

Determining crystalline atomic positions using XAFS, a new addition to the UWXAFS analysis package

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XAFS and x-ray diffraction (XRD) are complementary structure determination techniques. The combination of XAFS and XRD can be used to determine the complete crystal structure when diffraction can not be refined. This is often the case at high pressures or high temperatures where there is limited access to the samples and energy dispersive x-ray diffraction is used. A new method to determine the atomic positions within the unit cell using EXAFS data with the programs RUNFIT and MKFIT is described. These programs systematically produce and test models for the XAFS data that are consistent with the diffraction results. The programs were written to solve the structure of two intermediate high pressure phases of AgCl, and are distributed with a working example.

Keywords: crystal structure; atomic positions; high pressure temperature; UWXAFS.

1. Introduction

XAFS and x-ray diffraction (XRD) are complementary x-ray techniques. Diffraction patterns give the average long-range symmetries of the crystal structure. This includes the space group and the unit cell dimensions. Often at high pressures or extreme temperatures diffraction has been used to determine the space group of the crystal structure and the unit cell dimensions but there is insufficient data to determine the atomic positions within the unit cell. This is because the extreme conditions limit the access to the samples and energy dispersive x-ray diffraction is used, losing peak intensity information due to the variation of the source intensity with wavelength. XAFS probes the radial distribution of atoms about the absorbing atom in a crystal structure, which is determined by the space group and unit cell dimensions as well as the position of the atoms within the unit cell. Therefore the combination of XAFS and XRD can determine the complete crystal structure. A new method to determine the atomic positions within the unit cell using EXAFS data, with the programs RUNFIT and MKFIT, is described. These programs systematically produce and test models for the XAFS data that are consistent with the diffraction results. The programs were written to solve the structure of two intermediate high pressure phases of AgCl (Kelly *et al.*, to be published), and are distributed with a working example of the second high pressure phase (HPPII) of AgCl. RUNFIT automates the process of creating and testing different models for the structure to find atomic positions that result in XAFS spectra that are consistent with the XAFS and XRD data. RUNFIT uses MKFIT which generates the expressions for the radial distance between the absorbing atom and the neighboring atoms in terms of the unit cell parameters and the atomic positions for the atoms within the unit cell.

RUNFIT and MKFIT are written in Perl and have currently been tested on unix/linux platforms. They are a new part of the UWXAFS analysis package (Stern *et al.*, 1995) and can be obtained by sending e-mail to stern@u.washington.edu.

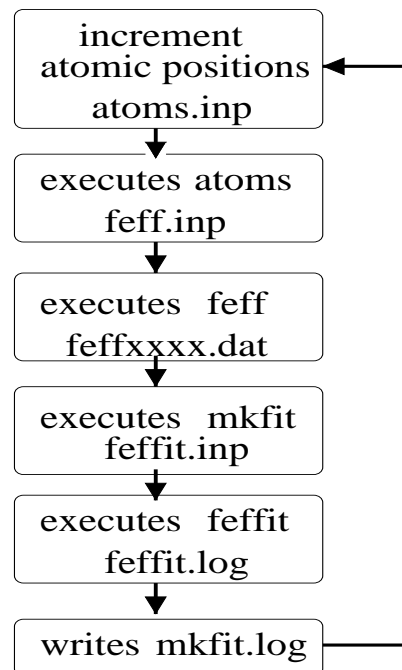


Figure 1 schematic of the RUNFIT process. RUNFIT automates the process of creating and testing XAFS models.

2. RUNFIT

RUNFIT automates the process of creating and testing XAFS models. To do this it executes several other UWXAFS programs. A schematic of the RUNFIT process is shown in Fig. 1. RUNFIT increments the atomic positions in a `atoms.inp` file, executes FEFF (Zabinsky *et al.*, 1995), makes a `feffit.inp` file, executes FEFFIT (Newville *et al.*, 1995) and then determines if the goodness-of-fit values are physically reasonable using user defined criteria. If so the fit is saved and the process starts over until all possible atomic positions have been sampled. For each set of atomic positions a small summary is written to a log file.

