

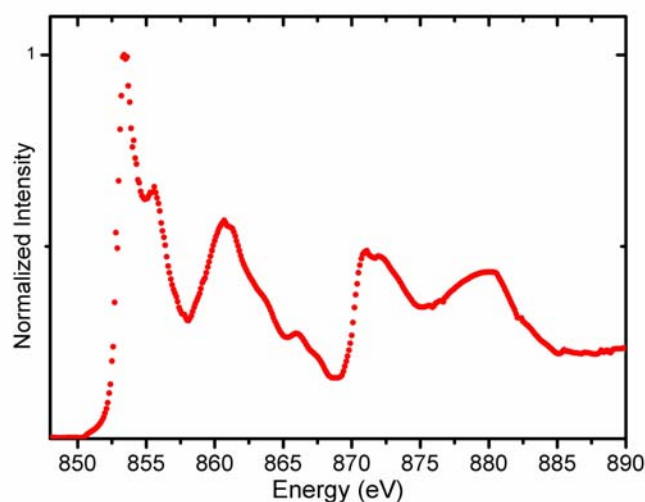
Photoemission calculations

In this section we discuss the photoemission spectra. In chapters 1 to 7, we have concentrated on XAS calculations. The main difference between XAS and XPS is that in XPS one excites an electron out of the system, in other words XPS is an ionising experiment. For the calculations this implies that we have to describe the excited electron within the model used.

X-ray photoemission (XPS) describes exactly the same process as x-ray absorption, i.e. the excitation of a core electron from the ground state to some excited state. A difference with x-ray absorption is the difference in measurement. XAS measures the variation in the absorption with respect to the excitation energy, while XPS measures the variation in the kinetic energy of the emitted electron at constant excitation energy. This immediately gives rise to the observation that one can combine XAS and XPS and measure the XPS spectra as a function of the x-ray excitation energy, for example while scanning through an absorption edge.

2p XPS spectra can be calculated with the same charge transfer multiplet model as 2p XAS spectra. The $3d^8 + 3d^9\bar{L}$ ground state is excited to $2p^53d^9 + 2p^53d^{10}\bar{L}$ in 2p XAS and to $2p^53d^8_s + 2p^53d^9\bar{L}_s$, where $_s$ is a free electron of s-character. A free electron is within the charge transfer multiplet model defined as an electron without correlation effects. Instead of an $_s$ electron, also excitations to a d-electron ($_d$) are calculated. The fact that in 2p XAS the electron is excited to a 3d-state implies that the 2p XAS process is self-screened. In contrast, the 2p XPS process is an ionizing effect that caused large screening effects. This also implies that it makes little sense to calculate 2p XPS spectra without charge transfer. In fact the effect of the core hole potential in the final state implies that one needs to include at least three configurations for a decent description of the spectral shape.

The figure below shows the experimental Ni 2p XPS spectrum. A rather rich spectrum is observed. In case of 2p XPS, the 2:1 ratio for the 2p_{3/2} and 2p_{1/2} peaks is better respected than for 2p XAS. However instead of two peaks the spectrum consists of a number of peaks and shoulders. Data from Altieri, PRB 61, 13406 (2000)



The procedure to calculate a 2p XPS spectrum is analog to a 2p XAS calculation. The ground state is identical and the final state involves a $2p \rightarrow d$ (or s) transition instead of $2p \rightarrow 3d$. The file als8ni2xps3.rcg is similar to the corresponding XAS inputfile. We discuss only the new features.

```

0          90999090          8065.47900      000000
10         14      0      0      1      1 INTER0
1          3 1 13 1 10      00      9 00000000 0 8065.4790 .00      1
D08 P06 D00
D08 P05 D01
Ni3+      1 1
Ni3+      2 1

-99999999.
0          90999090          8065.47900      000000
10         14      0      0      1      1 INTER0
1          4 1 14 1 10      00      9 00000000 0 8065.4790 .00      1
D09 P06 D09 D00
D09 P05 D09 D01
Ni3+      1 2
Ni3+      2 2

-99999999.
0          90999090          8065.47900      000000
10         14      0      0      1      1 INTER0
1          4 1 14 1 10      00      9 00000000 0 8065.4790 .00      1
D10 P06 D08 D00
D10 P05 D08 D01
Ni3+ 1 3
Ni3+ 2 3

-99999999.
0          80998080          8065.47900      000000
10         14      0      4      0      4 SHELL30000000 SPIN30000000 INTER2
1          3 1 13 1 10      00      9 00000000 0 8065.4790 .00      1
D08 P06 D10
D09 P06 D09
Ni3+P6D8L      4      0.0000      12.2341      7.5981      0.0832      0.0000HR99999999
Ni3+P6D9L2      2      0.0000      0.0742      0.0000      0.0000      0.0000HR99999999

-99999999.
0          80998080          8065.47900      000000
10         14      0      4      0      4 SHELL30000000 SPIN30000000 INTER2
1          3 1 13 1 10      00      9 00000000 0 8065.4790 .00      1
D09 P06 D09
D10 P06 D08
Ni3+P6D9L2      2      0.0000      0.0742      0.0000      0.0000      0.0000HR99999999
Ni3+P6D9L2      2      0.0000      0.0002      0.0000      0.0000      0.0000HR99999999

-99999999.
0          80998080          8065.47900      000000
10         14      0      4      0      4 SHELL30000000 SPIN30000000 INTER2
1          4 1 14 1 10      00      9 00000000 0 8065.4790 .00      1
D08 P05 D10 D01
D09 P05 D09 D01
Ni3+P5D8      8 862.3000      14.0221      8.7641      00.1122      11.5062HR99999999
      8.3503      6.3324      3.6034
Ni3+P5D9L      6 862.3000      00.1022      11.5072      7.7213      5.7874HR99999999
      3.2914

-99999999.
0          80998080          8065.47900      000000
10         14      0      4      0      4 SHELL30000000 SPIN30000000 INTER2
1          4 1 14 1 10      00      9 00000000 0 8065.4790 .00      1
D09 P05 D09 D01
D10 P05 D08 D01
Ni3+P5D9L      6 862.3000      00.1022      11.5072      7.7213      5.7874HR99999999
      3.2914
Ni3+P5D10L2      2 862.3000      11.5092      0.0000      0.0000      0.0000HR99999999

-99999999.
-1

```

The important change with respect to 2p XAS is that the dipole transition is changed from $D08 \ P06 \rightarrow D09 \ P05$ to $D08 \ P06 \ D00 \rightarrow D08 \ P05 \ D01$, meaning that the 2p core electron is excited to a free electron of d-character instead of the 3d-band. An additional calculation for a free s-electron should be added, in agreement with the dipole selection rule. The parameters that are given in the bottom part have been calculated for the configuration just neglecting the free electron and neglecting any ligand holes. That is, the parameters of $D08 \ P05 \ D10 \ D01$ (= 2p⁵ 3d⁸ d) are calculated with TTRCN for the configuration 2p⁵3d⁸. The ground state parameters are of course exactly the same for 2p-XPS as for 2p XAS. An important parameter is INTER2. This limits the interactions between the shells to the first two shells. The 2p and 3d shells are mixed, but the ligand hole shell (shell 3, either d₁₀, d₉ or d₈) and the free electron shell (shell 4, d₁ in the final state) are considered to be non-correlated. The als8ni2xps3.rac file is completely identical to the corresponding XAS file. Only the symmetry and the number of configurations matter. The als8ni2xps3.ban file has some new features though:

