Chapter 2

Experimental details

Chapter 2 provides details regarding the procedures and techniques employed for synthesizing the materials and characterizing their physical properties.

This part starts with the methodological demonstrations and steps used in the preparation of various compounds which have been used in our whole research works and this part is then followed by different experimental techniques used for investigating the various properties of the desired systems.

2.1 Sample synthesis technique:

The conventional solid-state reaction method for oxide polycrystalline solid sample synthesis is one of the most widely used techniques which uses a stoichiometric mixture of different starting powder materials as precursors. At room temperature, solids do not react with each other over normal time scales and thus, it is required to heat them to quite high temperatures, often to 1000 to 1500 °C so that the reactions may take place at an appreciable rate. The important aspect which mainly decides the solid-state reaction's workability and rate are the surface area of the solids, structural properties of the reactants, the reaction conditions, their reactivity, and the thermodynamic free energy change related to the reaction.

Throughout our research work, highly pure oxide powder materials have been used. The powders were taken in proper stoichiometry and then it was intimately ground for 1-2 hours in an agate mortar. This thoroughly mixed powder was then subjected to an initial heat treatment at the desired temperature (900-1000 ^{0}C). Once the temperature reaches room temperature, the powder was reground, and then it was put in a muffle furnace in the air at different desired temperatures (up to 1200 ^{0}C) for several days followed by intermittent grindings to get the pure phase formation. This was then ground finely and it was used to carry out the powder X-ray diffraction (XRD) experiment at 300 K, to check the phase purity. Finally, this powder was pressed into pellets using the hydraulic press under suitable pressure for final sintering at some higher temperatures depending on the systems (1250-1400 ^{0}C). These sintered samples were

undergone through different experiments to explore their properties, for example, structural, magnetic, spectroscopic, optical, electrical, etc. The detailed processes have been discussed in the working chapters. The generalized flow chart for the solid-state reaction techniques is shown below:

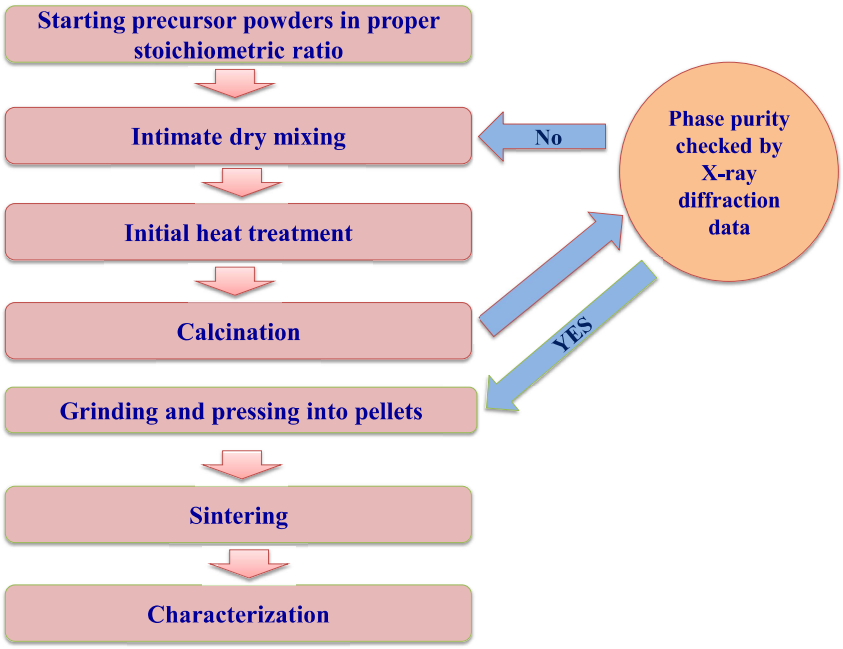

Fig. 2.1: The general flow chart for the solid-state reaction method.

2.2 Characterizing instruments and their brief working principle

2.2.1 X-ray diffractometer:

The XRD technique is a rapid analytical and non-destructive technique that is mainly employed for information on the phase formation of crystalline material that it also provides the knowledge of unit cell dimensions. The material used for this experiment requires finely ground, homogenized powder, and average bulk composition is obtained.

