UNIT I

STRUCTURAL CHARACTERIZATION

1.1 Principle of X-Ray Spectroscopy

- XRF works on methods involving interactions between electron beams and x-rays with samples.
- It is made possible by the behavior of atoms when they interact with radiation.
- When materials are excited with high-energy, short wavelength radiation (e.g., X-rays), they can become ionized.
- When an electron from the inner shell of an atom is excited by the energy of a photon, it moves to a higher energy level.
- When it returns to the low energy level, the energy which it previously gained by the excitation is emitted as a photon which has a wavelength that is characteristic for the element (there could be several characteristic wavelengths per element).
- Thus atomic X-rays emitted during electronic transitions to the inner shell states in atoms of modest atomic number.
- These X-rays since have characteristic energies related to the atomic number, and each element therefore has a characteristic X-ray spectrum which can be used to identify the element.

1.2 Small angle X Ray scattering

The term ''small-angle scattering'' (SAS) is somewhat ambiguous as long as the sample, type of radiation, and incident wavelength are not specified. Clearly, Bragg reflections of all crystals when investigated with highenergy radiation (e.g., γ rays) occur at small scattering angles (small 2θ) simply because the wavelength of the probing radiation is short. Conversely, crystals with large lattice constants could lead to small Bragg angles for a reasonable wavelength value of the radiation used. These Bragg reflections, although they might appear at small angles, can be treated in essentially the same way as the large-angle Bragg reflections with their origins laid out in all previous sections. However, in the more specific sense of the term, SAS is a scattering

phenomenon related to the scattering properties at small scattering vectors K (with magnitudes $K = 2 \sin \theta / \lambda$), or, in other words, diffuse scattering surrounding the direct beam.

SAS is produced by the variation of scattering length density over distances exceeding the normal interatomic distances in condensed systems. Aggregates of small particles (e.g., carbon black and catalysts) in air or vacuum, particles or macromolecules in liquid or solid solution (e.g., polymers and precipitates in alloys), and systems with smoothly varying concentration (or scattering length density) profiles (e.g., macromolecules, glasses, and spinodally decomposed systems) can be investigated with SAS methods. SAS intensity appears at low K values, that is, K should be small compared with the smallest reciprocal lattice vector in crystalline substances. Because the scattering intensity is related to the Fourier transform properties, it follows that measurements at low K will not allow one to resolve structural details in real space over distances smaller than $d_{min} \sim \pi / K_{max}$, where K_{max} is the maximum value accessible in the SAS experiment. If, for example, $K_{max} = 0.2 \ A^{\circ \ -1}$, then $d_{min} = 16 \ A^{\circ}$, and the discrete arrangement of scattering centers in condensed matter can in most cases be replaced by a continuous distribution of scattering length, averaged over volumes of about d^3_{min}. Consequently, summations over discrete scattering sites and the subsequent ones can be replaced by integrals. If we replace the scattering length fj by a locally averaged scattering length density r(r), where r is a continuously variable position vector.

$$I(K) = \left| \int_V \rho(r) e^{2piKr} \ d^3r \right|^2$$

where the integration extends over the sample volume V. The scattering length density may vary over distances of the order d_{min} as indicated earlier, and it is sometimes useful to express

$$\rho(r) = \Delta \rho(r) + r_0$$

where r0 is averaged over a volume larger than the resolution volume of the instrument (determined by the minimum observable value of K). Therefore, by discounting the Bragg peak, the diffuse intensity originating from in homogeneities is

$$I(K) = \left| \int_V \Delta\rho(r) e^{2piKr} \ d^3r \right|^2$$

1.3 X RAY PHOTOELECTRON SPECTROSCOPY

Photoelectron spectroscopy (PES) is an excellent technique for probing atomic and mole electronic energy levels. When an atom or molecule is subjected to high-energy rad photons in the radiation collide with and eject electrons from atoms leaving behind an Ejected electrons depart with different velocities and photoelectron spectroscopy measures d velocity distribution of the released electrons.

The process involved in photoelectron spectroscopy is sketched in Fig, where we deep in a few electrons (shown as circles) in some of the energy levels of an atom.
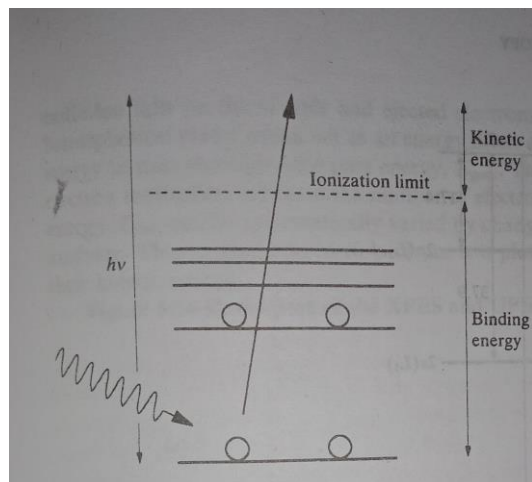
Electrons can be ejected from either the core or the valence levels of the atom, depending on the energy of the exciting radiation, and their kinetic energies are characteristic of the atom from which they have been emitted. If the atom is part of a molecule, the energy of its valence electrons (and, to a much lesser extent, its core electrons) will be modified by the bonding but are nonetheless characteristic of the orbital in question

When ionization occurs the kinetic energy acquired by the emitted electrons is not quantized, so that any incident energy highs than the ionization energy can be used for excitation. A higher energy is required to ionize inner core electrons, however, for which an X-ray source is suitable, the technique is then called X-ray photoelectron spectroscopy (or XPES). In this case the X-ray beam is produced by electron bombardment of a clean metal target, such as Al or Mg. melting in the emission of radiation at very specific energies; e.g. the k line for Al occurs at 1486.6 eV. If a very high intensity source is required, synchrotron radiation can be used, which has the further advantage that its emission frequency can be turned over a range.

Experimentally, the detection of electrons must be carried out in a high vacuum, as electrons are chemically active. There are no known window materials for He lamp sources, and so the lamp is usually mounted in a chamber which has a small hole into the sample compartment through which the emitted radiation can pass; continuous pumping maintains the high vacuum as helium leaks slowly through the hole. Obviously, the requirement for high vacuum means that measurements on solid samples are far easier than those on liquids and gases. However, modifications such as the use of flow techniques have ensured that a useful body of data has been obtained for the latter.
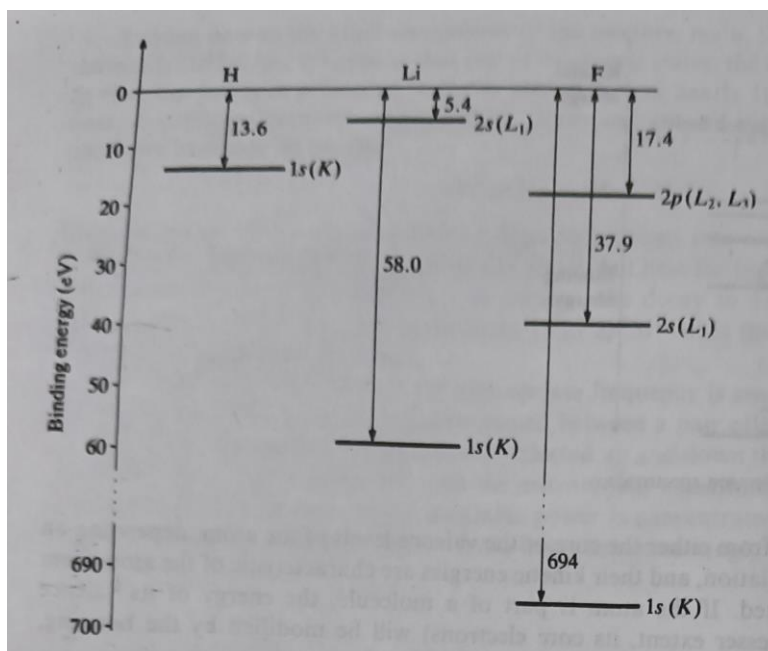
Figure shows the binding energies of electrons in the energy levels of three different dements. The levels are labeled with their term symbols (13, 2p, etc.) and with the X-ray rotation which is sometimes used in PES. In this notation the levels are given letters corresponding to their shell:

If necessary, a subscript denotes the sublevel from which the electron is ejected. The following examples show both notations for a few selected states:

Term symbol	$^1S_0$	$^2S_0$	$^2P_{1/2}$	$^2P_{3/2}$
X-ray notation	K	L_1	L2	L3

In XPES, the kinetic energy of the ejected electrons is measured using a hemispherical analyzer such as that shown in Fig. Monochromatic X-ray radiation falls on the sample and ejected electrons pass between a pair of electrically charged hemispherical plates which act as an energy filter, allowing electrons of only a particular kinetic energy to pass through-the pass energy. E_{pa}
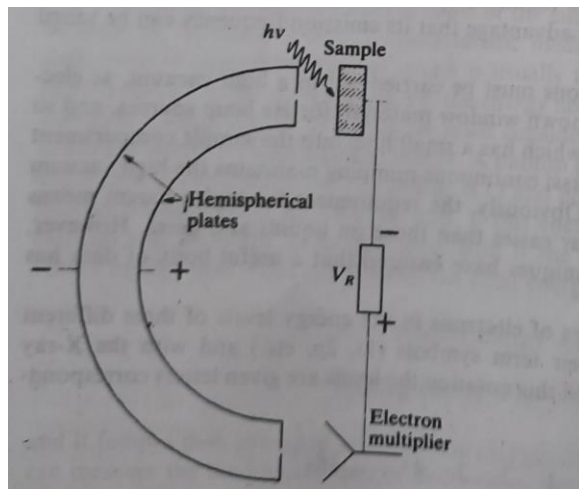
The resulting electron current, measured by an electron multiplier, indicates the number of electrons ejected from the surface with that kinetic energy. E_u can be systematically varied by changing the retarding voltage (V) applied to the analyzer. Thus a photoelectron spectrum is a plot of the number of electrons emitted against their kinetic energy.
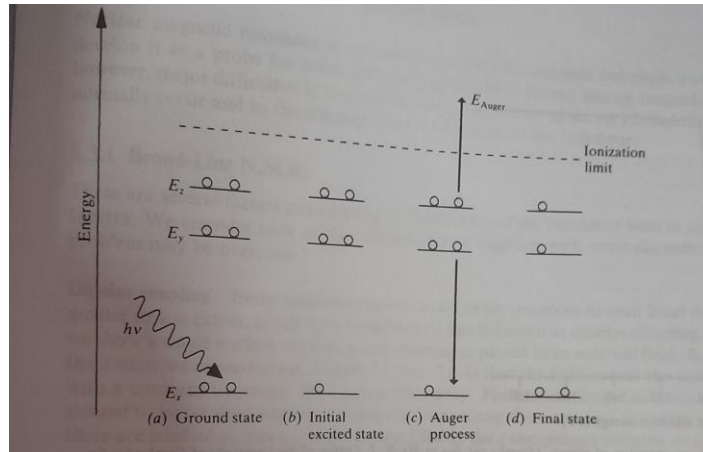
1.4 AUGER RELATION OF CORE HOLE

X-ray photoelectron spectroscopy and Auger electron spectroscopy are very closely related; in the former we look at electrons directly ejected from the inner core of surface atoms, while in the latter it is electrons emitted during secondary processes, after the emission of the first electron, which are studied. Another minor difference is that a high-energy electron beam (> I keV) is normally used in Auger work, rather than an X-ray beam, to eject the first electron. The equipment for detecting emitted electrons and analyzing their energies is very similar to that for PES spectroscopy.

To understand the Auger process we must imagine an electron to be ejected from a core level, E_x, of a surface atom in the ground state. The ion formed, with a vacancy or 'hole' in E_x, is shown as the initial excited state. The hole in E_x, can be filled by an electron dropping down from a higher level, E_y. This releases considerable energy ($E_x - E_y$). Part of which can be absorbed by an electron in a higher orbital, E_z, which will be ejected with kinetic energy representing the excess of $E_x - E_y$, over E_z. The latter is known as the Auger energy, E_{Auger}. The resulting ion, with 'holes' in both E_y, and E_z . Although this is referred to there as the final state, it is nonetheless higher in energy than the original ground state, and yet more electron rearrangements will subsequently occur, perhaps involving electron capture, or perhaps emission of successively less-energetic Auger electrons, often referred to as a cascade process, before the ground state is regained.

