Solid State Spectroscopy – Problem Set 7

Due date: June 29th, 2015

Problem 5.1 EXAFS Study of Mn/Fe substitution in Y(Mn$_{1-x}$Fe$_x$)$_2$O$_5$

From article « EXAFS, XANES, and DFT study of the mixed-valence compound YMn$_2$O$_5$: site-selective substitution of Fe for Mn » - F. Wunderlich et al., Phys. Rev. B ***82*** *014409 (2010).*

A- Parent Compound

YMn$_2$O$_5$ is a multiferroic material: at low temperature it presents simultaneously a magnetic order and a ferroelectric polarization. The coupling between the two types of order makes it potentially interesting for applications.

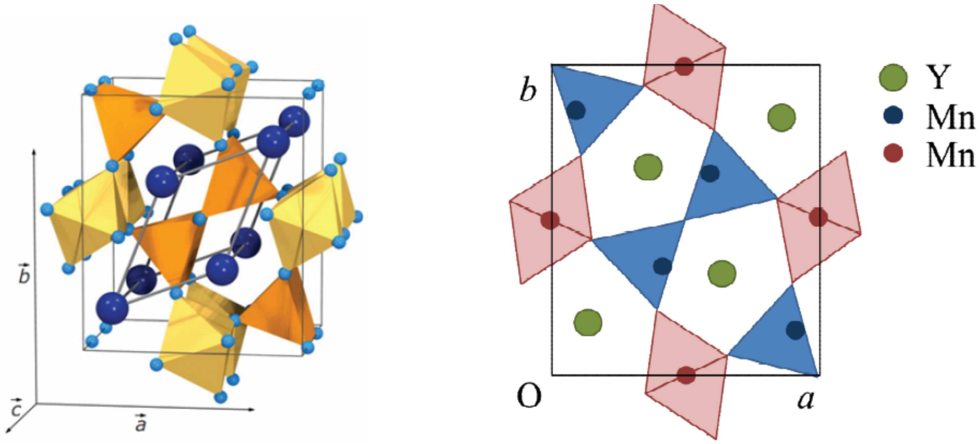


Fig. 1 Crystal structure of YMn$_2$O$_5$

1) YMn$_2$O$_5$ crystallizes in Pbam space group. Crystal unit cell is represented in Fig. 1. How many formula unit does it contain? In this unit cell, how many Mn atoms are sitting at an octahedral site? at a tetraedral site? What are the corresponding coordinations?

2) In the following table we give the possible oxidation states of Y, Mn, Fe and O.

Atom	Y	Mn	Fe	O
Possible oxidation state	+3	+2, +3, +4, +5, +6, +7	+2, +3, +4	-2

a- what is the average oxidation state of Mn in YMn$_2$O$_5$?

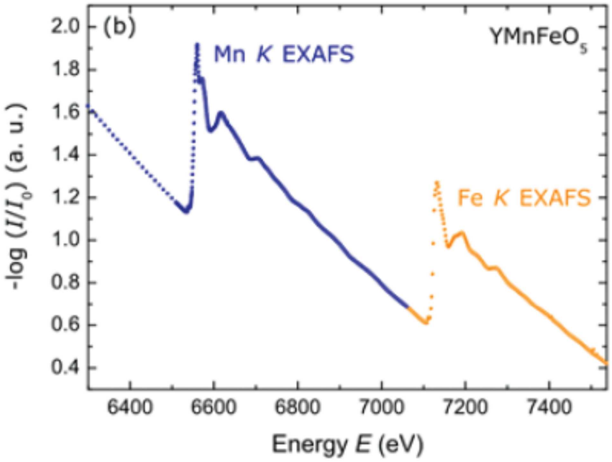
b- From simple geometrical considerations, guess the oxidation state of Mn in the tetraedral and in the octahedral sites.

c- The electronic structure of free Mn atoms is ([Ar]3d^{5}4s^2). The electronic structure of free Fe atoms is ([Ar]3d^{6}4s^2). What is the electronic configuration of Mn^{3+}, Mn^{4+}, Fe^{3+}, and Fe^{4+} ions? Do they carry a magnetic moment?

