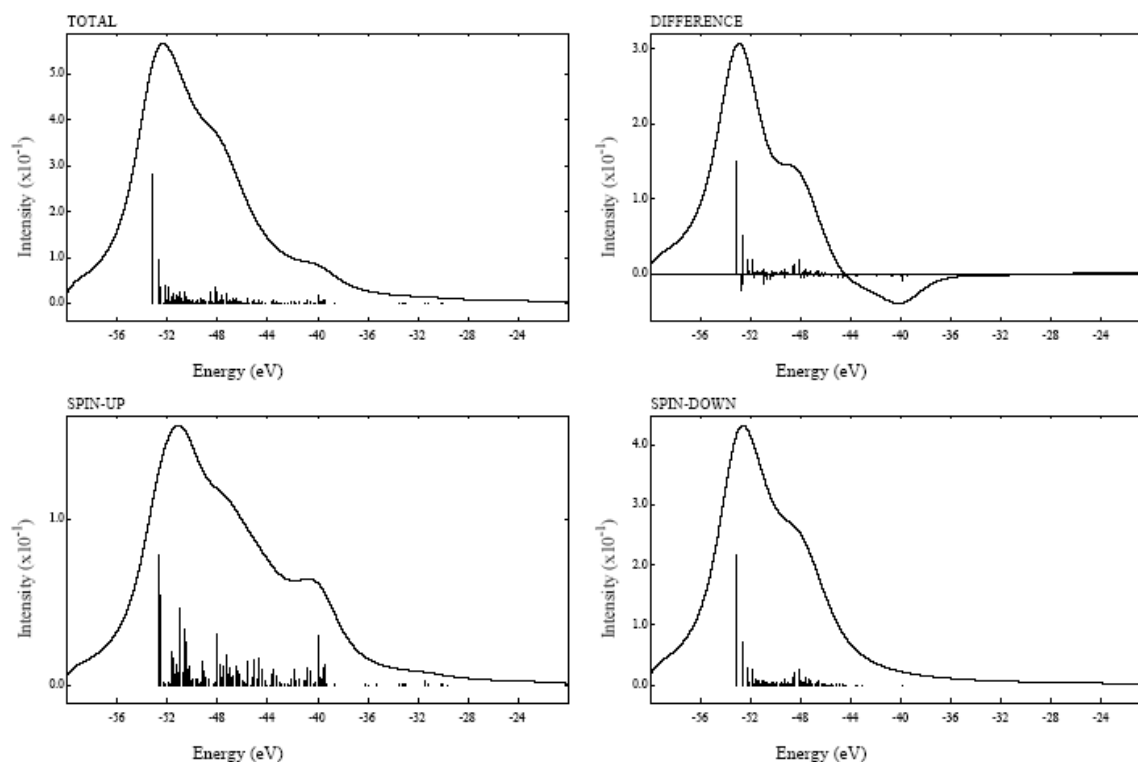
```
PRMULT
NCONF 3 3
N2 1
N3 1
def EG2 = -5.5 unity
def EF2 = -5.5 unity
def EG3 = -3.7 unity
def EF3 = -3.7 unity
XMIX 2      2.0 -1.0
4  1 1 2  1 2 3  2 1 2  2 2 3
XHAM 2  1.0  1.0
6  1 1  1 2  1 3  2 1  2 2  2 3
TRAN  3      1 1  2 2  3 3
TRIADS
s1+  1-  s0-  0
S1+  1-  S1-  0
S1+  1-  S1-  1
S1+  1-  ^S0- 0
S0+  1-  S0-  0
S0+  1-  S1-  0
^S0+  1-  S1-  0
^S0+  1-  ^S0- 0
```

The special features of this ban-file are the parameters used. Note that the energy of the second configuration is  $-5.5$  eV and of the third  $-3.7$  eV. The reason is that these 1s core states relate to the energies of a 1s XPS experiment. EG2 is given as  $\Delta - Q$  (corrected for multiplets). The final state energies have been chosen identical to the initial state values. This implies that we assume that the core hole potential of a 1s core hole is equal to that of a 3p core hole. This is not necessarily the case, but the difference will be negligible as far as 1s3p XES spectra are concerned.

The nikbct.plo reads:

```
inform
postscript nikbct.ps
landscape
rows_per_page 2
columns_per_page 2
horizontal_order
energy_range -60 -20
lorentzian 1.8 1e20
gaussian 0.5
band      nikbct.oba
frame_title SPIN-UP
spectrum istate ^S0+
frame_title SPIN-DOWN
spectrum istate S1+
frame_title TOTAL
addlines istate S1+
spectrum istate ^S0+
frame_title DIFFERENCE
addlines istate S1+
spectrum istate ^S0+ scale -1
end
```

Note that instead of the energy of the spin-down configuration, spin-up and spin-down are selected by symmetry. This is special for a  $1s13d8$  ground state as in this case both the spin-up and spin-down ground state have only a single (different) symmetry. It makes things easier because one does not have to look up the energy in the oba-file and add it to the plo-file.



This figure shows the result of the nikbct calculation, with the parameters as given above. Compared with the crystal field multiplet calculation (above), the spectra appear less structured. The general structure is maintained though.

