FeS_2 EXAFS

The post-mortem on an Artemis demonstration

Bruce Ravel
Synchrotron Science Group
National Institute of Standards and Technology
&
Beamline for Materials Measurements
National Synchrotron Light Source II

October 13, 2023

Copyright

This document is copyright © 2010-2015 Bruce Ravel.

This work is licensed under the Creative Commons Attribution-ShareAlike License. To view a copy of this license, visit http://creativecommons.org/licenses/by-sa/3.0/ or send a letter to Creative Commons, 559 Nathan Abbott Way, Stanford, California 94305, USA.

You are free:

- **to Share** — to copy, distribute, and transmit the work
- **to Remix** — to adapt the work
- to make commercial use of the work

Under the following conditions:

- **Attribution** – You must attribute the work in the manner specified by the author or licensor (but not in any way that suggests that they endorse you or your use of the work).
- **Share Alike** – If you alter, transform, or build upon this work, you may distribute the resulting work only under the same, similar or a compatible license.

With the understanidng that:

- **Waiver** – Any of the above conditions can be waived if you get permission from the copyright holder.
- **Public Domain** – Where the work or any of its elements is in the public domain under applicable law, that status is in no way affected by the license.
- **Other Rights** – In no way are any of the following rights affected by the license:
  - Your fair dealing or fair use rights, or other applicable copyright exceptions and limitations;
  - The author's moral rights;
  - Rights other persons may have either in the work itself or in how the work is used, such as publicity or privacy rights.
- **Notice** – For any reuse or distribution, you must make clear to others the license terms of this work.

This is a human-readable summary of the Legal Code (the full license).

The amplitude parameter

The amplitude parameter evaluates to something around 0.7 in the FeS_2 fit. This is at the low end of what is expected[1] for an S_0^2 parameter. Lots of things are correlated with amplitude:

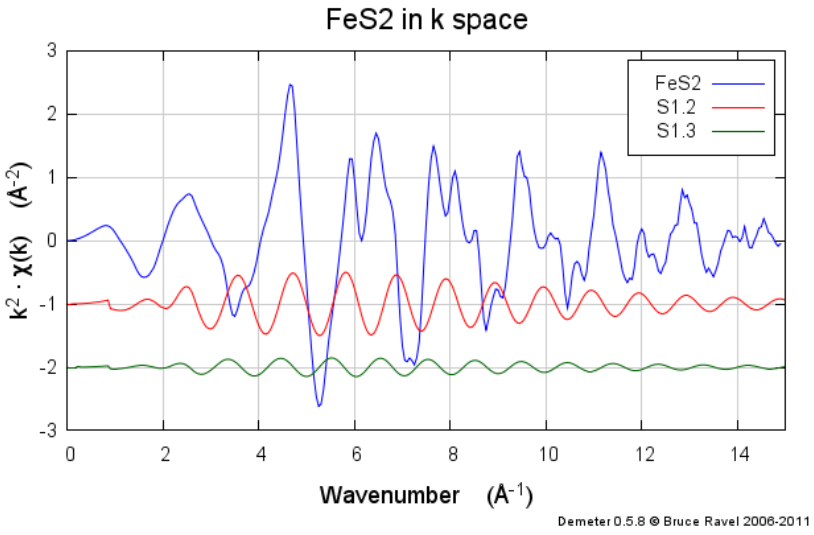
1. Coordination number, although this is a pure standard, so it is unlikely that coordination numbers are different from what we expect
2. Sample preparation: I do not know the provenance of these data. (They were taken from an on-line XAS data library.[2]) If the sample was not homogeneous, that would attenuate the amplitude[3] by the "pinhole efffect".
3. Again, without knowing the provenance, I cannot comment on the linearity of the detectors or any other aspect of the measurement.

Conclusion

A result of ~ 0.7 for amplitude seems acceptable.

1. G.G. Li, F. Bridges, & C.H. Booth *X-ray-absorption fine-structure standards: A comparison of experiment and theory*, Phys. Rev. B **52**:9 (1995) pp 6332-6348. DOI: 10.1103/PhysRevB.52.6332
2. http://cars9.uchicago.edu/~newville/ModelLib/search.html
3. K.-Q. Lu & E.A. Stern, *Size effect of powdered sample on EXAFS amplitude*, Nuclear Instruments and Methods **212**:1-3 (1983) pp 475-478, DOI: 10.1016/0167-5087(83)90730-5

The σ^2 constraint on the 2nd and 3rd shell S



Here we see the contribution in k of the scattering from the 6 S atoms in the 2nd shell and the 2 S atoms in the 3rd shell.

These shells are separated in distance by 0.15 Å, which is just enough to have them contribute almost completely out of phase.

