Chapter 2
Experimental Techniques

2.1 Introduction

In this chapter, the experimental techniques and working principles of the various instruments used in carrying out this piece of research work are described. The structural characterization was performed by X-ray diffractometry (XRD) and microstructure studies were carried out using scanning electron microscopy (SEM). The composition of the sample, LiFePO$_4$ in particular was determined by energy dispersive X-ray analysis (EDAX). Mössbauer Spectroscopy and Fourier Transform of Infrared Spectroscopy (FTIR) were used to analyze the phase purity at the Fe site, and the spectroscopic properties of the phosphate group respectively. The magnetic properties of the synthesized LiFePO$_4$ at low temperatures have been studied using Superconducting Quantum Interference Device (SQUID) and Mössbauer spectroscopy, while the high temperature behavior of the sample, order – disorder phase transition in particular has been studied by Fourier transform of Infrared Spectroscopy.

2.2 X-Ray Diffraction

![Schematic diagram of X-ray diffractometer](image)

A & B - collimator slits  
G – Counter  
C - Sample  
S – The line focal spot on the target  
E & H - Supporting table  
T- Target of the X-ray tube  
F – receiving slit  
O – Axis perpendicular to the plane of drawing

One of the simplest tools to obtain the structural details (e.g., average crystallite size and crystallite composition) about the nanocrystalline LiFePO$_4$ is the X-ray diffraction technique. Diffraction of X-ray beam from a lattice can occur only when the Bragg condition for diffraction,

\[ 2d_{hkl} \sin \theta = n\lambda \]  

(2.1)
is satisfied, where $d_{hk\ell}$ is the interplanar spacing between parallel planes.

- $\theta$ is the Bragg angle
- $\lambda$ is the incident wavelength and
- $n$ is order of diffraction.

The powder X-ray diffraction technique involves the diffraction of monochromatic X-rays by a powder specimen. Since single crystals are not always available, this technique is preferred to Laue method (wherein the wavelength of the X-rays is varied, keeping the incident angle constant) and polycrystalline samples may be examined nondestructively without any special preparation.

When X-rays of known wavelength are used, the diffractometer can measure the positions and line intensities of diffraction lines simultaneously and quickly. This method is especially suited for determining lattice parameters with high precision and for the identification of phases.

In this study we used PHILLPS X-ray diffractometer with a source providing Ni-filtered Cu-K$_\alpha$ radiation ($\lambda=1.54056$ Å). Bragg angle was varied by rotating the specimen. A radiation detector with associated electronic equipment forms the detector module.

The principle of operation [1] of this diffractometer is illustrated in the figure 2.1. The sample C is supported on a table which can be rotated about an axis O perpendicular to the plane of drawing and therefore parallel to the diffractometer axis O. X-rays diffracted from the sample are collected in the GM counter G after being focused at the slit F. A and B are special slits (soller slits) which define and collimate the incident and diffracted beams respectively. The beam from the x-ray tube contains not only K$_\alpha$ radiation but also weak K$_\beta$ line and some other components. The intensity of these weak and unwanted components is suppressed by passing the beam through a Ni filter. This filter is also used in a special holder in the diffracted beam to help decrease the background radiation originating in the specimen. The diffracted beam passes through another set of Soller slits (Fig.2.2) and the receiving slit F before entering the counter. Since the receiving slit defines the width of the beam admitted to the counter, an increase in its width will optimize the intensity of any diffraction line being measured. The intensity of the diffracted beam is measured directly by an electronic counter which converts the incoming X-rays into electric pulses counted by X-ray detector placed on the circumference of a circle centered on the thin film specimens as shown in fig (2.1) [1].
The counter is power driven at a constant angular velocity about diffractometer axis. It is connected to a scaler and set at a fixed value of $2\theta$ for a time, sufficient to make an accurate count of pulses from the counter. It is then moved to a new position and the operation repeated. The range of interest in $2\theta$ is covered in this fashion, and the curve of intensity ($I$) versus $2\theta$ plotted. When the continuation background between diffraction lines is being measured, the counter may be moved in steps of several degrees.