### K capture $1s3p$ x-ray emission

The effects of the excitation process can be studied by using two different excitation processes. Recently Glatzel and co-workers compared the usual above resonance x-ray excitation with K capture excitation for MnO (see [glatzel01b.pdf](#)). The x-ray excitation process follows the scheme as outlined above. The  $1s$  electron leaves the atom as a continuum electron and the spectrum is calculated by adding the  $1s3p$  spectra of the  $1s$  XPS spectrum states. In the K capture process the  $1s$  electron annihilates a proton and is captured in the core. The calculation is the same as for x-ray excitation as given above. A difference is the ordering of the configurations and the energy difference between  $1s^13d^5$  and  $1s^13d^6\bar{\downarrow}$  is equal to  $-Q$ . Because the core hole potential is larger than the charge transfer energy this is a negative number and the lowest energy configuration is  $1s^13d^6\bar{\downarrow}$ . In the case of K capture the  $1s$  electron that has 'left' is part of the nucleus and the total charge of the nucleus plus the  $1s$  core level is not modified. This implies that the outer valence electrons hardly notice any effect on the positions of the various configurations and the energy difference between  $1s^13d^5$  and  $1s^13d^6\bar{\downarrow}$  is equal that in the ground state, being  $\Delta$ . The K-capture spectrum is sharper and the satellite structure is found at a lower energy, which is a consequence of additional states in the x-ray excited spectrum. The simulated spectra correspond nicely with the experimental results.

### RIXS calculations at the K edge

In Resonant Inelastic X-ray Scattering (RIXS) spectroscopy a secondary monochromator (analyzer) with an energy bandwidth on the order of the lifetime broadening is used as a fluorescence detector. The first application of RIXS for 3d metal systems has been the effective removal of the 1s lifetime broadening, allowing the measurement of the K edge (or more precisely, a K edge like structure; see the discussion below) with unprecedented resolution. Since then, a number of applications of RIXS have been developed and demonstrated, for example the measurement of the spin-selective K edges, valence selective EXAFS and range extended EXAFS by using detection channels specific for a certain edge, valence and/or spin state.

The electronic states that form the edge of an absorption spectrum are resonantly excited states that subsequently decay. In case of a 3d transition metal ion the radiative decay with the highest probability after 1s core hole creation is a 2p to 1s transition or the K fluorescence emission. The spectroscopy is therefore denoted 1s2p RIXS to describe the core hole in the intermediate (1s) and final (2p) state. The fluorescence light emitted during the decay process can be recorded using a crystal analyzer with an energy bandwidth similar to that of the primary monochromator of the synchrotron beamline. The process can be viewed as an inelastic scattering of the incident photon at the 3d transition metal atom and is theoretically described by the Kramers-Heisenberg formula:

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

The intermediate state  $|n\rangle$  is reached from the ground state  $|g\rangle$  via a transition operator  $T_1$ . In a simplified picture using atomic configuration for  $\text{Fe}^{\text{III}}$  we can write  $|g\rangle = 3d^5$  and  $|n\rangle = 1s3d^6$ , i.e. a 1s electron is resonantly excited into a 3d orbital. The intermediate states  $|n\rangle$  in RIXS spectroscopy are the final states in conventional K-edge absorption spectroscopy.

The final states are reached via a 2p to 1s transition and  $T_2$  therefore identifies with the dipole operator. The 1s2p RIXS final state configuration  $|f\rangle = 2p^5 3d^6$  is identical to the final state configuration in soft x-ray L-edge absorption spectroscopy.

The incident energy as well as the emitted energy is varied in a RIXS experiment. The recorded intensity is proportional to  $F(\Omega, \omega)$  and is thus plotted versus a two-dimensional grid: the RIXS plane. In order to assign the total energy of electronic states to the axes of the contour plots one uses the incident energy axis (intermediate state energy) and the energy transfer axis  $\hbar\omega = E_g - E_f$  (final state energy). This choice of axes of the RIXS plane has also the advantage that the energy transfer axis relates to the excitation energy in L-edge absorption spectroscopy. The Kramers-Heisenberg equation contains two Lorentzian line shapes for the incident energy and the energy transfer. The lifetime broadenings  $\Gamma_K$  for the intermediate states and  $\Gamma_f$  for the final states thus apply in the  $\Omega$  and  $\omega$  direction, respectively. An experimental spectrum is further broadened by the energy bandwidths of the incident energy monochromator and the crystal analyzer.

Below, we discuss the potential of 1s2p RIXS for the analysis of 3d metals including experimentally obtained 2-dimensional energy grids and a detailed theoretical

analysis. As an example we use  $\text{FeAl}_2\text{O}_4$ , an octahedral  $\text{Fe}^{\text{II}}$  system. Octahedral systems are expected to have a K pre-edge structure that is completely dominated by direct quadrupole transitions, whereas tetrahedral systems have significant 3d4p admixture leading to mixed dipole and quadrupole contributions. All spectra will be analyzed using the crystal field multiplet code. The K pre-edge structure will be simulated using quadrupole 1s3d transitions. Finally the complete 1s2p 2D RIXS images will be calculated using the Kramers-Heisenberg formula and both the 1s3d quadrupole excitation (intermediate state) coupled to the 1s2p dipole decay (final state).

