

Modeling non-crystalline samples

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New Challenges and Solutions for XAS Data Analysis

Institute of Physics, Polish Academy of Sciences

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Introduction

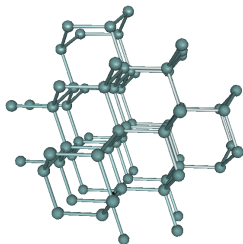
Earlier I demonstrated **ARTEMIS** by showing FeS_2 , which is a crystal. This allowed me to start with **ATOMS** and crystal data.

Atoms is just a tool

It is useful when it's useful.

In this short talk, I will suggest various ways to get started on samples that are not crystalline.

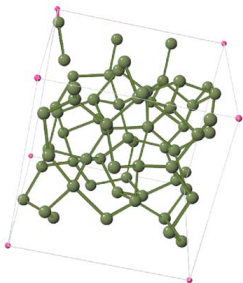
Crystalline and amorphous germanium



Ge crystallizes into an orderly, hexagonal close pack arrangement. Given EXAFS data on the crystalline material, it is fairly obvious how to begin: Run FEFF starting from the known crystal data.

```
space = f d 3 m
a      = 5.658
rmax   = 6.00
atoms
Ge     1/8  1/8  1/8
```

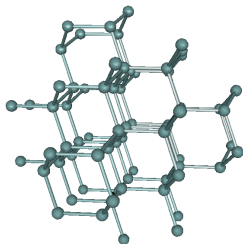
Amorphous Ge is a random continuous network.



aGe figure from V. Hugouvieux et al PRB 75, 104208 (2007)

DOI: [10.1103/PhysRevB.75.104208](https://doi.org/10.1103/PhysRevB.75.104208)

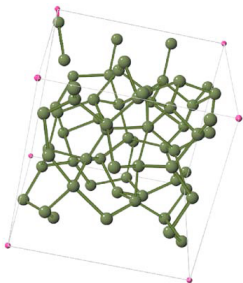
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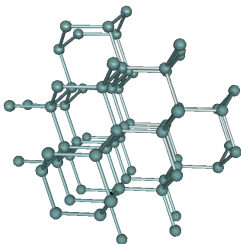
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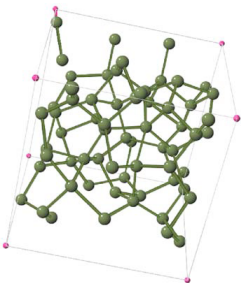
Do we have to run a molecular dynamics simulation just to then run FEFF?

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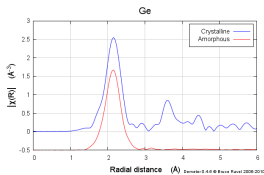
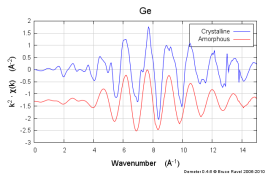
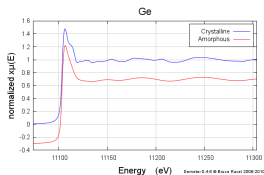
Amorphous Ge is a random continuous network.

Do we have to run a molecular dynamics simulation just to then run FEFF?

Happily, no.

Crytsalline and amorphous germanium

As always, let's start by looking at the data.

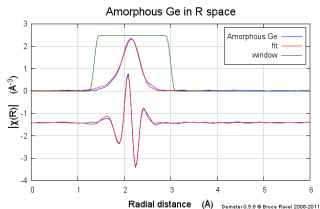
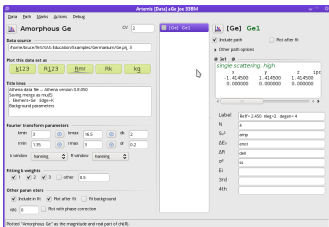


A random continuous network has a near-neighbor pair correlation nearly identical to its ordered counterpart. We see this behavior in our Ge data.

Fit to aGe

We import the data and the first path from the FEFF calculation on crystalline Ge.

We make a simple, first shell fitting model with terms for S_0^2 , ΔE_0 , ΔR , and σ^2 .



guess parameters:

amp	=	1.10	+/-	0.07
enot	=	3.94	+/-	0.75
delr	=	0.006	+/-	0.004
ss	=	0.00596	+/-	0.00040

We find that the bond length and coordination number for aGe is much the same as for cGe, while the disorder is a bit higher.