2.2.1.1 Basic principles of X-ray powder diffraction method:

In the year of 1912, Max von Laue first discovered that crystalline materials act as 3D diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. Hence, XRD has now become a famous approach for the investigations of crystal structures and crystalline size, etc. The XRD is depend upon constructive interference of monochromatic X-rays in a crystalline lattice. In this mechanism, the cathode ray produced the X-ray beams and these beams are filtered to obtain monochromatic radiation. After that on collimated to concentrate, they fall on the surface of the sample. The interaction of the incident X-rays with the sample results in the constructive interference producing a diffracted ray when conditions of Bragg's Law ($2d \sin \theta = n\lambda$) get satisfied. Where d is the interplane distance of atoms, n is the integer displaying the order of diffraction and λ is the wavelength of the incident X-rays. Finally, all the diffracted X-rays are then detected, processed, and counted. The all-possible diffraction directions of the lattice are covered by scanning the sample through a wide range of 2θ angles (because of the random orientation of the powdered material). Eventually, the conversions of the diffraction peaks to the corresponding d-spacings allow one to identify a particular crystalline compound since every compound has a unique set of d-spacings. Generally, this is done by comparing the d-spacings with standard reference data.

2.2.1.2 The experimental setup:

In performing the XRD experiments, monochromatic X-ray radiation of copper source (Cu-Kα = 1.5418 Å) has been used. A collimated beam of X-ray strikes the sample kept in powdered form on a glass slab and it produces the diffracted beams. This beam is collected by employing a moveable detector such as a Geiger counter, a scintillation counter, or an image plate that is linked to the chart recorder. XRD set-up has been demonstrated in Fig. 2.2 [145]. In regular use, the counter is driven to scan at a constant angular velocity over an angular range of 2Θ values (typically, we have used 10 to 90 degrees). In fact, the identification of single or multiple

phases of a system allows us to get an idea of the mechanism behind the formation of the sample.

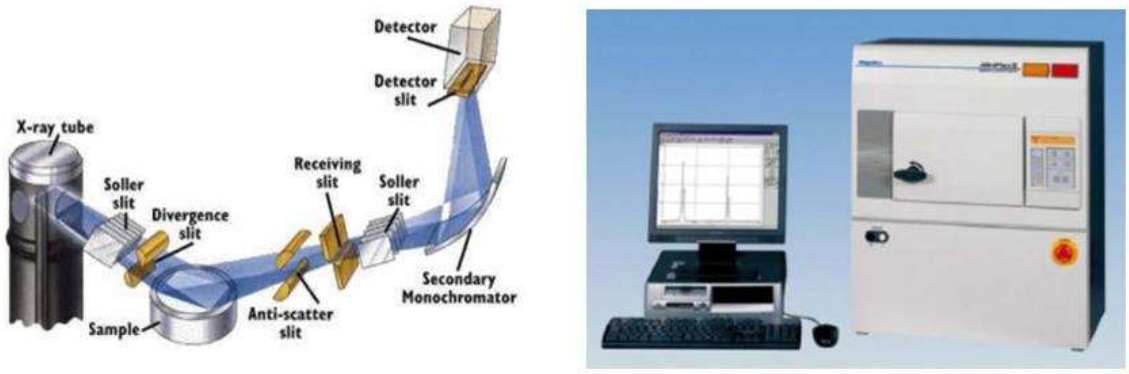

Fig. 2.2: The left figure depicts the schematic diagram of an XRD machine. The right figure is showing the X-ray diffractometer Rigaku Miniflex-II which we have used.

2.2.2 Neutron diffraction:

The neutron powder diffraction (NPD) is a powerful tool in the solid-state physics research field for determining the crystal structure as well as the magnetic micro-spin structure. Neutrons are neutral and deeply penetrating unlike other radiation sources e.g., x-ray and electrons. As a matter of fact, the wavelength of the incident neutrons with a similar order of magnitude as the inter-atomic distances of crystalline solids enables one to study the aspects of condensed matter at the atomic level.