Because energy is conserved, it is clear that the energy released by electron E_y, dropping down. ($E_x - E_y$) , must be equal to the energy taken up by the ejection of electron E, with kinetic energy $E_{Auger,}$ 50 we can write.

$$E_{Auger} + E_z = E_x - E_y$$

$$E_{Auger} = E_x - E_y - E_z$$

(a) Ground state (b) Initial excited state (c) Auger process (d) Final state

If, as here, we think of E_x, E_y, and E_z as the orbital energies of electrons in the ground state of the atom, this equation is not strictly accurate the Auger process deals with electrons in ionized states, which will have slightly different energies. This need not concern us here, how- ever; the important point is that the observed Auger energy is directly related to the binding energies of electrons in surface atoms, and so is characteristic of them Auger processes are more likely in the lighter elements, where the core electron energy is not very different from the energies of the outer electrons. AES is, therefore, widely used to detect light element contaminants on metals.

1.5 APPLICATION OF X-RAY PHOTOELECTRON SPECTROSCOPY

XPS can be used for both qualitative as well as quantitative analysis.

Qualitative analysis

Elemental analysis:
 The electron energy levels of an atom can be divided into two types, core levels, which are bound to the nucleus, and valence levels, which are only weakly bound. The valence levels of an atom are the ones that interact with the valence levels of other atoms to form chemical bonds in molecules and compounds. Their character (valence bond character) and energy are changed by this process, becoming characteristics of the new species formed.

The core-level electrons of an atom have energies that are nearly independent of the chemical species in which the atoms are bound since they are not involved in the bonding process. Thus, the identification of Core level binding energies thus provides unique signatures of the elements. All elements in the periodic table can be identified in this manner, except for H and He which have no core levels.

Quantitative analysis

Quantitative analysis requires the measurement of relative peak intensities and the intensity of the peak depends on the atomic concentration (N) of an element present in the surface film.

Chemical shift (chemical state analysis)

- Chemical shift is the difference in binding energy between the same atom in two chemically distinct states in the same molecule or in two separate compounds. It is characteristic of the nature and the number of atoms surrounding the ionized atoms of the sample. It can be used to see what kind of chemical bonding of atoms is on the sample surface.
- It concerns the chemical bonding nature, the nature of functional groups, and the oxidation states of atoms.
- An important capability of XPS is its ability to distinguish the same element in different chemical states, because of BE of an electron is different due to changes in charge density around that element by oxidation

- In-depth analysis
- Estimation of the in-depth distribution of elements in thin surface film is called in-depth surface analysis. It is done to know whether the thin film is homogeneous or not.

STRENGTHS OF XPS

Strengths of XPS include:

Non-destructive analysis of materials.

• Ability to detect all elements except for H and He. XPS surveys will obtain inventories of all elements present on material surfaces..

• Small shifts in binding energies can be measured (~0.1 eV) that provides information about the bound state of elements present these data are obtained by collecting spectra over limited energy range to reveal the fine structure of XPS spectra for a given element.

• Surface-sensitive analysis to determine composition of material surfaces a few atomic layers thick (~ 10 nm). Surface contaminants are usually easily removed using ion (Ar) beam sputtering methods. Semi-quantitative analyses can be obtained+10% atomic concentration. Depth profiles may be obtained to demonstrate chemical stratigraphy on the nm scale on material surfaces. Little or no sample preparation is required x-ray beams produce relatively little charging effects compared with electron beam methods; charging can easily be addressed with charge compensation methods using an electron flood gun. Some modern XPS instruments have imaging capabilities. Mature XPS databases exist to rapidly identify elements and their chemical state.

LIMITATIONS OF XPS

Limitations of XPS include

• XPS uses an ultrahigh vacuum chamber (< 10-9 Torr) and some samples are either not stable or volatilize under UHV conditions.

• X-ray beams cannot be focused in the same manner as electron beams; so the analyzed surface areas are significantly larger. Typically the analyzed area will be mm x mm or 10's or 100's of microns across at best--producing an averaged signal over these areas. Modern XPS instruments may have "small spot" capabilities, but this may be achieved by physically stepping down the beam size which reduces the count rate. Small spot XPS can be done via X-rays produced in a synchrotron source.

• Although charge compensation is often effective, some samples may produce severe charging problems that compromise the quality of the analysis. As a surface sensitive method, XPS is not an appropriate method for identifying bulk material substrates.

UNIT II

SPECTRAL CHARACTERIZATION

2.1 LASER SOURCES

A laser provides an almost ideal monochromatic source of narrow line width. It emits radiant energy that is coherent, parallel, and polarized. A laser beam can be kept us a very slim cylinder only a few micrometers in cross section. Laser operation involves three principles of physics: stimulated emission, population inversion, and optical resonance. Stimulated emission occurs when a photon strikes an excited atom or molecule and there- by causes that atom or molecule to emit its photon prematurely. This can occur only when the impinging photon has exactly the energy of the "stored" photon that would ultimately have been emitted spontaneously. The resulting emission falls precisely in phase with the electromagnetic wave that triggered its release and is identical in wavelength. Thus, the incoming photon is now joined by a second photon from the excited atom or molecule, resulting in a gain or amplification of photons and giving a perfectly coherent (in-phase) beam of radiation.

The precedence of stimulated emission over spontaneous emission is the basis for achieving laser action. For this to occur, a population inversion must take place; that is, there must be more molecules (or atoms) in the excited state than the ground state of the lasing material. This is possible only for a multilevel system, as illustrated in Fig. 8-6 for the He-Ne laser. A helium atom, excited by an electrical discharge to a long-lived triplet level, can only lose its energy by collision with another atom which has a comparable en- ergy level available. One excited state of neon lies only 313 cm below the excited helium state. As a result, a radiationless excitation of neon can occur on collision of the excited helium and ground-state neon atoms. The excited level of neon has a relatively long life- time before spontaneously decaying to the ground state with the emission of photons at 1153 and 632.8 nm. Thus, it is possible to build up a larger population of neon atoms in the excited state than in the ground state (population inversion). The spontaneous emission of a single photon at either of

these wavelengths can trigger a whole cascade of similar pho- tons by the process of stimulated emission. Optical pumping in employed to build up a population of atoms in an excited state. Population inversion is relatively easy for many organic molecules since their energy levels constitute a multilevel system.

Optical resonance is the third principle essential to laser operation. Resonance is achieved by placing the lasing medium in a cavity situated between a pair of parallel, plane mirrors. Making the spacing between the mirrors an integral multiple of the desired wavelength means that there will be a buildup of energy at the desired wave- length. If the resulting light is collinear with the optic axis and of a frequency falling within the bandwidth of one of the discrete optical frequencies, it will be reflected back and forth through the cavity. Growth of the wave will continue and, if the gain on repeated passages through the lasing medium is sufficient to compensate for losses within the cavity, a steady wave will be built up. Any wave that is inclined at an angle to the long axis of the cavity will be lost after only a few reflections, or perhaps without ever striking one of the mirrors. If one of the mirrors is semitransparent, a portion of the wave can escape through it, constituting the output of the laser. The output is radiation of low divergence, all of the same frequency, and all in phase. A crystal of LilO,, internal to the laser cavity, may be used to frequency double the available wavelengths.

To pump the laser, flash lamps, inert gas are lamps, or another laser have been used. Flash lamps are frequently used and are of two configurations: coaxial and linear. In t either configuration, high voltage from a low inductance capacitor is rapidly pulsed through the lamp. Coaxial arrangement offers very high pulse power but low repetition rates. Linear flash lamps do not provide peak powers comparable to coaxial flash lamps but can operate at higher repetition rates to yield the same average power. All pulsed systems generate copious amounts of radio frequency interference. Proper design and construction must be used to reduce radio frequency interference to acceptable levels, and equipment must be shielded to prevent upsetting nearby electronics.

The He-Ne laser line at 632.8 nm is favorably located in the spectrum where the least amount of fluorescent problems appears in routine

analyses. An argon laser possesses in- tense lines at 488.0 and 5143 nm; coupling with krypton adds two other major lines at 568.2 and 647.1 nm. The Ar-Kr laser is ideal for many experiments. Chances are that with at least one of the exciting lines, problems of photodecomposition, fluorescence, or absorption will be successfully circumvented. Tunable dye lasers, whose output frequency may be varied over a short range, are almost indispensable for studies involving resonance Raman. Several dyes are necessary to cover the entire wavelength range accessible to dye lasers; the appropriate dye solution is continuously pumped through the laser cavity. Prisms and gratings have been used to tune dye lasers.

2.2 LASER RAMAN SPECTROMETER

Intense monochromatic light source, sensitive detection, and high light-gathering power, coupled with freedom from extraneous stray light, must be built into a Raman spectrometer. Many of the commercial instruments employ a He-Ne laser as the light source. A double monochromator (often f/6 with a focal distance of 75 to 100 cm, 0.25 cm resolution) keeps stray light from the unshifted laser wavelength to a minimum, a special problem with powders and "dirty" samples. Scattered light is detected by a multiplier phototube with a red-sensitive response (if a He-Ne or Kr laser is the source). Visible-type optics are used throughout, and the entire spectral region is covered by a single grating. The schematic optical arrangement is shown in Fig.
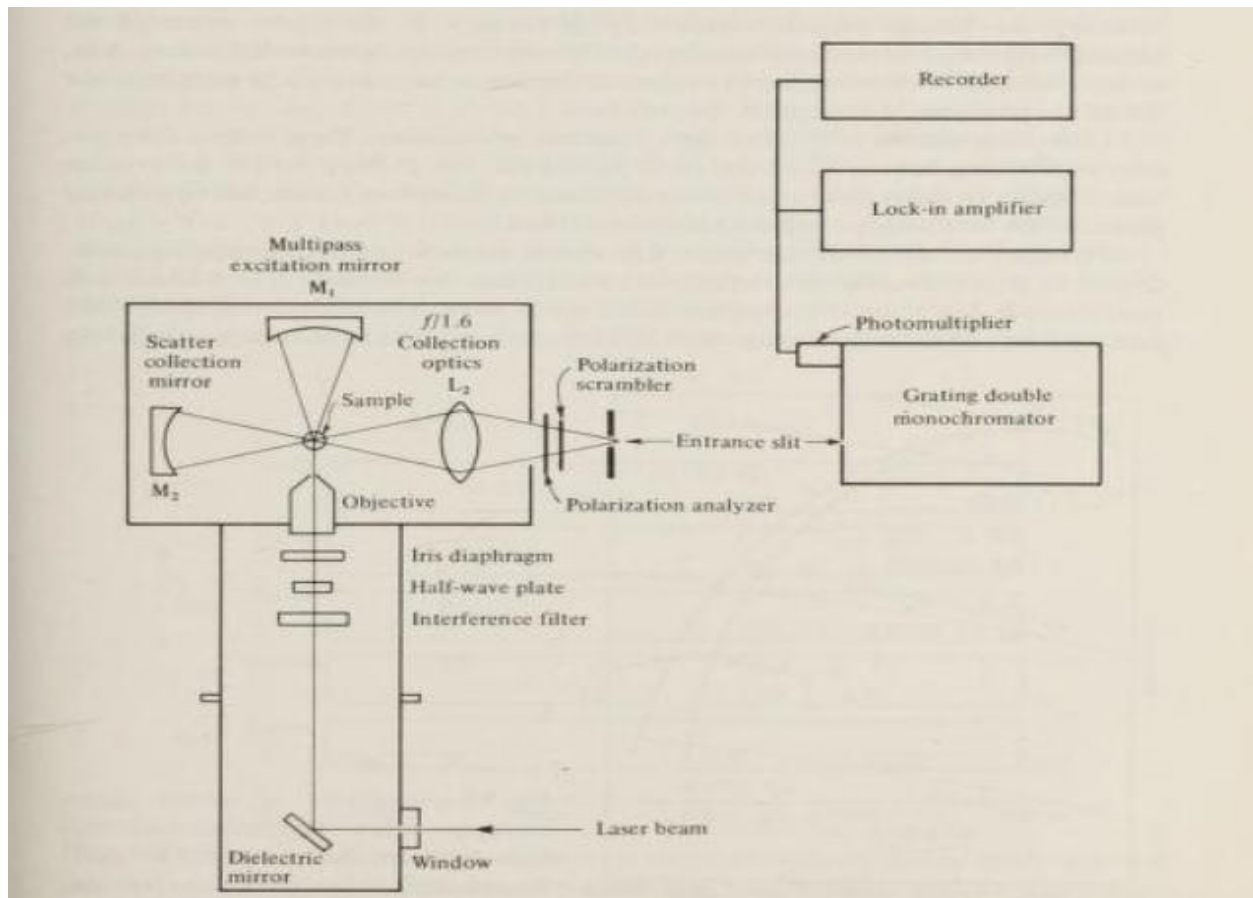
High-quality gratings are required for Raman work because imperfections in ruling that could lead to ghosts or other anomalies produce spectral artifacts in the Raman single-beam emission technique. Resolution and signal-to-noise ratio most often are limited by the effectiveness of the sample as a Raman scatterer because the Raman process is incredibly inefficient. The laser beam is focused into the sample by a lens system. Another lens collects and focuses the scattered light into the monochromator. A laser provides an almost ideal monochromatic source of narrow linewidth. It emits radiant energy that is coherent, parallel, and polarized. A laser beam can he kept as a very slim cylinder only a few micro- meters in cross section. Compared to the old mercury-arc sources, the sample image at the slit may be as much as 1000 times brighter with the laser. Sample volume can be diminished accordingly. The He-Ne laser line at 6328 A is favorably located in the spectrum where the least amount of fluorescent

problems appear in routine analyses. Although the Raman excitation efficiency decreases with the fourth power of the exciting frequency, fluorescence excitation efficiency usually decreases still faster. Also, strongly colored or photosensitive samples can frequently be examined by exciting in the red unless, of course, the sample is opaque to red.

