

Study of XAFS of some Fe compounds and determination of first shell radial distance

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Abstract. X-ray absorption fine structure (XAFS) of some Fe compounds have been studied using the latest XAFS analysis software *Demeter with Strawberry Perl*. The processed XAFS data of the Fe compounds have been taken from available model compound library. The XAFS data have been processed to plot the $\mu(E)$ versus E spectra. These spectra have been converted into K-space, R-space and q-space. R-space spectra have been used to obtain first shell radial distance in Fe compounds. Structural parameters like first shell radial distance is useful in determination of bond length in Fe compounds. Hence the study play important role in biological applications.

1. Introduction

X-ray absorption fine structure (XAFS) technique enables the measurement of fine structures in the X-ray absorption spectra, above the absorption edge of the atoms in a material. Generally an EXAFS spectrum extends from ~ 100 eV below the absorption edge of the particular atom, to ~ 700 eV above the absorption edge. The spectrum near the absorption edge (viz., the XANES part), gives information about the long range order existing in the sample and the oxidation states of the atoms involved, while the part of the spectrum well above the absorption edge (the EXAFS part) gives information regarding the short range order and local structure around the atomic species. With the advent of modern bright Synchrotron radiation sources, this technique has emerged as the most powerful technique for local structure determination, which can be applied to any type of material viz. amorphous, polycrystalline, polymers, surfaces and solutions.

A simplified EXAFS analysis method had been proposed previously for some transition metals^{1,2} and copper compounds³. In this procedure, the theoretical EXAFS data was generated, employing computer software *Mathcad*, for the first coordination shell around the absorbing atom, using standard EXAFS equation⁴. For this calculation, the required phase shift was extracted from the experimental data itself using LSS method⁵ and backscattering amplitude was taken from tables of Mackale⁶ for 2.5\AA radial distance from the central absorbing atom and Teo and Lee⁷. The other parameters were taken from crystallographic data⁸. First shell bond length has been calculated employing commonly used Fourier transform technique and compared with standard crystallographic value. In the present work analysis has been done on Fe foil and some Fe compounds using the latest XAFS analysis software *Demeter with Strawberry Perl*. The processed XAFS data of the Fe compounds have been taken from available model compound library. The XAFS data have been processed to plot the $\mu(E)$



verses E spectra. These spectra have been converted into K-space, R-space and q-space. R-space spectra have been used to obtain first shell radial distance in Fe compounds.

2. Experimental

Since EXAFS spectroscopy requires an intense polychromatic X-ray source, the most suitable light source is a synchrotron storage ring. The most common EXAFS beam-line works in transmission. It collects data measuring how the beam intensity decreases as it passes through the sample while scanning energy using a crystal monochromator. Experimental spectra are usually recorded by scanning energy from about 200 eV below the explored edge to 1000 eV above it. Energy steps can be of 0.1–2.0 eV, depending on the energy interval and the experimental setup.

3. Data Analysis

The purpose of EXAFS analysis is to obtain the parameters of the local structure of the absorbing atom from its experimental cross-section. Many analysis methods have been developed and in this section we will describe one of the most general and simple ones. The first step in data analysis is signal extraction by background removing. This delicate operation can be divided into three steps: a) choosing the threshold energy, for wave vector definition; b) pre-edge extrapolation (μ_0); c) atomic absorption modeling (μ). After these steps, it is possible to obtain the EXAFS signal as:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E)}$$

The EXAFS signal contains the contributions of all of the coordination shells. Each contribution can be approximated to a damped sinusoidal function in k-space, whose frequency is proportional to the absorber-scatterer distance.