2.2.2.1 Basic working principle:

Eventually, all the diffraction experiments rely on Bragg's law and there are mainly two ways of carrying out the experiment. In the first process, a monochromatic neutron beam of wavelength λ_0 is targeted on a sample and thus different inter-planar d-spacings are noted by moving a detector in a wide range of angles such that $\lambda_0=2d_{hkl}\sin\Theta_{hkl}$, where the Miller indices

(hkl) are related to the inter-planar spacing d_{hkl}. This method is usually used in most neutron diffraction facilities. However, there is an alternative method where the detector is kept fixed at an angle of Θ_0 and the wavelength is varied. This can be done by utilizing a white spectrum having a broad range of wavelengths and an energy dispersive detector. In this case, the d - spacings are found using the following relation: $\lambda = 2dsin\theta_0$.

The neutrons interact with matter in two main ways: firstly, the strong nuclear interaction which is related to the interaction occurring between the neutron and the nuclei of the sample, thus producing the nuclear scattering; secondly, the magnetic interaction, which is related to the interaction occurring between neutron spin and the atomic spins of the sample under investigation, thus giving rise to the magnetic scattering. Hence, the neutron diffraction technique has numerous advantages over the XRD technique. First, the scattering length which characterizes the nuclear interaction is not dependent on the atomic number Z, unlike the X-rays scattering length which is proportional to Z. This is the reason why for X-rays, the atoms having lighter weight are almost invisible (especially in the case when other heavy atoms are present), on the contrary, for the neutrons, both the light and heavy atoms may have comparable scattering lengths. Secondly, as the neutrons have magnetic spin moments, it interacts with the atomic spins of the sample and is capable of giving precise information about the spin structure of a system. Hence, the neutron diffraction technique is ubiquitous in the field of magnetism research.

The properties of neutrons are summarized below:

Mass = 1.674×10^{-27} Kg

Wavelength $\lambda = h/mv = h/ (2mE)^{1/2} = 0.0286/E^{1/2}$

Charge = 0

Spin (s) = ½

Magnetic dipole moment μ_N = -1.913

Neutron lifetime: 881.5±1.5 s (~15 min)

$n \xrightarrow{15\ min} p + e + \nu$

Neutron production is done in the reactor as follows:

Reactor source

$N + U^{235} \longrightarrow {}^{36}Ba + {}^{56}Kr + \text{neutron} + \text{betas}$

The fission neutrons have high KE 1-15 MeV

All of our neutron diffraction measurements were performed on the PD2 (Powder Diffractometer-2) neutron powder diffractometer (λ =1.2443 Å) at the Dhruva reactor in Bhaba Atomic Research Centre, Mumbai, India. The schematic diagram of the neutron diffractometer set up PD-2 is given below in Fig. 2.3 [146]:

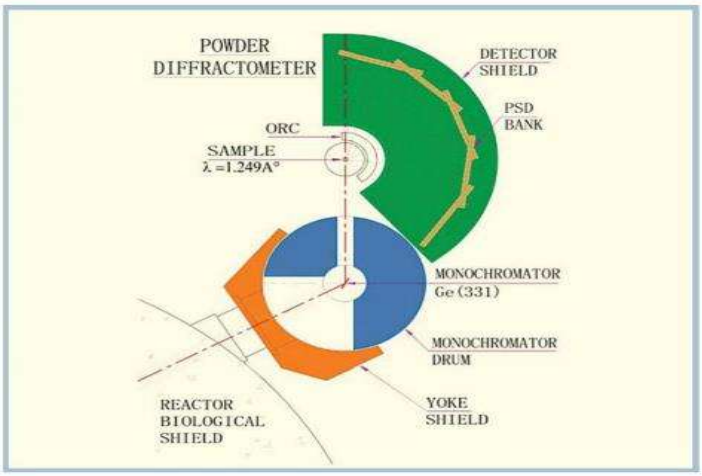

Fig. 2.3: Setup PD-2 (Powder Diffractometer-2) at Bhabha Atomic Research. Center, Mumbai, India.