This is the reason that the σ^2 parameter for the 3rd shell is so unreliable (indeed, negative when floated independently). The fit was relatively insensitive to that parameter because it could reduce the 2nd shell σ^2 to compensate for the unphysically small σ^2 from the 3rd shell.

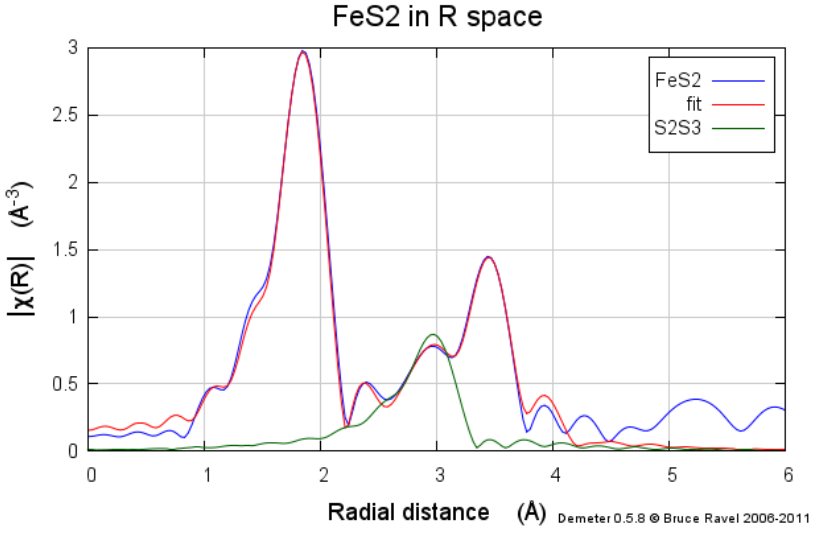
Conclusion

While it is certainly unphysical to constrain these two σ^2 parameters, the fit is more defensible with this constraint.

That σ^2 constraint examined in detail

Plot the data along with a VPath (i.e. the sum of two or more regular paths) constructed from the 2nd and 3rd shell S atoms.

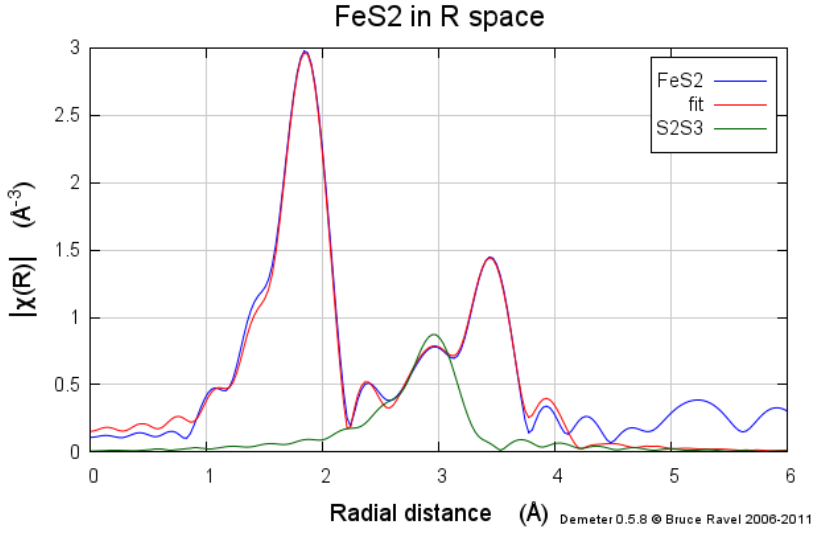
`def ss3 = ss2`




```
Number of variables          : 6
Chi-square                   : 6104.705744295
Reduced chi-square           : 493.543240341
R-factor                     : 0.009268899

ss2    =   0.00332806    # +/-   0.00130826
ss3    :=  0.00332806    # [ss2]
```

guess both ss2 and ss3




```
Number of variables          : 7
Chi-square                   : 5756.383603039
Reduced chi-square           : 506.316510008
R-factor                     : 0.009218088

ss2    =   0.00270523    # +/-   0.00164548
ss3    =   0.00014725    # +/-   0.00367061

correlation:  ss3 & ss2  -->  0.8050
```

The σ^2 constraints on the MS paths

The σ^2 parameters for the three paths involving collinear MS among the absorber and the 1st shell S atoms are all correct.*

The σ^2 parameters for the non-collinear MS paths are rather hokey approximations. The problem is that we don't have a good model to account for the effects on σ^2 of all the legs of the path nor of the disorder in scattering angle. I worry about introducing a new fitting parameter to account for a rather small effect in the data. We need to approximate.

Assertion

The σ^2 constraints for the triangle MS paths are non-physical approximations, but are a better solution than floating one or more new parameters in the fit.

