Homi Bhabha National Institute

SYNOPSIS OF PH.D. THESIS

1. **Name of the student**: Ms. Nitya Ramanan
2. **Name of the Constituent Institution**: Bhabha Atomic Research Centre
3. **Enrolment Number**: PHYS01200904022
4. **Title of the thesis**: XAFS characterization of disordered nanoclusters and augmentation of Indus-2 XAFS beamlines for extreme thermodynamic conditions
5. **Board of Studies**: Physical Sciences (08)

SYNOPSIS

Nanoclusters, i.e. clusters having diameter ~ 1-100nm, have immense technological importance in both fundamental science and industry due to their small size and ability to exhibit intriguing size-dependent properties. For many applications, small size is a necessity, for eg. (i) Electronic Device Industry: In electronic devices, where the idea is to accommodate maximum possible structures on a single chip, small individual elements would come in handy; (ii) Nanodrugs: Drugs have maximum potency when their size is comparable to the size of the target cell. The average size of human cell constituents is ~ 10-100nm. Therefore, to achieve good bioavailability, in vivo stability, solubility, intestinal absorption, sustained and targeted delivery to site of action, therapeutic effectiveness and low generalized side effects, nano-sized drugs are required. (iii) Plasmon Band: Several opto-electronic devices function on the basis of Surface Plasmon Resonance (SPR). SPR occurs due to scattering of conduction electrons by the nanocluster surface when the nanocluster diameter is less than the mean free path of the conduction electrons in the bulk metal. (iv) Sensors: Small size improves the efficiency and specificity of sensors.

Due to their small size, nanoclusters possess large surface to volume ratio, making them extremely reactive (since more surface is available to react) and hence potential candidates for catalysts. In fact, the reactivity becomes so remarkably high that even the so called noble metals (Au, Ag, Pt etc.) cease being noble in the nano-regime! Moreover, the high aspect ratio further simplifies the task of functionalizing nanocluster surfaces for various applications (from drug delivery to clothing insulation) simple.

In the nano-size regime, quantum size effects rule the properties of clusters. As a result, size becomes an additional degree of freedom, strongly influencing the optical, electric, magnetic, thermal and electronic properties. At this small size, nanoclusters are prone to various defects, mainly surface defects and vacancy. The strain induced by these defects makes the nanoclusters prone to disorder, resulting in a variety of interesting consequences, like alloying, de-alloying and segregation. X-ray Absorption Fine Structure (XAFS) is the only technique that can be used to obtain structural information on such highly disordered systems, and we have employed the same to investigate disordered clusters in different configurations. Due to the weak nature of XAFS oscillations, continuous energy spectrum, having high flux, high intensity and high resolution is required to override statistical noise and obtain good quality XAFS data. Synchrotron, due to its energy tunability, high brilliance and polarization represents the ideal source for XAFS experiments.

In parallel, we have also undertaken the task of augmentation of the XAFS beamlines at the Indus-2 synchrotron source for studying such systems at extreme thermodynamic conditions. Pressure and temperature offer additional control parameters to derive insights into the phase diagram of nanoclusters.

This dissertation is divided into two parts: (i) XAFS characterization of disordered nanoclusters and (ii) augmentation of Indus-2 XAFS beamlines for extreme thermodynamic conditions. In the former part, we have characterized disordered nanoclusters in different configurations, viz. embedded nanoclusters in thin films, bimetallic nanorods synthesized via swift heavy ion irradiation and nanomedicine. In the latter part, we present the newly installed low temperature and high pressure XAFS facilities at Indus-2. The dissertation is organized into nine chapters, which are summarized as follows:

Chapter 1: Introduction

In this chapter, we present a basic introduction to nanoclusters. Their various possible applications and the size dependence of their properties are discussed. We then move on to discuss one important consequence of small size – the presence of disorder in these clusters. The various techniques that can be used for characterization of such disordered clusters are discussed. Finally we emphasize the need for XAFS for characterization and highlight the new information that can be extracted using the same. The various systems studied in this dissertation are presented.

Chapter 2: Theory of XAFS

In this chapter, the underlying physics of XAFS is explained. The XAFS equation is derived and each of the terms in the equation is described in detail. The approximations used for derivation of the equation are summarized. The equation is extended to include effects due to multiple scattering. A brief overview of XANES (X-ray Absorption Near Edge Structure) phenomenon is also given. Finally, the strengths and limitations of XAFS in comparison with other techniques are discussed.