The EXAFS signal is Fourier transformed to obtain a radial distribution function. Fourier transform (FT) is the standard tool used for frequency separation. In fact, this operation transforms each sinusoidal component in a FT modulus peak, going from the $k(\text{\AA}^{-1})$ space to $R(\text{\AA})$ space. To minimize distortions and to avoid the presence of ripples (peak side-lobes which arise from the truncated integration) in the FT modulus, $\chi(k)$ is multiplied by a window $W(k)$. The height of peaks depends on the amplitude parameters of the EXAFS equation, while their position depends on phase parameters. Total or partial overlapping of more peaks often occurs. The position of a peak depends in the first approximation on the distance between absorber and scatterer and in the second approximation on the phase function. Since $\Phi(k)$ depends on k (always with a negative slope), peaks are shifted to lower R values. Once the peak associated to a single coordination shell has been recognized in the Fourier transform of the EXAFS, its contribution to the total signal can be obtained by an inverse Fourier transform carried out over the limits of the peak in R -space (otherwise the filter is calculated in a region containing more than one contribution). The outcome of this operation is the $\chi(k)$ function related to absorber-scatterer pairs whose interatomic distances belong to that specific integration interval.

Structural parameters can be obtained from $\chi(k)$ by means of a fitting procedure using known phase and amplitude functions. EXAFS analysis allows obtaining coordination numbers, interatomic distances and an estimate of the disorder around the central atom.

4. Results and Discussions

The experimental EXAFS data of the studied Fe foil and compounds have been taken from “the EXAFS model compound library” available at (<http://cars9.uchicago.edu/~newville/ModelLib/>). The analysis has been done using latest XAFS analysis software *Demeter with Strawberry Perl*. Figures 1(a)-(e) are showing the $\chi(E)$ verses E, $\chi(k)$ versus k, magnitude of Fourier transform versus radial distance and inverse Fourier transform versus q curves for Fe foil and its compounds. The value of first shell radial distance calculated from Fourier transform for Fe foil and its compounds have been

