Chapter 2

Experimental Techniques

2.1 Introduction

The aim of this chapter is to introduce the reader to all the experimental work carried out in this thesis with regard to the study of some of the double perovskites that are mentioned in the latter chapters. Along with the sample preparation technique, the method adopted for measurements, basic principle involved and the instruments used for all the experiments, are discussed below. In particular, to study the crystal structure and magnetic structure, techniques like X-ray diffraction and Neutron Powder Diffraction were employed. The transport and magnetic properties were investigated using four-probe resistivity and magnetization as a function of temperature and magnetic field. In order to gain an insight into changes occurring in the local structure of constituent atoms, X-ray absorption fine structure (XAFS) study has been undertaken.

2.2 Sample Preparation Technique

There are several techniques available that allow obtaining single-phase double perovskite samples. One can mention the wet chemistry methods (sol-gel) or solid-state reaction method. The Physical properties of the samples synthesized with different methods
can differ. However, this applies mostly to the microstructure and electrical transport properties.

2.2.1 Solid State Synthesis of Ceramic Samples

All the polycrystalline samples were synthesized by the standard solid state reaction method by taking stoichiometric amounts of La$_2$O$_3$, SrCO$_3$, Co(NO$_3$)$_2$.6H$_2$O, CuO and RuO$_2$. These starting powders were ground thoroughly, pressed into pellets and heated for a total of 48 hours at 1200°C and 1300°C with three intermediate regrinding steps. Prior to firing, the powders of La$_2$O$_3$, RuO$_2$ and SrCO$_3$ were pre-heated at 900°C and 700°C respectively to get rid of any adsorbed water.

2.3 Diffraction Methods

Diffraction methods have become a fundamental tool for the structural characterization and they have also been applied to the samples studied in this thesis. The X-ray diffraction (XRD) and Neutron Powder Diffraction (NPD) allow studying the long range ordering and thus a determination of the crystallographic structure on the one hand, and the deviations from a perfect ordering on the other hand. The usefulness of both the short x-rays and neutrons arises from the possibility to tune their wavelength so that it closely matches the interatomic distances in the solid (i.e. becomes of the order of $\sim$ 1Å).

2.3.1 X-ray Diffraction

X-ray diffraction is a widely used technique to determine the crystalline phase in the bulk materials. The wavelength of X-ray is comparable to the separation (d) between the crystal planes. Diffraction occurs when the Bragg condition which states that, the X-rays
Figure 2.1: The Bragg condition, \(2d \sin \theta = n \lambda\), where \(n\) is an integer, the extra distance traveled by the x-rays to the farther plane of atoms is equal to the multiple of the X-ray wavelength.

reflected from two neighboring planes of atoms must coherently interfere, is satisfied. This condition is fulfilled when the extra distance traveled by the x-rays to the farther planes of atoms is equal to the multiple of the X-ray wavelength, i.e. \(2d \sin \theta = n \lambda\), where \(n\) is an integer (as illustrated in the Fig 2.1) giving rise to diffraction in solids [1, 2]. An x-ray diffraction can be carried out on the polycrystalline (powder) samples or single crystals. The XRD pattern is a plot of the intensity of diffracted rays versus Bragg angle and contains information about the structure and composition of the basis. This information needs to be extracted from the pattern by employing a proper analysis procedure.

In the present study, the powder method is made use of wherein the samples were crushed into fine powder in an agate pestle and mortar and placed in a beam of monochromatic X-rays. The powder X-ray diffraction measurements are performed on powder samples using Rigaku X-ray diffractometer system in the department. The intensity of the Copper K\(_\alpha\) (\(\lambda = 1.5418\text{Å}\)) radiation diffracted from the powdered specimen was detected.
by a scintillation counter and recorded as a function of $2\theta$, where $\theta$ is the angle of incidence. The patterns were recorded in continuous mode in the $2\theta$ range of $18^\circ \leq 2\theta \leq 80^\circ$ with a step size of 0.02 at a speed of $2^\circ$/min. The diffraction peaks were indexed using a commercially available Powder Diffraction Package.