B- EXAFS

In the paper mentioned above, the authors study the effect of the substitution of some Mn atoms with Fe. As the two atoms have different electronic configurations new magnetic properties can in principle be expected. The details interaction between the magnetic moments depends on the site occupied by the ions, and it is therefore crucial to understand in which crystallographic site Fe goes.

We saw in class that the spectra resulting from an x-ray absorption experiment is composed of an absorption edge, followed by some oscillation. We consider the EXAFS (extended x-ray absorption fine structure) spectra of $Y(Mn_{1-x}Fe_x)_2O_5$ measured at room temperature close to Mn and Fe K-edges.



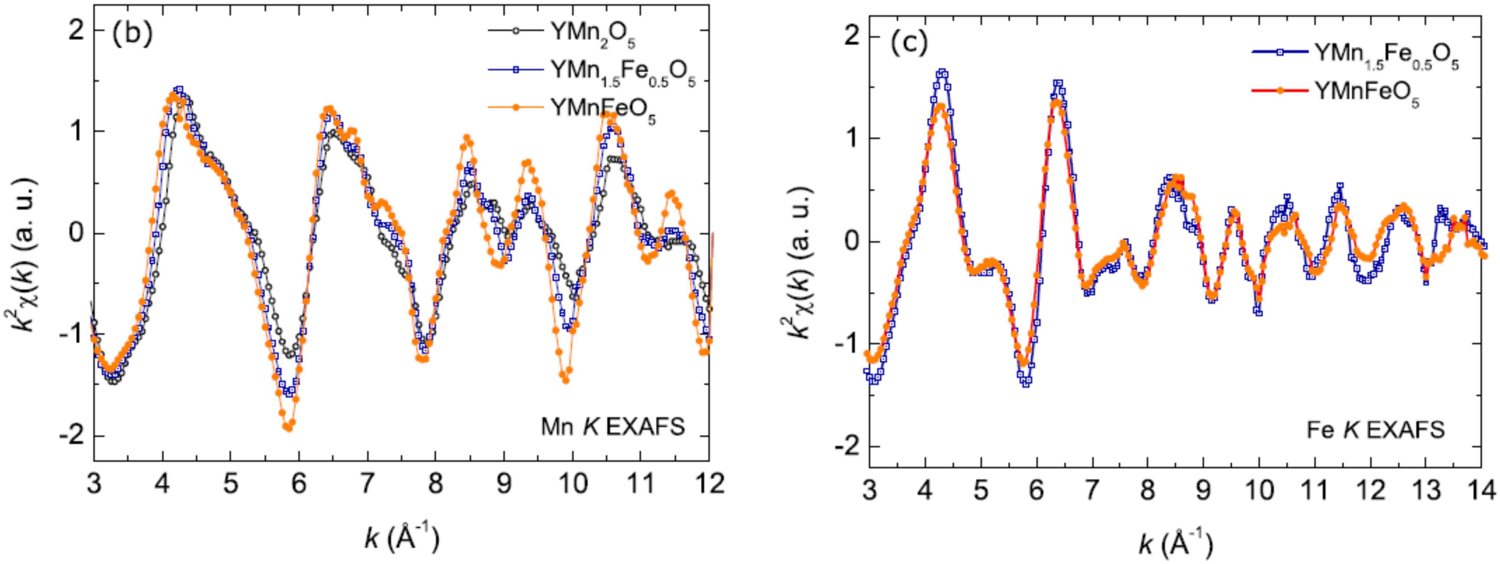
The fine structure of the oscillations in the absorption spectra above the edges is related to the back-scattering of photo-electrons on surrounding atoms. The oscillations are extracted from the spectra by subtracting the absorption of isolated atoms, and can usually be modelled by the EXAFS formula:

$$\chi(k) \propto \sum_i N_i \frac{|A_i(k,R_i)|}{kR_i^2} sin[2kR_i + \phi_i(k,R_i)] e^{-\frac{2R_i}{\lambda(k)}} e^{-2(k\sigma_i)^2}$$

where i refers to equivalent scattering paths (identical scattering centers located in a shell of size $2R_i$). The path degeneracy (ie the number of scattering atoms in shell of radius R_i) is N_i. The thermal induced disorder is included in the last term that contains the variance of Ri, σi.

