

## A Hands-on tutorial on CARD

F. d'Acapito, F. Benzi, 12/01/12

### Introduction

This tutorial is devoted to scientists wishing to learn using CARD. At present it is based on the CARD\_04 version. The exercise is based on data on a NiO layer (about 250 nm thick) deposited on an Al<sub>2</sub>O<sub>3</sub> substrate. The directory contains the following material:

File	Content
nio_0200.txt	Refl-exafs data collected at a nominal angle of 0.200 deg
nio_0311.txt	Refl-exafs data collected at a nominal angle of 0.311 deg
Nio_9000.txt	Reflectivity data collected at 9000 eV

In all cases the reflectivity is reduced to its absolute value and it will be care of the user to suitably treat the data of the beamline in order to obtain this.

This brief tutorial will permit the user to:

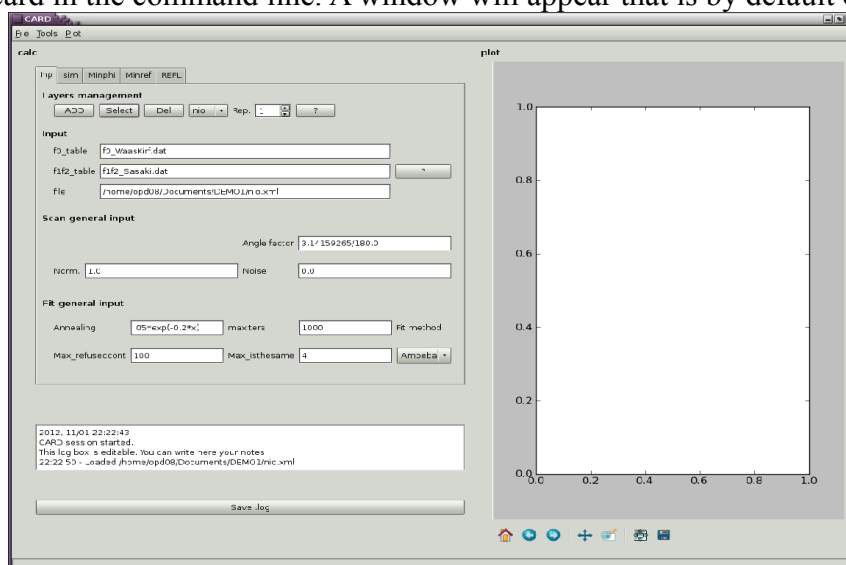
- create a model for the sample by fitting the reflectivity
- create the theoretical exafs paths for the two reflexafs spectra
- quantitatively analyze the spectra.

In the following the **shaded** text will refer to buttons or fields on the program windows.

*!! Careful. Look for "?" located in various points of the Grafical Interface, they give you useful hints. Look also at the bottom of the schreen as there is an integrated help (still in development). !!*

### Creating the layer model

Open the card code by double clicking on the icon in the installation window or by giving the command `./card` in the command line. A window will appear that is by default on the **Inp** menu.



Now we will create a model for the sample consisting in an alumina substrate and a NiO layer on it. Push the **ADD** button and create the substrate: in the popup window we will insert the following data

Layer name	sub
Thickness (Å)	0.0
Roughness (Å)	10.0
Density (g/cm <sup>3</sup> )	4.0
Composition	Al 2; O 3;

*!! Careful. If you insert a misspelled element name (Ak instead of Al) or forget the space between the element and the quantity (Al2 instead of Al 2) the window will close immediately. Rules for the layer name: a) the substrate layer name must be "sub" (without quotes) and b) the underscore "\_" character is forbidden.!!*