The receiving slits and counter are supported on the carriage E, which may be rotated about the axis O. The supports E and H are mechanically coupled so that the rotation of the counter through $2\theta$ degrees is automatically accompanied by rotation of the specimen through $\theta$ degrees. To preserve focusing conditions, the angles of incidence and reflection are made equal to one another and equal to the half the total angle of diffraction, using this $2\theta$-$\theta$ coupling.

Because of the focusing of the diffracted rays and the relatively large radius of the diffractometer circle (about 15 cm in commercial instruments), a diffractometer can resolve very
closely spaced diffraction lines. Indicative of this is the fact that the resolution of the Cu Kα can be obtained. Such resolution can only be achieved with a properly adjusted instrument, and it is necessary to so align the component parts so that the following conditions are satisfied for all diffraction angles:

1. Line of source, specimen surface and receiving slit axis are parallel.
2. The specimen surface contains the diffractometer axis and
3. The line source and receiving slit both lie on the diffractometer circle.

Figure 2.3 shows the block diagram of the detection system of a diffractometer [1].

The following information can be obtained from diffraction peak positions and the shape of XRD:

1. Position of the peak measured (2θ) yields size i.e., d spacing and crystal lattice parameter (size of the unit cell)
2. The shape (Full width Half Maximum, FWHM) of the XRD peak gives information regarding crystallite size and lattice imperfect ions.

The average crystallite sizes \( t \) of very small crystals (< 100 nm in diameter) can be measured from FWHM of their diffraction peaks by the Scherrer’s [1] formula,

\[
t = \frac{0.94 \lambda}{B \cos \theta_B}
\]

where \( \theta_B \) is the Bragg angle
\( \lambda \) is incident wavelength(nm)
B- FWHM (radians)

### 2.3 SEM and EDAX

The morphology of the samples was examined by Scanning Electron Microscope (SEM). For this purpose, pellets were prepared by compacting powder samples (prepared by Sol-gel synthesis) in a die. The morphology of the samples, as-prepared, was imaged to estimate the average size of the nano crystalline sample. The composition of the as-prepared samples was determined using Energy-dispersive analysis by X-rays (EDAX). The EDAX detector and electronics assembly was attached to SEM, from Hitachi series environmental SEM which works at an accelerating voltage of 20 kV, for chemical compositions of the sample (except for Lithium). During EDAX Analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms' own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an
outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray photon. The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established. The energy scale of the spectrometer was calibrated by recording ultra pure Au and Co samples spectra and the spectrum thus recorded was analyzed with software.

2.4 Fourier Transform of Infrared (FTIR) Spectroscopy:

Infrared spectroscopy is an important technique in materials physics and chemistry. It is an easy way to identify the presence of certain functional groups in a molecule. Also, one can use a library of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities. Two types of instrumentation are widely used to obtain infrared spectra:

1. Dispersive spectrophotometers, which use a monochromatic source of infrared radiation to produce a spectrum with one resolution element at a time.
2. Michelson interferometers, which use a moving mirror to create an interference pattern, or interferogram, from which all resolution elements are determined simultaneously.

![Figure 2.4. Schematic diagram of a FTIR spectrometer](image)

2.4.1 Theory of Interferometer operation

The interferometer requires two mirrors, an infrared light source, a detector, and a beam splitter as shown in figure 2.4. The beam splitter is the heart of the interferometer. Essentially a half-silvered mirror, the beam splitter reflects about half of an incident light beam while simultaneously transmitting the remaining half. One half of this split beam travels to the interferometer’s moving
mirror while the other half travels to the interferometer’s stationary mirror. The two mirrors reflect both beams back to the beam splitter where each of the two beams is again half reflected and half transmitted. Two output beams result one travels to the detector as the other travels to the source.