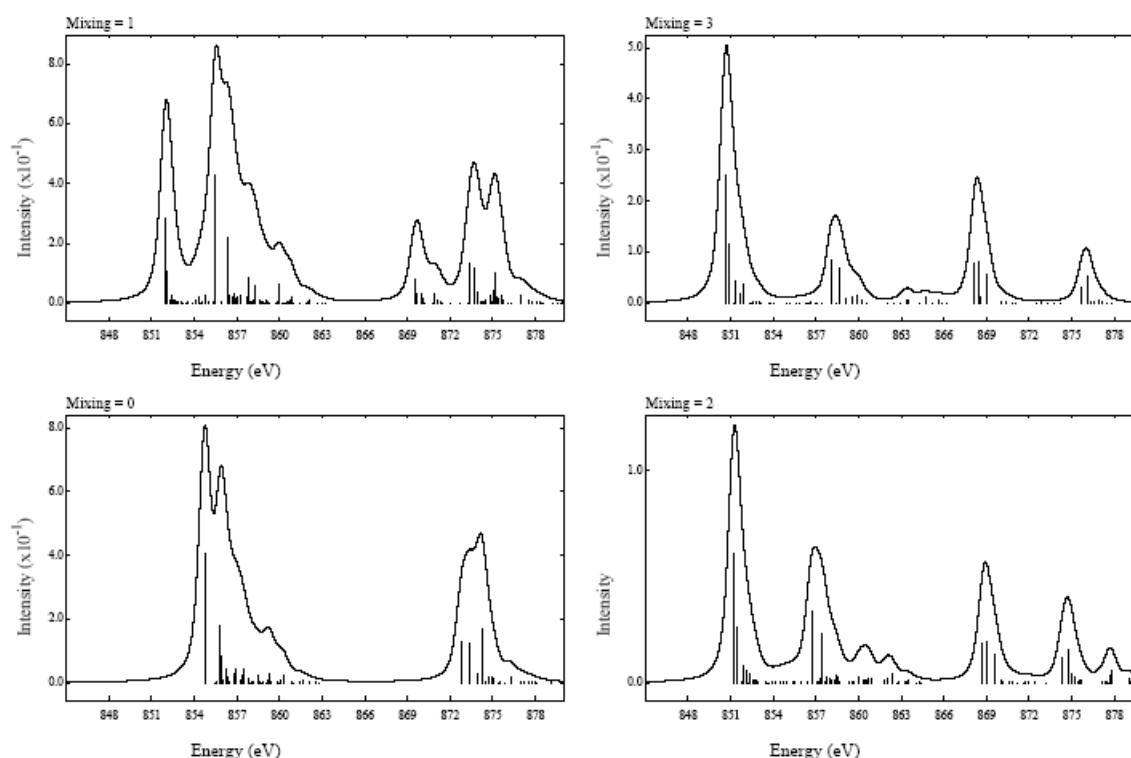
```

erange 0.3
NCONF 3 3
N2 1
N3 1
def EG1 = 0.0 unity
def EF1 = 0.0 unity
def EG2 = 3.5 unity
def EF2 = -5.0 unity
def EG3 = 14.0 unity
def EF3 = -3.0 unity
XMIX 4 3. 3. 1.5 1.5
2 1 1 2 1 2 3
XMIX 4 3. 3. 1.5 1.5
2 2 1 2 2 2 3
XHAM 4 1.0 1.0 0.0 0.0
6 1 1 1 2 1 3 2 1 2 2 2 3
TRAN 3 1 1 2 2 3 3
TRIADS
0+ 1- 1-
^0+ 1- 1-
1+ 1- 0-
1+ 1- ^0-
1+ 1- 2-
1+ 1- ^2-
2+ 1- 1-
^2+ 1- 1-
0+ ^0- ^0-
^0+ ^0- 0-
1+ ^0- 1-
2+ ^0- ^2-
^2+ ^0- 2-

```

For clarity the parameters EG1 and EF1 are added but kept at their default value of 0.0. The structure of the ban-file is equivalent to that of the corresponding XAS calculation (as given in chapter 6); what is completely different is the ordering of the states in the final state, as will be explained below. EG2 is set to 3.5 eV and EG3 to 14.0 eV. This implies that EG3 is effectively not part of the ground state. In the final state the value of $EF2 = EG2 - Q$ and $EF3 = EG3 - 3Q + U$, so both values 'shoot down' and actually become negative. This implies that in the final state we have a real 3-configuration calculation, where the lowest energy states are dominated by EF2 and EF3 (2p⁵3d⁹L and 2p⁵3d¹⁰L₂), so we have real charge transfer in these final states. It can be concluded that in case of 2p XPS it becomes important to include a third configuration 3d¹⁰LL' to the ground state because in the final state it is lowered in

energy and mixes with the $3d^8$ and $3d^9$ final states. 3s and 3p XPS follow the same energy scheme as 2p XPS. The multiplet effects of a 3p and a 3s core hole are different causing a different spectral shape.



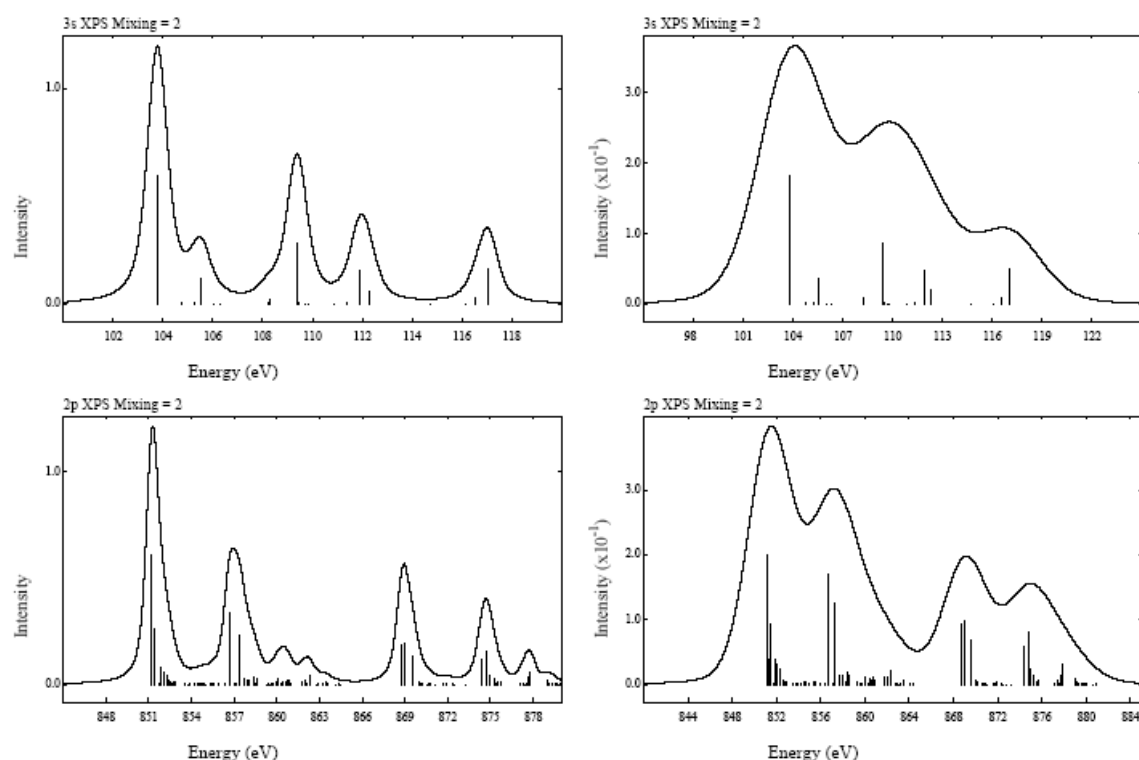
The figure above shows the result of the `als8ni2xps3.ban` calculation, where the mixing strengths are varied from 0 to 1, 2 and 3, as indicated above the figure. The mixing strength refers to the line `XMIX 4 3. 3. 1.5 1.5`, which is changed to `XMIX 4 2. 2. 1. 1.` etc. If the mixing is set to zero, one effectively has a single configuration ground state. The lowest energy configuration in the ground state is $3d^8$ and one obtains a pure $3d^8$ ground state. This implies that only the transition $3d^8 2p \rightarrow 3d^8 2p$ will obtain intensity. One can see in the figures that by switching on the mixing, the lowest lying peaks become visible, which indicates that now also the $3d^9$ and $3d^{10}$ configuration take part in the ground state. After some additional broadening, the calculated spectrum for a mixing of 2.0 corresponds roughly to the experimental 2p XPS spectrum. Actually the calculated spectrum is more similar to the 2p XPS spectrum of NiF₂ as will be discussed below.