RUNFIT has several parameters that can be specified in the initialization, `runfit.inp`, file. A template `runfit.inp` can be generated by RUNFIT. Some of the options include: (1) Cut off values for the R-factor and reduced-chi-squared value (Newville, 1994; Stern *et al.*, 1995) that determine whether the fit is good, and (2) the incremental step size for the atomic positions as well as their ranges. A more complete list of options is given in the RUNFIT documentation.

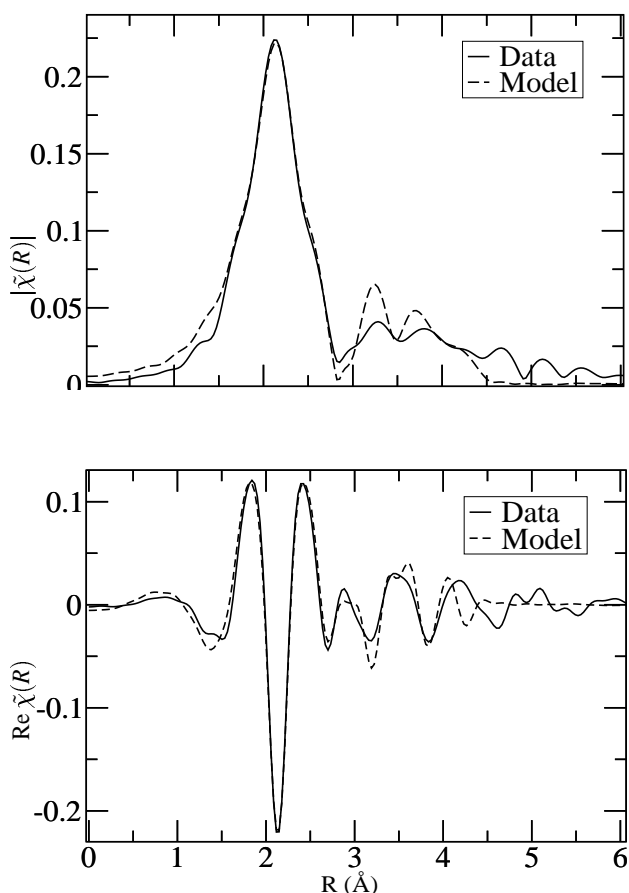


Figure 2
The magnitude, $|\tilde{\chi}(R)|$, and real part, $\text{Re } \tilde{\chi}(R)$, of the Fourier transform of the $\chi(k) \cdot k$ of a possible model run0002 and AgCl data for HPPII. Table 1 lists the Fourier transform parameters.

3. MKFIT

One major component of RUNFIT is the automatic generation of the `feffit.inp` file which contains the expressions for all path lengths included in the fit in terms of the unit cell dimensions and the atomic positions. This process is handled by a separate program MKFIT which is used by RUNFIT. By separating the increment of the atomic positions and creation of the `feffit.inp` file, MKFIT can be used independently. There are many situations where the unit cell dimensions and/or the atomic positions need to be slightly perturbed, for example at high pressures or high temperatures. In this situation MKFIT will write the expressions for all the path lengths given a partially completed `feffit.inp` or you can initialize MKFIT using a `mkfit.inp` file. Some of the options for RUNFIT are: (1) Guess or set values for energy shifts, σ^2 values and unit cell dimensions and (2) user defined expressions to determine one atomic position in terms of another as required by the space group. For example if two atoms within the unit cell are related according to (u,v,w) and $(u+0.5,v+0.5,w+0.5)$ then this information needs to be included so that only u,v , and w are determined in the fit. Also the paths to include in the fit may be specified using the maximum number of legs, the minimum amplitude ratio, and the maximum distance for the fit.