2.2.3 Magnetic Property Measurement System (MPMS): SQUID-VSM

A superconducting quantum interference device (SQUID) is a device that is used to observe small magnetic field changes with very high precision. The working principle of SQUID is

based on the theoretical works by Josephson and was experimentally realized in 1963 for the first time. There are two different types of SQUIDs which are made up of a superconducting ring interrupted at a point (radio frequency-SQUID) or two points (dc-SQUID) using a normally conducting or electrically insulating material. However, this interruption must be thin enough so that the superconducting Cooper pairs can tunnel through this layer (Josephson contact). The basic function of a SQUID is based on the Josephson effect and the flux quantization effect in superconducting rings. Eventually, only flows a magnetic flux that has the size of the integral multiple of the elementary magnetic flux quantum $\Phi_0 = 2.07 \times 10^{-15}$ Tesla-m^2 can flow by a superconducting ring.

2.2.3.1 Principles:

A radio frequency (RF) SQUID: It comprises one Josephson junction, which is mounted on a superconducting ring. An oscillating current is supplied to an external circuit, whose voltage changes as an effect of its interactions with the ring. The magnetic flux is then measured.

The DC SQUID: A DC SQUID is a simpler device that is formed by the two Josephson junctions connected in parallel on a closed superconducting loop as shown in Fig. 2.4(a) [147]. As already stated, a fundamental property of superconducting rings is that they can enclose flux quantum, $\Phi_0=2.07\times10^{-15}$ Tesla-m^2. In fact, the flux quantum is very small due to which this physical effect can be exploited to produce an extraordinarily sensitive magnetic detector known as the SQUID. The SQUIDs act as magnetic flux-to-voltage transducers where the sensitivity is set by the magnetic flux quantum. On application of the current to the SQUID (biasing it), it causes the Cooper pairs of electrons to tunnel through the junctions. However, the application of a magnetic field to the ring changes the flow. Actually, it alters the quantum-mechanical phase difference across each of the two junctions. The critical current of the SQUID is thus affected by these phase changes. As a consequence, a progressive rise or reduction in

the magnetic field gives rise to the oscillations of the critical current between a maximum value and a minimum one. The maximum occurs when the flux administered to the SQUID equals an integral number of flux quanta through the ring; the minimum value corresponds to a half-integral number of quanta. The flux applied to the SQUID can assume any value, unlike the flux contained within a closed superconducting ring, which must be an integral number. In practice, the current is not measured instead the voltage across the SQUID swinging back and forth under a steadily changing magnetic field is measured (Fig. 2.4(b)). A digital magnetometer is based on this SQUID where each "digit" corresponds to one flux quantum. As a matter of fact, conventional electronics can even detect voltages corresponding to changes in the magnetic flux of much less than one flux quantum. Hence, the SQUID can be realized as a flux-to-voltage transducer, transforming an extremely small change of magnetic flux into a voltage.

We have used the “Quantum Design MPMS 3” magnetometer throughout our research work for magnetic measurements. This MPMS set-up consists of three possible measurement modes, DC scan mode, AC susceptibility mode, and vibrating sample magnetometer (VSM) mode. In contrast to the dc magnetization measurements, an ac susceptibility measurement is a unique tool for probing the spin dynamics. The VSM is based on Faraday’s law of induction which states that an alternating magnetic field will induce an electric field and vice-versa. In VSM operation, a sample (powder/pellet) is kept within a uniform magnetic field and consequently, they get magnetized by aligning the magnetic domains in the direction of the field. However, the magnetization of the sample will in turn induce a magnetic field near the sample, known as a stray magnetic field of the sample. When the sample vibrates, this stray magnetic field alters as a function of time. This change is sensed by a set of pick-up coils. The pick-up coil is SQUID based and thus has a very high sensitivity. This induced current is directly proportional to the magnetization of the sample. The induction current is then amplified by a trans-impedance

amplifier and a lock-in amplifier. The various components are connected to computer resources. Controlling and monitoring software is used to perform several experiments following different protocols.