Recently it has been shown that in the case of the 2p XPS spectrum of NiO it is necessary to extend the impurity model to a larger cluster and to allow for non-local screening effects, that is the formation of completely screened core hole d^9 instead of normal E_p^*L while the valence hole moves to a neighbouring nickel to form a d^*L state (see [veenendaal93a.pdf](#)). From this discussion it can be concluded that the 2p XPS spectrum will contain large charge transfer satellites, while the 2p XAS spectrum in principle only shows a single peak (with its multiplet splittings). This difference between 2p XPS and 2p XAS can be summarized as follows: XPS is sensitive to the charge transfer effects or in other words the electronic configuration of the ground state, while XAS is sensitive to the symmetry of the ground state with its characteristic multiplet.

3s XPS

The calculation of 3s XPS spectra is analogous to 2p XPS. The ground state can be described again as $3d^8 + 3d^9L + 3d^{10}L^2$. In the final state, a 2p core hole is replaced by a 3s core hole, while the excited electron has p-character: $3s13d^8 p + 3s13d^9L p + 3s13d^{10}L^2 p$. The ligand holes are described as delocalized d-electrons again, which turns these final states into S01 D08 D10 P01, etc.

The files `als8ni23sxps.rcg` and `als8ni23sxps.rac` generate the matrices and `als8ni23sxps.ban` creates the outputfile `als8ni23sxps.oba`. The file `als8ni23sxps.plo` plots the result of this 3s XPS calculation with that of 2p XPS. For simplicity, we kept all parameters in the ban-files identical for 2p XPS and 3s XPS. In practice these parameters could be slightly different because the 2p core hole potential will be slightly larger than the 3s core hole potential.



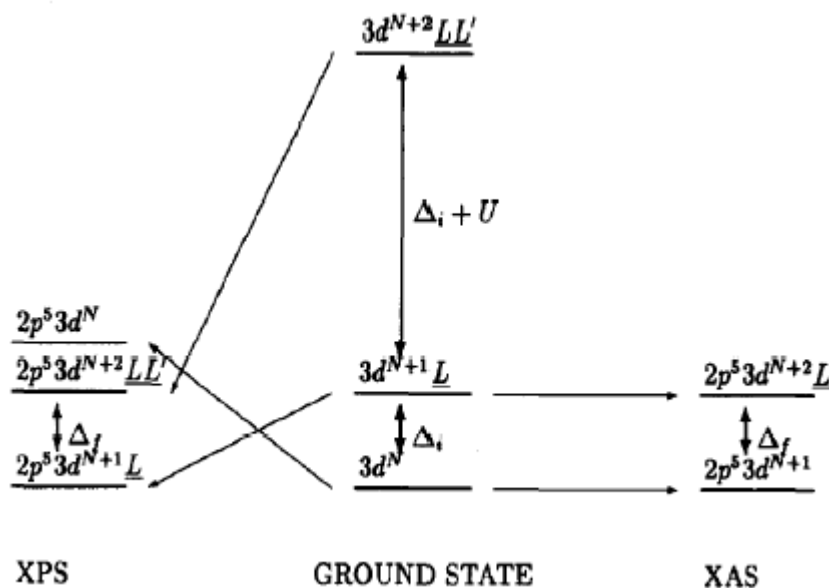
This figure shows the 3s XPS (top) compared with the 2p XPS (bottom). On the left a typical XAS broadening of 0.5 eV Gaussian is used, while on the right a more realistic 3.6 eV broadening (fwhm) has been used. Note that in the plo-file the broadenings are given as the hwhm, so they are given respectively as 0.25 eV and 1.8 eV. These calculated 3s XPS and 2p XPS spectra are similar to those calculated by Okada et al in [okada92a.pdf](#). In that paper also the comparison with experiment is made. The nickel-halides can be nicely explained with these calculations.

The creation of a 3s core hole has some additional aspects, in particular the interaction with a final state that contains two 3p core holes. The energy difference between $3s13d^8$ and $3p43d^9$ is small, which modifies the spectral shape ([bagus73a.pdf](#)). A recent study is [devries02a.pdf](#).

Difference between 2p XPS and 2p XAS

In the final state of both 2p XPS and 2p XAS a core hole is present which couples strongly to the d states via U_{2p3d} . This pulls down states with extra 3d electrons. The core hole in principle also couples to other valence states, but we assume that these couplings can be effectively included in U .

The four parameters, ϵ , t , U and Q determine the shape of the 2p XPS and 2p XAS spectra (neglecting multiplet effects). The energy of the core state and the core hole spin-orbit coupling determine the energy positions of the 2p ($L_{2,3}$) edge. The situation for a typical charge transfer insulator ($\epsilon = 3$, $U = 7$ eV) is visualized in this figure.



The ionic configurations are given and the effects of hybridization are not yet included. The arrows indicate the transitions in both XPS and XAS. In XPS the ordering of the final states is changed because of the effect of Q . The energy difference between the localized state and the band, $\epsilon_f(\text{XPS})$ is given as $-Q$, which is negative (-4) for this system. In XAS the ordering of states in the final state does not change because the 2p electron is excited directly into a 3d state, which causes the counteracting effects of U and Q . As discussed in chapter 6, Q is slightly larger than U , but here they are taken as equal. This has the consequence that $\epsilon_f(\text{XAS}) = \epsilon_i + U - Q = 0$.