Molecule file formats

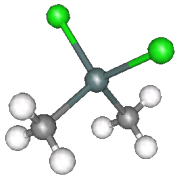
Just because a material is not a crystal does not mean that its structure is not known. Atomic structures of molecules from coordination complexes up to biological macromolecules are known from theory and experiment and are available in a variety of file formats.

FEFF needs a list of cartesian coordinates.

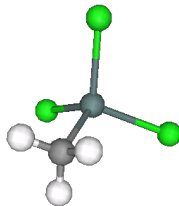
Sadly, the current version of ARTEMIS cannot help you convert a molecule file into a 'feff.inp' file, but it is not hard.

Methyl tin chloride

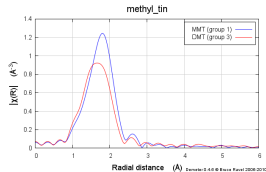
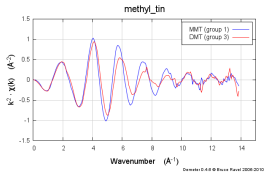
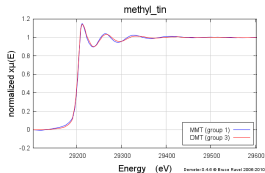
One of my standard teaching examples involves Sn K edge data on methyl tin chloride dissolved in an organic solvent.



Dimethyl tin dichloride



Monomethyl tin trichloride



Protein Data Bank file format

A bit of googling turned up a structure for dimethyl tin dichloride in the form of a [PDB file](#). It looks like this:

```
COMPND      5261536
HETATM      1  C1  LIG      1      -0.027      2.146      0.014      1.00      0.00
HETATM      2  SN2 LIG      1       0.002     -0.004      0.002      1.00      0.00
HETATM      3  C3  LIG      1       1.042     -0.716      1.744      1.00      0.00
HETATM      4  CL4 LIG      1     -2.212     -0.821      0.019      1.00      0.00
HETATM      5  CL5 LIG      1       1.107     -0.765     -1.940      1.00      0.00
HETATM      6 1H1  LIG      1       0.996      2.523      0.006      1.00      0.00
HETATM      7 2H1  LIG      1     -0.554      2.507     -0.869      1.00      0.00
HETATM      8 3H1  LIG      1     -0.537      2.497      0.911      1.00      0.00
HETATM      9 1H3  LIG      1       0.532     -0.365      2.641      1.00      0.00
HETATM     10 2H3  LIG      1       1.057     -1.806      1.738      1.00      0.00
HETATM     11 3H3  LIG      1       2.065     -0.339      1.736      1.00      0.00
END
```

The **red bits** are atomic species and cartesian coordinates — just what we need!

Feff6 input file

TITLE dimethyltin dichloride

HOLE 1 1.0 * Sn K edge (29200 eV), S0²

* mphase,mpath,mfeff,mchi

CONTROL 1 1 1 1

PRINT 1 0 0 0

RMAX 6.0

POTENTIALS

* ipot Z element

0 50 Sn

1 17 Cl

2 6 C

3 1 H

ATOMS

* x y z ipot

-0.027 2.146 0.014 2

0.002 -0.004 0.002 0

1.042 -0.716 1.744 2

-2.212 -0.821 0.019 1

1.107 -0.765 -1.940 1

0.996 2.523 0.006 3

-0.554 2.507 -0.869 3

-0.537 2.497 0.911 3

0.532 -0.365 2.641 3

1.057 -1.806 1.738 3

2.065 -0.339 1.736 3

- 1 Prepare 'feff.inp' boilerplate
- 2 Cut-n-paste the cartesian coordinates in the ATOMS list
- 3 Make a POTENTIALS list out the atomic species
- 4 The absorber **must** be potential #0, but it need neither be first in the ATOMS list nor be at (0,0,0)
- 5 The ATOMS list need not be in order of radial distance (or any other order)
- 6 This 'feff.inp' file can be imported directly into ARTEMIS

Now do a fit

Import each data set and one FEFF calculation into ARTEMIS. Use the relevant paths with each data set.