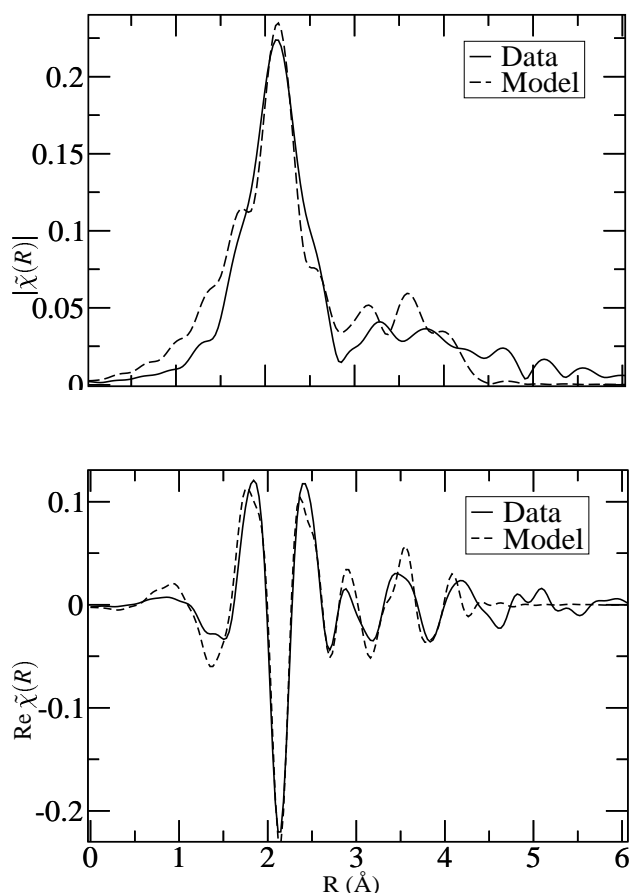


Figure 3
The magnitude, $|\tilde{\chi}(R)|$, and real part, $\text{Re } \tilde{\chi}(R)$, of the Fourier transform of the $\chi(k) \cdot k$ of a possible model, run0004, and AgCl data for HPPII. Table 1 lists the Fourier transform parameters.

4. Example: High Pressure Phase of AgCl

RUNFIT comes with a working example of a high pressure phase of AgCl. (Kelly *et al.*, to be published) The RUNFIT documentation details the initialization steps. Once the `runfit.inp` file has been set up, RUNFIT will try 10 different atomic positions and write a small note about each in a `runfit.log` file. All the fits that met the goodness-of-fit criteria are saved in the sub-directory called `saves`. The `feffit.log` files in this directory shows that FEFFIT found two minimum, `run0002.log` and `run0004.log`. Fig. 2 and Fig. 3 illustrates the data and model for both of these minimum. Table 1 lists the Fourier transform parameters and the degrees-of-freedom in the fit. Table 2 lists the goodness-of-fit values and the atomic positions for both of these models. The goodness-of-fit values are calculated by FEFFIT and their definitions can be found in the FEFFIT documentation (Newville *et al.*, 1995). Briefly, the values for χ^2 are often as large as several hundred because of the neglect of systematic errors. The final uncertainties of the fit parameters are increased to correct for the contribution of systematic errors by multiplying the initial error by χ^2_v . (Stern *et al.*, 1995)

