Laboratory EXAFS using photographic method

S K Joshi, A Gaur, A Johari and B D Shrivastava

1 Government College, Badnawar (Dhar)-454660, India
2 School of Studies in Physics, Vikram University, Ujjain-456010, India

Email: joshisantoshk@yahoo.com

Abstract. Laboratory EXAFS facilities have been used since long. However, EXAFS data analysis has not been reported as yet for the spectra recorded photographically. Though from our laboratory we have been reporting various studies employing X-ray spectrographs using the photographic method of registration of EXAFS spectra, but the data has never been analyzed using the Fourier transformation method and fitting with standards. This paper reports the study of copper metal EXAFS spectra at the K-edge recorded photographically employing a 400 mm curved mica crystal Cauchois type spectrograph with 0.5 kW tungsten target X-ray tube. The data obtained in digital form with the help of a microphotometer has been processed using EXAFS data analysis programs Athena and Artemis. The experimental data for copper metal foil have been fitted with the theoretical standards. The results have been compared with those obtained from another laboratory EXAFS set up employing 12 kW Rigaku rotating anode, Johansson-type spectrometer with Si(311) monochromator crystal and scintillation counter. The results have also been compared with those obtained from SSRL. The parameters obtained for the first two shells from the photographic method are comparable with those obtained from the other two methods. The present work shows that the photographic method of registering EXAFS spectra in laboratory set up using fixed target X-ray tubes can also be used for getting structural information at least for the first two coordination shells.

Keywords: Laboratory EXAFS, Cu metal K-edge
PACS: 78.70.Dm.

1. Introduction

Investigations in XAFS should preferably be carried out using X-ray beam from synchrotron. However, due to easy accessibility, many research workers are using laboratory XAFS set ups employing 12 kW rotating anode X-ray tubes. In such set ups, generally the spectrographs used are curved crystal Johann or Johansson types and the detectors used are proportional counters, scintillation counters, solid state detectors etc. [1-3]. Another kind of laboratory set ups for X-ray absorption spectroscopy use Cauchois type curved crystal spectographs employing X-ray films as detectors. Many workers [4,5] have been using such photographic technique and reporting the results about X-ray edge energies, edge structures, near edge structures and extended fine structures. The data has generally been analyzed qualitatively and empirically to yield useful information about molecular structure. The data has also been analyzed through some established relations to yield information about effective nuclear charge and average bond length. The data has seldom been analyzed using Fourier transform technique. To our knowledge, it has never been analyzed using the XAFS software packages like Athena and Artemis [6-8] The aim of the present investigation is to analyze the EXAFS data, obtained through photographic technique with 0.5 kW X-ray tubes, using these software packages and to compare the results with those obtained by another laboratory
method employing 12 kW rotating anode X-ray tubes and also with the results obtained from synchrotron EXAFS set ups. In the present study, we have focused only on Cu metal foil spectra.

2. Experimental

For the photographic method of recording spectra, we have used a 400 mm curved Cauchois-type transmission X-ray spectrograph employing mica crystal, oriented to reflect from (201) planes. The white radiation source was a 0.5 kW Machlett sealed tungsten target X-ray tube operated at 16 kV and 15 mA. The exposure time was 2 to 3 h on Kodak X-ray films. The absorbance versus energy data was obtained in the digital form with the help of Carl Zeiss G-II microphotometer. The dispersion of the spectrograph was about 0.8 eV/10^{-2} mm of the X-ray film, the movement of the microphotometer screw by 1 division being corresponding to movement by 10^{-2} mm on the X-ray film. The resolution of the spectrograph was 9 eV at 9.8 keV.

Another laboratory method [9] used by us employed a 12 kW rotating anode X-ray generator (Rigaku, 60 kV, 200 mA) with a focus size of 0.5 mm × 10 mm. The Johansson type curved crystal spectrometer based on the design of Tohji, et al has Rowland circle radius of 400 mm. Silicon crystal with (311) reflections have been used. For detection of signal scintillation counter has been used. Convenient menu-driven computer software had been used for control and data acquisition. Data can be directly acquired on a computer. The performance of the set up used by us at UGC-DAE Consortium for Scientific Research, Indore, India, was similar to that reported earlier [9]. Further, the EXAFS spectra were also recorded using synchrotron radiation at Stanford Synchrotron Radiation Laboratory (SSRL) in transmission mode. Using the above mentioned three methods, the spectra were recorded for copper metal foil at room temperature.