We start the calculation of the 1s2p RIXS spectrum of  $\text{FeAl}_2\text{O}_4$  by calculating its K pre-edge structure. The pre-edge of the (distorted) octahedral system is assumed to be quadrupole in nature and we have to calculate the 3d5 to 1s13d6 transition. The difference with the L edges discussed in chapters 1 to 3 is the quadrupole nature of the transition, which implies some modifications to the inputfiles.

The fe2q.rcn file is similar to the L edge case:

```
22 -9      2   10   1.0      5.E-06      1.E-09-2    130    1.0   0.65   0.0 0.50 0.0   0.70
26      Fe2+ 1S02 3D06      1S02 3D06
26      Fe2+ 1S01 3D07      1S01 3D07
-1
```

The program realised that this is a quadrupole transitions and prepares the following feal2o4.rcg file, where the numbers in red have been modified according the description in chapter 1:

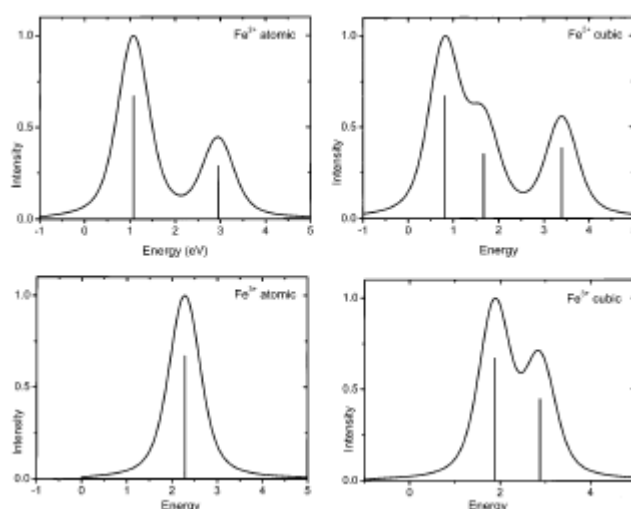
```
10      0      0   14   2   4   2   2 SHELL03000000 SPIN00000000 INTER8
0      80998080      8065.47800      00000000
1      2 1 12 1 10      00      9 00000000 1 8065.4790 .00      1
S 2   D 6
S 1   D 7
Fe2+ 1S02 3D06      4      0.0000      10.9661      6.8151      0.0002      0.0000HR99999999
Fe2+ 1S01 3D07      5      0.0000      11.6801      7.2581      0.0002      0.0584HR99999999
-99999999.
-1
```

That TTRCG has to perform a quadrupole transition is indicated with the two **blue 2 values**.

The feal2o4.rac file reads:

```
Y
% vertical 1 1
butler O3
to Oh
endchain
actor 0+ HAMILTONIAN ground PRINTEIG
OPER HAMILTONIAN
  BRANCH 0+ > 0 0+ 1.0
OPER SHELL2
  BRANCH 4+ > 0 0+ 4.0
actor 0+ HAMILTONIAN excite PRINTEIG
OPER HAMILTONIAN
  BRANCH 0+ > 0 0+ 1.0
OPER SHELL2
  BRANCH 4+ > 0 0+ 4.0
actor 2+ plan2 transi PRINTTRANS 050
oper MULTIPOLE
  branch 2+ > 0 2+ 1.000
actor ^1+ plan1 transi PRINTTRANS 050
oper MULTIPOLE
  branch 2+ > 0 ^1+ 1.000
RUN
```

The quadrupole operator has a 2+ (=D-electron-like) state in atomic symmetry. As we did see in chapter 2, a 3d-electron is split into T2 and E symmetry, which is exactly what also happens with the quadrupole operator. In octahedral symmetry the quadrupole operator has respectively 2+ (E) and ^1+ (T2) symmetry. This also implies that the quadrupole transition is angular dependent as given by the symmetries of the E and T2 states. An important addition to the rac-file is the statement **PRINTTRANS 050**. The consequence of this addition is that the matrix element is printed in the feal2o4.ora file, instead of the squared matrix element. The Kramers-Heisenberg formula needs the explicit matrix element of the quadrupole excitation to allow for interference effects in the intermediate state. If one would like to plot the K edge spectrum, the addition 050 should be omitted.

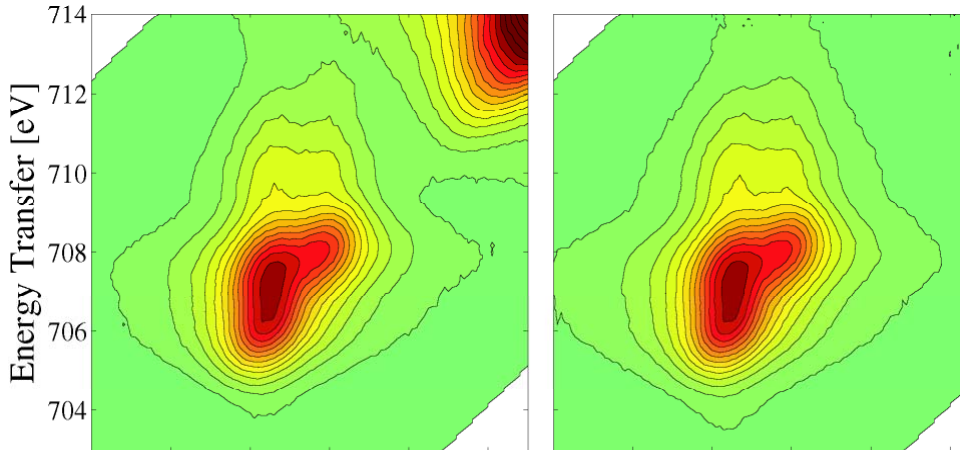


This figure shows the K pre-edge structures of FeII (top) and FeIII (bottom) for the atomic case (left) and after addition of a 1.0 eV crystal field (right). FeIII has a single pre-edge peak because its ground state is 6S and the only allowed transition is to a 5D state. FeII has two atomic transitions.