Note each output beam is composed half of the light that traveled from the moving mirror and half traveled from the stationary mirror. Also, the two output beams contain equivalent, but not necessarily identical information. This fact results from reflection-induced phase shifts at the beam splitter and subsequent interference. When the two beams return to the beam splitter, an interference pattern is generated. This pattern varies with the displacement of the moving mirror, that is, with the difference in path length in the two arms of the interferometer. The pattern, detected by the infrared detector as variations in the infrared energy level, ultimately yields spectral information. In the present work, the FTIR spectra have been recorded on JASCO FTIR (Model FT/IR-5300) and NEXUS FTIR (from Thermo–Nicolet) spectrometers. The spectra are recorded in the wavenumber range 400–2000 cm⁻¹ in the absorbance mode using KBr pellet method.

2.5 Mössbauer spectroscopy

Mössbauer spectroscopy is a method for measuring small shifts in nuclear energy levels with high precision. This method involves the ‘recoilless’ emission and absorption of gamma rays and utilizes the Doppler effect in order to use these gamma rays as a sensitive probe. The Mössbauer effect was discovered in 1958 by R. L. Mössbauer [2]. He showed that nuclear radiation can be emitted and absorbed recoilless if the atoms are in a solid state environment.

The Mössbauer spectrometer basically consists of a radioactive source, a drive to provide the relative Doppler velocity between the source and absorber (the material under investigation), a detector which counts the gamma radiation (in the transmission geometry) or the conversion electrons (in the backscattering geometry) and needful electronics for precise control and data acquisition.

The objective behind carrying out the Mössbauer experiments lies in its ability to probe shifts and splitting of the nuclear energy levels because of its exceptionally high intrinsic resolving power (10⁻¹⁰ to 10⁻¹⁴) when compared with the other spectroscopic techniques. The information is extracted by writing the total Hamiltonian as a sum of a Hamiltonian $\mathcal{H}_0$ exclusively for the atom and three more terms known as hyperfine interactions: $E_0$ which refers to Coulombic interactions between the nucleus and electrons, $M_I$ for magnetic interactions between the nuclear magnetic moment and the internal field at the nuclear site created by the atomic electrons, and $E_2$ for the electric quadrupole interaction.
interactions between the quadrupole moment of the nucleus and the electric field gradient created by the atomic electrons. Other higher order terms are neglected [3–5].

2.5.1 Isomer shift

In the process of $\gamma$-transition, the size of the nuclear volume alters which gives rise to the change in the nucleus–electron interaction energy. This change depends on the chemical environment that is the total surrounding electron charge density of the probed nucleus of the absorber. As this energy cannot be measured directly, it is always compared to a suitable reference. Figure 2.5 illustrates isomer shift in Mössbauer spectroscopy.

$$
\delta = \text{constant} \{ |\psi_s(0)_A|^2 - |\psi_s(0)_B|^2 \}
$$

where A and B stand for the absorber and source and $|\psi_s(0)|^2$ is the s-electron density at the nucleus including the indirect effect of $p$, $d$, and $f$ electrons on the s electron density. The isomer shift also gets affected with a change in temperature and pressure. The effect of pressure depends on the details of the electronic structure of the material.

2.5.2 Electric quadrupole interactions

If a nucleus has a spin quantum number $I > 1/2$, it has a non-spherical charge distribution given by

$$
e Q = \rho r^2 (3 \cos^2 \theta - 1) \, d\tau
$$

where $e$ is the charge of proton, $\rho$ is the charge density in a volume element $d\tau$, which is at a distance $r$ from the center of the nucleus and making an angle $\theta$ to the nuclear spin quantization axis. The sign of $Q$ depends upon the shape of the deformation, negative if oblate and positive if prolate along the spin axis. An asymmetric charge distribution around the nucleus causes an asymmetric electric field at the nucleus, characterized by the electric field gradient $\mathbf{J}_E$ [6]. There are two contributions to $\mathbf{J}_E$: lattice contributions from charges on distant ions, and valence contributions due to incompletely filled
electron shells. The electric quadrupole interaction between these two quantities gives rise to a splitting in the nuclear energy levels. $\int E$ does not work on the $I=1/2$ ground state, instead, it removes degeneracy in the excited state, splitting it into two sub states $m_I = \pm 1/2$ and $m_I = \pm 3/2$.