**Experimental Set-up for X-ray Diffraction**

The diffractometer consists of a x-ray source, a goniometer and a counter. Copper anode was used as the target in the X-ray source. The goniometer is designed to satisfy the focusing conditions geometrically. The sample lies at the center of the focussing circle and the plane of the circle at right angles with the axis of rotation of the goniometer. The plane of focussing circle involves the axis-I of focus of the target, the axis-II of the goniometer and the axis-III of the receiving slit. The radius of the focussing circle is a function of the angle $\theta$ formed by the surface of the sample with the extension line of the direct X-ray beam and the angle formed by the straight line connecting the axes II and III in $2\theta$. This angle is always accurately twice the angle $\theta$ formed by the surface of the sample with the extension line of the direct X-ray beam. Since in this goniometer, the X-ray beam from the line focus will irradiate the sample, the greater part of the X-ray beam is irradiated on the sample inclined against the focusing circle plane. When this angle of inclination is large, resolution of the diffracted X-ray beams and accuracy of the measured diffracted angle decreases. To minimize the angle of inclination, the soller slit is used.

The soller slit boxes have three slit holders for insertion of the diversion slit, the receiving slit and the scatter slit. The divergence slit determines the horizontal divergence angle of the x-ray beam irradiating the sample. The receiving slit is for limiting the width of diffracted beams entering the counter. It forms a pair with the divergence slit. The x-ray
Diffraction measurements were performed on powder samples using diffractometer system. The intensity of the $K_\alpha$ radiation diffracted from the powder specimen was detected by a scintillation counter and recorded as a function of the angle $2\theta$. The diffraction peaks were indexed to determine the crystallographic structures, space groups and lattice parameters of the samples.

2.3.2 Neutron Powder Diffraction

Neutron diffraction is a complementary technique to x-ray diffraction in structural studies. Neutrons interact with the atom nucleus and with the electron spin. Thus, magnetic ions give substantial scattering due to the interaction of the magnetic moment of the neutron with the unbalanced electron spin. The form factor $f$ used in XRD is replaced with the scattering length $b$ having units of length. The factor $b$ is dependent on the nuclear properties of the atom and has no simple correlation with the atomic number. It becomes negative for hydrogen, giving a large contrast when compared to other atoms. Moreover, due to the small size of the nucleus with respect to the thermal neutron wavelength (point-like scattering), there will be no dependence of $b$ with the scattering angle $\theta$.

In the case of ferromagnetic and antiferromagnetic materials, below certain ordering temperature, all the magnetic moments will become oriented with respect to some axis, within a magnetic domain. To each magnetic atom, magnetic scattering amplitude $D$ may be ascribed. Consequently apart from the Bragg diffraction peaks, arising from the three-dimensional ordering in crystal structure and nuclear scattering, additional peaks will appear being dependant on the ordering in the magnetic unit cell. If the magnetic unit cell is equivalent to the chemical unit cell, the magnetic and the nuclear Bragg peaks will be located at the same position in $2\theta$ units. On the other hand, if the magnetic cell
Figure 2.2: The Neutron Powder Diffractometer at BARC used for neutron diffraction measurements. The description of the instrument parameters can be seen on the right.

does not coincide with the chemical cell, magnetic Bragg peaks will occur in new positions corresponding to a super-structure long-range order. Above the ordering temperature, no magnetic order is present, and thus no long-range magnetic scattering contribution to the diffraction pattern will be present.

The NPD measurements presented in this thesis have been performed using the Powder diffractometer-2 which is a multi-PSD based instrument at the Dhruva reactor of BARC, Mumbai, covering a Q range upto $9.4\text{A}^{-1}$ as seen in the Fig.2.2. This part of the work has been done in close collaboration with Dr. Amitabh Das, SSPD, BARC.
2.4 Bulk Characterization Methods

A large number of macroscopic properties of the material can be investigated easily by means of experimental methods that can be generally called as bulk methods. In the case of materials being investigated in this thesis, these are the magnetometery and the four probe resistivity measurements.

2.4.1 Magnetometery

A large part of the work during the examination of the properties of the double perovskites investigated was dedicated to the magnetic properties of the material. The experiments have been performed both in high and low fields as a function of temperature and temperature ranges but not only under magnetic fields that can be easily obtained with the commercial use devices in the laboratories. Some large experimental facilities allowing the user to achieve very large fields have also been used.