2.3 RADIATION SOURCES

In the region beyond 5000 cm (2.0 µm), blackbody sources without envelopes com- monly are used. The same spectral characteristics cited for the tungsten incandescent lamp apply to these as well. Unfortunately, the emission maximum lies in the near- infrared. A fraction of the shorter-wavelength radiation will be present as stray light, and this will be particularly serious for long-wavelength measurements.

A close-wound Nichrome coil can be raised to incandescence by resistive heating. A black oxide film forms on the coil which gives acceptable emissivity. Temperatures up to 1100°C can be reached. The Nichrome coil requires no water-cooling and little or no maintenance and gives long service. This source is recommended where reliability is essen- tial, such as in nondispersive process analyzers and inexpensive spectrophotometers or filter photometers. Although simple and rugged, this source is less intense than other infrared sources.

A hotter, and therefore brighter, source is the Nernst glower, which has an operating temperature as high as 1500°C. Nernst glowers are constructed from a fused mixture of oxides of zirconium, yttrium, and thorium, molded in the form of hollow rods 1-3 mm in diameter and 2-5 cm in length. The ends of the rods are cemented to short ceramic tubes to facilitate mounting; short platinum leads provide power connections. Nernst glowers are fragile. They have a negative coefficient of resistance and must be preheated to be conductive. Therefore, auxiliary heaters must be provided as well as a ballast system to prevent overheating. A glower must be protected from drafts, but at the same time adequate ventilation is needed to remove surplus heat and evaporated oxides and binder.

The energy output is predominantly concentrated between 1 and 10 μm, with relatively low energy beyond 10 um. Radiation intensity is approximately twice that of Nichrome and Globar sources except in the near-infrared.

The Globar, a rod of silicon carbide 6-8 mm in diameter and 50 mm in length, possesses characteristics intermediate between heated wire coils and the Nernst glower. It is self- starting and has an operating temperature near 1300°C. The temperature coefficient of resistance is positive and may be conveniently controlled with a variable transformer. Its resistance increases with the length of time used so that provision must be made for increasing the voltage across the unit. It is often encased in a water-cooled brass tube, with a slot provided for emission of radiation. The spectral output of the Globar is about 80% that of a blackbody radiator. In comparison with the Nernst glower, the Globar is a less intense source below 10 μm, the two sources are comparable out to about 15 um, and the Globar is superior beyond about 15 um. It finds some use out to about 50 μm.

In the very far-infrared, beyond 50 μm (200 cm⁻¹), blackbody-type sources lose effectiveness since their radiation decreases with the fourth power of wavelength. High-pressure mercury arcs, with an extra quartz jacket to reduce thermal loss, give intense radiation in this region. Output is similar to that from blackbody sources, but additional radiation is emitted from a plasma which enhances the long-wavelength output.

2.4 FOURIER TRANSFORM INTERFEROMETER

Instead of using a monochromator, the infrared radiation, after passage through a sam- ple, can be analyzed by means of a scanning Michelson interferometer. This consists of a moving mirror, 4, a fixed mirror, 3, and a beamsplitter, C. Radia- tion from the infrared source, B, is collimated by mirror 2 and the resultant beam is divided at the beamsplitter, half of the beam passing to mirror 3 and half reflected to the moving mirror. After reflection the two beams recombine at the beamsplitter and, for any particu- lar wavelength, constructively or destructively interfere depending on the difference in optical paths between the two arms of the interferometer. With a constant mirror velocity the intensity of the emerging

radiation at any one particular wavelength modulates in a regular sinusoidal manner. In the case of a broadband infrared source the emerging beam is a complex mixture of modulation frequencies, which, after passing through the sample compartment, is focused onto the detector, G.
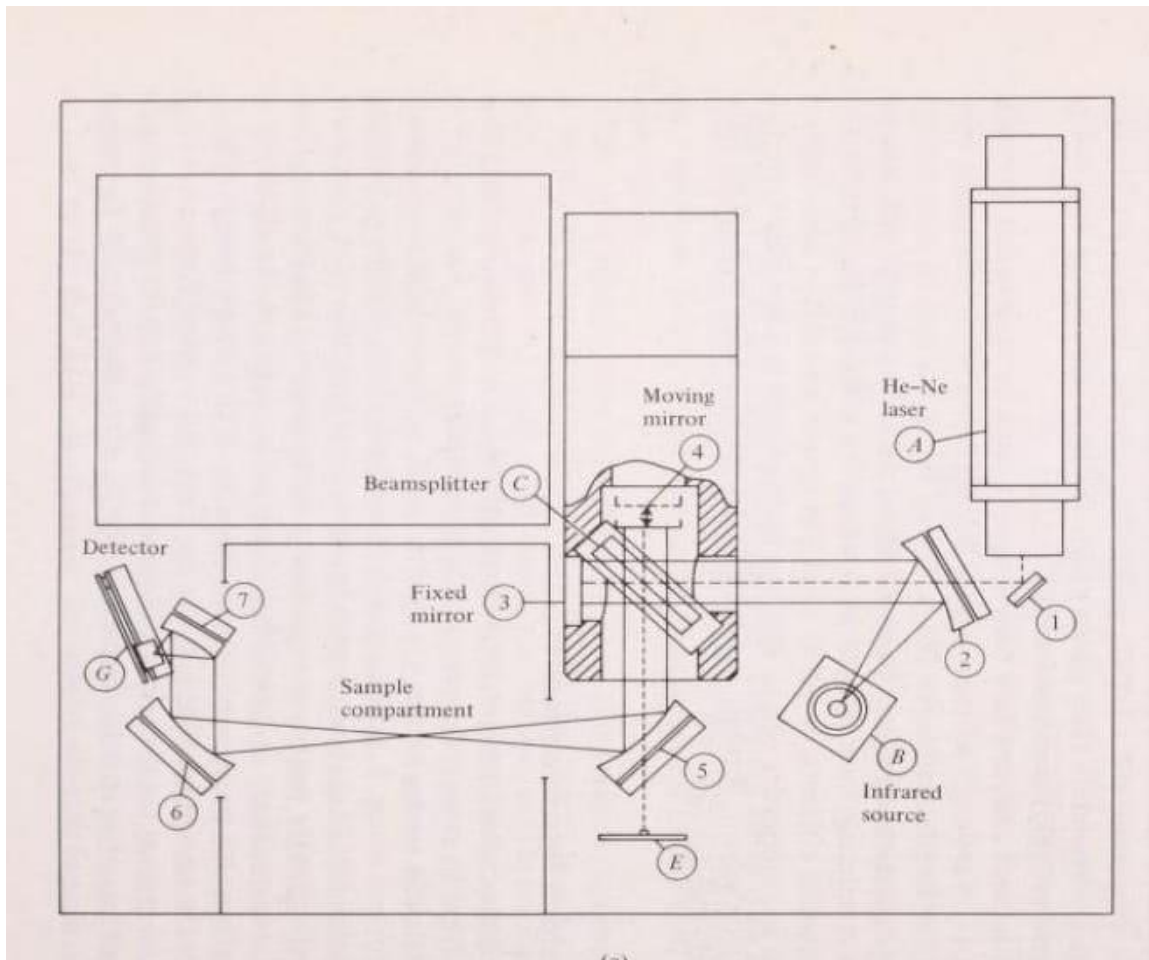
This detector signal is sampled at very precise intervals during the mirror scan. Both the sampling rate and mirror velocity are controlled by a reference signal from detector E produced by modulation of the beam from the helium-neon laser A. The resulting signal is known as an interferogram (memory 1) and contains all the information required to reconstruct the spectrum via a mathematical process known as Fourier transformation. This technique has several distinct advantages

over conventional dispersive techniques. There is only one moving part involved, mirror 4; this is mounted on a frictionless air bearing. Dispersion or filtering is not required, so that energy-wasting slits are not needed-a major advantage, particularly with energy a premium in the far-infrared. The use of a helium- neon laser as a reference results in near absolute frequency accuracy, better than 0.01 cm^1 over the range of 4800-400 cm. Because all wavelengths are detected throughout the scan, the scanning interferometer achieves the same spectral signal-to-noise ratio as a dispersive spectrometer in a fraction of the time (Fellgett's advantage).

2.5 BASIC PRINCIPLES OF NMR

The nuclei of certain isotopes possess an intrinsic spinning motion around their axes. The spinning of these charged particles, or their circulation, generates a magnetic moment along the axis of spin. If the nuclei are placed in an external magnetic field, their magnetic moment can align with or against the field. The individual nucleus spins around its axis and precesses about the force line of the applied magnetic field. These precessions are actually circular movements with respect to the force line and are restricted to a distinct number of angles between the field line and axis. The field aligns the spinning nuclei against the disordering tendencies of thermal processes. However, the nuclei do not align perfect y parallel (or antiparallel) to the imposed magnetic field. Instead, their spin axes are inclined to the field and precess about the field direction, behaving like a gyroscope in a gravitational field. Each pole of the nuclear axis sweeps out a circular path in the xy-plane. Increasing the strength of the field only makes the nuclei precess faster. The frequency of precession, Po, is known as the Larmor frequency of the observed nucleus.

2.6 NMR SPECTROMETER

There are many type of NMR spectrometers now available, but a general outline of a modern continuous wave (CW) (or field-sweep method) spectrometer will be given.

All high-resolution NMR spectrometers have a radio frequency (RF) source, sample holder, RF detector and a powerful magnet. The RF source and magnet have to have a high degree to field homogeneity. A resolution of 0.6 Hz in 60 MHz, i.e., 1 part in 108 is guaranteed, which means that the RF source and magnetic field are temperature-dependent. Therefore, accurate thermostating of the order of 10-5 is guaranteed, which means that the RF source and magnetic field are temperature- dependent. Therefore, accurate thermostating of the order of 10-5 K is required. The use of large polished magnets with aligned pole-faces further improve the homogeneity for the sample. Carefully shaped wire loops on the face of the magnet are called electric shims. Small currents when passed through these shims generate a local magnetic field. Properly adjusted shim coils improve the homogeneity by a factor of 103.

The compound under investigation is dissolved in a suitable solvent and a small amount of (<5%) of the reference compound is added. This sample (0.4 ml) is held in a glass tube of 0.5 cm outside diameter and 15 cm length for normal operation of 'H-NMR.

The suitability of a solvent is best dictated by, (a) high sample solubility, (b) absence of any signal from solvent in the region of interest and (c) symmetrical electron distribution.

CW-NMR

A NMR spectrometer differs in design from most spectrometers in that there is no clearly defined pub in space from the source to the detector through the sample. The radiation wavelength extends over less than a tenth of the wavelength. The block diagram of the components for a double coil NMR spectrometer is given. The sample is held in a glass tube with traces of the reference compound (e.g., TMS for 'H-NMR). The magnet poles are 20-30 cm in diameter and the gap between them is only 2-3 cm.

The RF oscillator bathes the sample in radiation of, say 60 MHz (for 'H-NMR) is made by means of current produced in the sweep generator fed to the field sweep coil around the magnetic recorder.