The energy lines now overlap with each other and give rise to a doublet in the Mössbauer spectrum. The separation between the energy levels is known as the quadrupole splitting and is given by

$$\Delta E_Q = e^2 q Q \sqrt{1 + \eta^2/3}/2$$

(2.4)

where $eq = d^2 V/dz^2$ with $V$ being the electrostatic potential, $\eta = (d^2 V/dx^2 - d^2 V/dy^2)/(d^2 V/dz^2)$, and $Q$ is the magnitude of charge deformation. The electric quadrupole interaction provides useful information about bond properties, molecular and electronic structure.

2.5.3 Magnetic hyperfine interactions

If the nucleus of the probe atom in the absorber is in a magnetic field caused by the electrons of the atom, or by an externally applied field, then magnetic dipole interactions occur. The Hamiltonian can be written as

$$\mathbf{H} = -\mu_N \mathbf{I} \cdot \mathbf{H}$$

(2.5)

where $\mathbf{I}$ is the nuclear spin, $\mathbf{H}$ is the total magnetic field, $\mu_N$ is the nuclear magneton, and $g$ is the nuclear g factor. Since both of the nuclear energy levels of the 14.4-keV (in case of iron) transition have spin and associated magnetic moments, they experience hyperfine splitting caused by the interaction of the magnetic moment of the nucleus with the magnetic field. These new levels are the magnetic sub states of the energy levels, which are degenerate in the absence of a magnetic field, and this result in more possible nuclear transitions. The transitions that are allowed are determined by the quantum selection rule, which states that $\Delta m_I = 0, \pm 1$ as illustrated in figure 2.7.
2.5.4 Combined magnetic and quadrupole interactions

The magnetic and quadrupole interaction are direction dependent. If the asymmetry parameter \( \eta = 0 \) and \( H \) is along the principal \( z \) axis of the electric Field gradient tensor, then the Hamiltonian is diagonal in \( I_z \). Then

\[
E(I_z) = -g \mu_N H I_z + E_Q(I_z) \tag{2.6}
\]

If the electric field gradient is axially symmetric and its principal axis makes an angle \( \theta \) with the magnetic axis and provided that \( e^2 q Q = \mu H \) then the eigen values are

\[
E_Q(I_z) = -g \mu_N H m_I + (-1)^m_1 \frac{1}{1} \left[ \left( \frac{e^2 q Q}{4} \right) \left( 3 \cos^2 \theta - 1 \right) \right] \tag{2.7}
\]

The separation of the outer lines in the HMF spectrum will be different from the inner lines [5].

2.5.5 Mössbauer Spectrometer

Mössbauer spectra can be recorded most commonly in two ways: 1) Employing a single line source with an absorber having different hyperfine interactions generated nuclear energy level splitting or 2) Employing a single line absorber with source having nuclear energy level shift. In either of the two ways the nuclear energy level splitting have to be matched with the recoil free \( \gamma \)-ray energy to record the resonance spectra. One immediate and convenient way of matching these energies is to impart a Doppler velocity to the single line source or absorber and hence giving a first order energy shift (\( \Delta E_\gamma \)) to the incident \( \gamma \)-ray energy (\( E_\gamma \)) equals to \( \Delta E_\gamma = \left( \frac{\nu}{c} \right) E_\gamma \), where \( \nu \) is the relative velocity between source and absorber. Depending on the variations of the Mössbauer natural line widths (FWHM) and energy level splitting. The range and precision of the Doppler velocities has to be selected. For example for the standard Mössbauer absorbers such as pure Fe (where Hyperfine Magnetic Field (HMF) \( \approx 330 \) kOe at RT), Fe\(_2\)O\(_3\) (HMF \( \approx 515 \) kOe at RT), Fe\(_3\)O\(_4\) (HMF \( \approx 455 \) kOe at 495 kOe at RT), Sodium Nitropruside or stainless steel a velocity range of \( \pm9, \pm12, \pm12, \pm4 \) and \( \pm2 \) respectively will be sufficient to record a spectra with good baseline and \(^{57}\)Fe source. Some other ways of recording Mossbauer spectra and designs of spectrometer depending on specific application are summarized in.
In our laboratory the Mössbauer spectrometer is operated in the constant acceleration mode and it has the following four basic building blocks:

1. Mössbauer source
2. Velocity drive and associated feedback systems
3. \( \gamma \)-Radiation detector system with associated electronics and
4. PC based Mössbauer data acquisition system.

a) Mössbauer Source:

The Mössbauer source was prepared by Du Pont Pharmaceuticals, USA by electrodepositing Co\(^{57}\) nuclei in 6\(\mu\)m thick Rhodium matrix and annealing at 1050°C for 72 hours under hydrogen atmosphere. The source has been sprayed with an acrylic coating. The strength of the source was 25.9mCi (958.3MBq) with a half life of 270 days.

b) Velocity drive and feedback system:

The velocity drive unit was fabricated locally by Nucleonix (model MD575) following the design of Kankeleit. It is an electromechanical transducer and consists of a coil connected to a rod, carrying the source. This coil is made of phosphor-bronze. This coil carries the driving velocity signal and is the energizing coil. The coil and rod assembly moves in a magnetic field produced by two permanent magnets. Another phosphor-bronze coil, known as the pick-up coil is also connected rigidly to the rod, and the rod is held with the transducer at either end with springs.

The magnetic flux \( (\varphi) \) linked with the pick-up coil is given by \( \varphi = \int nB.dA \), where \( n \) is the number of turns in the coil, \( B \) is the magnetic flux density and \( A \) is the area of the loop. When this coil moves in the magnetic field, then according to Lenz’s law, an induced emf is produced which is proportional to the rate of change of flux (\( d\varphi/dt \)) linked with the coil. This induced emf is a replica of the driving waveform and this is fed to the error stage of the feedback and power amplifier where it is compared with the reference velocity waveform. The reference velocity waveform is triangular (constant acceleration) in shape and is obtained by integrating the square input to the Mössbauer drive unit. The feedback network adjusts to produce zero difference between the driving waveform and the reference waveform. Apart from triangular waveform the other form possible is saw-tooth wave to produce constant acceleration. The specific velocity range required for different absorbers is obtained by changing the amplitude of the velocity waveform.
c) \(\gamma\)-Radiation detection system and associated electronics:

A gas-filled proportional counter from LND.INC, USA was used as the Mossbauer \(\gamma\)-ray detector. The gas mixture used was 97\% Xe +3\% CO\(_2\) at a pressure of 2 atmosphere with a Beryllium window 0.005” thick and having areal density 22.5 mg/cm\(^2\). A high voltage unit produced the detector bias; model HV 211 from ECIL, India. A preamplifier with very high input impedance and low output impedance was used, which was acting as a buffer (impedance matcher) between the detector and the spectroscopy amplifier. This FET input charge sensitive preamplifier was made by EG & G, ORTEC, USA. Spectroscopy amplifier, model PA572 from ECIL-India, was used for amplifying and shaping the detector output pulses. The output pulses from the spectroscopy amplifier were fed to a single channel analyzer (SCA), model SC6048 from ECIL-India, and the TTL output pulses of the SCA were fed to the ADC card for counting purpose. The detector bias, which was fed through the preamplifier, was selected from the plateau region of the number of counts (pulses) from the detectors vs. applied voltage curve with the Mössbauer source directly facing the detector. The bias voltage was set between 2600–2700 volts. This high voltage is achieved by using an oscillator coupled step-up transformer – a voltage multiplier – in the output stage and a feedback system to maintain the oscillator current and hence secondary voltage.