SQUID Magnetometery

Superconducting Quantum Interference Devices (SQUID) are the most sensitive detectors of magnetic flux available. A SQUID is in essence, a flux to voltage transducer, providing an output voltage that is periodic in applied flux with a period of one flux quantum, \( \Phi_0 = \frac{h}{2e} \approx 2.07 \times 10^{-15} \text{Wb} \). One is generally able to detect an output signal corresponding to a flux change much less than \( \Phi_0 \).

SQUIDs combine two physical phenomena, flux quantization - the fact that the flux \( \Phi \) in a closed superconducting loop is quantized [3] in units of \( \Phi_0 \) and second the Josephson tunneling [4]. There are two kinds of SQUIDs. The first [5], the dc SQUID, consists of two Josephson junctions connected in parallel on a superconducting loop and is so
Fe$_2$MnGa

* Check Ni substitution

(a) Ni - Mn - In
(b) Ni - Mn - Ga
(c) Ni - Fe - Ga

⇒ (d) Fe - Mn - Ga

Gemex
The corrections recommended by the referee have been duly carried out.

Examined

External Examiner: Guides
named because it operates with a steady state current bias. The second is the rf SQUID [6, 7] which involves a single Josephson junction interrupting the current flow around a superconducting loop and is operated with a radio frequency flux bias.

One of the simplest SQUID based instrument is the magnetometer. A pick-up loop is connected across a input coil to make a superconducting flux transform. The SQUID and the input coil are generally enclosed in a superconducting shield. If one applies magnetic flux $\delta \Phi^p$ to the pick-up loop, flux quantization requires

$$
\delta \Phi^p + (L_i + L_p)J_s = 0
$$

(2.1)

Here $L_i$ is the inductance of the input coil, $L_p$ is the inductance of the pick-up loop and $J_s$ is the supercurrent induced in the transformer. We have neglected the effects of the SQUID on the input circuit. The flux coupled into the SQUID, which we assume to be in flux locked loop is

$$
\delta \Phi = M_i|J_s| = \frac{M_i \delta \Phi^p}{L_i + L_p}
$$

(2.2)

where $M_i$ is the mutual inductance. We find the minimum detectable value of $\delta \Phi^p$ by equating $\delta \Phi$ with the equivalent flux noise of the SQUID. Defining $S_\phi^p$ as the spectral density of the equivalent flux noise referred to the pick-up loop, we find

$$
S_\phi^p = \frac{(L_p + L_i)^2}{M_i^2} S_\phi
$$

(2.3)

Introducing the equivalent noise energy referred to the pick-up loop we obtain

$$
\frac{S_\phi^p}{2L_p} = \frac{(L_p + L_i)^2}{L_i L_p} \frac{S_\phi}{2\alpha^2 L}
$$

(2.4)

We observe that eqn 2.4 has the minimum value

$$
\frac{S_\phi^p}{2L_p} = \frac{4\epsilon(f)}{\alpha^2}
$$

(2.5)
when \( L_i = L_p \). Thus a fraction \( \alpha^2/4 \) of the energy in the pick-up loop is transferred to the SQUID. It must be mentioned here that we have neglected the possible effects arising from noise in the SQUID, the fact that input circuit reduces the SQUID inductance and any possible coupling between the feedback coil and the input circuit.

The magnetic field resolution for \( L_i = L_p \) can then be written as

\[
B_{N}^{(p)} = \frac{(S_{\Phi})^{1/2}}{\pi r_p^2} = \frac{2\sqrt{2}L_p^{1/2}\epsilon^{1/2}}{\pi r_p^2\alpha}
\]

where \( r_p \) is the radius of the pick-up loop. Now \([8], L_p = \mu_0 r_p \ln(8r_p/r_0) - 2\), where \( \mu_0 = 4\pi \times 10^{-7} \) henries/meter and \( r_0 \) is the radius of the wire. For a reasonable range of values of \( r_p/r_0 \) we can obtain \( B_{N}^{(p)} = 2(\mu_0\epsilon)^{1/2}/\alpha r_p^{3/2} \). Thus one can improve the resolution indefinitely by increasing \( r_p \), keeping \( L_i = L_p \). However, in practice, the size of the cryostat sets the upper limit for \( r_p \). For a conservative values of \( \epsilon, \alpha \) and \( r_p \) one gets \( B_{N}^{(p)} = 5 \times 10^{-15} \text{TeslaHz}^{-1/2} \) which is much higher than any non-superconducting magnetometer.