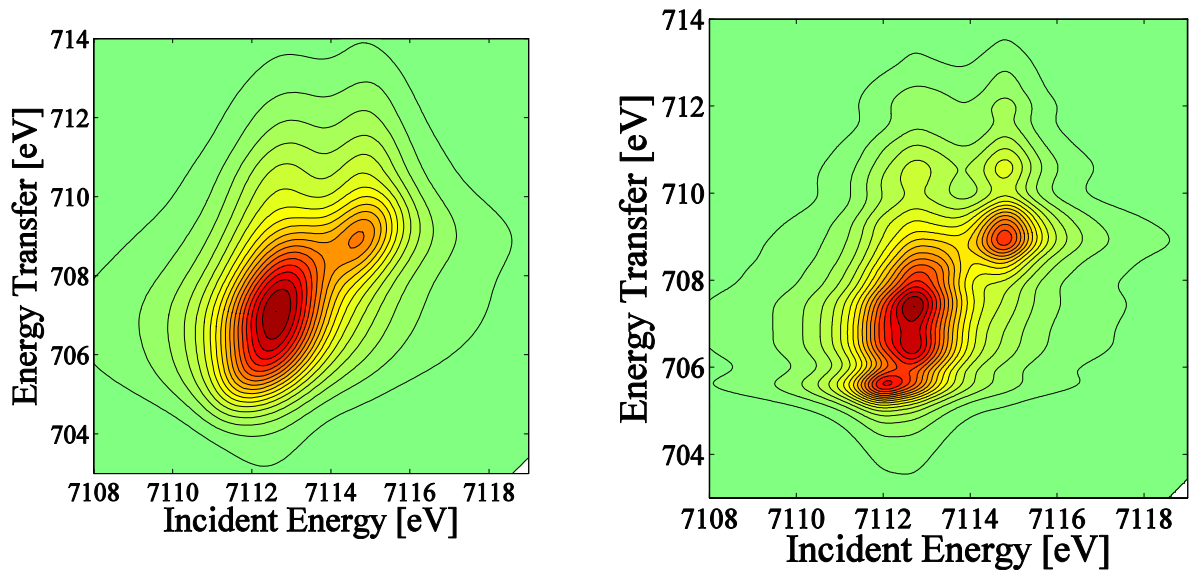
Next we have to calculate the matrix elements of the 1s2p XES channel. This is a normal dipole decay and the inputfiles are similar to those of non-resonant 1s3p XES

as discussed above. The only new feature is the addition of `PRINTTRANS 050` in the `rac`-file. This yields two outputfiles `feal2o4q.ora` for the  $1s3d$  excitation and `feal2o4qx.ora` for the  $1s2p$  decay. It is noted that the actual files as added to the program use D4H symmetry instead of OH, but this does not affect the present discussion (it allows to add a distortion from octahedral symmetry). The matrices are used in a MATLAB program written by Pieter Glatzel (now at ESRF, [glatzel@esrf.fr](mailto:glatzel@esrf.fr)).

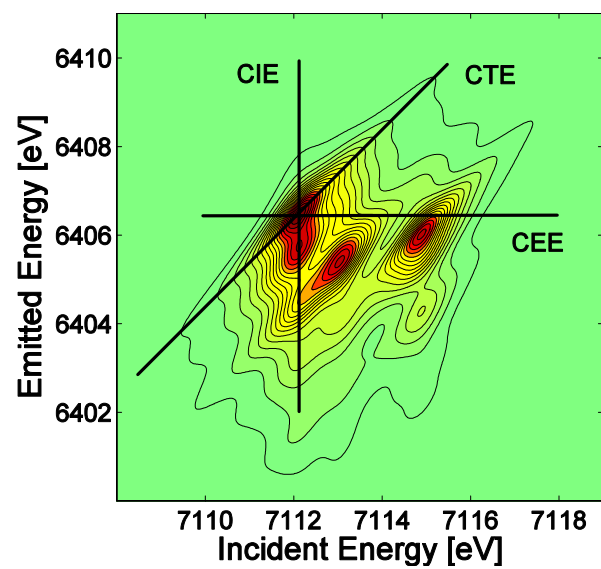
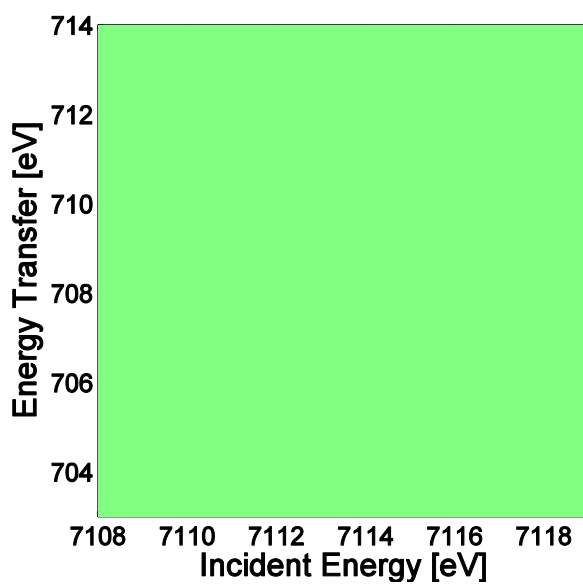
The MATLAB-disprixs program allows one to plot the 2D-RIXS image and perform a range of additional data analysis options. I refer to the manual of the program for further details. Below the experimental  $1s2p$  RIXS spectra of FA77 are given.