As is fairly easy to change the magnetic field smoothly and also, as a is fairly easy to maintain the RF frequency, technically, this method is by far the simplest.
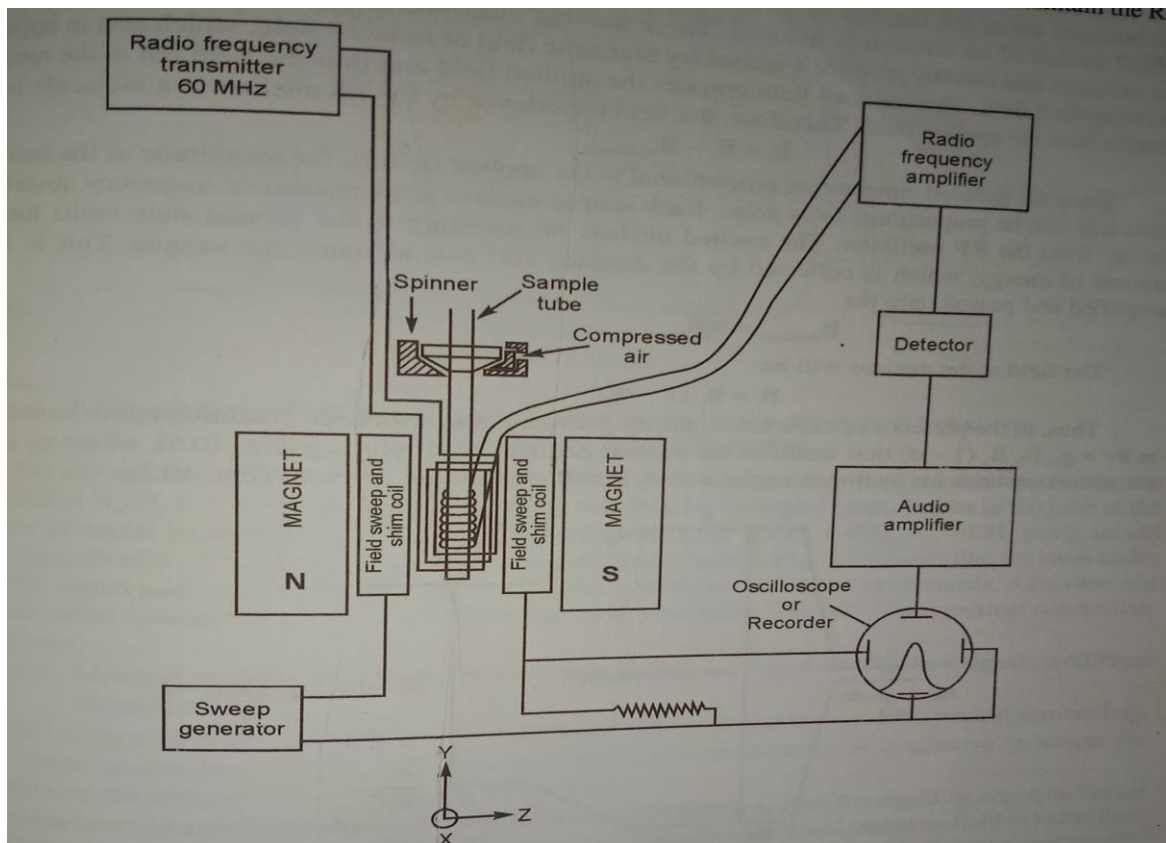

2.7 PRINCIPLES OF ESR

ESR spectroscopy is based on the absorption of microwave radiation by an unpaired electron when it is exposed to a strong magnetic field. The electronic energy levels of the atom or molecule will split into different levels. The magnitude of the splitting is dependent on the strength of the applied magnetic field. The atom or molecule can be excited from one split level to another in the presence of an external radiation of frequency corresponding to the frequency obtained from the difference in energy between the split levels. Such an excitation is called a magnetic resonance absorption. The magnetic resonance frequency will hence be influenced by the local environment of the atom or molecule.

2.8 ESR SPECTROMETER

The principle components of an ESR spectrometer are (1) a source of microwave radiation of constant frequency and variable amplitude; (2) a means of applying the microwave power to the sample-the microwave bridge; (3) a homogeneous and steady magnetic field to provide the magnetic field (spectroscopic) splitting; (4) an ac field superimposed on the steady field so as to sweep continuously through the resonance absorption of the sample; (5) a detector to measure the microwave power absorbed from the microwave field; and (6) an oscilloscope or a graphic x-y recorder. A simplified block diagram of an ESR spectrometer.
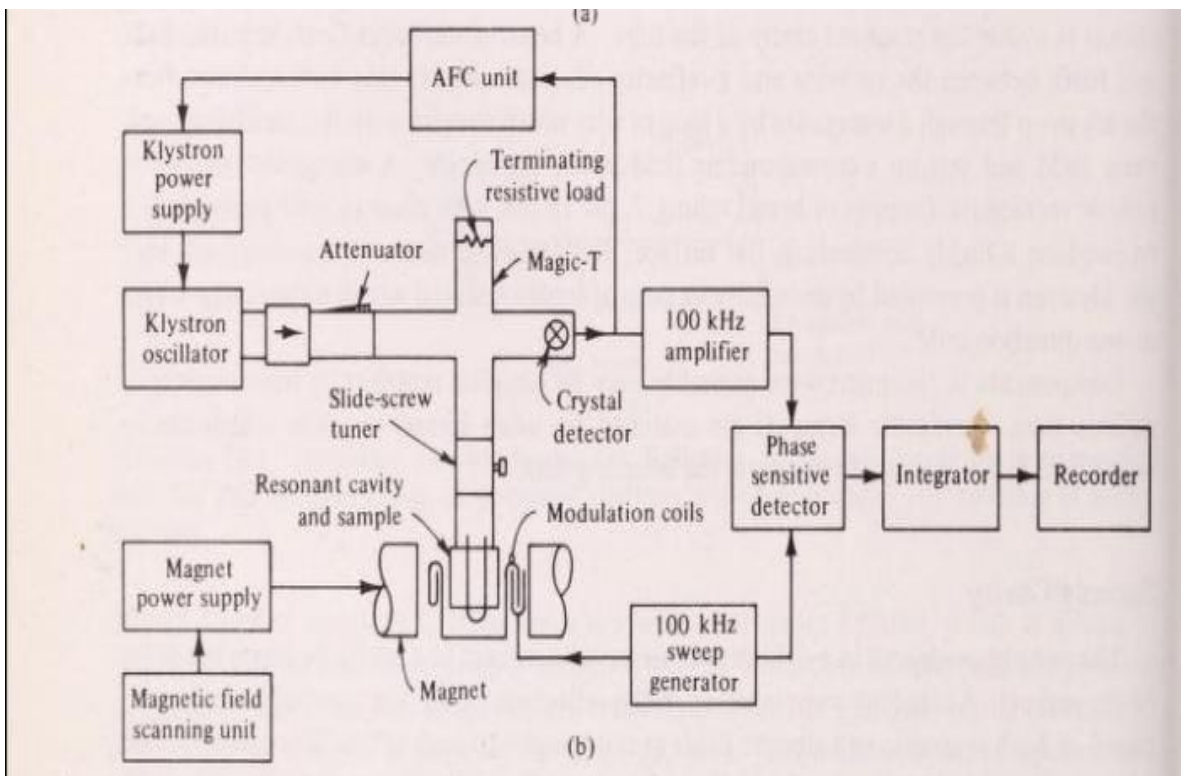
Source

Most ESR spectrometers employ radiation obtained from a klystron oscillator operating in the microwave X-band (3-cm wavelength) region. In a klystron the whole oscillating circuit is within the resonant cavity of the tube. A beam of electrons flows in pulses back and forth between the cathode and a reflector filament. Power may be withdrawn from the klystron through a waveguide by a loop of wire which couples with the oscillating magnetic field and sets up a corresponding field in the waveguide. A waveguide consists of hollow rectangular (copper or brass) tubing, 2.2 X 10 cm, with silver or gold plating inside to produce a highly conducting, flat surface. Reflection of microwave power back into the klystron is prevented by an isolator-a strip of ferrite material which passes microwaves in one direction only. Components in the microwave assembly may be coupled together by irises or slots of various sizes. Waveguide elements are matched by using screws or stubs which can be positioned in the waveguide or across the coupling slits.

Sample Cavity

The sample, contained in a cylindrical quartz tube, is held in a cavity between the poles of the magnet. A standing wave is set up in the reflection cavity; the standing wave is com- posed of both magnetic and electric fields at right angles to each other. The cavity is anal- ogous to a tuned circuit-a parallel LC combination. To minimize any influence of a high dielectric constant when such material is the sample, the sample tube is located in the cavi- ty in a position of maximum rf magnetic field and minimum rf electric field. Tubing of 3-5 mm i.d. with a sample volume of 0.15-0.5 ml can be used with samples which do not possess a high dielectric constant. For samples with a high dielectric constant, flat cells with a thickness of about 0.25 mm, and sample volume of 0.05 ml, are often used. Ro- tatable cavities are used for studying anisotropic effects in single crystals and in solid samples.

Dual sample cavities are used for simultaneous observation of a sample and a reference material. Slots can be machined into the walls of the cavity to allow ultraviolet irradiation of the sample. The two cavity sections are separately

modulated, one section by a 0.1- MHz field modulation and the other section by a 400-Hz field modulation. When the sig nals are fed through an appropriate 400-Hz amplifier and phase-sensitive detector, or a similar 0.1-MHz network, both resonances can be displayed on the recorder and superim- posed, Both samples are literally in the same cavity. Thus, sources of error in intensity measurements are automatically compensated by comparing relative signal heights.

Magnet and Modulation Coils

An electromagnet capable of producing steady fields ranging from 50 to 5500 G is required to handle samples whose g-factor ranges from 1.5 to 6. The g-factor is given by

$$g = \mu_e/\mu_B \, M_s$$

where g, called the spectroscopic splitting factor, has a value which is a function of the electron's environment (a value close to two for a free electron): is the Bohr magneton, a factor for converting angular momentum to magnetic moment. Because ESR spectrometers employ a sample resonant cavity to amplify the microwave signal, it is only feasible to vary the magnetic field. The cavity would not remain at resonance if the microwave frequency were varied. Also, it is difficult to vary the frequency of a klystron oscillator linearly and reproducibly. Field homogeneity and stability of one part in 106 are adequate for most ESR studies.

Microwave Bridge

The bridge enables the microwave system to be operated as a balanced bridge with all the advantages of null methods in electrical circuits. The micro- wave bridge will not allow microwave power to pass in a straight line from one arm to the arm opposite. Power entering arm A will divide between arms B and C if the impedances of B and C are the same, so that no power will enter arm D. Under these conditions the bridge is said to be balanced. Arm C usually contains a balancing load. If the impedance of arm B (the sample cavity) changes because of some ESR resonance absorption by a sample in it, the bridge becomes

unbalanced and some microwave power enters into arm D containing the detector- a semiconducting silicon-tungsten crystal which acts as a rectifier, converting the microwave power into direct current.

A set of coils mounted on the walls of the sample cavity and fed by a 0.1-MHz sweep generator provides modulation of the dc magnetic field at the sample position. As the main magnetic field is swept slowly through resonance over a period of several minutes, a dynamically recurring imbalance in the microwave bridge is detected and amplified for presentation on a recorder as the derivative of the microwave absorption spectrum against the magnetic field . Because of instrumental considerations associated with the signal-to-noise ratio, ESR spectra are nearly always recorded as first-derivative spectra. For low-frequency modulation (400 Hz or less) the coils can be mounted outside the cavity and even on the magnet pole pieces. Higher modulation frequencies cannot penetrate metal effectively and the modulation coils must be mounted inside the sample cavity.

Sensitivity

The ultimate sensitivity at room temperature of practical X-band (9500 MHz) ESR spectrometers is often expressed as

$$N_{min} = 1 \times 10^{11} \, \Delta H / \sqrt{T}$$

where N_{min} is the minimum number of detectable spins per gauss, ΔH is the width between deflection points on the derivative absorption curve, and is the time constant of the detecting system which is inversely proportional to the bandwidth of the detection circuit. For a sample of very small dielectric loss, the minimum concentration is in the order of 10M to barely see the line. For aqueous solutions, 10-7M represents a reasonable lower limit. For structure determinations and quantitative analysis, the concentration should be about 10-M. The limiting factor is generally the noise level in the spectrometer due to crystal noise and klystron noise. Working at higher magnetic field strengths gives a higher sensitivity. For example, at 35,000 MHz (K-band spectrometer) the sensitivity is 20 times greater.

UNIT III

OPTICAL CHARACTERIZATION

3.1 INSTRUMENTS FOR ABSORPTION PHOTOMETRY

Instruments for absorption photometry may be classified as spectrophotometers or filter photometers. Dispersive spectrometers are expensive but offer the advantage of continuous wavelength selectability. They are typically limited by light throughput, light scatter, and size. A monochromator is an inefficient device for transferring optical energy and energy loss is serious. For example, if an exit width of 0.1 nm with a height of 10 mm is used, the resultant aperture to the detector is on the order of 10 mm. To sense this small amount of energy a photomultiplier tube is generally required. The photomultiplier tube, inherently noisy, further degrades the signal-to-noise ratio and places severe demands on the detector if high precision is to be obtained.

Filter photometers offer an economic advantage over dispersive instruments, as well as increased luminosity, particularly when utilizing the interference-type filter. Of course, filters must be kept in stock for all wavelengths of measurement. If an analysis requires a measurement at a wavelength for which no filter is available, less than maximal sensitivity must be accepted. Because of the higher transmission efficiency, a more efficient optical system can be employed, markedly reducing effects of nearby emission or absorption features, and providing higher signal-to-noise ratios than can normally be obtained with a monochromator. The aperture to the detector can easily be opened to a centimeter in diameter, resulting in an effective detector aperture of 0.79 cm (as compared to 10 mm for monochromators). The detector receives a signal many magnitudes greater, allowing the use of such devices as vacuum photodiodes or semiconductor detectors rather than photomultiplier tubes. Not only do these detectors have better noise characteristics, but they are much less expensive. For routine or repetitive analyses, the stability of filters offers definite speed advantages. Pushbutton selection is possible. There is no danger of incorrect wavelength setting or of drift from the peak wavelength during operation, nieces- stating readjustment or recalibration.