Mössbauer spectra were recorded in transmission geometry with \(\gamma\)-rays, collimated using lead block. The radiations emitted from the Mössbauer source were 6.3 keV X-rays, 14.4 keV and 136 keV \(\gamma\)-rays. The high-resolution proportional counter was detecting all these three radiation and corresponding pulses were produced. However we were interested only in the 14.4 keV \(\gamma\)-rays. So for obvious reasons we had to block the pulses produced by other radiations to enter in to the counting system. This was achieved by setting the SCA input voltage gates appropriately. Before setting these gates we recorded the so-called pulse height spectrum (PHS) without putting any absorber between the source and the detector and by keeping the SCA in the ‘WINDOW’ mode, in which the difference between the upper and lower level voltages are fixed. The spectroscopy amplifier gain, pulse shaping time, base line restoration and polarity were properly set by observing the amplified detector pulses on the oscilloscope. Care was taken in choosing these parameters of the spectroscopy amplifier so that there were not many saturated output pulses. In the PHS we observed well-resolved two peaks (apart from the low voltage escape peak) in different voltage intervals proportional to the 6.3 and 14.4 keV incident radiations. The sum peak corresponding to the (6.3 keV + 14.4 keV) was also observed with low intensity. The SCA lower and upper voltage levels were set to the voltage values close to starting of 14.4 keV peak and ending of the sum peak respectively and it was put in the NORMAL mode (where pulses between the upper and lower level only were accepted and all other pulses were rejected). In this way 14.4 keV \(\gamma\)-rays pulses were chosen and hence the signal to noise was improved.
d) PC based Mössbauer data acquisition system

In designing the Mössbauer data acquisition system one need to use a multi channel analyzer (MCA) operating in the multi channel scaling (MCS) mode, the mode in which different channels are accessed at different time intervals. The time intervals correspond to the times during which the drive is moving with velocity ‘v’ to ‘v+dv’. In implementing this operation it is convenient and cost effective to use a microprocessor based data acquisition system (MPDS) rather than a conventional MCA with involved hardware. What all one has to do is to open a memory bank (channels) to store the counts (standard pulses from the output of the SCA) in synchronization with the velocity of the drive. Different channels correspond to different velocities of the source and in turn different energies. Thus the counts vs. channel number data represent the Mössbauer spectrum. Standard samples (e.g. pure Fe) Mössbauer data are recorded to calibrate the channel numbers to velocities from the known separations of the Mössbauer lines in terms of velocity from other sources [15]. In principle we can increase the number of channels to have better resolution of velocity but not up to ad-infinitum as it may deteriorate the spectrum quality due to even marginal non-linearity in the drive velocity waveform. Most commonly 256, 512, or 1024 channels are addressed.

Our design of the data acquisition system was based on the PCL208 High Performance Data Acquisition Card (or ADC card) of Dynalog Microsystems, India. The card was plugged into the expansion slot of a PC to implement MCS function of a MCA. The I/O card has an AD converter, an Intel 8254 programmable interval timer, and DA converter on board. The timer IC has three 16 bit down counters/timers. The counters were set to binary counting mode to enable them to count from 0 to 65535. The counter registers and the counters control register were configured to get the following counter operations. Counter 1 was internally coupled with a clock of frequency 1MHz and is used to generate the dwell time of 100 μ-seconds. We organized 1024 (512 + 512) channels for our spectrometer. To implement this, Counter 2 was set to down count by 1024 and give the current channel position by reading its contents on the fly to reduce the dead time in the MCS to the order of 0.5 μ-seconds. The third timer (Counter 0, internally coupled with 100 kHz clock) keeps track of the number of SCA TTL output pulses that come from the radiation detector. For the purpose of synchronization the square wave to drive the Mössbauer velocity drive is obtained by software checking the counter, which divides the dwell time by 1024. If there is a channel advances then the DAC is output with zero for a current timer value greater than 512 and FF for a value less than 512. The frequency of this square wave, fed to the Mössbauer drive unit, was 10 Hz.