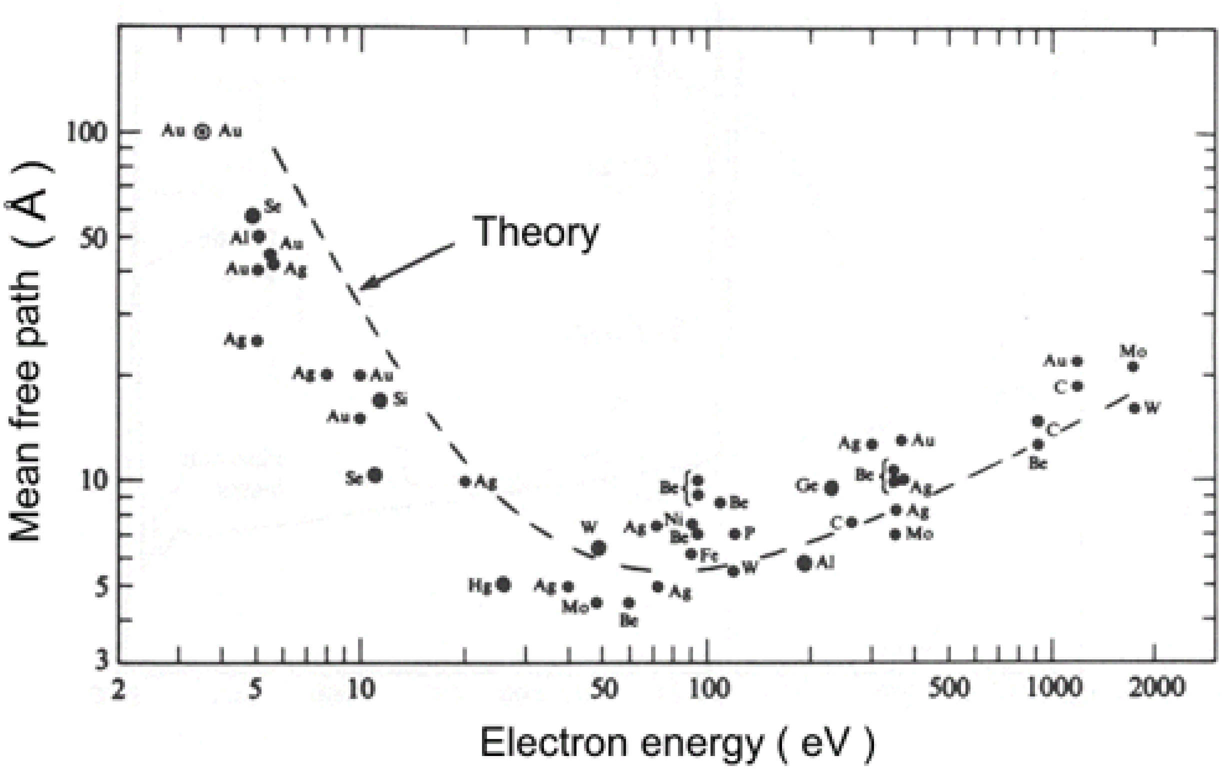
$A_i(k,R_i)$ and $\phi_i(k,R_i)$ are respectively the scattering amplitude and phase associated with path i. λ(k) is the photoelectron mean free path.

In the following figure the quantity $k^2\chi(k)$ is plotted as function of the momentum k of the photoelectron for various Fe concentrations (x= 0, 0.25 and 0.5).



1) To which physical process the term e^{-2R_i/λ_i} in the above formula can be associated?