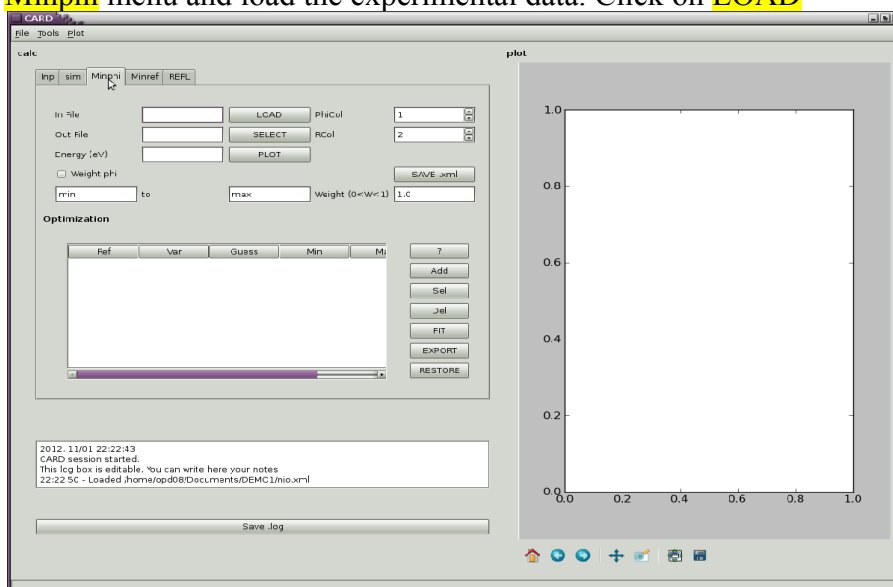
Click **OK** and the substrate is created. We can now insert the data for the NiO layer by clicking again **ADD**

Layer name	nio
Thickness (Å)	250.0
Roughness (Å)	10.0
Density (g/cm <sup>3</sup> )	6.67
Composition	Ni 1; O 1;

It is now time to save our work. Go in the menu of the top part of the window and click **File->Save** as and create an xml file, say nio.xml, in the DEMO directory.

### Fitting the reflectivity at fixed energy $R_E(\phi)$

Now go in the **Minphi** menu and load the experimental data. Click on **LOAD**



and choose the nio\_9000.txt file. Set also an output file for the fit as nio\_9000.out and set the **Energy** at 9000 eV. Click the **PLOT** button to see the experimental (blue) and theoretical (green) curves together.

We insert now the fitting variables. In general we have two sets of variables names one for the substrate and the layer and one for scan variables due to imperfections in the data collection. The variables for layer and substrate are "density", "roughness" and "thickness"(valid only for layers). The variable for the scan are the "angleshift" (accounts for possible errors in the absolute angle determination), "noise" (a constant background) and "norm" (a multiplicative term to compensate possible errors in the absolute reflectivity determination) . You can add the parameters by pushing the **Add** button, selecting the variable family (**scan**, **sub** or **layer**) and providing the variable name, **guess** (initial) value and **max** and **min** limits.

*!! Careful. Provide the variable name with quotes " ", otherwise the code could not save the .xml file correctly !!*

click on **SAVE .xml** to save your precious work done so far.

Now click on **FIT** and wait until the **FIT** button is back to a light color. Note that a window in the background informs you on the evolution of the fit. Now you can save again the xml file and export the fit results pushing the **EXPORT** button : save the file with a name like nio\_9000\_minphi.out.

File nio\_9000\_minphi.out

2012, 11/01 22:51:25

Fit results for /home/opd08/Documents/DEMO1/nio\_9000.txt

Method(s) used for the fit: Amoeba

No weight specified, setting default weight to 1.0

List of fit variables:

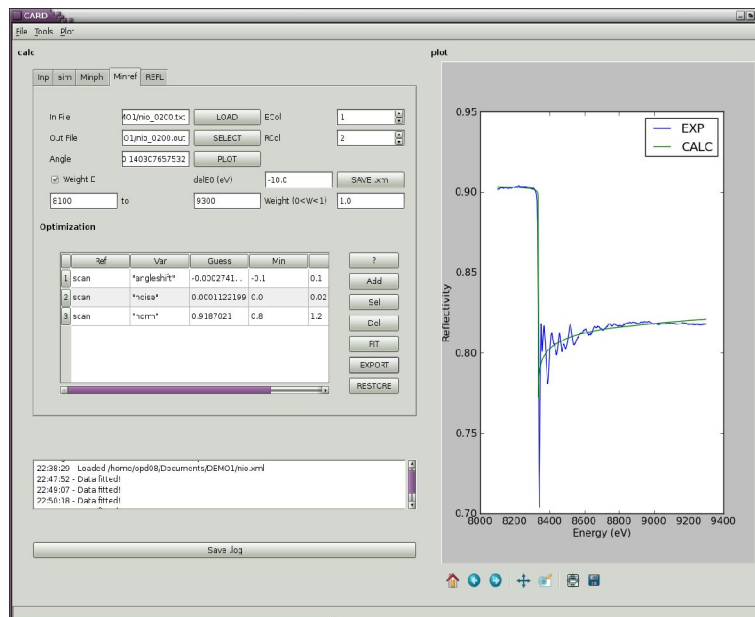
```
sub "roughness" 9.798327
nio "thickness" 217.2345
nio "roughness" 11.47892
nio "density" 5.613082
scan "angleshift" -0.00204928611607
scan "noise" 0.008260114
scan "norm" 1.027465
```

Output file: /home/opd08/Documents/DEMO1/nio\_9000.out

We possess now a model of the sample (in terms of thickness, roughness, ...) for the following fit of the reflectivity at fixed angle.

### **Fitting the reflectivity at fixed energy $R_{\phi}(E)$**

We click now on the **Minref** button and load the first reflexafs spectrum; namely nio\_0200.txt. Also in this case we will define an output file like nio\_0200.out. Put the nominal **Angle** value for this data set that is 0.2 deg in this case.



Clicking on **PLOT** you will see the comparison between the theoretical reflectivity and the experimental one. A shift in the energy position of the edge is possible and the **delE0** field can be used to compensate for this, in the present case a value of -10 eV is OK.

We will suppose that the differences in reflectivity are all due to errors in the scan so we will create a new fit with scan variables only. (Actually; there is no reason to change geometrical values for the sample like the thickness or the roughness whereas it is well possible that the absolute reflectivity were not correctly estimated in the RefLEXAFS spectrum as well as a possible background increase due to fluorescence...). Once the variables and their guess, min and max values determined save the project; in this case you must use a different name for the xml file (namely, nio\_0200\_minref.xml) otherwise you will lose the fit setup for the **Minphi** menu. Also here you can export the fit results by pushing the **EXPORT** button (put a name like nio\_0200\_minref.out).

File nio\_0200\_minref.out

2012, 12/01 01:11:48

Fit results for TEMP\_files/rebinned

Method(s) used for the fit: Amoeba

No weight specified, setting default weight to 1.0

List of fit variables:

scan "angleshift" -0.0594668885541

scan "noise" 0.0002810232

scan "norm" 0.9186448

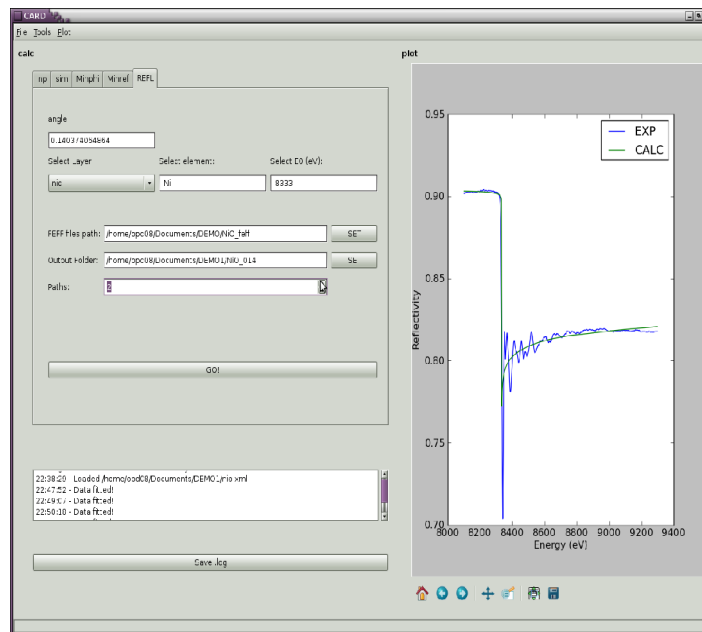
Output file: /home/opd08/Documents/DEMO1/nio\_0200.out

You will notice an appreciable change in the angular value that results to be at the origin of the previous disagreement in the reflectivity curves. The value is now set at about 0.14 deg.