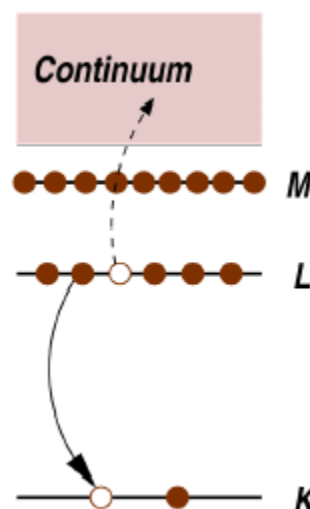
More soon:

1. 3p XPS in NiO
2. Valence band photoemission

Resonant Photoemission and Auger calculations

In this section we discuss the resonant photoemission and Auger spectra. The Auger decay process is given in the figure on the right. After a K (1s) core hole is created, an L electron fills the K hole while another L electron uses this energy to escape into the continuum. By measuring the kinetic energy of this Auger electron, the Auger spectrum can be measured.

Assume that one excites a 2p core electron in NiO. Then this 2p core hole can be filled by any electron that has a higher energy. This includes the 3s, 3p and 3d electrons. The energy that is created by this decay can be used to excite another 3s, 3p or 3d electron out of the solid.



	all electrons	partly filled	direct XPS
ground state	$2p^6 3s^2 3p^6 3d^8$	$3d^8$	-
2p core hole (resonant)	$2p^5 3s^2 3p^6 3d^9$	$2p^5 3d^9$	-
2p3s3s Auger	$2p^6 3s^0 3p^6 3d^9 +$	$(3s^0) 3d^9$	no
2p3s3p Auger	$2p^6 3s^1 3p^5 3d^9 +$	$3s^1 3p^5 3d^9$	no
2p3p3p Auger	$2p^6 3s^2 3p^4 3d^9 +$	$3p^4 3d^9$	no
2p3s3d Auger	$2p^6 3s^1 3p^6 3d^8 +$	$3s^1 3d^8$	3s XPS
2p3p3d Auger	$2p^6 3s^2 3p^5 3d^8 +$	$3p^5 3d^8$	3p XPS
2p3d3d Auger	$2p^6 3s^2 3p^6 3d^7 +$	$3d^7$	3d XPS

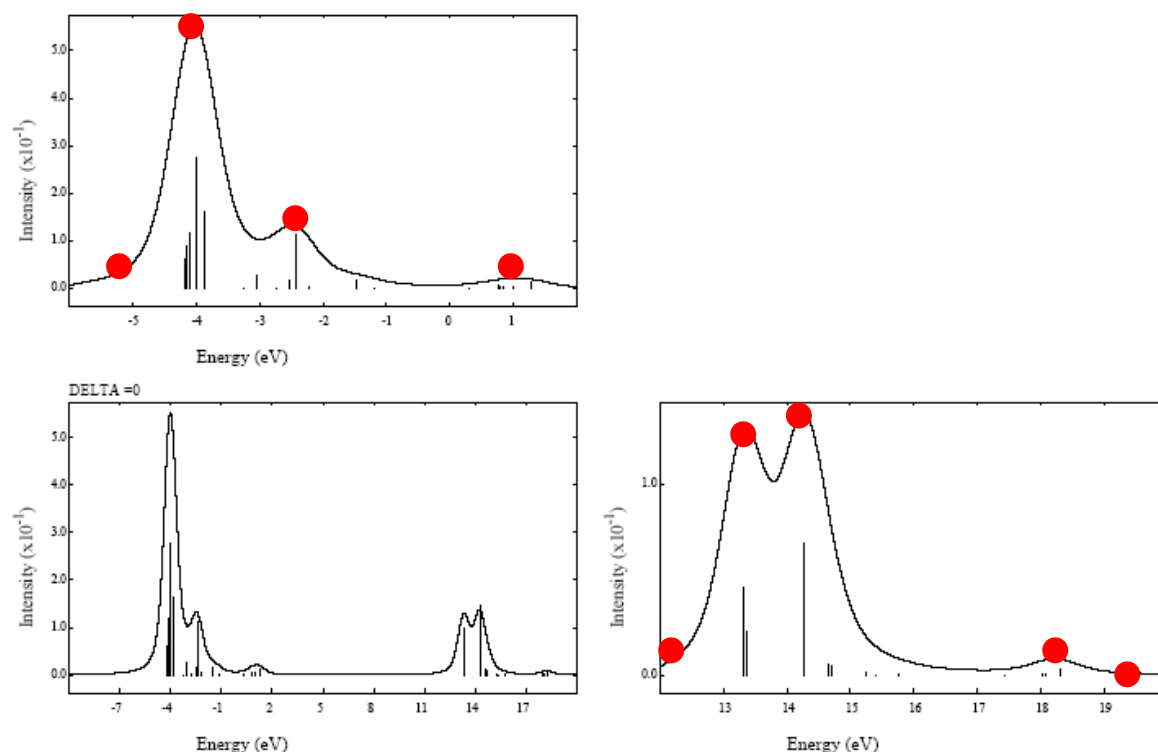
The table above gives all 6 possibilities to fill a 2p core hole from a combination of 3s, 3p and 3d electrons. The final states of the last three combinations (3s3d, 3p3d, 3d3d) can also be reached by direct photoemission. This means that at the 2p XAS excitation energy there will be two processes that start from the same ground state and reach the same final state, implying that they will interfere. This is the basis for resonant photoemission. Before the 2p XAS edge only direct 3p photoemission occurs, but at the edge a second channel is switched on that reaches the same final state: the resonant photoemission.

In contrast all Auger transitions that do not involve a 3d electron (3s3s, 3s3p and 3p3p) reach a final state that cannot be reached by direct photoemission. This implies that these channels are close before the 2p edge and are switched on at the 2p edge. No interference occurs at these resonant Auger transitions.

We can use the multiplet program to describe all these resonant photoemission and resonant Auger processes. The calculations are quite different from XAS and XPS calculations, because in addition to dipole transitions, we also have to calculate Auger matrix elements. Because the Auger process is an ionising experiment one needs at least two configurations for a decent description. This implies that the $3d^9 L$ state is added to the $3d^8$ state in the ground state. The intermediate and final states all have their second corresponding configuration added, for example the 2p3s3s resonant