3. Results and Discussions

The microphotometer curve is an optical density curve. In the small region of energy of interest, the optical density is proportional to the X-ray intensity I transmitted after absorption from the absorber [10]. The incident intensity I_0 is taken to correspond to the maximum optical density on the X-ray film. For the spectra recorded photographically, the energy calibration was done with the help of reference emission lines 74 W Lα_2 and 74 W Lβ_4 which were present in the spectrum. The digital values obtained from the microphotometer were entered as input in the computer software Athena version 0.8.056 for data analysis [11]. The EXAFS data were background-subtracted and normalized to a unit edge step. The normalized spectrum of μ(E) vs. E is shown in figure 1. The data from the rotating anode set up and the SSRL were also processed in the same way and their normalized spectra are also shown in figure 1. Figure 2 shows the χ(k) vs k plots. In both these figures, the spectra have been shifted vertically by suitable values so that the three spectra may be easily compared with each other. For the present analysis, the input parameter that determines the maximum frequency of the background R_{bkg} was set to 1.25 Å. The background subtracted normalized χ(k) data was then imported into the Artemis version 0.8.012 and the corresponding Fourier transformed data was obtained. The magnitude of the Fourier transformed data |χ(R)| are shown in figure 3. The Fourier transform parameters used were w=2, k_{min}=2.3 Å^{-1}, k_{max}=14.3 Å^{-1} and dk=1 Å^{-1} for SSRL data; w=2, k_{min}=2.8 Å^{-1}, k_{max}=9.6 Å^{-1} and dk=2 Å^{-1} for rotating anode data; w=2, k_{min}=2.6 Å^{-1}, k_{max}=11.3 Å^{-1} and dk=2 Å^{-1} for photographic data. The theoretical model for copper metal was generated in Artemis using the software Atoms, available in Artemis. Theoretically modeled data were fitted to the experimental data in the R space and the corresponding fits are shown in figure 3. The SSRL data, rotating anode data and photographic data were fitted using k_{min}=2 to present these data sources on equal footing. Fits were performed in the R ranges of 1.5-3.8 Å for SSRL data, 1.4-3.7 Å for rotating anode data and 1.35-3.7 Å for photographic data, i.e., only for the first and second coordination shells. We have used the third path along with the first and second paths in the fitting procedure because the third path (R_{eff} = 3.829 Å) leaks into the region of first and second peaks in the Fourier transformed spectra.
Figure 3. Magnitude of the Fourier transform of experimental data (solid line) along with theoretically modeled fit (dashed line). (a) Photographic, (b) Rotating anode and (c) SSRL data. The photographic data, rotating anode data and SSRL data have been fitted by using a $k^2$ weight of 2 for better comparison. Only first three scattering paths have been used for fitting. Fitting parameters are given in the text.

Table 1. Local structure parameters for copper metal

| Experimental techniques | 1st shell | 2nd shell |
|------------------------|----------|----------|
|                         | N        | R (Å)    | del r (Å) | $\sigma^2 (Å^2)$ | N | R(Å) | del r(Å) | $\sigma^2 (Å^2)$ |
| Photographic           | 12       | 2.56     | 0.010(0.017) | 0.0015(0.0022) | 6.0 | 3.58 | -0.025(0.012) | 0.0045(0.0014) |
| Rotating anode         | 12       | 2.50     | -0.052(0.005) | 0.0122(0.0019) | 6.0 | 3.44 | -0.174(0.014) | 0.0101(0.0027) |
| SSRL                   | 12       | 2.54     | -0.011(0.004) | 0.0083(0.0009) | 6.0 | 3.69 | 0.080(0.007)  | 0.0088(0.0010) |