SQUID magnetometers usually employ flux transformers made of Nb wire. An important variation of the flux transformer is a gradiometer which can either be of first order measuring \( \delta B_z/\delta z \) or a second order measuring \( \delta^2 B_z/\delta z^2 \). The gradiometer discriminates strongly against distant noise sources which have a small gradient, in favour of locally generated signals. One can thus use a second order gradiometer in an unshielded environment. Our magnetization measurements were recorded on the SQUID magnetometer: the Magnetic Properties Measurements System (MPMS) from Quantum Design Inc. at Tata Institute of Fundamental Research, Mumbai. Figure 2.3 shows a general wiring diagram of this SQUID magnetometer. This uses a second order gradiometer.

The coils are wound in a second-derivative configuration in which the upper and lower
Figure 2.3: General wiring diagram of the SQUID Magnetometer from Quantum Inc.

single turns are counterwound with respect to the two-turn center coil. As mentioned above, this configuration strongly rejects interference from nearby magnetic sources and lets the system function without the need for a superconducting shield around the SQUID sensing loop. The general diagram of the coils is shown in Figure 2.4.

The normal measurement process used in the MPMS is to position the sample below the detection coils with the sample transport set at its lower limit of travel, and then raise the sample through the coils while measuring the output of the SQUID detector.

In its initial position, the sample should be well below the detection coils so that the SQUID does not detect the sample moment. The sample is then typically measured by repeatedly moving the sample upward some distance and reading the voltage from the SQUID detector. If the SQUID voltage is read at large number of points, the voltage can be plotted as a function of sample position, as shown in Figure 2.5. A set of such data is known as scan.
Figure 2.4: Diagram of the second order Gradiometer coils

Figure 2.5: A typical 'scan' of the SQUID Magnetometer
Data Measurement and Analysis

The raw data from a measurement are a set of voltage readings taken as a function of position as the sample is moved upward through the sensing loops. At each position, the SQUID output voltage is typically read several times, and many vertical scans can be averaged together to improve the measurement resolution. The magnetic moment calibration for the system is determined by measuring palladium standard over a range of magnetic fields, and adjusting the system calibration factors to obtain the correct moment of the standard. The standard is a right circular cylinder approximately 3mm diameter x 3mm high. With pickup coil geometry used in MPMS, samples of this size or smaller are effectively point sources to an accuracy of about 0.1%.

After the raw data have been collected, one of the three methods is used to compute the magnetic moment of the sample. Using the full scan method the moment is calculated as the square root of the sum of the squares, normalized for the number of data points and the system calibration factors. This process minimizes errors due to volume variations of the sample. This analysis works well when the signal is large compared to the noise of the system. However, when the sample response becomes comparable to the system noise, this technique effectively sums the noise signal as well as the signal, rather than trying to average the noise to zero.

The other two methods available for moment calculation are Linear Regression and Iterative Regression. These methods calculate the EMU value by fitting a theoretical signal to the measured data and using the best fit to calculate the EMU. The regression calculations eliminate noise more effectively, and the iterative calculation corrects the sample position by adjusting for vertical displacement before calculating the EMU.
Sample Mounting Considerations

The sample holder can be a major contributor to the background signal, but this contribution can be minimized by choosing materials with low magnetic susceptibility and by keeping the mass of these materials to a minimum. The materials used in the sample holder must also perform well over the temperature range to be used. In a gradiometer-type magnetometer, like the one used here, the geometrical arrangement of the background and the sample is critical when their magnetic susceptibilities will be of similar magnitude, and thus the sample holder should optimize the positioning of the sample in the magnetometer. The sample should also be rigidly mounted to avoid extraneous motion of the sample during measurements.