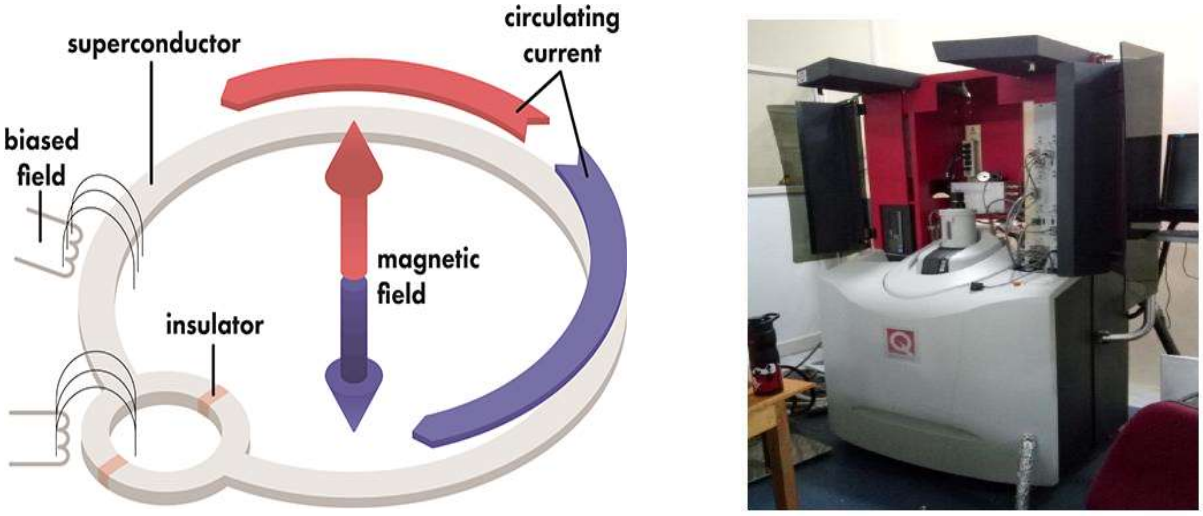

Fig. 2.4**:** (a) depicts the Josephson junction, (b) shows the picture of the Quantum Design MPMS SQUID VSM facility in our institute.

The XPS which is also called photoelectron spectroscopy for Chemical Analysis (ESCA), is a powerful technique used to collect chemical information about the surfaces of solid materials viz., oxidation states, elemental composition, ligand coordination, etc. Both the insulators and conductors can easily be investigated in surface areas from a few microns to a few millimeters in depth. In fact, the XPS is used as a surface-sensitive tool since it mainly identifies those electrons produced near the surface. The photoelectrons of interest have comparatively small kinetic energy. As a consequence of the inelastic collisions in the sample's atomic structure, photoelectrons producing more than 20 to 50 Å beneath the surface cannot escape with sufficient energy to be detected in this technique.

2.2.4.1 Working principle:

The sample under investigation is kept inside an ultrahigh vacuum ambiance (typically ~10^{-10} torr) and then it is exposed to a monochromatic, low-energy X-ray source. The X-rays incident on the sample results in the ejection of core-level electrons from sample atoms. In fact, the energy of a core electron produced in such a photoemission process is a function of its binding energy and is a characteristic of the element from which it was emitted. As a matter of fact, the primary data used for XPS is the energy analysis of the photo-emitted electrons. When the incident X-ray ejects the core electron, an outer electron fills the core hole. By the emission of an Auger electron or a characteristic X-ray, these energies get compensated. Further, in XPS Auger electron's energy can also be utilized along with the emitted photoelectrons.