The results obtained from fitting are given in Table 1, which gives the local structure parameters obtained from the EXAFS analysis for Cu metal. As the coordination number for Cu metal is well known, we have constrained N to its crystallographic value for the first shell and used $S_0^2$ as fitting parameter. For the second shell we have fixed the $S_0^2$ value thus obtained. The $S_0^2$ values for the three spectra are comparable to each other. However, $S_0^2$ is slightly higher in the case of photographic data than the other two data, the error bar also being much higher in the case of photographic data. The del $E_0$ values for the three spectra are also comparable to each other. The first shell distance determined from photographic data is higher than the crystallographic distance ($R_{eff}=2.553$ Å) by 0.010 Å, while this value is -0.011 Å for SSRL data and -0.052 Å for rotating anode data. For the second shell, the distance determined from photographic data and rotating anode data is shorter than the crystallographic distance ($R_{eff}=3.610$ Å) by 0.025 Å and 0.174 Å.
Å, respectively. However, in case of SSRL data, the distance is greater by 0.08 Å than the crystallographic distance. The Debye-Waller factor $\sigma^2$ for the first shell is 0.0105 Å$^2$ for photographic data and 0.0122 Å$^2$ for rotating anode data, but is 0.0083 Å$^2$ for the SSRL data. Similarly, this factor for the second shell is 0.0045 Å$^2$ for photographic data, 0.0101 Å$^2$ for rotating anode data and 0.0088 Å$^2$ for SSRL data. The higher values of this factor are due to the fact that all the measurements have been made at the room temperature. The values of goodness-of-fit parameter, i.e., reduced chi-square ($\chi^2$) are 2.0, 4.3, 369 for photographic, rotating anode and SSRL data, respectively. It may be mentioned herewith that when we fit the third shell also in the SSRL data, then the parameters obtained are: $S_0^2$=0.72, del E$=2.90$ eV, R=4.442 Å ($R_{eq}=4.4213$ Å), N=24, del r = 0.020 Å, $\sigma^2=0.012$ Å$^2$.

In the photographic method, we are getting the third and fourth shell peaks also in the Fourier transformed spectra, but we have not been able to fit them satisfactorily. Hence, we have restricted our analysis up to the first two coordination shells only and have observed that the local structure parameters obtained from the photographic EXAFS data are sufficiently comparable to those obtained from the SSRL data. The present analysis of the copper K-edge EXAFS has thus amply shown that the photographic method can also be used for determining the local structure parameters for the first two shells.

The aim of the present work is to demonstrate the usefulness of the laboratory EXAFS set ups having low power X-ray fixed target tubes and photographic method of registration of spectra. There is a large population around the world that does not have ready access to synchrotron. The method outlined by us can be useful when the synchrotron facility is not available and also when the laboratory does not have a rotating anode X-ray generator. Fixed target X-ray tubes are mostly available in the laboratories and a Cauchois type X-ray spectrograph can be indigenously fabricated and hence the laboratory EXAFS set ups employing photographic technique can be easily installed. Such set ups could then be used by physicists, chemists, biologists etc. for easy and quick determination of the local structures at least up to the first two shells in their own laboratory and without much loss of accuracy. Further, the method outlined by us can be used to screen the samples in advance of a rare and possibly expensive visit to synchrotron.

4. Acknowledgements
Thanks are due to Professor E. A. Stern for recording the spectra at SSRL. Thanks are due to MPCST, Bhopal (India) for a research grant.

References
[1] Stern E A 1980 Laboratory EXAFS Facilities ( New York, American Institute of Physics )
[2] Koningsberger D C and Prins R 1988 X-ray Absorption - Principles, Applications, Techniques of EXAFS, SEXAFS AND XANES ( New York; Wiley - Interscience )
[3] Kurisaki T, Matsuo S, Toth I and Wakita H 2008 Anal. Sci. 24 1385
[4] Joshi S K, Shrivastava B D, Shrivastava Bhakta D and Mishra A 2004 X-Ray Spectrom 33 466
[5] Joshi S K, Katare R K, Shrivastava B D 2007 X-Ray Absorption Fine Structure XAFS 13 p - 821 ( New York, American Institute of Physics )
[6] Ravel B and Newville M 2005 J. Synchrotron Rad. 12 537
[7] Newville M G 1995 Local Thermodynamic Measurements of Dilute Binary Alloys using EXAFS (Ph.D. Thesis, University of Washington, Seattle)
[8] Kelly S D, Hesterberg D and Ravel B 2008 Methods of Soil Analysis, Part 5, Mineralogical Methods Chapter 14 ( Medison ; Soil Science Society of America)
[9] Deshpande S K, Chaudary S M, Pimpale A, Nigavekar A S, Ogale S B and Bhide V G 1991 Pramana - J. Phys. 37 373
[10] Blokhin M A 1962 X-ray Spectroscopy ( Delhi, Hindustan Publishing Corporation )
[11] Rehr J J and Albers R C 2000 Rev. Mod. Phys. 72 62