In case of a second order gradiometer, moving a long homogeneous sample (which extends well beyond the ends of the coil during measurement) through the pickup coil will not produce any signal. For this reason the drinking straw, which is light weight, homogeneous plastic tube, is often used as an important part of the sample holder. Since a homogeneous sample that extends well beyond the pickup coils does not produce a signal, yet a small sample does produce a signal, there must be a cross over between the two limits. The sample length should not exceed 10mm along the field direction to obtain most accurate measurement. It is important to keep the sample susceptibility constant over its length as well the sample should be kept close to the centerline of the magnetometer to get the most accurate measurements.

When the background contribution of the sample holder will be similar in magnitude to the sample signal, the relative position of the sample and the materials producing the background is important. If there is a spatial offset between the sample and the
background along the axis of the magnet, the signal produced by both of them will be highly distorted and will not be characteristic of the dipole moment that is being measured.

In our measurements, samples in the form of rectangular pieces, typically of 5mm height by 3mm breadth were used. Magnetization (M) was measured as a function of temperature and as a function of field. M(T) was measured in an applied field of 50 Oe and 1000 Oe in the temperature range of 5 to 300 K. The sample was initially cooled from 300K to 5 K in zero applied field and the data was recorded while warming up to 300 K in the applied magnetic field (referred to as ZFC curve) and subsequent cooling (referred to as FC curve) back to 5 K. It may be emphasized here that care has been taken to make sure that the remanent field of SQUID magnetometer was less than ±13 Oe during the low field measurements. Magnetization as a function of field was measured under sweep magnetic fields up to ±5T at various temperatures. Before each M(H) was recorded, the sample was cooled in zero field from 300 K to the desired temperature of measurement. Magnetization was measured while increasing H to 50 kOe (virgin curve). Measurement of M was then continued with the cycling of H between 50 and -50 kOe.

2.4.2 Four Probe Resistivity

In the investigation of the electrical properties, a method for measuring the resistivity of the material is of great importance. The simplest way to measure the resistance of the material is to make two contacts and measure the drop of voltage while letting the current pass through the contacts. Temperature dependant electrical resistivity measurements on all the samples were made using the in-house conventional d.c four probe setup. This resistivity inset has a sample holder with four equidistant copper contacts. The sample
X-ray Photoelectron Spectroscopy

is mounted onto this holder using G-varnish that electrically isolates the sample from the rest of the insert while maintaining a good thermal contact. A manganin heater radially wound just above the sample holder serves to control the temperature of the sample. Here the desired current through the sample is passed through the outer two contacts using a Keithley 224 programmable constant current source and the potential developed across the inner two contacts made on the sample is measured using a Keithley 2182A nanovoltmeter. The entire system is evacuated and cooled in a liquid Nitrogen dewar and the temperature is measured with a calibrated Platinum resistor (Pt-100) having an accuracy of 0.1K using Keithley 2010 multimeter. Using this set-up measurements in the temperature range of 77K to 350K can be made.

Rectangular bars with dimensions \( \approx (2\text{mm} \times 5\text{mm} \times 1\text{mm}) \) were cut from the sample and used for the measurements. The data acquisition was carried in the cooling and warming cycles in the temperature range: 77K to 300K.

2.5 X-ray Photoelectron Spectroscopy

Electrons in condensed matter are classified into core electrons and outer electrons (or valence electrons). The core electrons are well localized inside the atom, and so they keep their properties in the free atom state, irrespective of the chemical surroundings. On the other hand, the outer electrons are more extended and contribute to the inter-atomic bond, so that their properties are different for different materials even with the same atomic origin. In the core level spectroscopy, a core electron is excited by an incident photon or by an incident electron, and the spectra associated with the core level excitation, provide us with important information on the properties of outer electrons, as
X-ray Photoelectron Spectroscopy