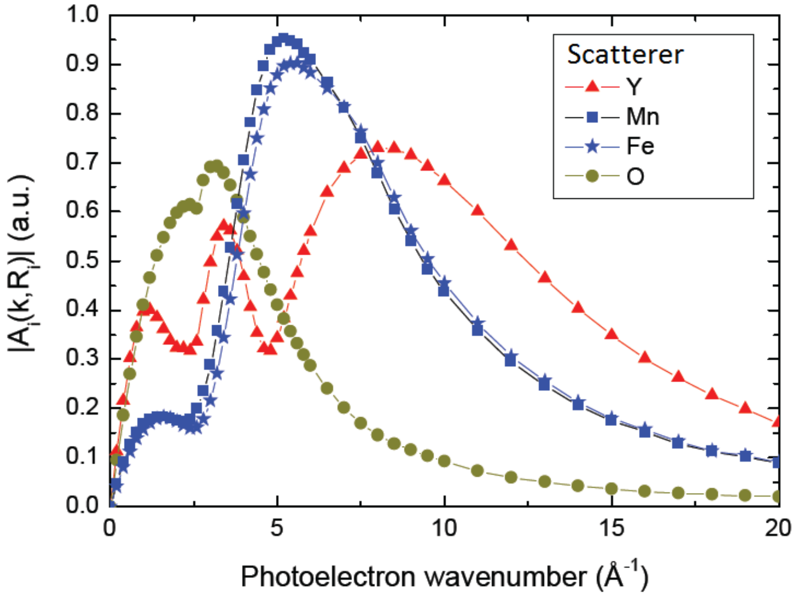
In the following figure the mean free path of an electron as function of its kinetic energy is given. From this figure and the EXAFS plot given above, estimate the radius probed by EXAFS around the absorbing atom in the considered experiment (hint: convert the momentum range of the photo-electron in the experimental spectra into kinetic energy)



2) What is the point of performing a Fourier transform of $\chi(k)$?

3) The oscillations are recorded on a finite interval of photoelectron momentum. What is the practical consequence on the Fourier transformation of $\chi(k)$? What does this physically correspond to? Perform numerical estimate.

4) The backscattering amplitudes used in the EXAFS formula $A_i(k, R_i)$ for the different atoms of the compound are given in the following figure. Discuss the chemical sensitivity of EXAFS.



5) From the previous considerations, to conclude about the site occupied by Fe, one has to measure EXAFS at the K-edge of Fe and determine whether this is the EXAFS signal of an atom in tetrahedral, octahedral or mixt site, and do the same for Mn. This requires a complex analysis of the EXAFS spectra that will not be (and in fact cannot be) performed here. From simple considerations we can however determine whether the substitution is completely random or not.

We call $\chi_o(k)$ and $\chi_T(k)$ the EXAFS signal of absorbing atoms in octahedral and tetrahedral sites, respectively. x is the fraction of Mn atoms substituted with Fe (x<=1/2), and δ the fraction of Fe atoms at a tetrahedral site. Using the results of part 1, show that the K-edge Fe EXAFS signal (normalized by the number of absorbing atoms) can be written as $\chi_{Fe}(k) = [8x\ \delta\chi_T(k) + 8x\ (1-\delta)\chi_o(k)]/8x$. Similarly, express the K-edge Mn EXAFS signal as function of $\chi_o(k)$, $\chi_T(k)$, x and δ.

6) We consider the following cases:

- Fe substitution is random
- Fe are only on octahedral sites
- Fe are only on pyramidal sites
- Fe is preferentially on one of the two sites.

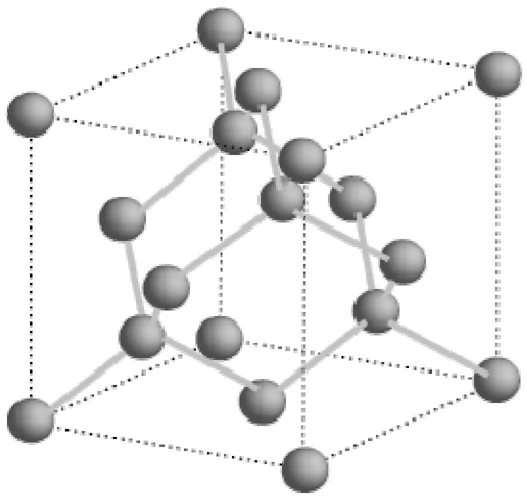
Determine in each case whether the EXAFS signals of Fe and Mn are identical or not, and if they depend on x or not. Confront this to the Fe and Mn K-edge data shown above and conclude whether the substitution is random or not.

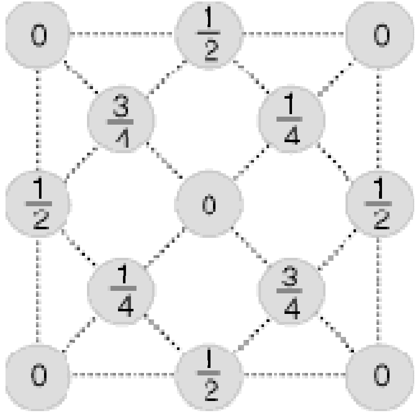
7) Why would this conclusion have been difficult to reach with standard diffraction?