### Creating the theoretical paths.

In order to proceed with this step you should have already calculated the standard theoretical paths for NiO with feff and saved in a suitable directory, say NiO\_feff.

Then push the **REFL** button and you will get this screenshot:



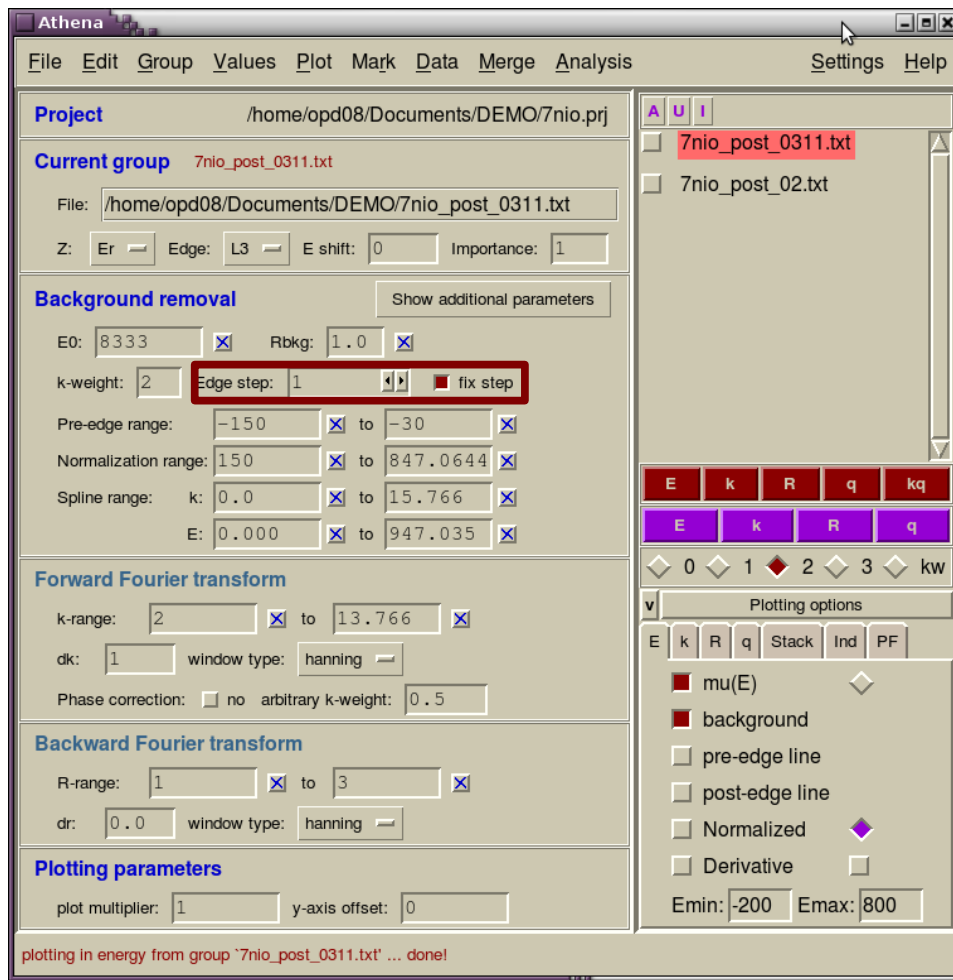
in the **angle** field you will find the data collection angle as calculated by the reflectivity fit. You have to select the layer where you element is (**Select layer**), the element and the edge position. Then you provide (**SET**) the program with the directory containing the conventional EXAFS paths (NiO\_feff) and with the name of the directory for the new paths (NiO\_014) . Finally you declare the number of **Paths** to recalculate (2 is sufficient for 1<sup>st</sup> and 2<sup>nd</sup> shell of NiO) and click on **GO!**

The calculation takes some time, wait until **GO!** Comes to a light color again.