well as atomic arrangements. One of the most important aspects of core level spectroscopy is that many body effects of outer electrons are often reflected sensitively in the spectral features. In magnetic materials which contain incompletely filled f or d electrons, the core holes couple strongly with f or d electrons resulting in splitting of core level spectra. One of the origins of the splitting is known as the exchange splitting, where the core hole spin $s$ is coupled with the local spin $S$ of f or d electrons on the core hole site through the exchange interaction given by $U = -J.S.s$. When the core hole has a finite value of orbital angular momentum, the exchange splitting is generalized to the multiplet splitting. The exchange or multiplet splitting is essentially of atomic origin [9]. When monochromatic source of x-rays are used to remove core electrons, the photoelectron spectroscopy is referred to as X-ray Photoelectron Spectroscopy (XPS). If an electron is ionized from a core level with non zero orbital angular momentum, the spin of the whole state can couple to its orbital angular momentum leading to two different $J$ values, $(J = 1 \pm 1/2)$ i.e. $J_1 = 3/2$ and $J_2 = 1/2$ for the final state. As the energy of these two final states are different, the spectrum of any such core level shows a doublet structure corresponding to the different $J$ values in absence of any other interaction. The 2p levels of the first row transition metal oxides, the 3p ad 3d levels of second row transition metal oxides are known to show such spin-orbit couples doublet structure in XPS spectra. The energy difference $\Delta E_{ni}$, between the two peaks corresponding to the two different $J$ values is known as the spin orbit splitting. Besides the doublet structure corresponding to different $J$ values, XPS spectra of transition metal compounds (3d, 4d), rare earths (4f,5f) where electron correlation are strong, show evidence of satellites next to the core level peaks [10, 11, 12] due to multielectronic excitations. These satellites can appear on the higher
(shake up) or on the lower energy side (shake down) of the main core level peaks. When a core-hole is created in one of the levels, the nuclear charge felt by the other electrons increases nearly by +1 and the outer electrons relax in this new attractive potential. The relaxation energy thus produced can cause an outer electron to make a transition to an unoccupied state. If such a transition takes place, the energy of the photoejected electron decreases or increases by an amount equal to the energy of the transition and an extra peak appears in the photoelectron spectrum. Energy separation and intensity of the satellite with reference to the main peak for a given metal ion depend on the nature of the ligand, and gives the energy difference between bonding and antibonding levels.

X-ray photoelectron spectra at Co (2p) and Ru (3d) levels were recorded using Thermo Fisher Scientific Multilab 2000 (England) instrument with Al Kα radiation (1486.6 eV). The binding energies reported here is with reference to graphite at 284.5 eV having an accuracy of ±0.1 eV.

2.6 X-ray Absorption Fine Structure Spectroscopy

X-ray Absorption Fine Structure commonly known as XAFS is a technique employed to study the chemical environment of the atoms in a crystal. When a high energy X-ray photon is absorbed, a core level electron is emitted if the incident energy of the photons exceeds its binding energy. This causes a sharp dip in the transmitted intensity which is called as "absorption edge". The outgoing photo-electron can be thought of as a spherical wave expanding in all directions. When such a wave reaches the neighboring atoms, it will be partially back-scattered. The back-scattered wave interferes with the outgoing electron wave causing a constructive or destructive interference. The net effect is the
modulation of the transmitted X-rays through the absorber up to about 1000 eV from the absorption edge. The interference pattern depends mainly on the number, nature and distance of the surrounding atoms. Thus XAFS proves to be a useful tool for the study of the atoms in a solid. The XAFS experiment can be divided into three parts, the experimental set-up, the sample preparation and the data analysis procedure. The first two parts will be discussed below while the actual procedure for data analysis is discussed with LaSrCoRuO$_6$ XAFS as an example and presented in the next Chapter.

2.6.1 Experimental Setup

The X-ray absorption experiment can be carried out in the transmission as well as fluorescence mode. All the experiments presented in this thesis were carried out using the Co and Ru edge in transmission mode at room temperature using the beamline 12C at the Photon factory, Tsukuba, Japan. The X-ray source here is the bending magnet type with 1.2 T field and the energy ranges from 2 - 2.4 GeV with injection current of 300 mA (© 2 GeV) and 130 mA (©2.4 GeV). The Fig.2.6 shows the schematic of a typical XAFS experiment for both, transmission and fluorescence geometries. The main components are: the monochromator used to select the X-ray energy, the slits and the ion chambers used to sample the incident and transmitted X-ray intensities. Polychromatic X-rays are produced by the synchrotron radiation source or by bremsstrahlung from a conventional laboratory source and a desired energy band of approximately 1 eV bandwidth is then selected by diffraction from monochromator. The monochromator consists of two channel-cut silicon crystals held parallel to each other. Only those X-ray photons that are of correct wavelength $\lambda$ ($\lambda = hc/E$, where $h$ is the Planck's constant and $c$ is the speed of light) to satisfy the Bragg condition $n\lambda = 2dsin\theta$ at the selected angle $\theta$ will be
Figure 2.6: Schematic of the XAFS experiment. The setup for both the transmission and fluorescence geometries is depicted.