The calculated RIXS spectra are given with two different broadenings, 1.0 eV excitation plus decay (left) and 0.3 eV excitation plus decay (right). The 1.0 eV calculations reproduce the experiment, but it is clear that the improvement of the resolution to 0.3 eV will be important for the use of  $1s2p$  RIXS as an analysis tool.



Below we give the 1s2p RIXS spectrum of FeSiO, plotted in two different ways. On the left we use the energy transfer as y-axis and on the right the emitted energy. The three lines CIE, CEE and CTE refer to three useful cross sections through the 2D RIXS plane.

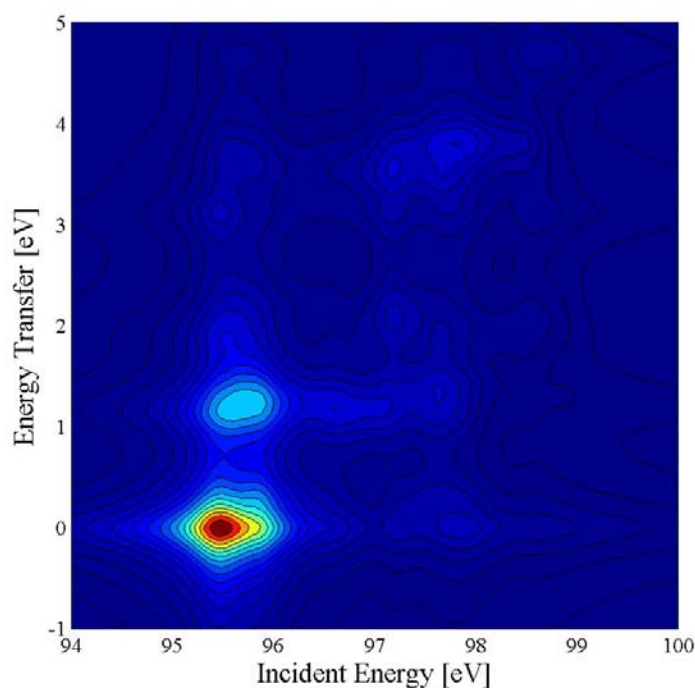
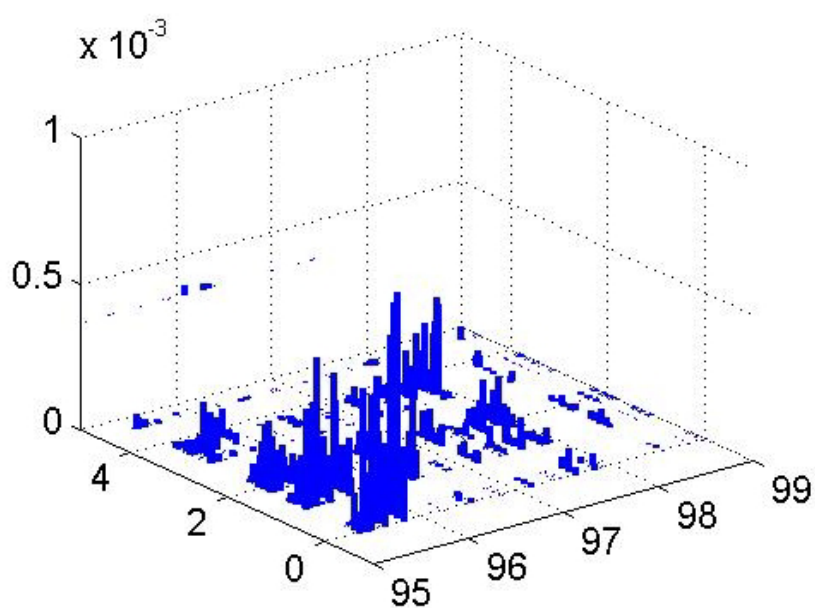




**Soft x-ray RIXS****Calculating NiO**

The calculation the 2p3d RIXS spectrum is analogous to that of the 1s2p RIXS spectra. The calculation involves the 2p to 3d excitation and the 3d to 2p decay. Actually this is two times the same calculation with only the initial state and final state configurations reversed. The files nix2p3d.rcg and nix2p3d.rac generate the XAS matrix elements and the files nix3d2p.rcg and nix3d2p.rac generate the XES matrix elements. These matrix elements are then read by the rixsmaster program under MATLAB.