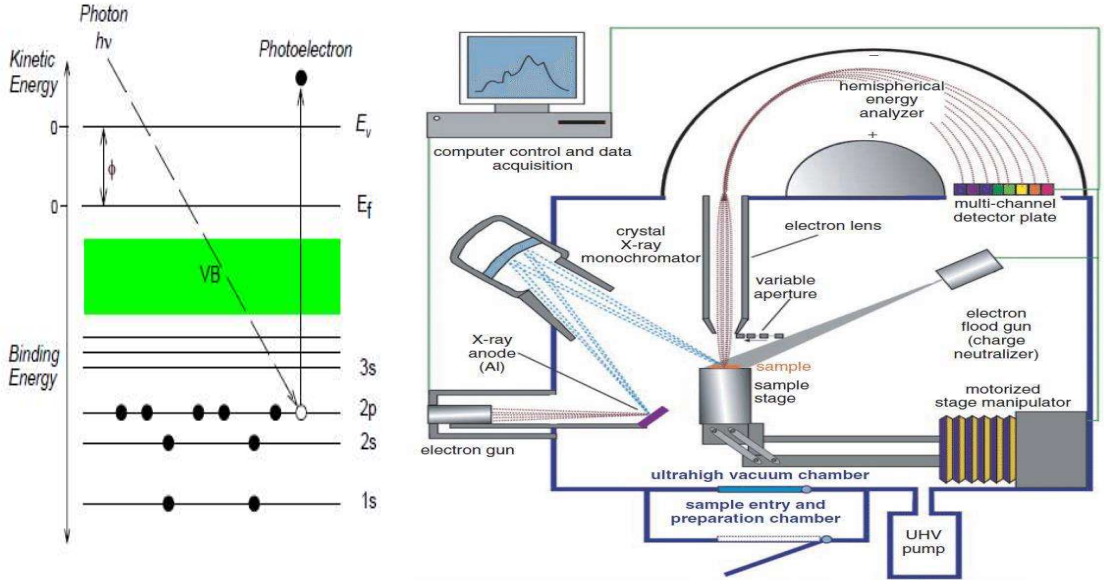

Fig. 2.5: The left figure shows the schematic diagram of the photoelectric effect. The right figure depicts the schematic diagram of an XPS setup.

The following equation is used for the energy of each of the photoelectrons which is purposed by Ernest-Rutherford (1914):

$$E_{\text{kintetic energy}} = h\nu - (E_B + \phi) \quad 2.1$$

Here, E_B represents the binding energy of the electron, $h\nu$ represents the energy of the incident X-ray photons being used, $E_{\text{Kinetic energy}}$ represents the kinetic energy of the electron that is measured by the spectrometer and the work function of the spectrometer is known as ϕ. This is illustrated in the schematic diagram Fig. 2.5 (left).

The different instrumental units of an XPS machine as demonstrated in the schematic Fig. 2.5-right) [148].

Hemispherical electron energy analyzer

1. X-ray source.
2. Ar-ion gun.
3. Vacuum system.
4. Neutralizer or electron flood gun.
5. Multi-channel detector plates.
6. Sample stage or holder.
7. Electronic control units.
8. Computer.

2.2.5 Raman Spectroscopy:

In the year 1928, Raman and Krishnan discovered Raman spectroscopy. However, during his discovery, very crude instrumentation was available such as he used sunlight as the source, a telescope as a collector and he used his eyes as the detector. Thereafter, lots of improvements were furnished. At first, the innovation of a good excitation source was looked for. Then, the detector system was invented and a commercial Raman spectrometer was available. Since then,

it remained a novel qualitative and quantitative spectroscopic technique for probing the dynamic crystal structure by the scattering of radiation.

2.2.5.1 Basic principle:

During the scattering of the light from a molecule or crystal, most photons are elastically scattered. Hence, such scattered photons have exactly the same energy and, therefore, wavelength, as the incident light. As a matter of fact, only a small fraction of light (approximately 1 in 107 photons) suffers inelastic scattering, leading to a change in its frequency. The mechanism leading to the inelastic scattering is known as the Raman Effect. In fact, Raman scattering can occur giving rise to a change in vibrational, rotational, or electronic energy of a molecule. The case of elastic scattering is known as Rayleigh scattering.