Artemis [Feff] Atoms and Feff

Name of this feff calculation: methyltin

Description

```
# dimethyltin dichloride
# This paths.dat file was written by Deuser 0.5.6
# The central atom is denoted by this token: @
# Cluster size = 6.00000 Angstroms, containing 10 atoms
```

Scattering Paths

Degen	Reff	Scattering path	Imp.	legs	Type
0000	2	2.1502 @ C @	2	2	single scattering
0001	2	2.3602 @ C @	2	2	single scattering
0002	6	2.7155 @ H @	2	2	single scattering
0003	12	2.9779 @ C H @	0	3	other double scattering
0004	6	3.2402 @ C H C @	0	4	dog-leg
0005	12	3.6055 @ H C @	0	3	other double scattering
0006	6	3.8055 @ C C H @	0	4	dog-leg
0007	2	3.9057 @ C C @	0	3	other double scattering
0008	8	4.0976 @ C @	0	3	other double scattering
0009	8	4.2710 @ C H @	0	3	other double scattering
0010	2	4.2874 @ C @	0	3	other double scattering
0011	2	4.3004 @ C @ C @	1	4	rattle
0012	2	4.3004 @ C @ C @	0	4	hinge
0013	16	4.4491 @ C H @	0	3	other double scattering
0014	4	4.4710 @ H H @	0	3	other double scattering
0015	12	4.4956 @ H H H @	0	4	dog-leg
0016	8	4.5104 @ C @	0	3	other double scattering

Artemis [Data] Data group 1

Dimethyl Tin

State source: Include path Plot other fit

Other path options

0 @

single scattering, high

χ	σ	μ	ρ
-2.212102	-0.024071	0.000000	0.000000
0.000000	-0.004000	0.000000	0.000000

Label: feff-2.3602 step-2 argon-2

N : 2

S_{eff} : 1

ΔE_{eff} : none

ΔR_{eff} : none

σ^2 : none

Δ : none

ΔR : none

Δ : none

Transfer related groups to plotting list

Artemis [Data] Data group 1

Monomethyl tin

State source: Include path Plot other fit

Other path options

0 @

single scattering, high

χ	σ	μ	ρ
-2.212102	-0.024071	0.000000	0.000000
0.000000	-0.004000	0.000000	0.000000

Label: feff-2.3602 step-2 argon-2

N : 3

S_{eff} : 1

ΔE_{eff} : none

ΔR_{eff} : none

σ^2 : none

Δ : none

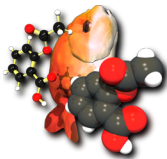
ΔR : none

Δ : none

Transfer related groups to plotting list

See the methyltin [example](http://bruceravel.github.io/XAS-Education/) and [presentation](http://bruceravel.github.io/XAS-Education/) available at <http://bruceravel.github.io/XAS-Education/>.

How could this be made better?

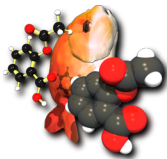


Open Babel (<http://openbabel.org/>) is a chemical toolbox that, among other things, translates between 98 different atomic structure file formats.

Integrating Open Babel with **FEFF** and **ARTEMIS**

- 1 Open Babel is written in C++
- 2 File format I/O is handled by small extension modules, also written in C++
- 3 Need a '**feff.inp**' I/O module written and donated to the Open Babel project
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See recent versions of Larch.

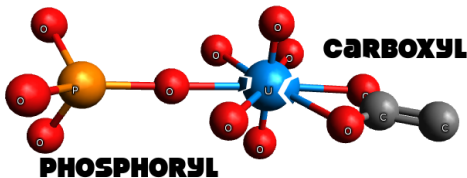
Matt and Mauro have made a lot of progress in this area in recent releases of Larch!!

Sorbed species

Here's a paper you should read

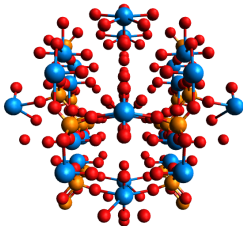
X-ray absorption fine structure determination of pH-dependent U-bacterial cell wall interactions, S.D. Kelly, et al. *Geochimica et Cosmochimica Acta* 66:22 (2002) 3855-3871 [DOI: 10.1016/S0016-7037\(02\)00947-X](https://doi.org/10.1016/S0016-7037(02)00947-X)

In it, the authors measure the pH dependence of the cell wall functional groups responsible for the absorption of aqueous UO_2^{2+} to *B. subtilis* from pH 1.67 to 4.80.