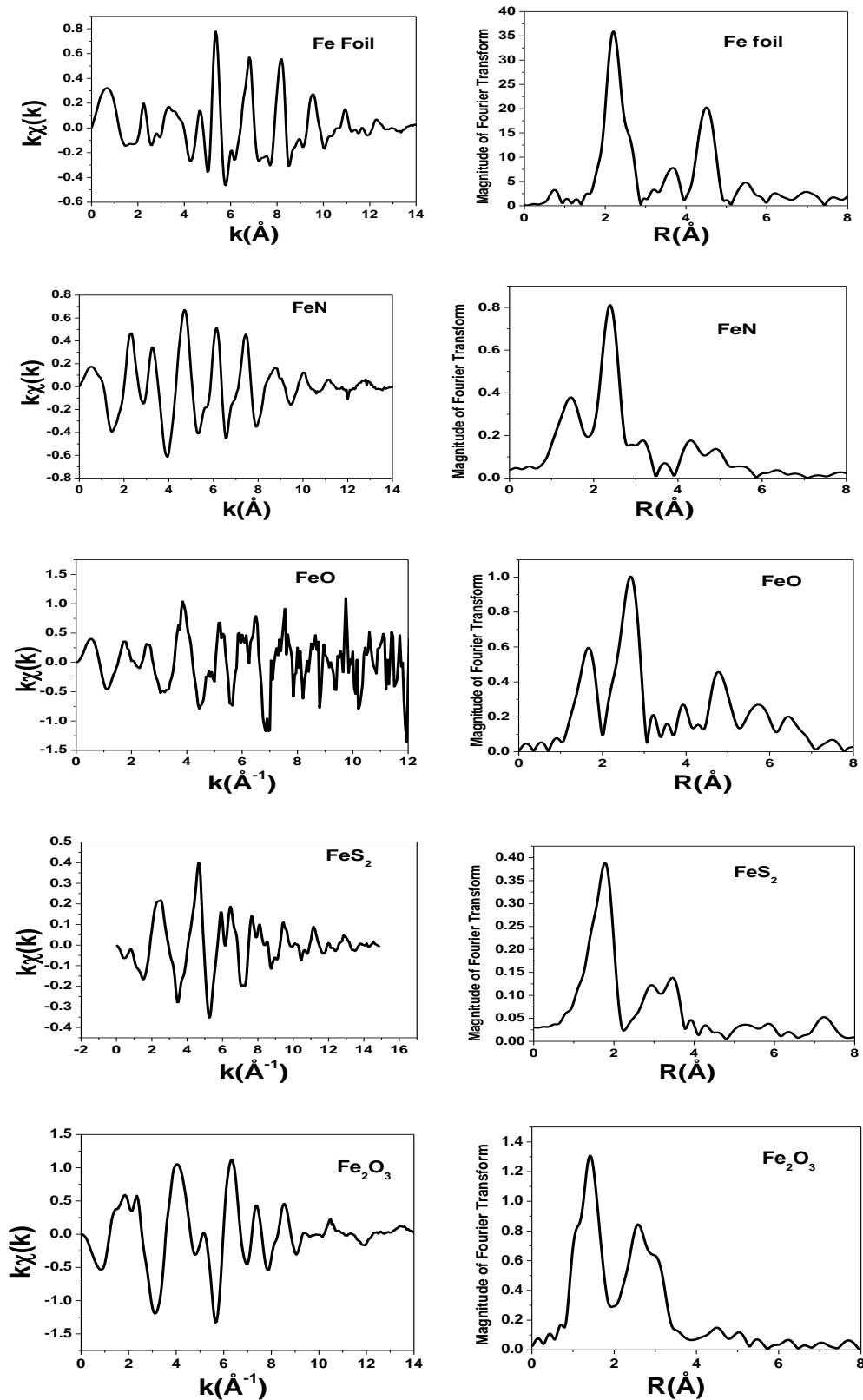


Figure 1. $\chi(k)$ versus k , magnitude of Fourier transform curves of Fe metal foil and compounds at room temperature.

shown in table 1. The values of first shell radial distance for the Fe metal foil and compounds are in good agreement with the standard crystallographic values except Fe_2O_3 . Hence the proposed method of data analysis using the latest XAFS analysis software *Demeter with Strawberry Perl* is useful and efficient for the determination of structural parameters like inter atomic distances.

Table 1. First shell bond length for the Iron compounds.

S. No.	Compounds	$R_{\text{Crystallographic}}$ [Å]	$R_{\text{experimental}}$ [Å]
1	Fe	2.48	2.16
2	FeN	1.97	2.31
3	FeO	2.00	2.58
4	FeS_2	2.26	1.83
5	Fe_2O_3	2.03	1.39

5. Conclusions

EXAFS has developed into a mature technique with numerous applications in physics, chemistry, materials science, biology, and environmental science. The range of application of EXAFS will be further extended when third generation synchrotron radiation sources come on-line. The method outlined in the present work can be used for easy and quick determination of the first shell bond lengths, before one prefers to use elaborate and time consuming method of analysis of EXAFS data.

References

- [1] Parsai N, Mishra A and Shrivastava B D 2012 *X-Ray Spectrum* **41** 219
- [2] Mishra A, Parsai N and Shrivastava B D 2011 *Indian J. Pure App. Phys.* **49** 25
- [3] Mishra A, Parsai N and Shrivastava B D 2012 *Solid State Phys. AIP Conf. Proc.* **1447** 173
- [4] Rehr J and Albers R C 2000 *Rev. Mod. Phys.* **72** 621
- [5] Lytle F W, Sayers D E and Stern E A 1975 *Phys. Rev. B* **11** 4825
- [6] McKale A G, Knapp G S and Chan S K 1986 *Phys. Rev. B* **33** 841
- [7] Teo B K and Lee P A 1979 *J Amer. Chem. Soc.* **101** 2815
- [8] 1962 *International tables for X-ray crystallography* vol III ed Caroline H MacGillavry and Gerard D. Rieck (Kynoch press, Birmingham, UK) p 277