Mössbauer spectra with good counting statistics (~0.5M counts/channel) were recorded. The spectrum recorded in the first 512 channels was the mirror image of the spectrum recorded in the next
512 channels. Therefore the spectra in these two halves were added by folding the overall spectrum with respect to the zero velocity channels in both the halves to increase the statistics of each spectrum (~1M counts/channel in the folded spectrum). SCA gates were set to get very good signal – to – noise ratio.

2.5.6 Mössbauer absorber preparation

There are various ways of preparing Mössbauer absorber. It can be in the form of a foil or in the form of powder – either compacted in the form of pellet or as it is. In our studies, absorbers were prepared by spreading the fine powder as uniformly as possible in the central hole (~9mm diameter) of a copper plate fixed on a cello tape; in this way the sample was also stuck to the cello tape. Another piece of cello tape was fixed from top so that there was no chance of the sample to fall and the copper plate with sample were firmly stuck to cello tape pieces from both sides. The amount of powder for the absorber was calculated so that the natural Fe contents in the absorbers were closed to 10 mg/cm², which is ideally required according to Margulies and Ehrman [16]. Hence we could safely assume no correction in the lines due to thickness broadening and that all our absorbers were with in the thin absorber limit.

2.6 Superconducting Quantum Interference Device (SQUID)

The sensitivity of a Josephson junction to an applied magnetic field increase with the area of the junction, which justifies making the devices arge so that the control currents can be reduced to a minimum. The switching speed of the junction, however, decreases as the area increases. In recent devices, the conflicting demands of speed and sensitivity are met by replacing a single junction with two or more junctions connected by a continuous superconducting loop. Such a multi-junction device is called a Josephson interferometer or a Superconducting Quantum Interference Device (SQUID). Using a SQUID, the minutest changes in magnetic fields can be measured with more sensitivity than with any other device.

2.6.1 Principle

In the case of two Josephson junctions, connected in parallel, as the magnetic flux \( \Phi \) threading a superconducting loop is changed, the critical current of two junctions oscillates with a period equal to the flux quantum \( \Phi_0 \). These oscillations are a result of the interference between the macroscopic wave functions at the two junctions. This phenomenon of “superconducting quantum interference” forms the basis of a SQUID.

2.6.2 Requirement
The I–V characteristics of a dc-SQUID must be non-hysteric which is ensured by adding an external shunt with a sufficiently low resistance. When the flux through SQUID is changed, the I–V characteristics oscillate between two extreme values. If the SQUID is biased with a constant current, the voltage across the SQUID becomes periodic in the applied flux.

2.6.3 Working of a SQUID
SQUID, a device which makes use of flux quantization and Josephson tunneling, is a flux-to-voltage transducer that converts a change in magnetic flux to a change in voltage which can be easily detected with conventional electronics. It can operate at temperatures below the superconducting transition temperature and is a magnetic-flux detector of incomparable sensitivity. A typical response curve for a SQUID magnetometer is shown in figure 2.8.

In practical SQUID measuring instruments, the flux through the SQUID loop is held constant by means of a negative feedback with an additional coil. The strength of the feedback current necessary for this is then a measure of the magnetic flux to be measured. A particularly high sensitivity is achieved if a low frequency signal is superposed on the feedback current, the low frequency voltage thereby caused is detected by a lock-in amplifier. With the help of superconducting flux transformers, one can also measure magnetic fields which do not lie at the location of the SQUID loop. With an optimally designed SQUID, such high sensitivities are possible that they correspond to an energy resolution of the magnetic field of about $1 \times 10^{-33}$ Joules per Hertz of measured bandwidth, which is about two times the Planck constant ($\hbar$) [8].

2.7 Electrochemical Characterization

The sample LiFePO$_4$ synthesized in our laboratory has been tested for its electrochemical activity and the details have been given elsewhere in this thesis.

References


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