* E.A. Hudson et al., *Polarized x-ray-absorption spectroscopy of the uranyl ion: Comparison of experiment and theory*, Phys. Rev. B **54** (1996) pp. 156-165 DOI: 10.1103/PhysRevB.54.156

The fourth shell S

Because the σ^2 for the 4^{th} shell S atom is so large, we see no improvement to the fit by introducing this scatterer.

Why is its σ^2 so large?

That's hard to say without help from theory, but clearly the relative positions of the absorber and this rather distant atom have a large thermal disorder.

Conclusion

It is safe to exclude this scatterer from the fit. Indeed, the fit is improved by not having its frail σ^2 parameter in the fit.

It would be interesting to measure this material at 10 K to see if the signal from this distant atom could be observed.

The remaining MS paths

Nine of the first 15 paths from the FEFF calculation were included in the fit. The remaining 6 paths are MS paths with small amplitudes. We got a sensible fit with a model which excluded these paths. It would be a good exercise to figure out a sensible parameterization of their σ^2s, include them in the fit, and determine if the fit is improved by having them.

Conclusion

It was safe to exclude these paths, but this should be verified by examining the fits with and without those paths.

The parameterization of ΔR

FeS_2 is a cubic crystal. In this case, there are only two parameters that determine the locations of **all** the atoms in the cluster – the lattice constant a and the position of the S atom in the unit cell. For now, we neglect the effect of the position of the S atom.

Why is the parameterization that sets $\Delta R = \alpha \cdot R_{eff}$ acceptible for all paths?

- The distance between *any two atoms in a cubic crystal* is some geometrical factor multiplied by the lattice constant. That factor depends on the positions of the atoms in the unit cell, but is a pure number.
- Thus, from the FEFF calculation, $d_{eff}(i,j) = C_{ij} \cdot a_0$ for any two atoms i and j
- We consider an isotropic expansion (or contraction) of the unit, which is reasonable for a cubic lattice that does not undergo a phase transition. So $a = (1 + \alpha) * a_0$.

$$
\begin{aligned}
d_{ij} &= d_{eff}(i,j) + \Delta d(i,j) \\
&= C_{ij} \cdot a \\
&= C_{ij} \cdot (1 + \alpha) \cdot a_0 \\
&= C_{ij} \cdot a_0 + C_{ij} \cdot \alpha \cdot a_0
\end{aligned}
\qquad
\begin{aligned}
\therefore\ \Delta d(i,j) &= C_{ij} \cdot \alpha \cdot a_0 \\
&= \alpha \cdot d_{eff}(i,j)
\end{aligned}
$$

Conclusion

$\alpha \cdot d_{eff}$ works for all legs of any SS or MS path in a cubic crystal (if there are no internal degrees of freedom). The R of a path is the sum of d for each leg, thus ΔR for a path is the sum of Δd for each leg.

*This trick is **only** valid for a cubic crystal.*

Improving on the parameterization of ΔR

In the crystal data for FeS_2, the S atom is at position (0.384, 0.384, 0.384), or $(\frac{3}{8}+\delta, \frac{3}{8}+\delta, \frac{3}{8}+\delta)$, where $\delta = 0.009$.

The effect of changing δ can be incorporated into the math expressions for ΔR for any path that includes a S atom. Doing so is beyond the scope of this document.

Exercise for the reader

Examine the `'feff.inp'` file for FeS_2. Think about how to incorporate the effect of δ into a fit.

Correlations

We have a pretty robust set of parameters in our fit. Only two of the correlations are above 60%.

ΔE_0 and α This correlation is about 86%. That is reasonable. Those are the only two parameters effecting the phase of the fit. This is a common level of correlation for such parameters.

1^{st} shell σ^2 and amplitude This correlation is about 81%. Again, this is pretty common for two things that have such an effect on overall amplitude of the fit.

Conclusion

The correlations we see are within acceptable limits.

The happiness "parameter"

Always remember

Happiness is a semantic parameter and should NEVER be reported in a publication – NEVER!

We have decades of knowledge of how the parameters of an EXAFS fit should behave. "Happiness" attempts to encode that general knowledge into a single, non-statistical, entirely semantic parameter.

- The $\mathcal{R}$-factor should be small. An $\mathcal{R}$-factor below 0.02 gives no penalty. Above that, the penalty scales linearly to some maximum.
- A penalty is assessed if more than 2/3 of the number of independent points are used.
- A penalty for each Path with a negative S_0^2 or σ^2 value.
- A penalty for each E_0, ΔR, or σ^2 path parameter that is "too big".
- A penalty is assessed for each correlation above 0.95.
- A penalty is assessed for each non-zero restraint.

The evaluation of the happiness is tunable via configuration parameters.