The MATAB-disprixs program can generate a number of outputs, for example stick diagrams or contour plots. Below the Ni 2p main peak is given at 95.5 eV. (More soon)



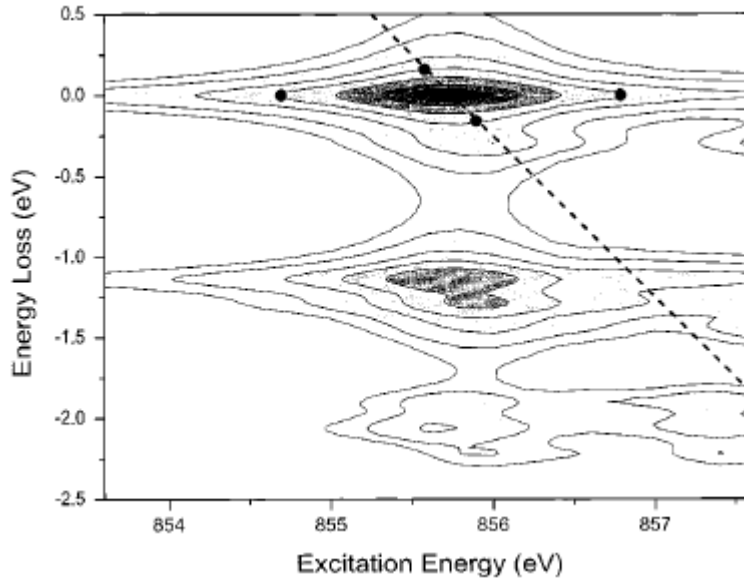
## 2p x-ray emission

The 2p core levels of the 3d transition metals are positioned in the soft x-ray range between 400 and 1000 eV. As discussed in section III, the 2p x-ray absorption spectra are dominated by multiplet effects and do show a complex multi-peaked spectral shape. This makes 2p x-ray emission ideally suitable for resonance studies. Therefore we will start with a discussion of the resonant 2p x-ray emission spectral shapes. Both 2p3s and 2p3d resonant x-ray emission will be discussed.

If the core hole is created with an energy close to the 2p absorption edge, the x-ray absorption and x-ray emission processes do occur coherently and the overall 2p3d process (of a  $3d^5$  ground state) is described with the Kramers-Heisenberg formula:

$$I(\omega, \omega') \sim \left| \sum_{2p^5 3d^6} \frac{\langle 3d^5 | \hat{e}' \cdot r | 2p^5 3d^6 \rangle \langle 2p^5 3d^6 | \hat{e} \cdot r | 3d^5 \rangle}{E_{2p^5 3d^6} - E_{3d^5} - \hbar\omega - i\Gamma_{2p}} \right|^2 \quad (\text{Eq. 17})$$

This formula forms the basis of all resonant x-ray processes. The intensity (I) is given as a function of the excitation ( ) and the emission ( ') energies. The initial state ( $3d^5$ ) is excited to an intermediate state ( $2p^5 3d^6$ ) with the dipole operator ( $\hat{e} \cdot r$ ) and the second dipole operator ( $\hat{e}' \cdot r$ ) describes the decay to the final state ( $3d^5$ ). The denominator contains the binding energy of the intermediate state and its lifetime broadening. A resonance occurs if the excitation energy is equal to the binding energy of the intermediate state. Looking at the MnO 2p x-ray absorption spectrum of figure 11, each multiplet line can give rise to a different resonant 2p3d x-ray emission spectral shape.



The general spectral landscape can be viewed as a two-dimensional space with axis and '. This figure shows a contour-plot of the 2p3d resonant x-ray emission spectrum of  $\text{Ni}^{\text{II}}$  using a crystal field of 1.12 eV to simulate NiO. The darkest area has the highest intensity. The horizontal axis shows the x-ray excitation energy. The main peak of the 2p x-ray absorption spectrum of NiO has an energy of 855.7 eV with a shoulder at 857.5 eV<sup>50</sup>. The vertical axis shows the x-ray energy loss, that is the energy of 0.0 eV means that the 2p3d decay energy is equal to the 2p3d excitation energy, in other words this refers to resonant elastic scattering. There is a large peak visible with its peak position at (855.7 eV, 0.0 eV). There is a second peak at an

energy loss of 1.1 eV. This peak relates to a ligand field excitation from the  $^3A_2$  ground state to the  $^3T_2$  excited state. A third peak is visible at approximately -2.0 eV.

A number of cross sections can be made. This paper focuses on the (resonant) x-ray emission spectral shape excited with a fixed energy. This will be indicated as  $I_{\text{XES}}(\omega')$ . In figure 25 this relates to vertical cross sections. For example the resonant x-ray emission spectrum excited at 855.7 eV relates to a vertical line at 855.7 eV. If the excitation energy is (far) above a resonance this is normal x-ray emission or fluorescence. Close to a resonance, it is called *resonant x-ray emission*. With 2p3d resonant x-ray emission one studies the elementary excitations by probing the energy difference between the initial and final state. These spectra can be plotted in two ways: (1) as resonant x-ray emission spectra i.e.  $I_{\text{XES}}(\omega')$ , or (2) as *resonant inelastic x-ray scattering*  $I_{\text{XES}}(\omega, \omega')$ . These spectra are of course exactly the same, but if one compares spectra excited at different excitation energies, the resonant x-ray emission spectra shift with the excitation energies, while the RIXS spectra align all elementary excitations. RIXS can be used to study, for example, the dd-excitations in transition metals as will be discussed below.<sup>41</sup>

Another cross section is to measure the x-ray absorption spectrum at a fixed emission energy:  $I'_{\text{XAS}}(\omega)$ . This relates to the diagonal line.