reflected from the first crystal. The parallel second crystal is used as a mirror to restore the beam to its original direction. However, along with the fundamental edge energy E, the monochromator crystals can pass higher order harmonics (like 2E, 3E, etc) into the experimental beam. Making the two crystals slightly non-parallel by detuning the second crystal eliminates the higher order harmonics that would interfere with the fundamental reflections. The harmonics rejection is further achieved by using X-ray mirrors made of metals with high atomic number viz. Rh or Pt.

The slits placed after the monochromator define the size of the beam that strikes the sample. The dimensions of the slits are so chosen as to strike a balance between two contrasting aspects: maximizing the throughput and maximizing the energy resolu-
Sample Preparation

The throughput is increased by opening the slits as more photons pass through. However, due to the angular divergence of the X-ray source and the geometry of the monochromator, there is a speed of energies compromising the energy resolution. The slit window at EXAFS beamline at Photon factory, Tsukuba, Japan has a rectangular geometry and all four sides can be adjusted to attain a critical size of the beam incident on the sample. The incident and transmitted X-ray fluxes are monitored usually with gas ionization chambers. The ion chambers are basically, parallel plate capacitors with high voltage maintained across the plates. The region in between the plates is filled with gas that gets ionized when x-rays travel through it. The associated electronics measures the current produced and hence determines the proportional x-ray intensity. The choice of a particular gas or mixture of gases that fills the ion chambers is made on the basis of the x-ray edge to be measured. Finally, the sample is affixed onto a motorized sample stage with monochromatic movement to facilitate the movement of the sample into the beam. For the XAFS measurement at ambient conditions, sample is in direct contact with the surroundings. XAFS can also be carried out in wide range of sample environment conditions with suitable modifications at the sample holder stage.

2.6.2 Sample Preparation

The form of the sample for XAFS experiment is just as important as the technique of measurement and needs to be prepared in much the same way with due consideration to absorption of X-ray photons. The most important characteristics of an XAFS sample are its thickness, homogeneity and purity. The sample thickness is determined by optimizing the signal to noise ratio. This corresponds to an edge step absorption coefficient of about 1.0 while total absorption coefficient does not exceed 2.5. The homogeneity of the sample
Sample Preparation

is important because the XAFS signal gets attenuated if part of the x-rays do not pass through the sample. The particle size of the powder sample should be fairly uniform.

Taking into consideration all these factors, absorbers for the XAFS experiments were made by spreading very fine powder of the sample on a scotch tape avoiding any sort of sample inhomogeneity and pin holes. Small strips of the sample coated tape were cut and were held one on top of the other. This assembly of the sample coated tape was sandwiched in between the scotch tape and held onto the sample holder plate. Enough number of such strips were adjusted to give absorption edge jump, $\Delta \mu X \leq 1$. XAFS at Ru and Co K-edges were recorded in the transmission mode using Si(111) as monochromator. The K-edge energies of Ru and Co are given in the table.

The measurements were carried out at room temperature and liquid Nitrogen temperature. The incident and transmitted photon intensities were simultaneously recorded using gas-ionization chambers filled with mixtures of He-N$_2$ for Ru edge and Ar-N$_2$ for Co edge. Measurements were carried out from 300 eV below the edge energy to 1000 eV above it with a 5 eV step in the pre-edge region and 2.5 eV step in the EXAFS region. At each edge, three scans were collected for each sample.

Data analysis was carried out using IFEFFIT [13] in ATHENA and ARTHEMIS programs [14]. Here theoretical fitting standards were computed with ATOMS and FEFF6 programs [15, 16].
References


References