The Raman effect is based on molecular deformation in electric field E determined by molecular polarizability α. The laser beam can be considered as an oscillating electromagnetic wave with electric vector E. After interaction with the sample, it induces electric dipole moment $P = \alpha E$ which deforms the molecule. Due to the periodical deformation, molecules start vibrating with characteristic frequency ν_m. The amplitude of vibration is defined as nuclear displacement or it can be realized in another way: monochromatic laser light ν_0 excites molecules and transforms them into oscillating dipoles. That oscillating dipoles emit light of three different frequencies as ν_0, $\nu_0-\nu_m$, and $\nu_0-\nu_m$ which are known as Rayleigh, stokes, and Anti-stokes scattering (as shown in Fig. 2.6) [149].

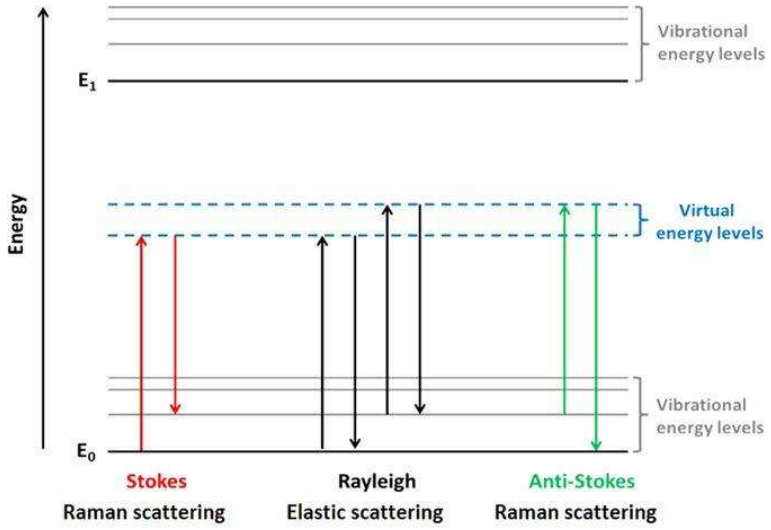

Fig. 2.6: Energy level diagram showing states involved in the Raman effect.

2.2.6 X-ray absorption spectroscopy:

In X-ray spectroscopy studies, the involved transitions are related to either absorption (XAS) or emission (XPS) of X-rays, in which the former measures the ground state to the excited state transitions, while the latter investigates the decay process from the excited state. However, both techniques can probe the chemical states and local environment of atoms in molecules. In XAS, the incident X-ray photon excites an electron in the core level to an unoccupied conduction level following the intra-atomic dipole selection rule. Since the energy difference between the core level and conduction level are specific to the elements, XAS is an element-specific probe. The synchrotron-based XAS is a spectroscopic tool to probe the electronic states of a matter. The synchrotron-based XAS facilities provide a wide range of X-ray energies that are capable of sensing most of the elements in the periodic table. In contrast to the other methods (such as optical or UV absorption, magnetic susceptibility, fluorescence, electrochemistry, etc.,), the XAS technique uses a previously chosen energy of the incident X-rays to identify the specific element being probed. For the last few decades, it is being widely used due to its element specificity, sensitivity to spin orientation, and surface sensitivity. Like XPS, XAS is used for

quantitative analysis of the oxidation states of the elements of the material. However, additionally, XAS has an intrinsic capability to sense magnetic ordering also. The circular polarization of the synchrotron X-ray makes it possible to investigate the spin orientation of the magnetic materials. This information of magnetic ordering is embedded in the same multiplet structure which is used to specify the presence of different chemical species. The signature of FM or AFM etc. order is seen as an increase or decrease of some peak intensities in a particular multiplet pattern. Therefore, it is necessary to have knowledge of both the shape of the spectra signifying a specific element as well as the possible alterations in those spectra which accompany the different types of magnetic orderings. Thus, if we have this information beforehand, the magnetic information can be extracted not only for a specific element but also for different chemical phases of that same element.