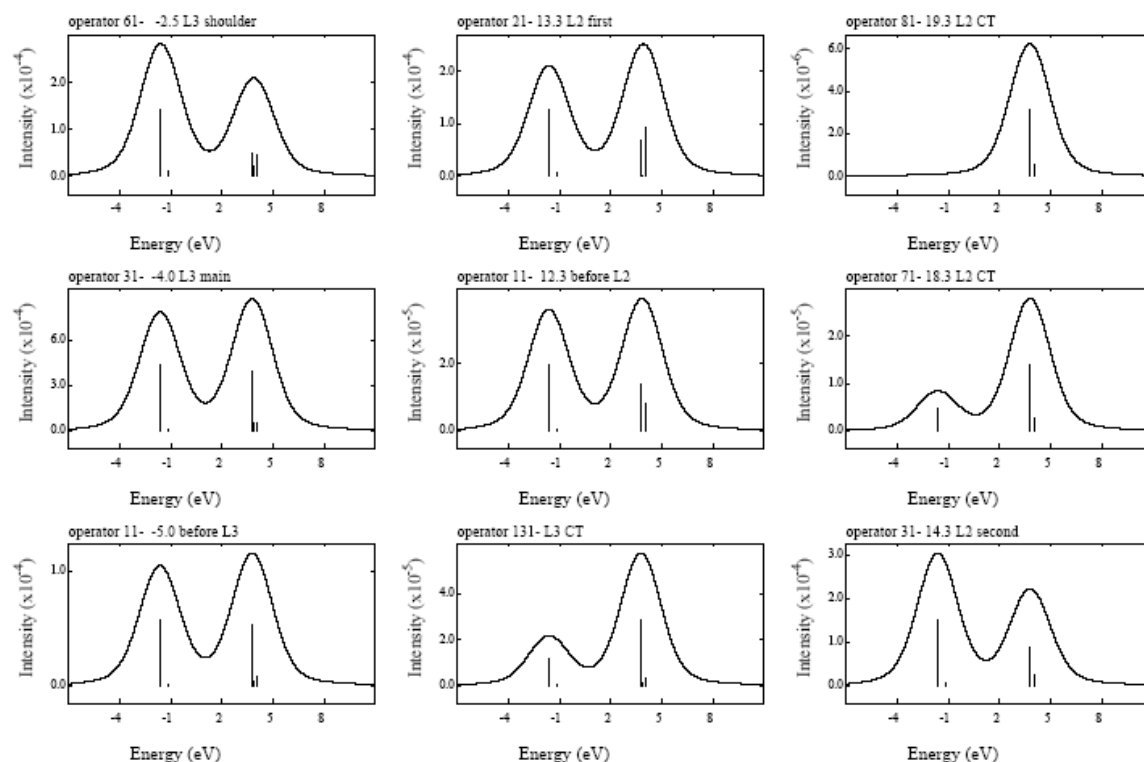
Auger final state is $(3s^0)3d^9 + (3s^0)3d^{10}\underline{L}$, etc. Before we calculate the resonant Auger spectra, we first re-calculate the 2p XAS spectral shape, which is centred at zero. This spectrum will be used to determine the energies at which the resonant Auger spectra will be calculated.

The files als9ni2x1.rcg, als9ni2x1.rac, als9ni2x1.ban and als9ni2x1.plo generate the following figure:



The bottom left shows the complete 2p XAS spectrum of NiO, between -10 and +20 eV. The top left shows a close-up of the L3 edge and the bottom right a close-up of the L2 edge. We will use this spectrum to set the energies at which the resonant Auger spectra will be excited. We have chosen 9 energies as indicated with the red circles, respectively -5.0 eV, -4.0 eV (=L3 peak), -2.5 eV (=L3 shoulder), +1.0 eV (=L3 charge transfer), 12.3 eV, 13.3 eV (=L2 first), 14.3 eV (=L2 second), 18.3 eV (L2 CT1) and 19.3 eV (L2 CT2).

The files als9pssp.rcg, als9pssp.rac, als9pssp.ban and als9pssp.plo generate the following figure:



This figure shows nine 2p3s3s resonant Auger spectra. It can be seen that all spectra consist essentially of two peaks, which vary in intensity ratio depending on the excitation energy. The experimental spectrum at resonance is similar to this calculation as has been explained in finazzi99a.pdf. In the case of 2p3s3s resonant Auger, it is relatively easy to assign the two peaks because the final state relates to $(3s^0)3d^9 + (3s^0)3d^{10}\underline{L}$. In this final state the 3s-states are empty, the ligand hole state is non-correlated the free electron is non-correlated, which leaves only 3d⁹ and 3d¹⁰, which both are essentially single peaks, i.e. 3d⁹ is only affected by the 3d spin-orbit coupling. Thus the two peaks present in the spectrum are respectively the 3d⁹ and the 3d¹⁰L peaks, or more precisely their bonding and anti-bonding combinations.

Chapter 5

PHOTOEMISSION AND AUGER

Before continuing with the more interesting spectra of the other resonant Auger and resonant photoemission spectra, we first discuss the new features of the inputfiles. The file als9pssp.rcg reads:

```

10      0      0      14      0      0      1      1  SPIN000000000 SHELL000000000 INTER0
0
1      4 1 14 2-10      00      9 00000000 0 8065.47800 00000000
P 6 S 2 D 8 P 0
P 5 S 2 D 9 P 0
P 6 S 0 D 9 P 1
Ni2+ 3d8
Ni2+ 2p5 3d9
Ni2+ 3s0 3d9 p
p5 3d09 -s0 3d9 p
-99999999.
10      0      0      14      0      0      1      1  SPIN000000000 SHELL000000000 INTER0
0
1      5 1 15 2-10      00      9 00000000 0 8065.47800 00000000
P 6 S 2 D 9 D 9 P 0
P 5 S 2 D10 D 9 P 0
P 6 S 0 D10 D 9 P 1
Ni2+ 3d9
Ni2+ 2p5 3d10
Ni2+ 3s0 3d10p
p5 3d10 -s0 3d10p
-99999999.
10      0      0      14      4      4      0      4  SPIN000000000 SHELL300000000 INTER1
0
1      2 1 12 1 10      00      9 00000000 0 8065.47800 00000000
D 8 D10
D 9 D 9
Ni2+ 3d8      4      .0000      12.2341      7.5981      .0002      .0000HR99999999
Ni2+ 3d9      2      .0000      .0002      .0000      .0000      .0000HR99999999
-99999999.
10      0      0      14      4      4      0      4  SPIN000000000 SHELL003000000 INTER3
0
1      5 2-15 2-10      00      9 00000000 0 8065.47800 00000000
P 5 S 2 D 9 D10 p 0
P 6 S 0 D 9 D10 p 1
P 5 S 2 D10 D 9 p 0
P 6 S 0 D10 D 9 p 1
Ni2+ 2p5 3d09      6      .0000      11.5072      .0002      7.7213      5.7874HR99999999
3.2914
Ni2+ 3s0 3d9 p      6 1000.0000      .0942      .0002      .0003      .0004HR99999999
p5 3d09 -s0 3d9 p 1      .19665      .00005      .00005      .00005      .00005HR99999999
Ni2+ 2p5 3d10      2      0.0000      11.5092      .0000      .0000      .0000HR99999999
Ni2+ 3s0 3d10p      2 1000.0000      .0002      .0000      .0000      .0000HR99999999
p5 3d10 -s0 3d10p 1      .19275      .00005      .00005      .00005      .00005HR99999999
-99999999.
-1