3.2 PHOTOLUMINESCENCE PRINCIPLES

When a semiconductor is illuminated by a light source having photon energy greater than the band-gap energy (E_g) of the material, electrons are promoted to the conduction band, leaving holes behind in the valence band. When an electron-hole pair recombines, it emits a photon that has a wavelength characteristic of the material and the particular radiative process. Photoluminescence spectroscopy is a technique for extracting information about the electronic structure of the material from the spectrum of light emitted. In the basic process of PL at low temperature (liquid nitrogen temperature and below), an incoming photon is absorbed to create a free electron-hole pair. This transition must be essentially vertical to conserve crystal momentum, since the photon momentum is quite small. At cryogenic temperatures the electrons (holes) rapidly thermalize to the bottom (top) of the conduction (valence) band by emitting phonons. For this reason there is typically no observable luminescence above the band-gap energy. Once they have relaxed to the band edges, an electron and hole can bind together to form an exciton, which then recombines radiatively as described below. Alternatively, the electron or hole (or both) can drop into a defect state by nonradiative recombination and then undergo radiative recombination.

3.3 UV- ABSORPTION SPECTROSCOPY:

UV-Spectroscopy is used to study the optical properties of materials. Ultraviolet and visible spectroscopy is the electronics spectroscopy. When a molecule absorbs light of a particular wavelength an electron can be raised from its highest occupied molecular orbit causing an electronic transition.
 UV and visible light have sufficient energy to cause only the two electronic transitions namely n→π* and π→π*, this means that only compounds with π electrons or nonbonding electrons can produce UV spectra.
Silver chloride, if exposed to sunlight will undergo change in color and finally become black. Ritter found that the action considerably increases. If silver chloride is exposed beyond the action considerably region of 400nm to 10nm is called an ultraviolet spectrum. Sun is the natural source of UV radiations detection of UV radiations can be done by four methods.

- Photographic plates, which quickly blackens, when exposed to UV radiation. Fluorescence, process by which certain substance emit visible light when exposed to UV
- Phosphorescence process by which substances continuous to emit visible light even exposed UV is removed.
- Photo electric effect, using UV as light source to emit electrons.
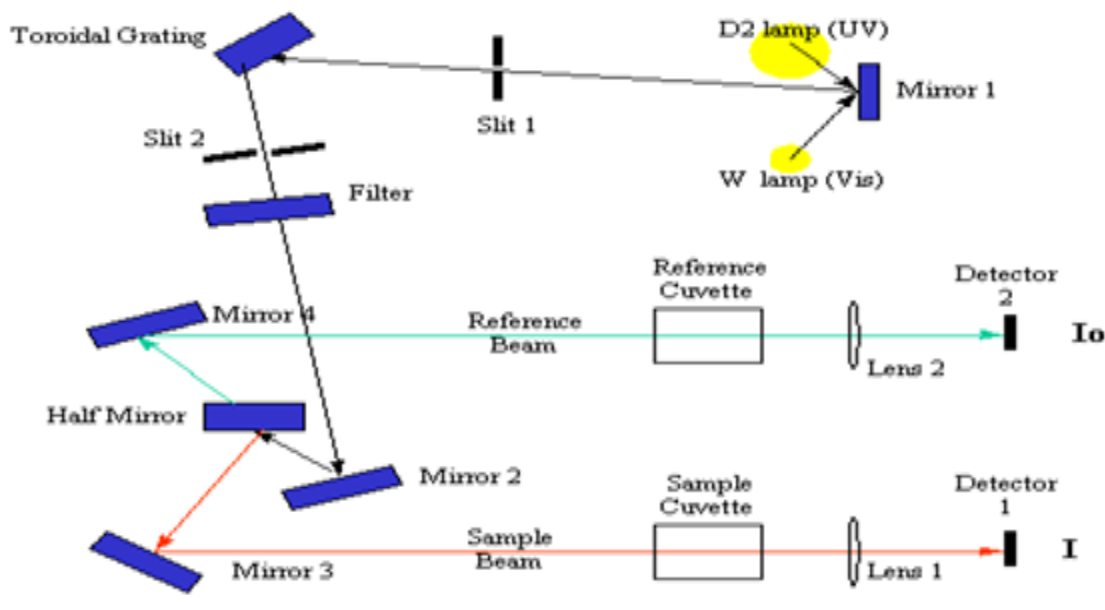
The functioning of this instrument is relatively straight forward. A beam of light from a visible or UV light source is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic beam in turn is split into two equal beams by a half-mirrored device.

One beam, the sample beam passes through a small transparent container containing a solution of the compound being studied in a transparent solvent. The other beam, the reference passes through an identical cuvatte containing only the solvent.

The intensities of these light beams are then measured, be electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined asI0. The intensity of the sample beam is defined as I. Over a short period of time, the spectrometer automatically scans all the component wavelength in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm.

Application of UV visible spectroscopy:
- UV absorption spectroscopy is used to determine the dissociation constants of acids and bases.
- UV absorption spectroscopy is generally used for the qualitative determination of compounds that absorb UV.
- UV absorption spectroscopy is one of the best methods for defecting impurities in organic compounds.
- UV absorption spectroscopy can characterize those type of compounds whiz absorb UV radiation.
- UV absorption spectroscopy can be used to study the kinetics of reaction.

3.4 PRINCIPLE BEHIND IR SPECTROSCOPY

The absorption of the infra red radiation causes excitation of the molecule from the lower to the higher vibrational level. We know that each vibrational level is associated with a number of spaced rotational levels. Clearly the infra red spectra is considered as vibrational – rotational spectra. All the bonds in a molecule are not capable of absorbing infra red radiation but only those which are accompanied by a change in dipole moment will absorb in the infra red region .Such vibrational transitions which are accompanied by a change in dipole moment of the molecule are called infra red active transitions. Thus these are responsible for absorption for absorption of energy in the infra red region .On the other hand the vibrational transitions which are not accompanied by a change in dipole moment are not directly observed and these are infra red inactive. Fof, vibrational transitions of $C=O, N-H, O-H$, etc bands are accompanied by a change in dipole moment and thus

absorb in the infra red region. But transitions in carbon - carbon bonds in symmetrical alkenes and alkynes are not accompanied by the change in dipole moment and hence do not absorb in the infra red region.
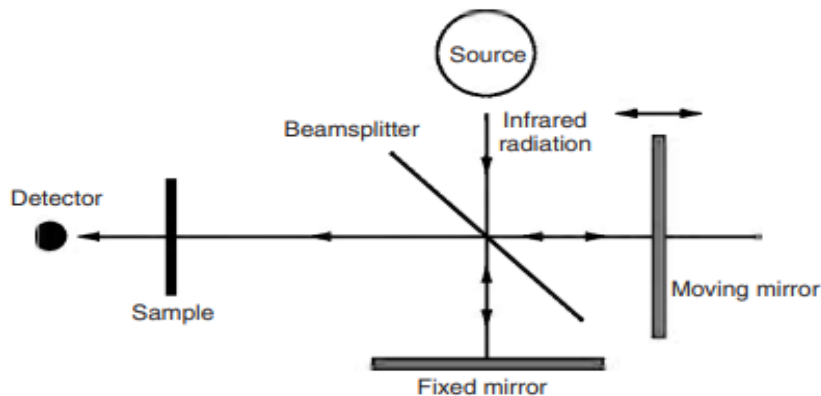
3.5 FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier Transform Infrared Spectroscopy FTIR is the most widely used vibrational spectroscopic technique. FTIR is an infrared spectroscopy in which the Fourier transform method is used to obtain an infrared spectrum in a whole range of wave numbers simultaneously. It differs from the dispersive method that entails creating a spectrum by collecting signals 298 9 Vibrational Spectroscopy for Molecular Analysis at each wave number separately. Currently, FTIR has almost totally replaced the dispersive method because FTIR has a much higher signal-to-noise ratio than that of the dispersive method.

Working Principles

The key component in the FTIR system is the Michelson interferometer. The infrared radiation from a source enters the Michelson interferometer. The interferometer is composed of one beam splitter and two mirrors. The beam splitter transmits half of the infrared (IR) beam from the source and reflects the other half. The two split beams strike a fixed mirror and a moving mirror, respectively. After reflecting from the mirrors, the two split beams combine at the beam splitter again in order to irradiate the sample before the beams are received by a detector. The function of the moving mirror is to change the optical path lengths in order to generate light interference between the two split beams. If the moving mirror is located at the same distance from the beam splitter as the fixed mirror, the optical paths of the two split beams are the same; thus, there is zero path difference. An optical path difference (δ) will be introduced by translating the moving mirror away from the beam splitter. Changing the optical-path difference is similar to what happens in diffraction of crystallographic planes . The two split beams will show constructive and destructive interference periodically, with continuous change of δ value. There will be completely constructive interference when $\delta = n\lambda$, but completely destructive interference

when $\delta = 1\ 2 + n\ \lambda$. A change of δ value is realized by a change in the position of the moving mirror.

Fourier transformation is necessary to convert an interferogram into an infrared spectrum, which is a plot of the light intensity versus wave number. The Fourier transform is based on a fact that any mathematical function can be expressed as a sum of sinusoidal waves. All the information of wave intensity as a function of wavelength is included in the sum of sinusoidal waves.

A computer equipped with a FTIR instrument constructs the infrared spectrum using a fast Fourier transform (FFT) algorithm that substantially reduces the computation time. The Fourier transform as a mathematical when discussing the relationship between real space and reciprocal space. Here, it is emphasized as a tool that transfers information between a function in the time (t) domain and its corresponding one in the frequency (ω) domain.

$$F(\omega) = 1\ \sqrt{2\pi} \int_{-\infty}^{\infty} f(t)e^{-i\omega t}\, dt$$

In an FTIR instrument, the Fourier transform converts the intensity versus optical path difference to the intensity versus wave number. The optical path difference can be considered as in the time domain because it is obtained by multiplying time with the speed of a moving mirror. The wave number can be considered as in the frequency domain because it is equal to frequency divided by the light speed.

3.6 STRENGTH OF FTIR SPECTROSCOPY

There are three principal advantages for an FTIR spectrometer.

The multiplex or Fellgett's advantage.

This arises from the fact that information from all wavelengths is collected simultaneously. It results in a higher signal-to-noise ratio for a given scan-time for observations limited by a fixed detector noise contribution (typically in the thermal infrared spectral region where a photodetector is limited by generation-recombination noise). For a spectrum with m resolution elements, this increase is equal to the square root of m. Alternatively, it allows a shorter scan-time for a given resolution. In practice multiple scans are often averaged, increasing the signal-to-noise ratio by the square root of the number of scans.

The throughput or Jacquinot's advantage.

This results from the fact that in a dispersive instrument, the monochromator has entrance and exit slits which restrict the amount of light that passes through it. The interferometer throughput is determined only by the diameter of the collimated beam coming from the source. Although no slits are needed, FTIR spectrometers do require an aperture to restrict the convergence of the collimated beam in the interferometer. This is because convergent rays are modulated at different frequencies as the path difference is varied. Such an aperture is called a Jacquinot stop. For a given resolution and wavelength this circular aperture allows more light through than a slit, resulting in a higher signal-to-noise ratio.

The wavelength accuracy or Connes' advantage.

The wavelength scale is calibrated by a laser beam of known wavelength that passes through the interferometer. This is much more stable and accurate than in dispersive instruments where the scale depends on the mechanical movement of diffraction gratings. In practice, the accuracy is limited by the divergence of the beam in the interferometer which depends on the resolution.

Another minor advantage is less sensitivity to stray light, that is radiation of one wavelength appearing at another wavelength in the spectrum. In dispersive instruments, this is the result of imperfections in the diffraction gratings and accidental reflections. In FT instruments there is no direct equivalent as the apparent wavelength is determined by the modulation frequency in the interferometer.