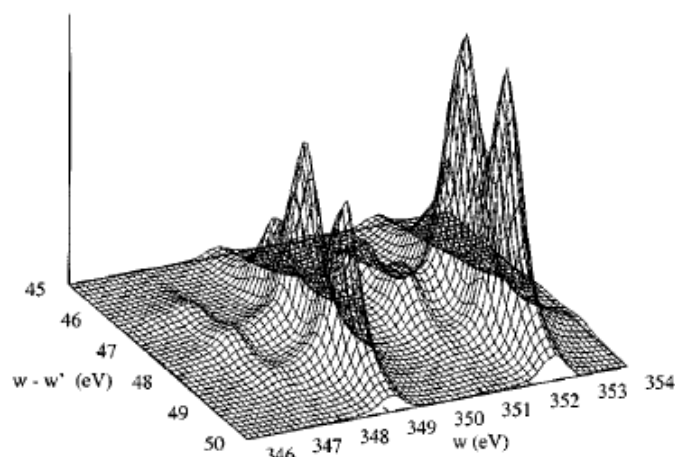
### 2p3s resonant x-ray emission

Before returning to the 2p3d resonant x-ray emission spectra, we will first discuss the 2p3s resonant x-ray emission spectra as the 2p3s case gives a good opportunity to describe essentially all peaks with a simple model. We will follow the calculation of the 2p3s resonant x-ray emission spectra of  $\text{CaF}_2$ . In resonant 2p3s x-ray emission, one is exciting at all these 7 peaks in the absorption spectrum and measures the 2p3s x-ray emission spectral shape. The 3s2p inelastic x-ray scattering cross section is dominated by resonant scattering via the  $2p^5 3d^1$  intermediate states. It has been shown that one can reduce the calculation to the transitions of  $3d^0$ , via  $2p^5 3d^1$ , to  $3s^1 3d^1$  states. The effects of charge transfer are small and can be neglected. Both the x-ray absorption and x-ray emission steps essentially conserve the local charge and it has been shown that in those experimental conditions ionic systems like  $\text{CaF}_2$  can be described in close detail by the ligand field approximation. One has to fill in the x-ray absorption and x-ray emission steps in the Kramers-Heisenberg formula:

$$I(\omega, \omega') \sim \left| \sum_{2p^5 3d^1} \frac{\langle 3s^1 3d^1 | \hat{e}' \cdot r | 2p^5 3d^1 \rangle \langle 2p^5 3d^1 | \hat{e} \cdot r | 3d^0 \rangle}{E_{2p^5 3d^1} - E_{3d^0} - \hbar\omega - i\Gamma_{2p}} \right|^2 \quad (\text{Eq. 18})$$

This calculation can almost be carried out 'by hand'. Starting from the situation in  $\text{CaF}_2$  with all bands completely full, one has the advantage of strong restrictions on the possible symmetry states. Ligand field multiplet calculations have been performed for the  $3d^0$  initial state, the  $2p^5 3d^1$  intermediate states, and the  $3s^1 3d^1$  final states in cubic symmetry. The  $3d^0$  initial state consists of only one state with  $^1A_1$  symmetry. The only  $2p^5 3d^1$  intermediate states that can be reached in x-ray absorption must have  $T_1$  symmetry, and as there will be seven of those states. The  $3s^1 3d^1$  final states are split by only two interactions, the 3s3d exchange and the cubic crystal field. This gives a total of four peaks in the final state. The complete calculation is then the transition of one initial state via seven intermediate states to four final states. The results of these seven absorption matrix elements and 28 (in fact 49 due to degeneracies<sup>31</sup>) emission matrix elements are fed into the Kramers-Heisenberg formula.

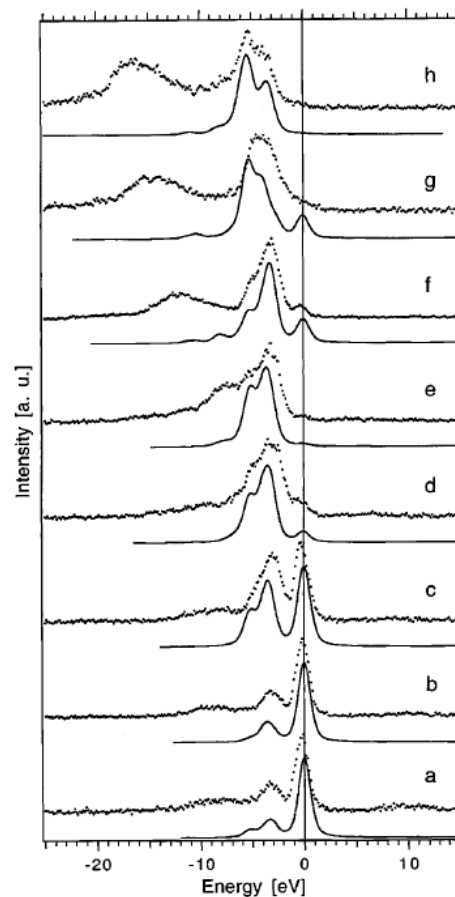
This figure gives the resulting resonant 2p3s x-ray emission spectral shapes. One can observe that in all comparisons of interference-on (solid line) and interference-off (dashed) the integrated intensities of the solid and dashed line are equivalent or in fact identical as the integrated intensity is conserved by a sum rule. Relatively large interference effects can be seen for the spectra excited at 347.5 and 348.1 eV. These two energies relate to weak excitations, hence the decay spectrum is dominated by the Lorentzian tails of the neighbours. That is, interference effects are largest if two channels have a comparable effective strength at a certain energy. The experimental results are reproduced with these calculations.