```

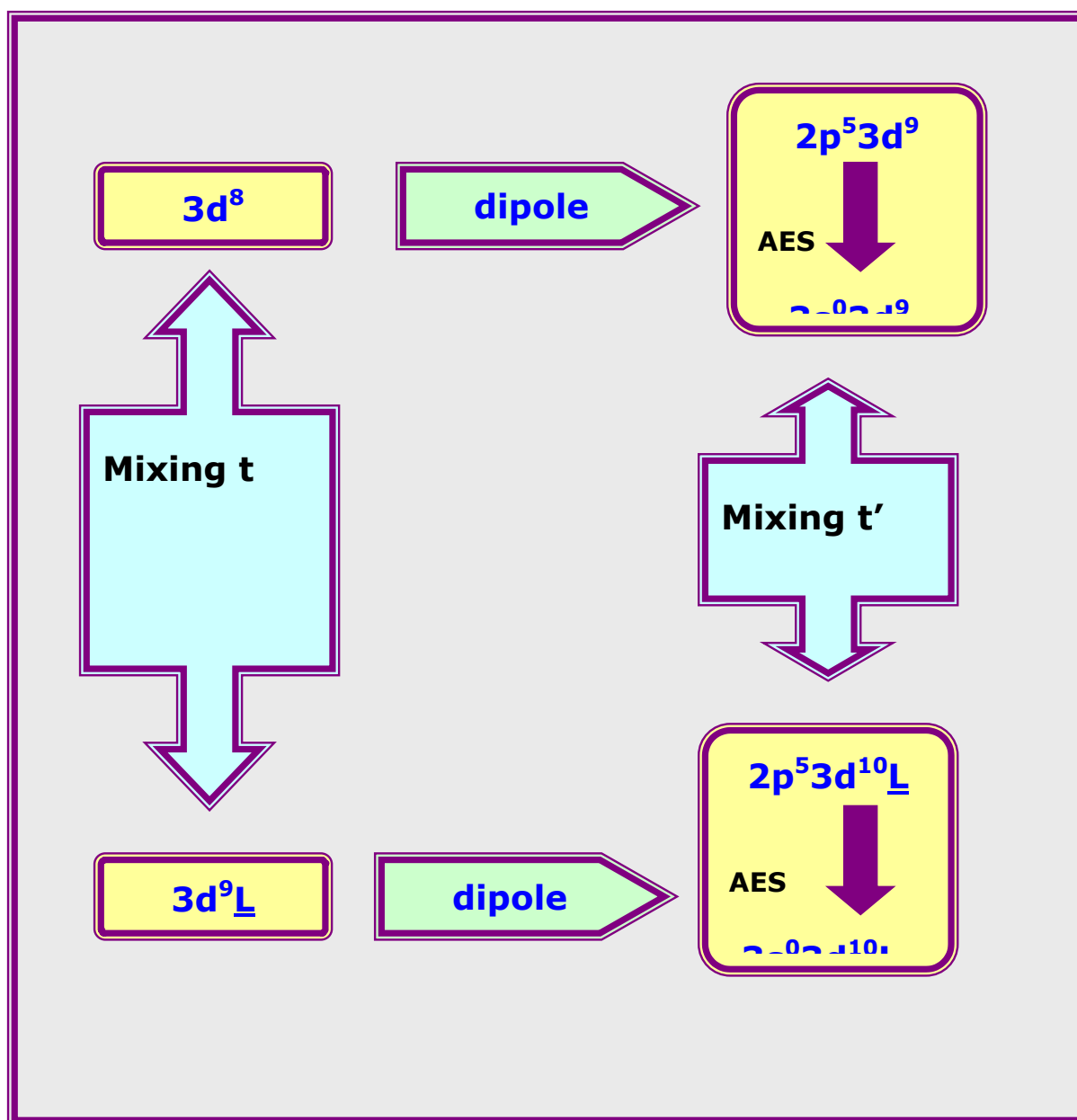
The main change with respect to XAS and XPS calculations is that there now are three (or more) configurations in each sub-calculation, instead of just the initial and final state. For example, the first dipole calculation involves:

```

P 6 S 2 D 8 P 0
P 5 S 2 D 9 P 0
P 6 S 0 D 9 P 1

```

These are respectively the initial $3d^8$ state, intermediate $2p^5 3d^9$ states and final $3s^0 3d^9 p$ states. There is an extra line that indicates that the intermediate and final states are mixed because they have the same symmetry. More details will be explained later. The coupling scheme can be given as:



The main change is in the fourth calculation, where the intermediate and final states are coupled. There are four configurations coupled:

P	5	S	2	D	9	D10	p	0
P	6	S	0	D	9	D10	p	1
P	5	S	2	D10	D	9	p	0
P	6	S	0	D10	D	9	p	1

The coupling between $2p^5 3s^2 3d^9$ and $3s^0 3d^9 e$ is in fact the Auger matrix element. The Auger matrix elements are given as additional inputlines. The line

p5	3d09	-s0	3d9	p	1	.19665	.00005	.00005	.00005	.00005	HR99999999
----	------	-----	-----	---	---	--------	--------	--------	--------	--------	------------

gives this Auger matrix element. In case of a $2p 3s 3s p$ Auger the matrix has the form $\langle 3s3s | 1/r | 2p p \rangle$. There is only one term in the evaluation of this matrix, which

is given as 0.1966 eV. This value is actually multiplied with 0.27 as indicated in the line with the reduction factors (more details later).

The file als9pssp.rac is equivalent to the XAS and XPS calculations, but the file als9pssp.ban is quite different. als9pssp.ban reads:

```
PRMULT
NCONF 2 2
N2 1
def EG2 = 3.5 unity
def EF2 = 2.0 unity
XMIX 2 2.2 -1.1
1 1 1 2
XMIX 2 1.8 -0.9
1 2 1 2
XHAM 2 1.0 0.7
4 1 1 1 2 2 1 2 2
TRAN 2 1 1 2 2
DIP 1.83761
AUGER
GAMMA 0.3
NO 1 CI 1 DIP 0.0
DEF EF2 = -4.5 unity
NOMEGA 20 ESTART -5.0 ESTEP 0.5
ENDAUGER
TRIADS
^1+ 1- 1- 0
^1+ 1- 2- 0
^1+ 1- ^1- 0
^1+ 1- ^0- 0
```

The beginning of the file till the line with TRAN is similar to an XAS calculation. In this particular case the mixing was chosen different for the initial state respectively the intermediate and final states, but this was also used in als9ni2x1.ban. Also the end of the file with the TRIADS is equivalent to XAS. In between there are some additional lines, starting with DIP.