UNIT IV

THERMAL AND MECHANICAL CHARACTERIZATION

4.1 THERMAL METHODS

Thermal analysis includes a group of techniques in which a physical property of a substace is measured as a function of temperature while the substance is subjected to a controlled temperature program. A complete modern thermal analysis instrument measures temperatures of transitions, weight losses in materials, energies of transitions, dimenensional changes, modulus, and viscoelastic properties. Current applications include environmental measurements, product reliability, compositional analysis, stability, chemical reactions and dynamic properties.There are three major methods of thermal analysis. They are

- Differential thermal analysis – physical and chemical processes related to thermal effects can be characterized.
- Thermogravimetry analysis – mass changes due to evaporation, decomposition and interaction with the atmosphere.
- Thermomechanical analysis – differential changes, deformations, viscoelastic properties, transitions, density

4.2 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetry (TG) provides the analyst with a quantitative measurement of any weight change associated with a transition. For example. TG can directly record the loss in weight with time or temperature due to dehydration or decomposition. Thermogravimetric curves are characteristic for a given compound or system because of the unique sequence of physicochemical reactions which occur over definite temperature ranges and at rates that are a function of the molecular structure. Changes in weight are a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to the evolution of volatile products or the formation of heavier reaction products. From such curves data are obtained concerning the thermodynamics and kinetics of the various chemical reactions, reaction mechanisms, and the intermediate and final reaction products. The usual temperature range is from ambient to 1200°C with inert or reactive atmospheres.

The derivative in TG is often used to pinpoint completion of weight-loss steps or to increase resolution of overlapping weight-loss occurrences.

Instrumentation

For TG the sample is continuously weighed as it is heated to elevated temperatures. Samples are placed in a crucible or shallow dish that is attached to an automatic-recording balance. The automatic null-type balance incorporates a sensing element which detects a deviation of the balance beam from its null position. One transducer is a pair of photo- cells, a slotted flag connected to the balance arm, and a lamp. Once an initial balance has been established, any changes in sample weight cause the balance to rotate. This moves the flag so that the light falling on each photocell is no longer equal. The resulting nonzero signal is amplified and fed back as a current to a taut-band torque motor (the pivot point of the balance) to restore the balance to equilibrium. This current is proportional to the weight change and is recorded on the y-axis of the recorder. Changes in mass can also be detected by contraction or elongation of a precision helical spring whose movement is detected by the movement of an attached core in a linear variable differential transformer. With either type balance the sample container is mounted inside a quartz or Pyrex housing which is located inside the furnace, Furnace temperature is continuously monitored by a thermocouple whose signal is applied to the x-axis of the recorder. Linear heating rates from $5°$ to $10°C/min$ are generally employed. In differential thermogravimetry the actual measurement signal is derived from a solid. state resistance-capacitance circuit which uses the direct output of the electrical weight. change signal from the thermobalance for the primary signal input. The resulting output is the derivative, Aw/Ar, which is used in kinetic interpretations. Sample sizes range from 1 to 300 mg, and sensitivities down to a few micrograms of weight change are common.
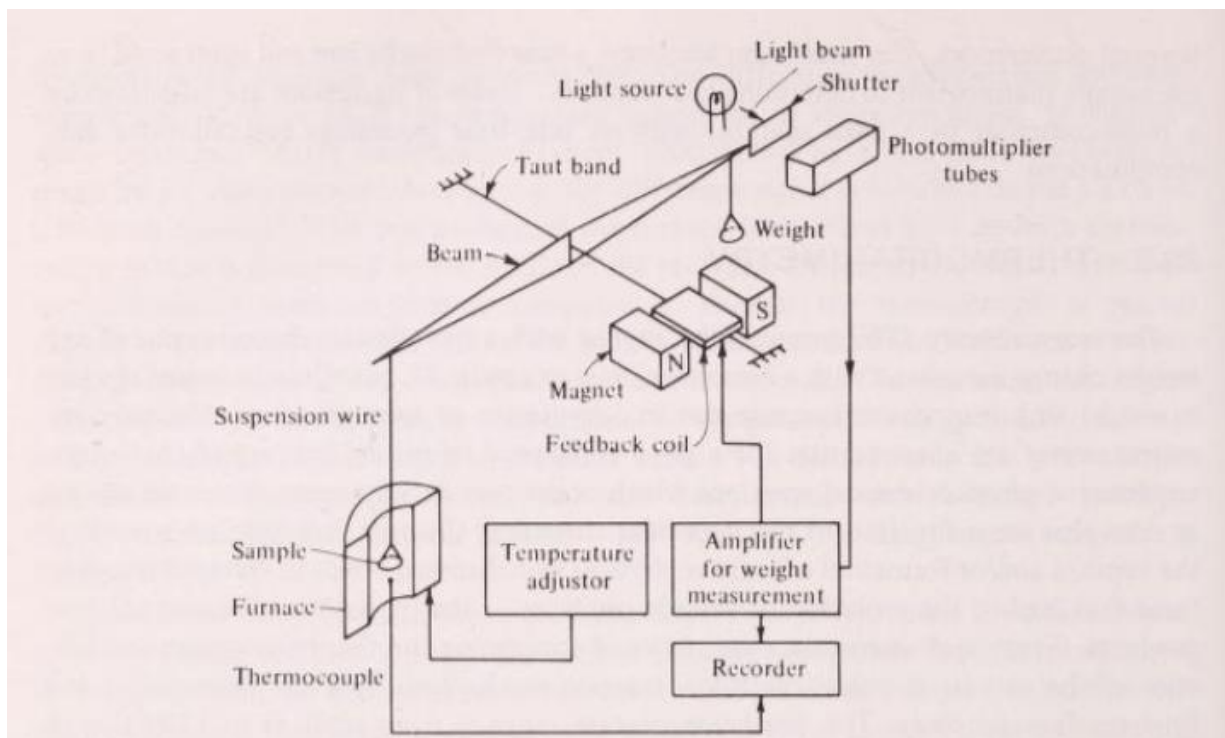
4.3 DIFFERENTIAL THERMAL ANALYSIS

In differential thermal analysis (DTA) the temperature of a sample and a thermally inert reference material are measured as a function of temperature (usually sample temperature), Any transition which the sample undergoes will result in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. This differential temperature versus the programmed temperature (T) at which the whole system is being changed tells the analyst the temperature of transitions and whether the transition is exothermic or endothermic.

Instrumentation
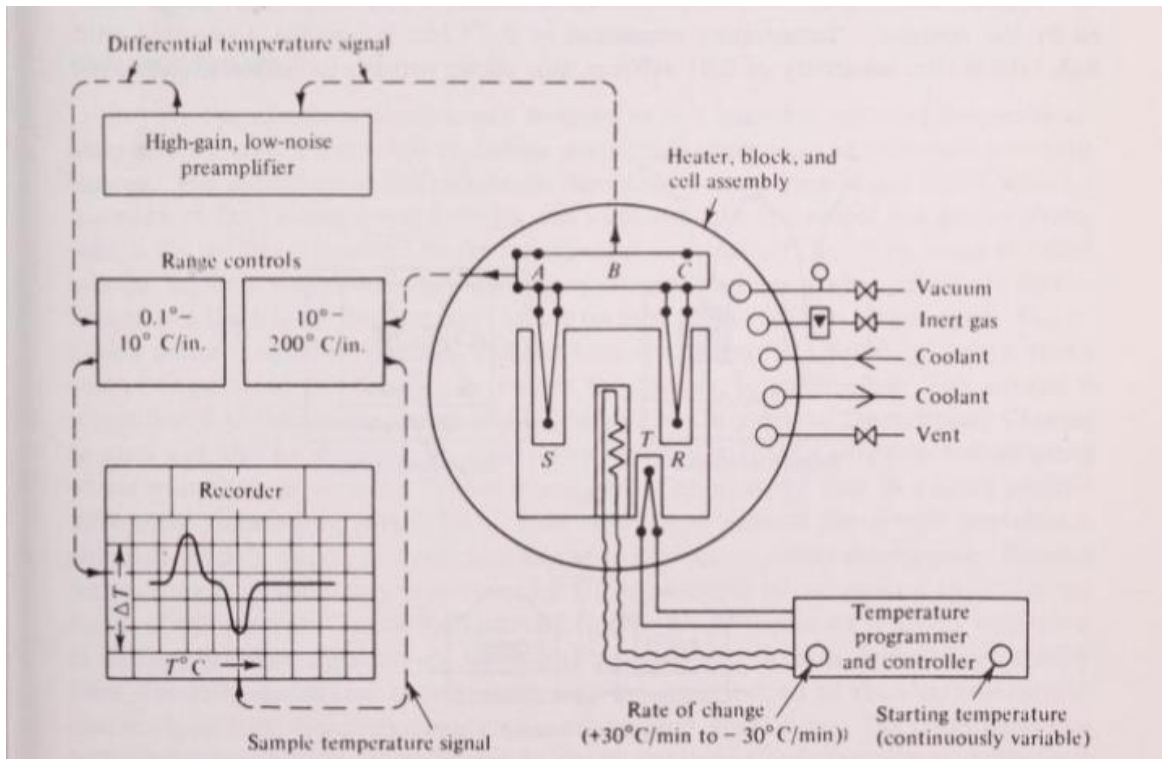
Typical DTA equipment is illustrated in Fig. The furnace contains a sample block with identical and symmetrically located chambers Each chamber contains a cen- tered thermocouple. The sample is placed in one chamber and a reference material, such as a Alg0,, is placed in the other chamber. The furnace and sample block temperature are then increased at a linear rate, most often 5 to 12°C/min, either by increasing the volt age through the heater element by a motor-

driven variable transformer or by a thermocouple-actuated feedback type of controller. The difference in temperature between sample and reference (S, R) thermocouples, connected in series-opposition, is continuously measured. After amplification (about 1000 times) by a high-gain, low-noise, de amplifier for the microvolt-level signals, the difference signal is recorded on the y-axis of a millivolt recorder. The temperature of the furnace is measured by a separate thermo- couple which is connected to the x-axis of the recorder, frequently through a reference ice junction or room-temperature compensator. Because the thermocouple is placed directly in the sample, or attached to the sample container, the DTA technique provides the highest thermometric accuracy of all the thermal methods. The area under the output curve, however, is not necessarily proportional to the amount of energy transferred in or out of the sample. If maximum calorimetric accuracy is desired, the sample and reference thermocouples are removed from direct contact with the sample. The temperature range is between -190 and 1600°C. Sample sizes range from 0.1 to 100 mg.

Quantitative heats of transition require area integration to determine the total amount of energy transferred into or out of the sample. Precise measurement requires enlargement of the thermogram for accurate area measurements and a time-base display rather than the temperature base thermogram. Also, precise quantitative heat capacity measurements are typically made at high sensitivity settings. Microprocessors avoid the necessity for running several thermograms. A disk memory retains all occurrences at maximum sensitivity. An expanded thermogram can be replotted automatically over a temperature range select ed by the operator. Temperature expansion to 0.2°C/cm is possible. Combined with high calorimetric sensitivity of 0.01 mW/cm, this allows virtually unlimited expansion of thermal occurrences. For maximum accuracy, a base line can be run and subtracted from the sample thermogram to determine heat capacity. Heats of transitions are calculated by a microcomputer in a data analyzer without time-base recordings and laborious data computations.

4.4 MECHANICAL PRINCIPLES: STATIC AND DYNAMIC MEASUREMENT

Static measurements

Here we use a piezoelectric bimorph cantilever to act as the detecting sensor. The main body of the detector is a steel strip, and both the upper and lower surfaces of the steel strip are bonded with piezoelectric patches. An

indenter was welded onto the free end of the cantilever to provide contact with the sample during testing. For soft materials testing, the tip radius of the indenter is fairly large, 5 mm, to enlarge the indentation force and protect the sample. The indentation force is measured by a strain gauge bonded on the piezoelectric cantilever, which also monitored the indenter displacement of the cantilever. The testing sample is fixed on a 3-D piezoelectric motor platform with the displacement resolution of 0.05 mm.

To get the quasi-static mechanical properties of soft materials, the indentation force - depth (F-h) curve of the sample is measured during the indentation process. The indentation force is measured by the strain gauge with the cantilever stiffness calibrated in advance. The indentation depth is the Z displacement of the ultrasonic motor platform minus
the indenter displacement of the piezoelectric cantilever. After obtaining the F-h curve, the quasi-static mechanical properties of the sample can be extracted using different material models. In this work, the finite deformation neo-hookean model is used to describe the indentation behavior of soft material. This model is applicable to soft materials during the indentation process, which is more accurate than the Hertz contact model. According to

$$\mu_0 = E_s/2(1 + v_s), \quad E^0 = \left(\frac{1 - v^2_t}{E_t} + \frac{1 - v^2_s}{E_s}\right)^{-1}$$

,for $v_s = 0.5$, and with $E_t \gg E_s$, we get $E^* = E_s.4/3$ and $\mu_0 = E_s/3$, we get $E^* = 4\mu_0$. Substitute this relationship into the formula $F = 4E^*/3 \sqrt{(h3R)}$, the F-h relationship during indentation is.

$$F = 16/3 \ \mu_0\sqrt{Rh} \ h$$

where h is the indentation depth and R is the tip radius of the indenter, the initial shear modulus (μ_0) of the material can be obtained by fitting the above formula with the measured F-h data.
The sensitivity of the quasi-static indentation method is defined as

$$s_\varepsilon = \partial\varepsilon/\partial\mu_0$$

for the measurement parameter of the quasi-static pressing method is the strain ε at the fixed end of the piezoelectric cantilever, which represents the strain change of piezoelectric cantilever caused by the change of initial shear modulus of the testing sample, and the larger the sensitivity, the better. The piezoelectric cantilever beam

is equivalent to a homogeneous beam with the modulus of E, the length of L, the width of a, and the thickness of b. The strain at the fixed end of the cantilever can be obtained as $\varepsilon = 6LF/Eab2$, thus we have:

$$S_\varepsilon = 32 \sqrt{Rh} \, hL/Eb^2 a$$

DYNAMIC MEASUREMENT

For dynamic mechanical testing, the indentation force (or indentation depth) is fixed and the contact resonance frequency (CRF) of the piezoelectric cantilever-sample system is tracked. To obtain the indentation depth dependent mechanical properties of the sample, the indenter can be pressed into the sample continuously by using the piezoelectric motor platform. At each prescribed indentation depth, the CRF of the piezoelectric cantilever is tracked using an impedance analyzer to obtain the LCS between the indenter and the sample. The dynamic elastic properties of the sample under different loads can then be obtained by using the Hertz contact model.