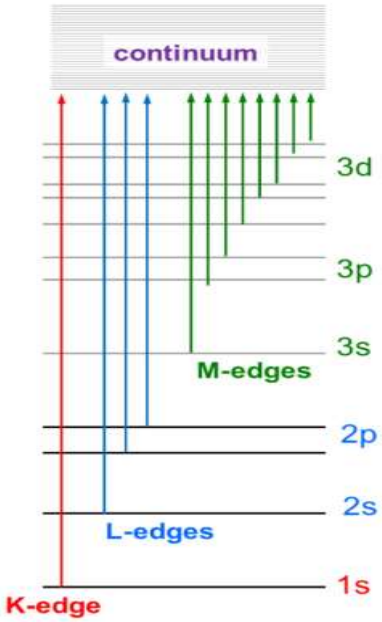

Fig. 2.7: Transitions between the core electron which rise near the XAS edges.

The schematic diagram of the XAS spectra is illustrated in Fig. 2.7 [150]. The XAS of any system such as atomic or molecular in nature is characterized by sharp rises in absorption at specific X-ray photon energies that are the characteristic feature of the absorbing element. These sudden rises in absorption are known as absorption edges. It is related to the energy necessary to eject a core electron into the LUMO or to the continuum thus producing a photoelectron. The absorption discontinuity rises due to the photoelectron originating from a 1s core level known as K-edge. It is called L-edge when the ionization is from a 2s or 2p electron. Similarly, it is called the M-edge when the photoelectrons excite from 3d electrons.

In the present thesis, we have performed all of our XAS measurements at the BL14 beamline of Hiroshima Synchrotron Radiation Centre, Hiroshima University, Japan. A defined protocol which has been considered while performing the XAS measurements is: total electron yield (TEY) mode, base pressure of $4\times10^{-8,}$ and the photon energy range of the beamline was 400-1200 eV.

2.2.7 X-ray magnetic circular dichroism:

X-ray magnetic circular dichroism (XMCD) spectroscopy is defined as a difference between two XAS spectra. These two XAS spectra are obtained from left circularly polarized light and right circularly polarized light, in the presence of the magnetic field. The information of the magnetic properties of the atom can be obtained by the XMCD measurement, particularly about their spin and orbital magnetic moments. The circularly polarized X-rays are provided by an undulator, which then irradiates the sample, which is kept magnetized by an applied magnetic field.

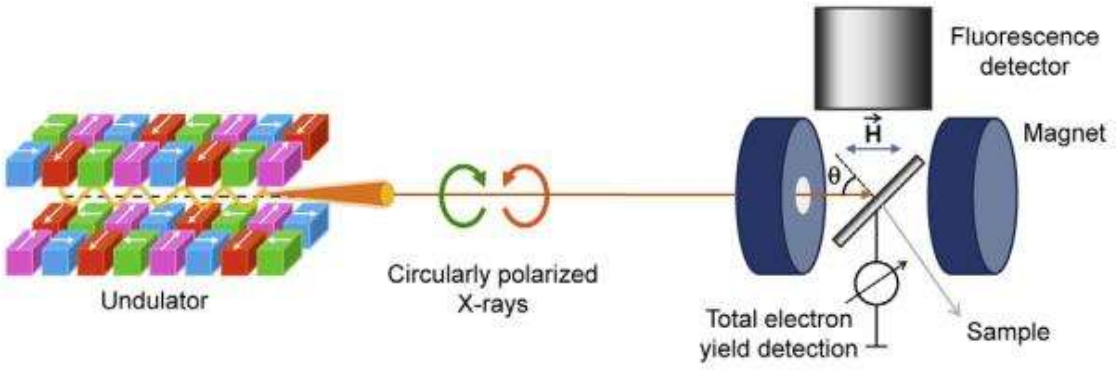

Fig. 2.8: Experimental setup for an XMCD experiment.

A schematic view of two beamlines XMCD experimental setup is illustrated in Fig. 2.8 [151]. The sample is positioned at the center of a superconducting magnet, which is illuminated with polarized and monochromatic X-ray. The magnetic field is applied along the direction of the incoming beam. The observation of the polarized dependent XAS is achieved by fluorescence yield (FY) or TEY. Later is regularly used in soft X-ray regimes. The fluorescence detectors are (single or multi-anode) ion-implanted silicon photodiodes which are characterized by high efficiency in the X-ray range, fast time response, excellent linearity, and nearly insensitivity to the magnetic field.