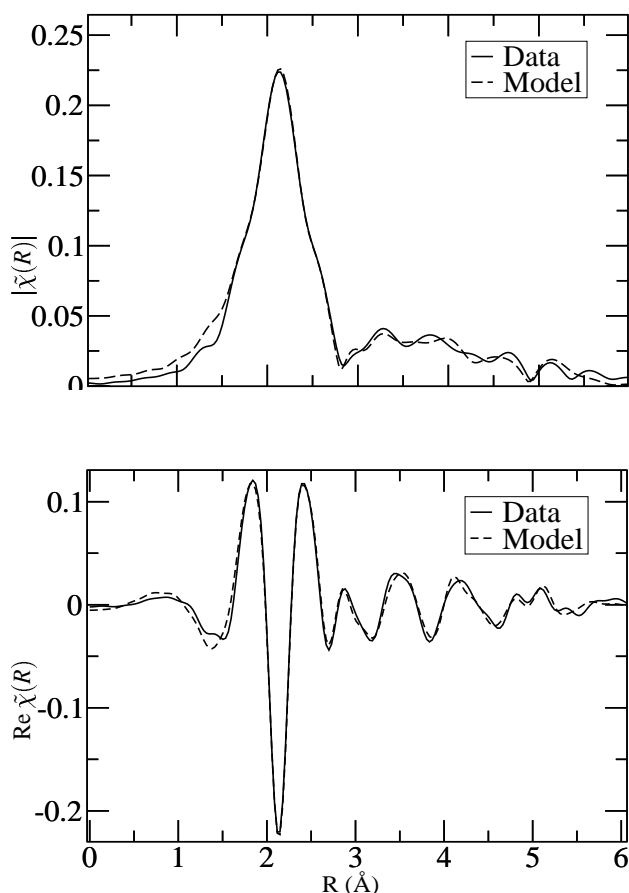


Figure 4
The magnitude, $|\tilde{\chi}(R)|$, and real part, $\text{Re } \tilde{\chi}(R)$, of the Fourier transform of the $\chi(k) \cdot k$ of the final model and AgCl data for HPPII. Table 1 lists the Fourier transform parameters.

Table 1
The data range, Δk , the fit range, d_r , the degrees of freedom in the fit, ν , the number of variables determined in the fit, N_{var} , and the number of independent points in the fit, N_{idp} . Both data sets were processed with k -weight = 1 in the Fourier Transform of the data and with the full width of the Hanning window sill, $dk=2$ (\AA^{-1}).

Model	Δr (\AA)	Δk (\AA^{-1})	N_{idp}	N_{var}	ν
MKFIT	[1.6 : 5.2]	[2.6 : 12.4]	24	7	17
final	[1.6 : 5.2]	[2.6 : 12.4]	24	13	11

The next step is to run ATOMS with these atomic positions and correct some of the gross approximations made by MKFIT. During this process the fit based on run0004 was abandoned because it did not give a reasonable fit to the data (χ^2_ν within two standard deviations of the fit found starting with model run0002). The final model is shown in Fig. 4 which is based on run0002. Table 1

list the Fourier transform parameters and the degrees-of-freedom in the fit. As shown in this table we needed to increase the number of variables from 7 used in the models by MKFIT to 13 in our final model. This is because RUNFIT works best with as few parameters as possible in the initial search for atomic positions. Table 2 list the goodness-of-fit values and the atomic positions for the final model. For this part of the analysis it was useful to use only MKFIT by itself to generate the `feffit.inp` file as described above.

Table 2
The best-fit values for the atomic positions, Ag1_1y and Cl2_2y, and the goodness-of-fit parameters for the two minimum found by RUNFIT, run0002 and run0004, and the final model.

Model	Ag1_1y	Cl2_2y	\mathcal{R}	χ^2_ν
run002	0.4009 ± 0.0008	0.1377 ± 0.0013	0.015	821
run004	0.3954 ± 0.0011	0.1573 ± 0.0020	0.030	1008
final	0.3997 ± 0.0013	0.1346 ± 0.0030	0.003	171

5. Is RUNFIT the right tool?

The use of RUNFIT will not result in a perfectly refined fit, see Fig 2 and Fig. 3. RUNFIT uses crude σ^2 values as determined by the Correlated Debye function with a single Debye temperature for each atom type. RUNFIT also uses crude energy shifts, one for each atom type independent of the distance from the core atom. These approximations mean that RUNFIT will only be able to find approximate solutions.

RUNFIT is ideal if the space group and unit cell dimensions are known from previous diffraction data, but there are a few atomic position variables that have yet to be determined. This is often the case at high pressures and high temperatures where there is limited access to the samples and energy dispersive diffraction is used losing the peak intensity information because of the variation of the source intensity with wavelength. Most of the atomic position variables will be related to each other as determined by the space group so that even if there are many atoms in the unit cell there are only a few unknown parameters. In this situation RUNFIT will systematically explore the parameter space for these atomic positions and save only a few possibilities.

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