The piezoelectric indentation system is simplified into the mechanical model, where L is the length of the piezo-electric bimorph, hp and 2hm are the thickness of the piezoelectric material (PZT) layer and that of the steel layer, respectively. The contact interaction between the cantilever indenter and the sample was modeled by a linear spring with the stiffness kt, neglecting the sample's added mass and damping here for simplicity. The indenter is simplified to a single mass mt, ρb andρm are the density of the PZT and steel strip, respectively. By derivation, we have.

$$k_t = m_t \omega^2_0 + k_b \lambda^3_{b0} \, \frac{1 + \cos \lambda b_0 L \cosh \lambda b_0 L}{\cos \lambda b_0 L \sinh \lambda b_0 L - \sin \lambda b_0 L \cosh \lambda b_0 L}$$

where k_b is the equivalent stiffness of the piezoelectric cantilever, ρ_b is the mass per unit length of the cantilever, we have

$$\bar{k}_b = \frac{2}{3} a \left[\frac{1}{S^E_{P11}} ((h_p + h_m)^3 - h^3_m) + \frac{1}{S_{m11}} h^3_m \right]$$

$$\bar{\rho}_b = 2a(\rho_p h_p + \rho_m h_m),$$

where a is the width of the piezoelectric cantilever.

S^E_{p11} and S_{m11} are the elastic compliance of the PZT and steel strip, respectively, and ω_0 is the resonance frequency of piezoelectric cantilever,

$$\lambda_{b0} = (\omega_0^2 \bar{\rho}_b / \bar{k}_b)^{1/4}$$

4.5 INSTRUMENTATION OF EXTENSOMETER ANALYSIS

The extension of the specimen must be measured with an extensometer in order to obtain the displacement corresponding to a given load. There are various ways to measure small displacements with great accuracy. One technique that has become very popular is the so-called clip-on gage. This gage consists of two spring arms attached to a small block. Strain gages are attached to both spring arms and are connected to form a Wheatstone bridge similar to the load cell. However, the calibration is done in terms of displacement, and it is possible to measure very small displacements with great accuracy using this instrument. While some indication of the specimen deformation can be obtained by monitoring the displacement of the crosshead (or hydraulic ram, depending on the nature of the test machine), it is, of course, preferable to attach an extensometer directly to the specimen. In this way the extension of the specimen is measured unambiguously.

Two problems arise if the extension of the specimen is equated to the displacement of the lower crosshead or piston:
(1) the gage length is assumed to be the region between the shoulders of the specimen and, more importantly,
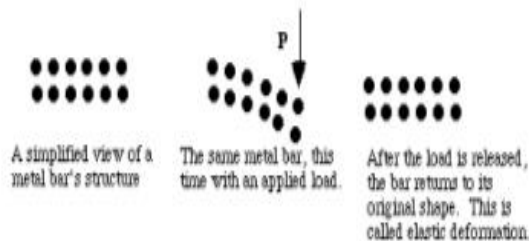 (2) deflection in the load train occurs to a rather significant degree.

Thus, unless the machine stiffness is known and factored into account, the extension of the specimen will be overestimated. In addition, even if the machine stiffness is accounted for, the rate of straining of the specimen will be variable throughout the plastic region since the proportion of actual machine and specimen deflection changes in a nonlinear way. Given these sources of error it is highly desirable to measure the machine deflection directly using an extensometer. Of course this is not always possible, especially when testing in severe environments and/or at high temperatures. In such cases other techniques must be used to obtain reasonable estimates of the strain in the specimen.
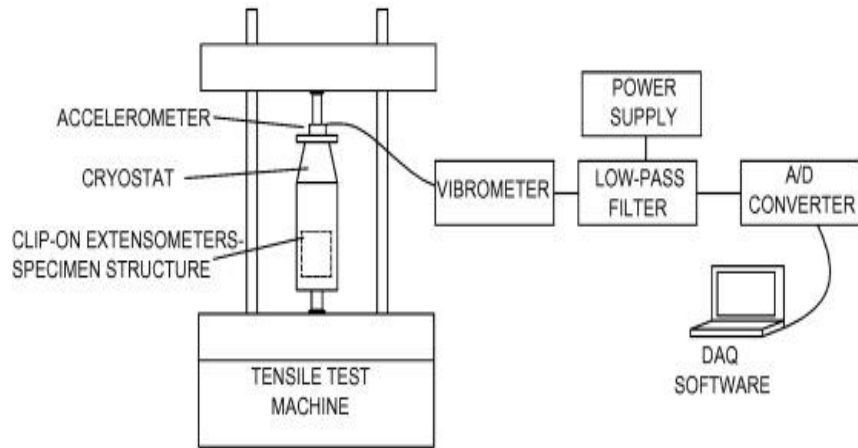
4.6 BENDING PROPERTIES OF MATERIALS:

When small loads (stresses) are applied to metals they deform, and they return to their original shape when the load is released. Bending a sheet of steel is an example where the bonds are bent or stretched only a small percentage. This is called elastic deformation and involves temporary stretching or bending of bonds between atoms.

When higher stresses are applied, permanent (plastic) deformation occurs. For example, when a paper clip is bent a large amount and then released, it will remain partially bent. This plastic deformation involves the breaking of bonds, often by the motion of dislocations.

A simplified view of a metal bar's structure   The same metal bar, this time with an applied load.   After the load is released, the bar returns to its original shape. This is called elastic deformation.

Dislocations move easily in metals, due to the delocalized bonding, but do not move easily in ceramics. This largely explains why metals are ductile, while ceramics are brittle.
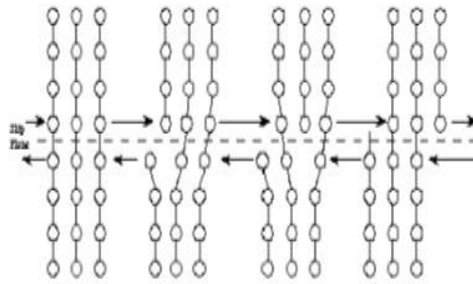
If placed under too large of a stress, metals will mechanically fail, or fracture. This can also result over time from many small stresses. The most common reason (about 80%) for metal failure is fatigue. Through the application and release of small stresses (as many as millions of times) as the metal is used, small cracks in the metal are formed and grow slowly. Eventually the metal is permanently deformed or it breaks (fractures).

4.7 IN- PLANE IMPACT TESTING

Figure, shows the working procedure of impact testing. The pivoting arm is raised to a specific height, which is the potential energy and then this arm gets released
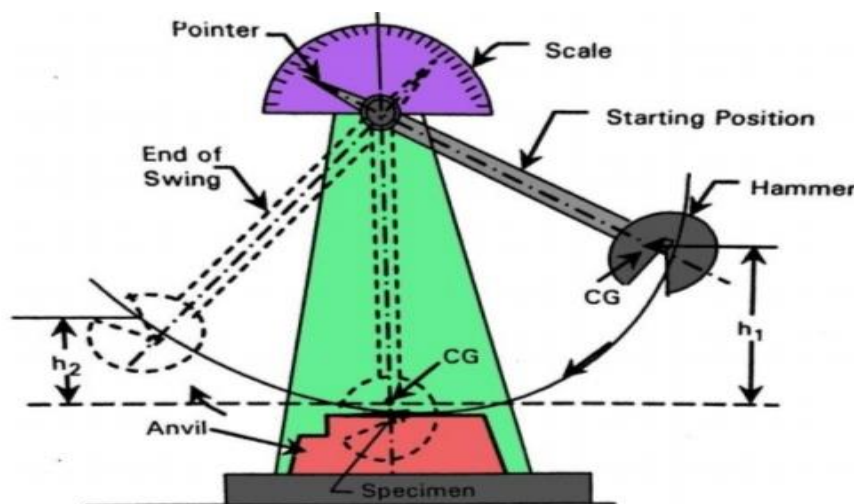
The arm swings down hitting a notched sample, available on the specimen holding vise, and breaking the specimen. The energy absorbed by the sample is measured from the height the arm swings to after hitting the sample. The fracture energy (Joule) is determined from the swing-up angle of the hammer and its swing-down angle. A notched sample is generally used to determine impact energy and notch sensitivity. Some of the standards are followed worldwide for the test they are ASTM D6110, ASTM E23, and ASTM D256 etc...,. In Charpy test , a test

specimen having a V-shaped notch is placed on the holder in such position that the notched section is in the center of the holder and the specimen is broken by striking the back of the notched section with the hammer. The Charpy impact value (kJ/m2) is calculated by dividing the fracture energy by the cross-section area of the specimen. If a test specimen having a V- shaped notch is fixed vertically, and the specimen is broken by striking it from the same side as that of the notch by the use of the hammer, this is called Izod test. The Izod impact energy value (J/m,) is calculated by dividing the fracture energy by the width of the specimen.

UNIT V

MORPHOLOGICAL CHARACTERIZATION

5.1 SCANNING ELECTRON MICROSCOPE-SEM

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum in conventional SEM,

Principles

"When the accelerated primary electrons stricks the sample, it produces secondary electrons. These secondary electron are collected by a positive charged electron detector which in turn gives a 3D detector which in turn gives a 3D image of the sample."

The signals used by a scanning electron microscope to produce an image result from interactions of the electron beam with atoms at various depths within the sample. Various types of signals are produced including secondary electrons (SE), reflected or back-scattered electrons(BSE), characteristic X-rays and light (cathodoluminescence) (CL), absorbed current (specimen current) and transmitted electrons. Secondary electron detectors are standard equipment in all SEMs Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnifications is possible, to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. Scanning Electron Microscopy (SEM) - Instrumentation Construction It consists of an electron gun to produce high energy electron beam. A magnetic condensing lens is used to condense the electron beam and a scanning coil is arranged in between magnetic condensing lens and the sample. The electron detector (Scintillator) is used to collect the secondary electrons and can be converted into electrical signal. These signals can be fed into CRO through video amplifier as shown in fig

Working

Stream of electrons are produces by the electron gun and theses primary electrons are accelerated by the grid and anode. These accelerated primary electrons are made to incident on the sample through condensing lenses and scanning coil. These high speed primary electrons on falling over the sample produce low energy secondary electrons. The collection of secondary electrons is very difficult because of their low energy. Therefore, to collect this secondary electron a very high voltage is applied to the collector
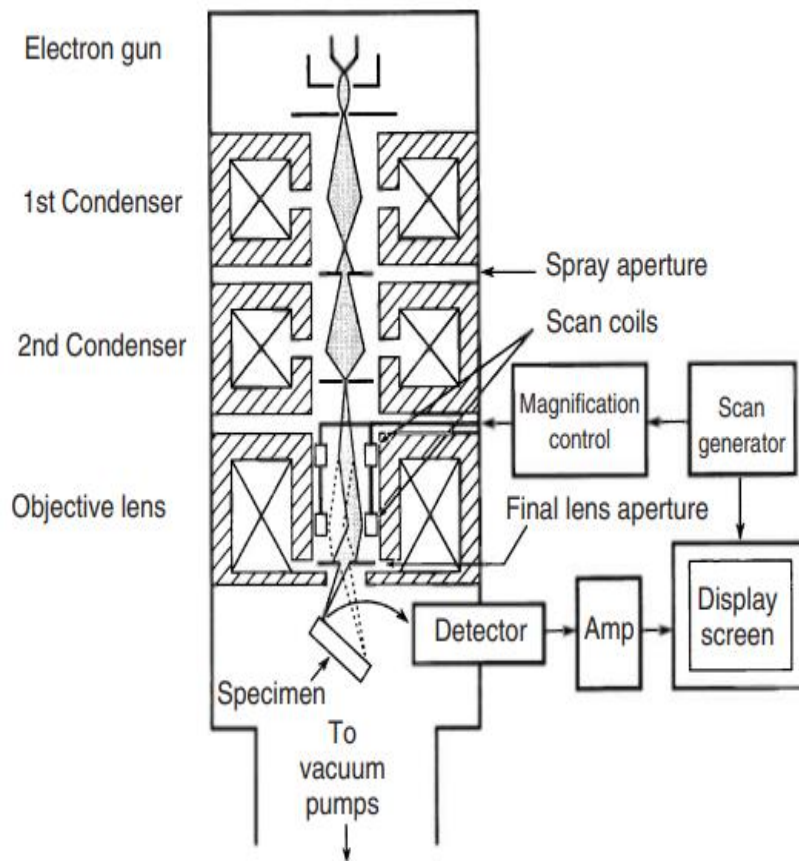
These collected electrons produce scintillation on photo multiplier tube (detector) and are converted into electrical signals. These signals are amplified by

the video amplifier and are fed to the CRO. By similar procedure the electron beam scan the sample from left to right and again from left to right etc., similar to we read a book and the whole picture of the sample is obtained in the CRO screen.