A topic not discussed in this paper are the consequences of intermediate state decay/relaxation, also known as post-collision interactions, as observed in the experimental spectra. These decay channels do give rise to non-resonant x-ray emission. Far above the edge the situation is clear and these non-resonant channels are the normal fluorescence lines at constant energy, but the non-resonant channels close to and even at resonance present a theoretical challenge as they can (and will) be different both from resonant x-ray emission and also from the normal non-resonant channels. To shed light on this situation one has to understand in great detail what happens exactly in the various relaxation and decay channels, both elastic as inelastic. In solids this is a dramatically complex situation and little is known quantitatively.

### 2p3d resonant x-ray emission

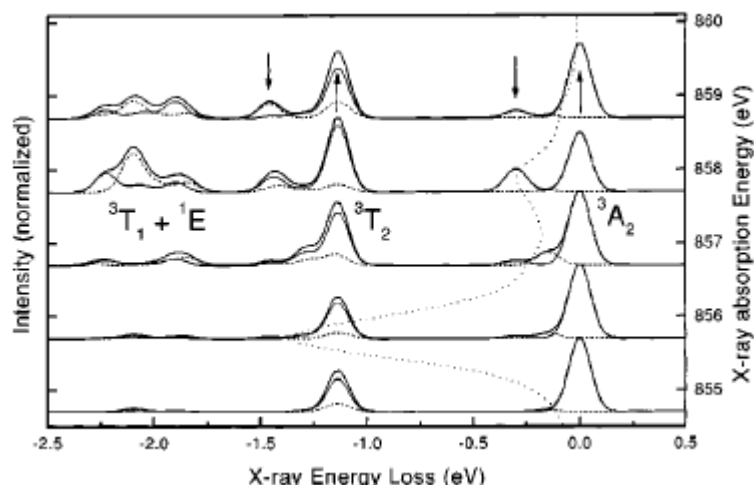
This figure shows the 2p3d RIXS spectra of MnO. One can see the elastic peak related to transitions of the  $3d^5$  ground state via any  $2p^5 3d^6$  intermediate state back to itself. In addition one observes peaks at constant energy-loss, for example at about -4.0 eV. These peaks relate to dd-transitions. They essentially map the Tanabe-Sugano diagrams of the electronic configurations of a  $3d^5$  ground state. It is important to notice that the relative intensity of these various peaks is not constant over the excitation energies, but varies. This is an indication of the relative matrix elements from the  $2p^5 3d^6$  intermediate states back to the  $3d^5$  states. In the spectra f, g and h one also observes a peak shifting to higher energy losses. This is a signal of the off-resonant 2p3d fluorescence that is visible because of the relaxation of the intermediate states.



### Spin-flip transitions

Above we have seen that resonant 2p3d x-ray emission can give information on dd-excitations and charge transfer excitations. Also other low-energy excitations can be studied, for example it has been that spin-flip transitions can be observed in resonant 2p3d and 3p3d x-ray emission of nickel and copper oxides.

This figure shows the resonant 2p3d x-ray emission spectra at the 2p x-ray absorption spectrum of NiO. This figure is related to figure 25 discussed above. The resonant elastic peak of  ${}^3A_2$  symmetry is visible at 0.0 eV and the dd-transitions to the  ${}^3T_2$ ,  ${}^3T_1$  and  ${}^1E$  states are visible at energies of 1.1 eV and at about 2.0 eV energy loss. However some additional peaks are visible at low energy loss.



For example a peak is visible at about 0.25 eV. This peak can be assigned to a spin-flip transition in which a  $\text{Ni}^{\text{II}}$  ion flips its spin-state from +1.0 to -1.0 (or reversed). The consequence of this spin-flip is that the anti-ferromagnetic neighbours now see an apparent ferromagnetic neighbour and the energy involved is the energy loss observed in resonant x-ray emission. The spin-flip peak is highest at an excitation energy of 858 eV that is at the shoulder of the 2p x-ray absorption spectral shape. The reason is that this shoulder relates to a state in which the 2p and 3d electrons are essentially anti-parallel aligned, in contrast to the parallel alignment of the main peak. This anti-parallel alignment facilitates the spin-flip transitions to occur.

It is good to note that in the literature two completely distinct transitions are called spin-flip. There is the spin-flip as described above that is related to the transition of a  $m_s = -1$  state to a  $m_s = +1$  state. The other usage of the term spin-flip is given to transitions in which the spin 'flips' from for example a sextet state to a quartet state. These types of 'spin-flip' can be seen in all but the elastic transition. The total spin-state has been modified in such spin-flip transition. In my opinion it is better to refer to such transitions simply as dd-transitions.

The measurement of spin-flip transitions is important for the study of the anti-ferromagnetic coupling in transition metal oxides. There is however an experimental complication, which is that the overall resolution of the experiment should preferably be in the order of 0.2 eV. This is at the edge of the present technology and still suffers from low intensities.

More soon on the usage of the MATLAB programs