Chapter 3: Experimental Apparatus for XAFS

In this chapter, we describe the instrumentation required for carrying out XAFS experiments. The experimental setup for XAFS is broadly classified into source and beamline instrumentation. Synchrotrons are the ideal source for XAFS experiments, and we discuss their strengths. The different generations of synchrotron sources, viz. bending magnet, insertion devices and free electron lasers are described. XAFS experiments require streamlined optics for getting good quality data. We describe in detail the optical components of XAFS beamlines and detectors for transmission and fluorescence mode XAFS, sample holders for various XAFS experiments and the sample preparation method for XAFS. Finally, we discuss the methods to eliminate noise in XAFS data.

Chapter 4: XAFS data analysis

In this chapter, we explain the method of analysis of XAFS data using the IFEFFIT fitting package. XAFS data analysis breaks up into (i) data processing, (ii) data modelling and (iii) data fitting. We discuss each of these steps in detail.

Chapter 5: Augmentation of Indus-2 XAFS beamlines for extreme thermodynamic conditions.

The synchrotron source in India, Indus-2, is a second generation source operating at 2.5 GeV ring energy and 300mA current. Presently two XAFS beamlines are operational at Indus-2 – one operates in energy dispersive mode and the other operates in energy scanning mode. Recently, we have upgraded these beamlines to accommodate experiments under extreme conditions, viz. low temperature and high pressure. This chapter describes (i) installation displex closed cycle cryostat and assessment of the possibility of performing experiments using the same by measuring XAFS on standard Au foil, and (ii) modification of optical layout of dispersive XAFS beamline for experiments under high pressure.

Chapter 6: XAFS characterization of embedded bimetallic nanoclusters in multilayer film

In this chapter, we characterize bimetallic clusters embedded in C matrix. These clusters were formed following ion irradiation of a Pt/Ni/C multilayer film. TEM, X-ray Reflectivity and X-ray Fluorescence measurements on the film pre- and post- irradiation provided information on layer periodicity and roughness, and also revealed cluster formation with irradiation. But they could not ascertain the composition and configuration of these clusters; neither could they determine the nature of the formed clusters. We have used XAFS in X-ray Standing Wave mode to derive this information. With rigorous XAFS coordination analysis, we have de-coupled the interfacial and layer contributions and derived the structure of the clusters to be Ni centered Ni/Pt bimetallic alloy clusters, highly disordered beyond first nearest neighbour. The possible applications of the same are discussed.

Chapter 7: XAFS characterization of bimetallic nanorods synthesized via Swift Heavy Ion Irradiation

In this chapter, we characterize bimetallic nanorods in silica matrix synthesized via Swift Heavy Ion Irradiation (SHII) of co-sputtered metal/metal//silica film. Although several methods have been previously used for synthesis of such nanorods, this is the first time they have been synthesized by SHII. We present two systems – Ag/Pt (bulk immiscible) and Ag/Au (bulk miscible). These are amorphous and crystalline respectively pre-SHII. We attempt to understand the relative effect of SHII on these two systems by deriving their composition and configuration using XAFS.

Chapter 8: XAFS characterization of Ayurvedic nanomedicine

In the absence of scientific evidence towards their claimed non-toxicity, Ayurvedic drugs are facing a world-wide ban due to their heavy metal content. In this chapter, we investigate the structure of Hg based ayurvedic drug, ‘Rasasindura’, with the objective of finding evidence towards its putative non-toxicity. Our results establish that the system contains HgS nanocrystals in stable α-HgS configuration and that metallic Hg^0 is completely absent, ensuring absence of Hg-based toxicity. With rigorous, novel XAFS analysis strategies, we have estimated the number and nature of defects, confirming the robust structure of the HgS nano-crystals (<3% defects). This ensures integrity of the nano-crystals during the drug-delivery process.

Chapter 9: Conclusions and future directions

In this chapter, we summarize the main conclusions of this dissertation. (i) The utility of XAFS to deduce the structure of disordered nanoclusters has been clearly demonstrated. XAFS successfully helped in understanding the composition and configuration of these clusters. Additionally, XANES characterization of these clusters led us to understand the chemical nature of cluster formation. (ii) The XAFS beamlines at Indus-2 have been augmented for performing experiments under low temperature and high pressure. We have assessed the feasibility of performing experiments using these new setups.