You have now the tools for making a quantitative analysis of the RefLEXAFS data.

### Data extraction

The RefLEXAFS data extraction will be done with ATHENA. Remember that you will fit the oscillating part of the reflectivity that is *per se* an absolute quantity. For this, the only point to care of is to define a fixed **Edge step** equal to one.

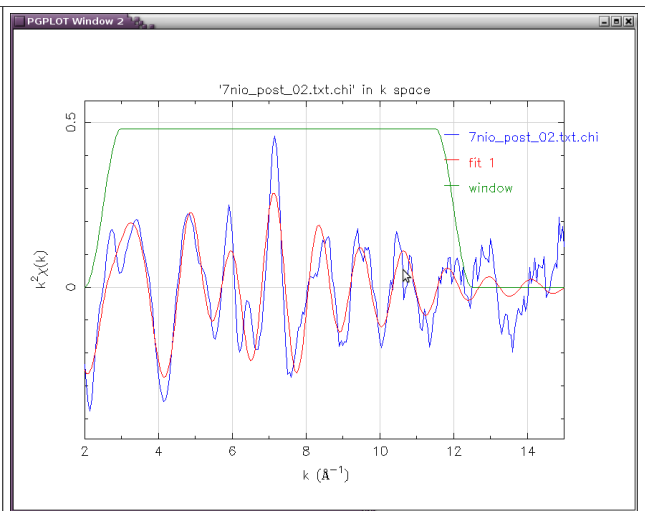
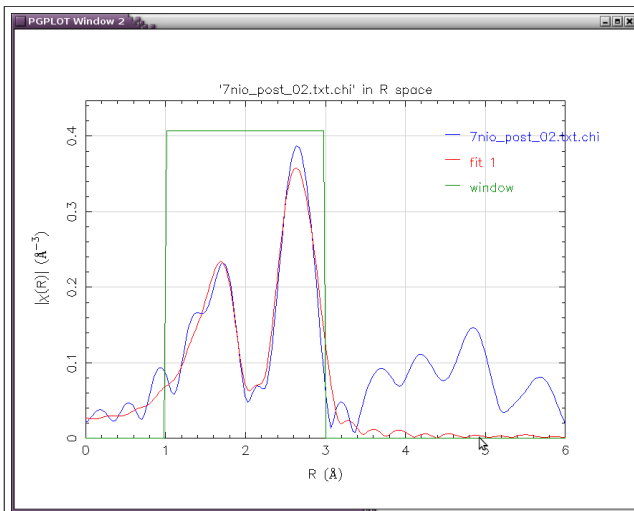


Also have a look to the E0 and fix it to the correct value if the code calculates a bad one. Check the correct subtraction of the atomic background and save the .chi function.

### Data fitting.

To carry out the last step we will use ARTEMIS. Under the FILE menu open the .chi file. In theory ARTEMIS makes the calculation of the theoretical paths in the Theory menu but we have already done this job. The trick to have ARTEMIS to open our paths is to open a New Feff input template under Theory and then choosing a blank page. Now you go under Paths and choose to Add a feff path and you will pick feff0001.dat and feff0002.dat under the directory NiO\_014 you created previously.

Here below you can find the results of the fit:



Sample	amp	$R_{\text{NiO}}$ (Å)	$\sigma^2_{\text{NiO}}$ (Å <sup>2</sup> )	$R_{\text{NiNi}}$ (Å)	$\sigma^2_{\text{NiNi}}$ (Å <sup>2</sup> )	DE0
nio_0200	1.05	2.08	0.0027	2.96	0.0075	4.29
nio_0300	1.06	2.07	0.0086	2.96	0.0079	3.91

Note that the results on the total reflection (nio\_0200) and high incidence angle (nio\_0300) perfectly compatible.