Advantages

1. It can be used to examine specimens of large thickness.

2. It has large depth of focus.

3. It can be used to get a 3D image of the object.

4. Since the image can be directly viewed in the screen, structural details can be resolved in a precise manner.

5. The magnification may be upto 3,00,000 times greater than that of the size of the object.

Disadvantage

1. The resolution of the image is limited to about 10-20 nm, hence it is very poor.

Applications

The SEM is routinely used to generate high-resolution images of shapes of objects (SEI) and to show spatial variations in chemical compositions:

1) acquiring elemental maps or spot chemical analyses using EDS, 2)discrimination of phases based on mean atomic number (commonly related to relative density) using BSE, and

3)The SEM is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM.

5.2 TRANSMISSION ELECTRON MICROSCOPY

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image. The specimen is most often an ultrathin section less than 100 nm thick or a suspension

on a grid. An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen. The image is then magnified and focused onto an imaging device, such as a fluorescent screen, a layer of photographic film, or a sensor such as a charge-coupled device
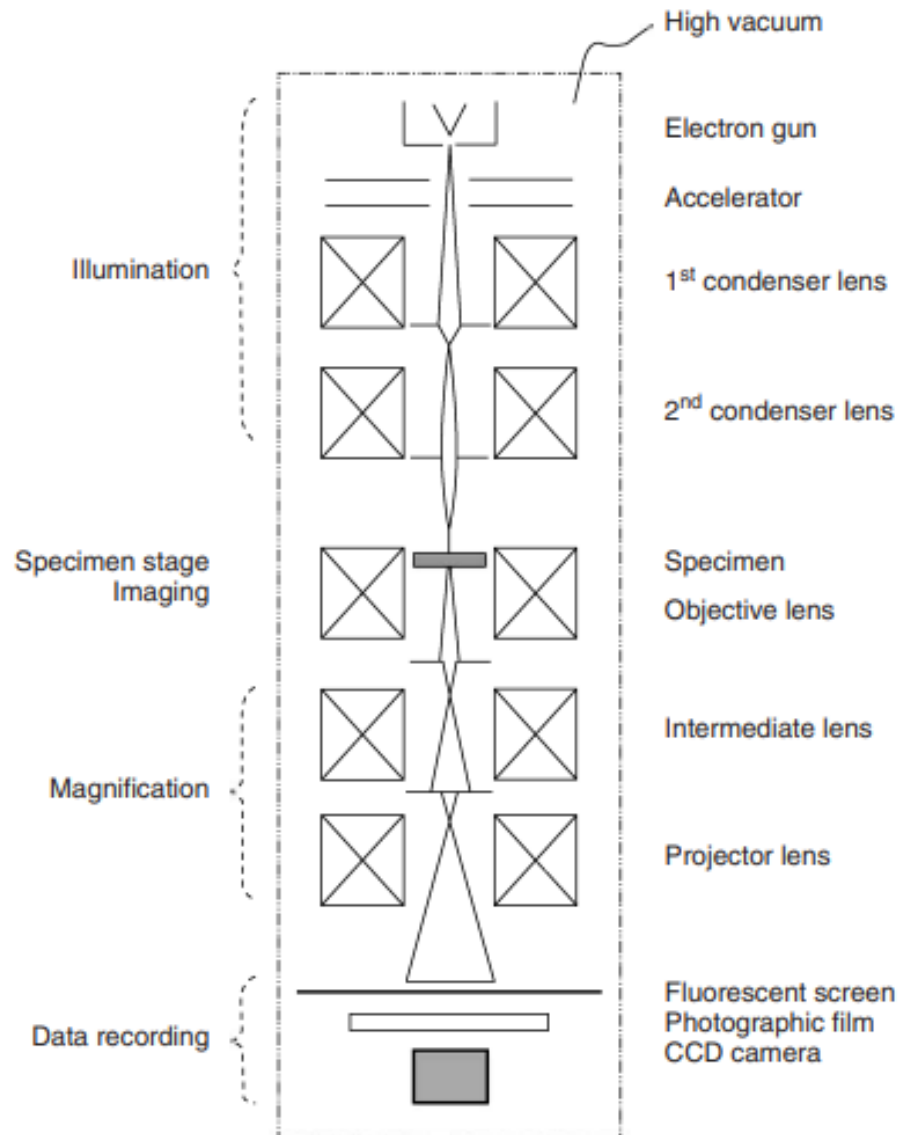
Principle

Electrons are made to pass through the specimen and the image is formed in the fluoresce screen, either by using transmitted beam (Bright field image) on by using diffracted beam (Dark field image).

Construction

It consists of an electron gun to produce electrons. Magnetic condensing lens is used to condense the electrons and is also used to adjust the size of the electron that falls onto the specimen. The specimen is places in between the condensing lens and objective lens as show in fig . The magnetic objective lens in used to block the high angle diffracted beams and the aperture is used to eliminate the diffracted beam (if any) and in turn it increases the contrast of the image.The magnetic projector lens is places above the fluorescent screen in order to achieve higher magnification. The image can be recorded by using a florescent (Phosphor) screen or (CCD- charged Coupled Device) also.

Working

Stream of electrons are produced by the electron gun and is made to fall over the specimen using the magnetic condensing lens. Based on the angle of incidence, the beam is partly transmitted and partly diffracted, as shown in fig. Both the transmitted beam and the diffracted beams are recombined at the E-wald sphere (sphere of reflection which encloses all possible reflections from the crystal/specimen, satisfying Bragg's law), to form the image as shown in fig . The combined image is called the phase contrast image.The magnified image is recorded in the fluorescent screen (or) CCD. This high contrast image is called Bright field image. Also, it has to be noted that the bright field image obtained is purely due to the elastic scattering (no energy change) i.e., due to transmitted beam alone

High vacuum

Electron gun

Accelerator

Illumination

1st condenser lens

2nd condenser lens

Specimen stage
Imaging

Specimen
Objective lens

Intermediate lens

Magnification

Projector lens

Fluorescent screen
Photographic film
CCD camera

Data recording

Advantages

1. It can be used to examine the specimen of size upto 0.2 nm.

2. The magnification is 10,00,000 times greater than the size of the object.

3. It has high resolution

4. The resolving power is 1Å to 2 Å .

5. We can get high contrast image due to both transmitted beams (bright field) and diffracted beam (Dark field).

Disadvantages

1. The specimen should be very thin.

2. It is not suitable for thick samples.

3. There are changes for the structural change, during sample preparation .

4. 3D image can't be obtained

5. In case of biological sample, the electron may interact with the sample, which may even damage the sample.

Application

1. The main application of TEM is in Nano science (Nano-tubes, micro machines etc.), used to find the internal structures of nanomaterial.

2. It is used to find the 2D image of very small biological cells. Virus, bacteria etc.
3. It is used in thin film technology, metallurgy, bio-chemistry, micro-biology etc.
4. It is used to study the compositions of paints, papers, fibers, composite materials, alloys etc.

5.3 Scanning Tunneling Microscopy

STM relies on a tunneling current across a gap between the probe tip and a surface atom for surface examination. An electric current may penetrate an isolation gap between two conductors if high voltage is applied, but this is not the tunneling current. The tunneling current is a phenomenon of quantum mechanics. It results from electrons penetrating an energy barrier larger than the electron energy. To generate the tunneling current (I_t), a bias voltage is applied across a gap between the tip and the sample when the tip is kept near the sample. Without much knowledge of quantum mechanics, we may quantify the tunneling current through the following equation

$$I_t = V_b \exp(-Cd)$$

V_b is the bias voltage applied between the tip and the surface, C is a constant that depends on the nature of the sample material, and d is the nearest distance between the tip and the sample surface.

For generating a tunneling current, only a small bias voltage (typically between 1 mV and 4 V) is necessary when the gap is on the scale of the interatomic distance. In an STM, the tunneling current (It) is between 10 pA and 10 nA. The tunneling current varies exponentially when the distance changes. The tunneling current decays by an order of magnitude when the vacuum gap is changed by 0.1 nm
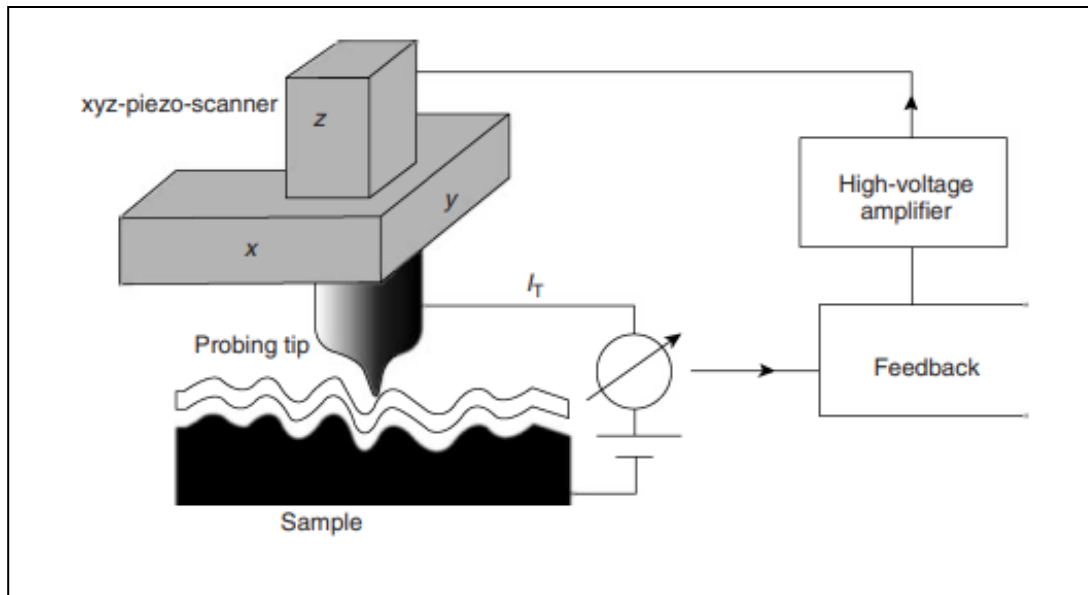
Operational Modes

There are four operational modes in the STM: constant current, constant height, spectroscopic, and manipulation modes. Mostly used are constant current and constant height mode.

In the constant-current mode, the feedback loop controls the scanner moving up and down to maintain a constant tunneling current. A corrugation contour of the LDOS during scanning can be obtained in the constant-current mode.

The constant-height mode can provide much higher scanning rates than that of constant current. The constant-height mode can be obtained by turning off the feedbackloop control. This mode requires that the sample surface is well leveled without tilt.

Advantages

STM is helpful because it can give researchers a three dimensional profile of a surface, which allows researchers to examine a multitude of characteristics, including roughness, surface defects and determining things about the molecules such as size and conformation.

Other advantages of the scanning tunneling microscope include:

1.It has a high resolution in atomic level, which is considered to be 0.1 nm lateral resolution and 0.01 nm depth resolution.

2. 3D mapping image can be easily obtained.

3. It is capable of capturing much more details than lesser microscopes.

4. STM is also versatile. They can be used in ultra high vacuum, air, water and other liquids and gasses.

5. They will operate in temperatures as low as zero Kelvin up to a few hundred degrees Celsius.

Disadvantages

The four major downsides to using STMs are:

1. STM can be difficult to use effectively. There is a very specific technique that requires a lot of skill and precision.

2. STM require very stable and clean surfaces, excellent vibration control and sharp tips.

3. STM only can be used to scan not easily oxidized and well conductive samples.
4. STM use highly specialized equipment that is fragile and expensive.

Applications

Several surfaces have been studied with the STM. The arrangement of individual atoms on the metal surfaces of gold, platinum, nickel, and copper have all been accurately documented. The absorption and diffusion of different species such as oxygen and the epitaxial growth of gold on gold, silver on gold, and nickel on gold also have been examined in detail.