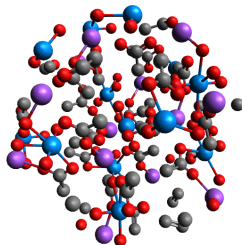


Using crystal analogs as Feff structures

Triuranyl diphosphate tetrahydrate contains a monodentate U-P moiety.

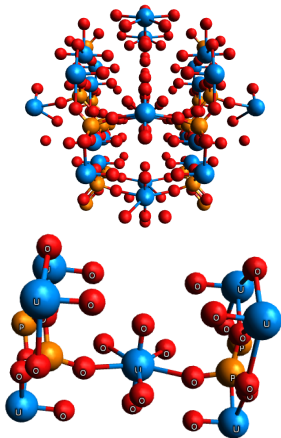


Sodium uranyl triacetate contains a bidentate U-C moiety.

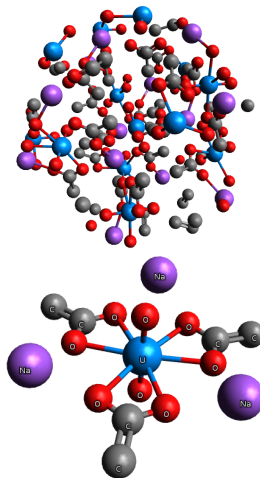


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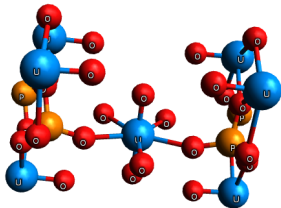


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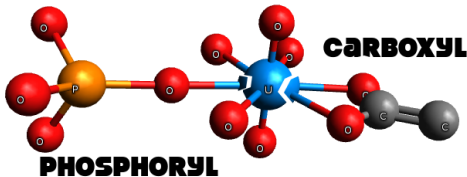
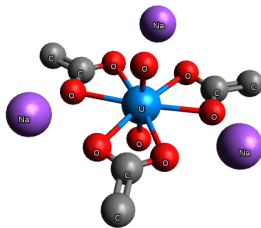


Choosing paths selectively from crystal analogs

The monodentate U-P from the crystal resembles the phosphoryl coordination structure we are looking for:



The bidentate U-C from the crystal resembles the carboxyl coordination structure we are looking for:



The moral of this story

The practical version

The structure used in the FEFF calculation doesn't need to be "perfect". Close is usually good enough to get started.

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The practical version

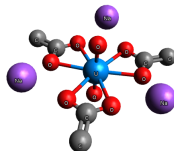
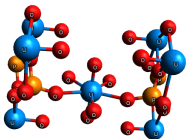
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The technical version

Small changes in local coordination do not result in large changes to the complex scattering factor ($F(k)$ and $\Phi(k)$ in the EXAFS equation). EXAFS **is** sensitive to small changes in local coordination, but this is due to the $\sin(2kR)$ term.

A high quality EXAFS analysis can suffer an approximation to the local coordination environment in the calculation of the theoretical fitting standards so long as the fitting model is parameterized in a way to capture the details of that local coordination.

Using crystal analogs in Artemis



Here's the outline:

- 1 Import each crystal structure into ARTEMIS
- 2 Run ATOMS, run FEFF
- 3 Examine the path list, select those SS and MS paths you need to describe your structure
- 4 Parameterize, fit

Take-home messages

Close is probably good enough

Running `FEFF` on a structure that resembles the actual data is usually adequate. More technically — the computation of the scattering factor is not acutely sensitive to atomic positions.

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Use your prior knowledge of your sample. If you have a hunch (even a weak suspicion) about the local configuration, you have enough to get started with `FEFF`.

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Some information is better than no information

At the end of the day, you may only be able to extract a little bit of information about the local configuration. Scientific progress is made in tiny steps.