

# EXAFS Phase Shifts

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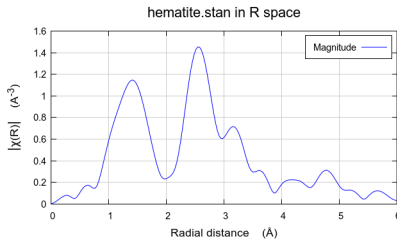
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# The EXAFS Phase Shift in Hematite

Here is  $\tilde{\chi}(R)$  for hematite,  $\text{Fe}_2\text{O}_3$ .



Hematite has a known crystal structure\* with Fe in a six-coordinated oxygen octahedron. There are 3 near neighbor oxygen atoms at 1.95  $\text{\AA}$  and 3 others 2.12  $\text{\AA}$ .

Why is the first peak in  $\tilde{\chi}(R)$  at about 1.4  $\text{\AA}$  when the nearest neighbor is at 1.95  $\text{\AA}$ ?

\*R.L. Blake, R.E. Hesseck, T. Zoltai, L.W. Finger American Mineralogist 51 (1966) 123-129, *Refinement of the hematite structure*

# EXAFS Equation

Here's the EXAFS equation:

$$\chi(k, \Gamma) = \frac{(N_{\Gamma} S_0^2) F_{\Gamma}(k) e^{-2\sigma_{\Gamma}^2 k^2} e^{-2R_{\Gamma}/\lambda(k)}}{2 k R_{\Gamma}^2} \sin(2kR_{\Gamma} + \Phi_{\Gamma}(k)) \quad (1)$$

$$\chi_{\text{theory}}(k) = \sum_{\Gamma} \chi(k, \Gamma) \quad (2)$$

$$R_{\Gamma} = R_{0,\Gamma} + \Delta R_{\Gamma} \quad (3)$$

$$k = \sqrt{2m_e(E_0 - \Delta E_0)/\hbar^2} \approx \sqrt{(E_0 - \Delta E_0)/3.81} \quad (4)$$

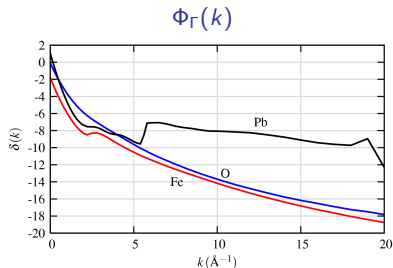
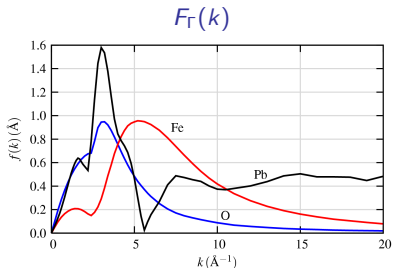
The oscillatory term is a function not of  $2kR$ , but of  $2kR + \Phi(k)$ .

The integral that makes  $\tilde{\chi}(R)$  is usually done over  $2k$ , i.e.

$\tilde{\chi}(R) = \int d(2k) k^{kw} \cdot \chi(k)$ . This makes  $\tilde{\chi}(R)$  look somewhat like a radial distribution function with peaks near sensible values of  $R$  (half-path-length), rather than  $2R$  (full-path-length).

# Scattering Amplitudes and Phase Shifts

Remember that the complex scattering function (for which  $F(k)$  is the amplitude and  $\Phi(k)$  is the phase) is structured and Z-dependent. Here are some representative examples for elements from different rows of the periodic table.

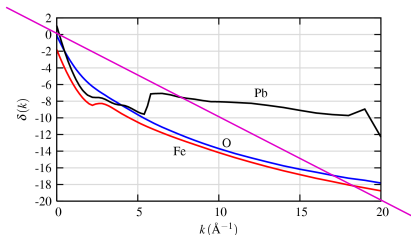


Very heavy elements have a discontinuity in  $\Phi(k)$ , like Pb at about  $5.5 \text{\AA}^{-1}$ .

Lighter scatterers, like O and Fe, have fairly smooth phase functions.

# Examining the Phase Function

The phase functions for the lighter elements are valued near 0 at  $k = 0 \text{ \AA}^{-1}$  and decrease to almost 20 at  $k = 20 \text{ \AA}^{-1}$ . To some level of approximation, these phase functions can be described by a line of slope -1, i.e.  $\Phi(k) \approx -1 \cdot k$



Using that crude approximation, the oscillatory term of the EXAFS equation is  $\sin(2kR - k) = \sin\left(2k \cdot \left(R - \frac{1}{2}\right)\right)$ . When the integral is done over  $d(2k)$ , the first peak in the resulting  $\tilde{\chi}(R)$  shows up around  $(R - \frac{1}{2}) \text{ \AA}$ .

# This is why the first peak is shifted inward

Obviously, the approximation of  $\Phi(k)$  as a straight line is inaccurate. The peak shift is not exactly  $\frac{1}{2} \text{ \AA}$ . And for heavier scatterers, the approximation is even worse.

But this explains in a hand-waving sense why the peaks are shifted to lower  $R$  in  $\tilde{\chi}(R)$ .

This is yet another reason why  $\tilde{\chi}(R)$  is **NOT** a radial distribution function.