Problem 5.2 Powder diffraction

We consider the crystalline structure of Silicon plotted below. It is cubic.

1) What is the lattice? What is the pattern?





2) Define the reciprocal lattice vectors. Calculate the scattering amplitude (i.e. the structure factor) F_{hkl} at reciprocal lattice point $\mathbf{q}$ = h.$\mathbf{a^*}$ + k.$\mathbf{b^*}$ + l.$\mathbf{c^*}$ = $\mathbf{Q_{hkl}}$. What are the existence conditions of a reflection (hkl)? Which extinctions are related to the lattice? to the pattern?

3) We want to look at the diffraction pattern from a Silicon Powder. What is a powder from the micro-structural point of view? What does it tell us about the powder diffraction pattern?

4) Calculate the lattice spacing d_{hkl}. Are there reflections?

5) In the following table are listed all the reflections that can be seen in a simple cubic lattice. From this, index the powder diffraction diagram of Si.

hkl	h^2+k^2+l^2	Multiplicity	hkl	h^2+k^2+l^2	Multiplicity	hkl	h^2+k^2+l^2	Multiplicity
100	1	6	321	14	48	431	26	48
110	2	12	400	16	6	510	26	24
111	3	8	410	17	24	511	27	24
200	4	6	322	17	24	333	27	8
210	5	24	411	18	24	520	29	24
211	6	24	330	18	12	432	29	48
220	8	12	331	19	24	521	30	48
221	9	24	420	20	24	440	32	12
300	9	6	421	21	48	441	33	24
310	10	242	332	22	24	522	33	24
311	11	24	422	24	24	530	34	24
222	12	8	430	25	24	433	34	24
320	13	24	500	25	6	531	35	48

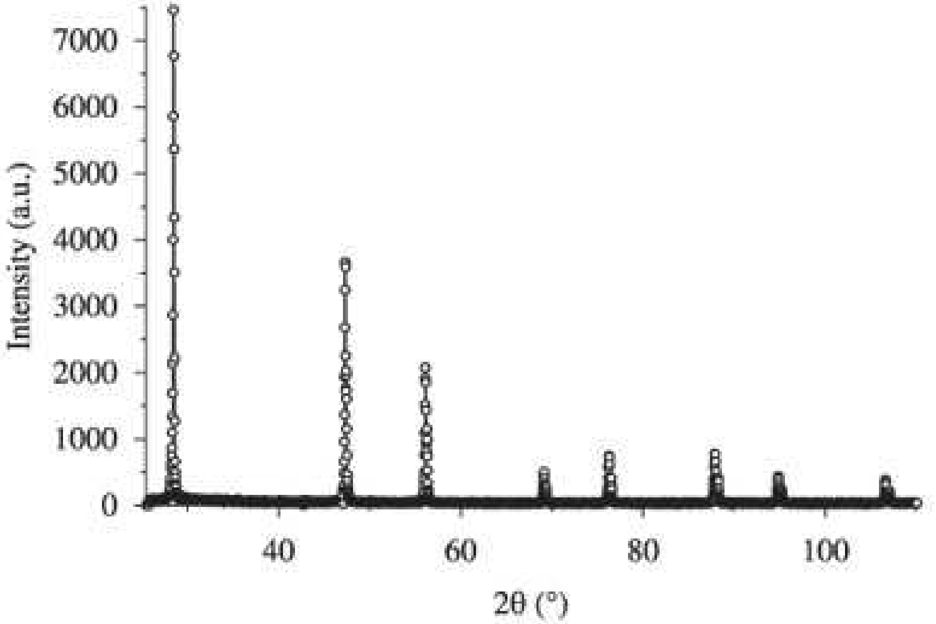


Figure 1. XRD pattern of standard silicon powder.

6) The first diffraction peak is seen for Bragg angle $2\theta = 28.436^{o}$ for x-rays with $\lambda = 1.54$ Å. Deduce the lattice parameter of Si.