This Chapter is concluded by bringing out the future scope of the work.

Publication in Refereed Journals:

b. Published

1. Nitya Ramanan, Sumalay Roy, Debdutta Lahiri, Surinder M. Sharma and B.N. Dev, 'Ascertaining the nano-cluster formation within ion-irradiated Pt/Ni/C multi-trilayer, with X-ray Absorption Spectroscopy', *Journal of Synchrotron Radiation*, **20**, 137 (2013).
2. Nitya Ramanan, Sumalay Roy, Debdutta Lahiri, Surinder M. Sharma and B.N. Dev, 'XSW-XAFS characterization of ion-irradiated Pt/Ni/C Multilayer', *Journal of Physics: Conference Series*, **430**, 012063 (2013).
3. Debdutta Lahiri, Tomohiro Shibata, Soma Chattopadhyay, Nitya Ramanan, Swati Pandya, P D Kulkarni, A Thamizhavel, A K Grover, S Ramakrishnan and Surinder

M. Sharma, 'XAFS understanding of "repeated" magnetic compensation in $Nd_{0.8}$ $Tb_{0.2}Al_2$' *Journal of Physics: Conference Series*, **430**, 012106 (2013).

4. Nitya Ramanan, Debdutta Lahiri, Nandini Garg, D. Bhattacharyya, S.N. Jha, N K Sahoo and Surinder M Sharma, 'High Pressure experiments at the XAFS beamline, Indus-2', *Journal of Physics: Conference Series*, **377**, 012011 (2012).

c. Accepted

1. Nitya Ramanan, Parasmani Rajput, S.N. Jha and Debdutta Lahiri, 'Assessing the feasibility of Low temperature XAFS experiments at Indus-2, India: first results', in press, *Nuclear Instruments and Methods in Physics Research A.*

d. Under review

1. Nitya Ramanan, Debdutta Lahiri, Parasmani Rajput, Ramesh Chandra Varma, A. Arun, T.S. Muraleedharan, K.K. Pandey, Nandita Maiti, S.N. Jha and Surinder M. Sharma, 'Investigating structural aspects to understand the putative/claimed non-toxicity of Hg-based Ayurvedic drug "*Rasasindura*", using XAFS', under review, *Journal of Synchrotron Radiation*.
2. Nitya Ramanan, Debdutta Lahiri, Ashwani Kumar, Parasmani Rajput, K. Thankarajan, D. Bhattacharyya and S.N. Jha, 'First phase commissioning of High Pressure XAFS setup at ED-XAFS beamline, Indus-2 Synchrotron Radiation Source, India', under review, *Journal of Optics (Optical Society of India).*

e. Other publications

1. 'Investigating alloying/de-alloying of Ag/Pt and Ag/Au nanorods under Swift Heavy-ion Irradiation', manuscript under preparation.
2. N. Ramanan, D. Lahiri, D. Bhattacharyya and S. N. Jha, 'Calibration of standard Ni foil XAFS data recorded at the EXAFS Beamline, INDUS-2 SRS', BARC report, *BARC/2012/E/009* (2012).
3. N. Ramanan, D. Lahiri, S.M. Sharma, N.C. Das, D.V. Udupa and A.D. Patil, 'Development of a bendable mirror for studying materials under high pressure using EXAFS beamline at INDUS-2 SRS', BARC report, *BARC/2010/E/12* (2010).

Signature of the Student: [signature]

Date: 12/02/2015

Doctoral Committee:

S.No.	Name	Designation	Signature	Date
1.	Prof. S.M. Sharma	Chairman	Surinder M Sharma	13/2/15
2.	Prof. M.N. Deo	Guide/Convener	[signature]	12/02/2015
3.	Prof. N.K. Sahoo	Member	[signature]	12/02/2015
4.	Prof. S.K. Dhar	Member	Skdhar	12/02/2015

AK Mohanty
13-2-2015

प्रोफेसर ए.के. मोहान्ती / Prof. A. K. Mohanty
डीन-शैक्षणिक / Dean-Academic
भौतिक एवं गणितीय विज्ञान / Physical & Mathematical Sciences
होमी भाभा राष्ट्रीय संस्थान / Homi Bhabha National Institute
भा.प.अ.कें / Bhabha Atomic Research Centre
मुंबई / Mumbai - 400085