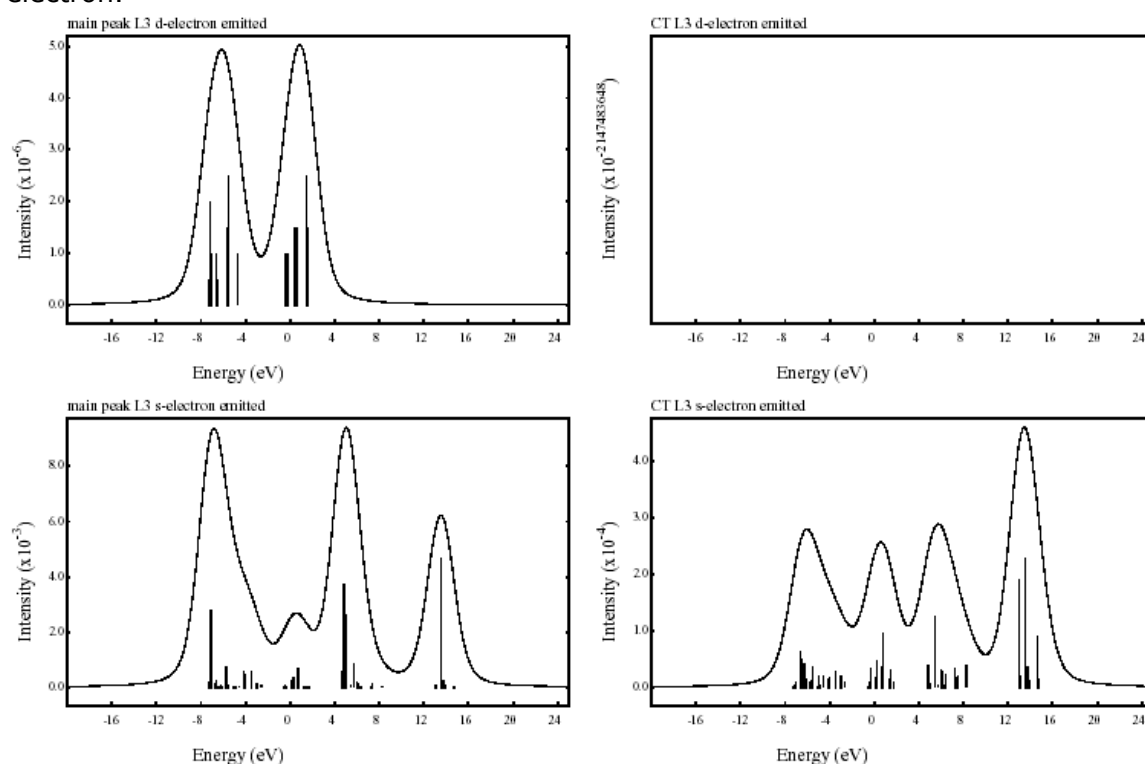
- **DIP 1.83761** gives the strength of the dipole transition (if present).
- **AUGER** tells that the Auger input starts
- **GAMMA 0.3** gives the lifetime broadening of the intermediate states, which is important for interference and line overlap effects.
- **NO 1 CI 1 DIP 0.0** gives the first Auger line, which has no direct channel (DIP 0.0). In the examples we give, there will always be just one Auger channel.
- **DEF EF2 = -4.5 unity** gives the energy position of the second configuration in the final state, after the Auger decay. Thus the energy of the second configuration is 3.5 eV in the initial state, 2.0 eV after XAS and -4.5 eV after XAS and Auger. The change in the Auger-step is similar to XPS as both are ionising experiments.
- **NOMEGA 20 ESTART -5.0 ESTEP 0.5** gives the energies in the XAS spectrum for which the resonant Auger spectrum is calculated. NOMEGA gives the number of points. ESTART is the start energy and ESTEP the energy difference to the next calculation. In this case there are 20 points calculated between -5.0 and +4.5 eV.

By adding these lines to the TTBAN inputfile the resonant Auger spectra are calculated that yield the spectra as given above. The final task is to plot the resonant Auger spectra. The direct photoemission spectrum is given with the operator 1-. Then a

number of operators are given starting from 11-, which gives the first resonant state, so in the present example at -5.0 eV in the 2p XAS spectrum. The next spectrum at -4.5 eV has the name 21-, etc.

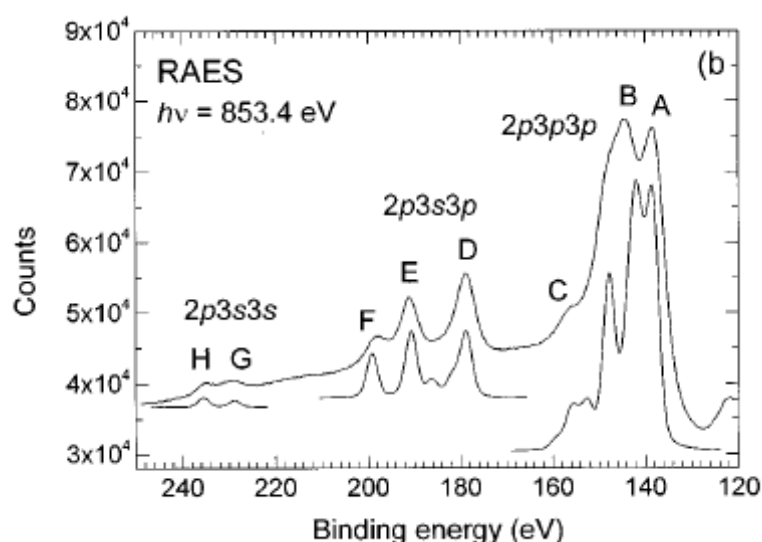
2p3s3p resonant Auger

All other resonant Auger are calculated similar to the 2p3s3s Auger. The files als9psps.rcg, als9psps.rac and als9psps.ban calculate 2p3s3p resonant Auger spectrum, where the excited electron has s-character. The Auger matrix elements have the form $\langle 3s3p | 1/r | 2p s \rangle$. The excited electron can also be of d-character and the files als9pspd.rcg, als9pspd.rac and als9pspd.ban calculate 2p3s3p resonant Auger spectrum, where the excited electron has d-character. The file als9pspd.plo plots the resonant Auger spectrum at -4 eV and at +1 eV for the emitted s-electron and d-electron.



The figure shows that the intensity of the spectrum where an s-electron is emitted is much higher (8×10^{-3}) than the emitted d-electron (5×10^{-6}), which is related to the much stronger Auger matrix elements (see below). The 2p3s3p resonant Auger spectrum is a rather rich multiplet spectrum separated over more than 20 eV. The final state has a 3s hole and a 3p-hole that couple to the 3d⁹ and 3d¹⁰L valence states. The reason is the very large exchange interactions between the 3s, 3p and 3d electrons. The 3s3p exchange is largest followed by the 3p3d (multiplet) exchange and the 3s3d exchange, as can be checked in the rcg-file below.

Comparison with experiment shows that this resonant Auger calculation gives approximately the correct spectral shape. The figure below shows the comparison between theory and experiment. Note that the 2p3s3p spectrum is reversed with respect to the spectra given above, i.e. the lowest energy states in the calculation have the lowest binding energy. For more details see finazzi99a.pdf.



P 5	S 2	P 6	D 9	D10	S 0				
P 6	S 1	P 5	D 9	D10	S 1				
P 5	S 2	P 6	D10	D 9	S 0				
P 6	S 1	P 5	D10	D 9	S 1				
Ni2+	2p5	3d09		6	.0000	11.5072	.0002	7.7213	5.7874HR99999999
	3.2914								
Ni2+	3s1	3p5	3d9	s 8	1000.0000	1.4002	.0002	14.3893	21.7354HR99999999
	13.5824		17.7844		10.8434				
p5	3d09	-s1	3p5	3d2	.19415	.23675	.00005	.00005	.00005HR99999999
Ni2+	2p5	3d10		2	0.0000	11.5092	.0000	.0000	.0000HR99999999
Ni2+	3s1	3p5	3d10s	3	1000.0000	1.4002	21.5044	.0004	.0004HR99999999
p5	3d10	-s1	3p5	3d2	.18995	.23485	.00005	.00005	.00005HR99999999

The bottom part of the als9psps.rcg file shows the coupling of the 2p53d9 state with its corresponding 3s13p53d9 state and as well with 2p53d10L and 3s13p53d10L. The largest Slater integral is the 3s3p exchange interaction (21.73 eV), followed by the G1-term of the 3p3d multiplet interaction (17.78 eV) and the 3s3d exchange interaction (13.58 eV). Note that the parameters in the rcg-file follow the sequence of unfilled correlated shells that are given. In the present case this are the 2p shell and the 3d shell for the intermediate states and respectively the 3s, 3p and 3d shells for the final state. For example the 3s13p53d9 configuration has as parameters respectively the 3p and 3d spin-orbit coupling, the 3p3d F2 Slater integral, the 3s3p exchange, the 3s3d exchange and the 3p3d G1 and G3 Slater integrals.

Calculate Auger matrix elements

One can observe in the rcg-file above that the Auger matrix elements end with a 5. These Auger matrix elements can be calculated with the TTRCN program. The file als9ni2p3s3p.rcn reads:

22	-9	2	10	1.0	5.E-08	1.E-11-2	130	1.0	0.65	45.0	0.50	0.0	0.70
28		Ni2+	3d8			3D08							
28		Ni2+	2p5	3d09		2P05	3D09						
28		Ni2+	3s1	3p5	3d9	s	3S01	3P05	3D0999S01				45.0
28		Ni2+	3s1	3p5	3d9	d	3S01	3P05	3D0999D01				45.0
-1													

The first line will be discussed later. The second line describes the ground state (3d8) and the third line the intermediate state (2p53d9). The next two lines describe the

possible final states of 2p3s3p Auger. The difference between the two lines is the character of the emitted electron, which is respectively s and d. The number at the end of the line is the energy of the emitted electron in Rydbergs. This number is approximately equal to the binding energy of the 2p electron minus the binding energies of 3s and 3p, i.e. $852 \text{ eV} - 110 \text{ eV} - 66 \text{ eV} = 676 \text{ eV} \approx 49 \text{ Rydberg}$. The exact number that is used in the rcn-file is not very important, as long as it is in the correct energy range.

The outputfile als9ni2p3s3p.rcn reads:

Ni2+ 3d8	4	0.0000	12.2341	7.5981	0.0832	0.0000	HR99999999
Ni2+ 2p5 3d09	6	860.1660	11.5072	0.1022	7.7213	5.7874	HR99999999
3.2914							
Ni2+ 3s1 3p5 3d9 s11	-9500.0000	1.4042	0.0942	14.3893	21.7354	HR99999999	
13.5824	0.0004	17.7844	10.8434	0.0004	0.0004		
Ni2+ 3s1 3p5 3d9 d18	-8500.0000	1.4042	0.0942	0.0002	14.3893	HR99999999	
0.0003	0.0003	0.0003	21.7354	13.5824	0.0004	17.7844	
10.8434	0.0004	0.0004	0.0004	0.0004	0.0004		
p5 3d09 -s1 3p5 3d2	0.19415	0.23675	0.00005	0.00005	0.00005	HR99999999	
p5 3d09 -s1 3p5 3d2	-0.01005	0.00615	0.00005	0.00005	0.00005	HR99999999	
s1 3p5 3d-s1 3p5 3d4	0.00005	0.00005	0.00005	0.00005	0.00005	HR99999999	
Ni2+ 3d8	Ni2+ 2p5 3d09	-0.18503	(2P//R1// 3D)	1.000	HR	36-100	
Ni2+ 3d8	Ni2+ 3s1 3p5 3d9 s	0.00000	(//R1//)	0.000	HR	0 0	
Ni2+ 3d8	Ni2+ 3s1 3p5 3d9 d	0.00000	(//R1//)	0.000	HR	0 0	
	-99999999.						
-1							

This file gives all the atomic parameters, including the Auger matrix elements (in green). The Auger matrix elements are given below the lines with the Slater integrals. It is found that the Auger matrix elements for an emitted s-electron are respectively 0.1941 and 0.2367. These numbers relate respectively to the R^1 and R^0_E terms. In case of an emitted d-electron, the R^1 and R^2_E terms have the values of -0.0100 and 0.0061. It is found that the values for an emitted s-electron are some 20 times larger, which effectively will give a much larger cross section for the emitted s-electron.

The selection rules for Auger transitions dictate that the parity of the initial and final state (in the Auger process) are the same. This implies that a 2p3s3p Auger transition must yield an even-parity emitted electron, i.e. s, d, etc. One might wonder if it would be possible to emit an electron of g-symmetry. (Further selection rules say that it is not possible, but if one is not sure one could try to calculate it). If one adds this line to the rcn-file

28	Ni2+ 3s1 3p5 3d9 d	3S01 3P05 3D0999G01	45.0
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the program will give only zero terms, indicating that this channel has no intensity, in other words is not allowed.

The nature of the emitted electron is important for the angular dependences of the Auger transitions, in particular in combination with the spin-polarization. A number of publications of van der Laan and Thole deal with this subject.

Resonant photoemission

If we look at the 2p3p3d resonant Auger the calculation procedure is equivalent to that described above. However, there is one additional feature, which is that the final state can also be reached by direct photoemission. Starting from a 3d8 ground state, one can follow two paths:

1. 3d8 > 2p5 3d9 > 3p5 3d8 +
2. 3d8 > 3p5 3d8 +

Because the initial and final state are equivalent, interference occurs between these two paths. This can be expressed mathematically as (taken from martensson99a):

$$w = 2\pi \sum_f \left| \langle f | V_i | g \rangle + \sum_m \frac{\langle f | V_A | m \rangle \langle m | V_f | g \rangle}{E_g - E_m - \frac{i\Gamma_m}{2}} \right|^2 \times \delta(E_f - E_g) \quad (1)$$

$|g\rangle$ indicates the 3d8 initial state, $|m\rangle$ the 2p53d9 intermediate state and $|f\rangle$ the 3p5 3d8 + final state. Because one first adds the matrix elements and then squares, interference effects occur.

Valence band resonant photoemission follows the same procedure:

1. 3d8 > 2p5 3d9 > 3d7 +
2. 3d8 > 3d7 +

The experimental results can be found in tjernberg96a.

An important ingredient in resonant photoemission that is not included in the calculations as discussed, is the interplay between so-called resonant and normal Auger channels. The calculations as given above only deal with resonant channels, i.e. channels that use a core hole resonance. In addition, there are so-called 'normal' Auger channels. These channels are not described by an x-ray absorption step to a localized state, but instead they are described by a transition to a 'delocalized' state which loses the excited electron (in the intermediate state). The paths could be written as:

resonant: 3d8 > 2p5 3d9 > 3d7 + A

normal: 3d8 > 2p5 3d8 + p > 3d6 + A + p

A distinguish is made between the emitted Auger electron (A) and the emitted photoelectron (p). The normal Auger path ends up with one less valence electron, but if charge transfer is included in the description, this difference becomes small as the final state ordering occurs. In principle one can describe both paths by the program using the scheme as given above. Effectively this is:

resonant: 3d8 > 2p XAS > 2p3d3d Auger

normal: 3d8 > 2p XPS > 2p3d3d Auger

Note that if one would detect the energy of the photoemission electron and the Auger electron simultaneously, one could obtain even more information. This is the mechanism of coincidence spectroscopy (see bartynski apecs.pdf for details).

Chapter 5

PHOTOEMISSION AND AUGER

More soon.