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MOSSBAUER SPECTROSCPY

Vijaya Durga* and Chandana and Padmalatha

Vijaya Institute of Pharmaceutical Sciences, Enikepadu.

*Corresponding Author: Vijaya Durga

Vijaya Institute of Pharmaceutical Sciences, Enikepadu.

ABSTRACT

Mossbauer spectrometry provides unique measurements of electronic, magnetic, and structural properties within materials. A Mossbauer spectrum is an intensity of γ-ray absorption versus energy for a specific resonant nucleus such as 57Fe or 119Sn. Mossbauer spectrometry looks at materials from the "inside out," where "inside" refers to the resonant nucleus. For one nucleus to emit a γ-ray and a second nucleus to absorb it with efficiency, both nuclei must be embedded in solids, a phenomenon known as the "Mossbauer effect." Mossbauer spectra give quantitative information on "hyperfine interactions," which are small energies from the interaction between the nucleus and its neighbouring electrons. The three important hyperfine interactions originate from the electron density at the nucleus (the isomer shift), the gradient of the electric field (the nuclear quadrupole splitting), and the unpaired electron density at the nucleus (the hyperfine magnetic field). Over the years, methods have been refined for using these three hyperfine interactions to determine valence and spin at the resonant atom. Even when the hyperfine interactions are not easily interpreted, they can often be used reliably as "fingerprints" to identify the different local chemical environments of the resonant atom, usually with a good estimate of their fractional abundances. Mossbauer spectrometry is useful for quantitative phase analyses or determinations of the concentrations of resonant element in different phases, even when the phases are nanostructured or amorphous.

KEYWORDS: Mossbauer spectroscopy, Mossbauer Effect, Mossbauer spectroscopy with synchrotron radiation, Nuclear forward scattering, Nuclear in-elastic scattering, Sample preparation.

INTRODUCTION

Mossbauer spectrometry is based on the quantum mechanical "Mossbauer effect," which provides a nonintuitive link between nuclear and solid-state physics. Mossbauer spectrometry measures the spectrum of energies at which specific nuclei absorb γ rays. Curiously, for one nucleus to experimenter can accept short radioisotope half-lives, cryogenic temperatures, and the preparation of radiation sources in hot cells.

Most applications of Mossbauer spectrometry in materials science utilize "hyperfine interactions," in which the electrons around a nucleus perturb the energies of nuclear states. Hyperfine interactions cause very small perturbations of 10–9 to 10–7 eV in the energies of Mossbauer γ rays. For comparison, the γ rays themselves have energies of 104 to 105 eV. Surprisingly, these small hyperfine perturbations of γ-ray energies can be measured easily, and with high accuracy, using a low-cost Mossbauer spectrometer.

Interpretations of Mossbauer spectra have few parallels with other methods of materials characterization. Perhaps NMR spectrometry is the best analogy, although the excitation energies are very different. A Mossbauer spectrum looks at a material from the "inside out," where "inside" means the Mossbauer nucleus. The method is often useful because nuclear energy levels are altered by hyperfine interactions between the nucleus and its nearby electrons. With some interpretation, these hyperfine interactions can reveal the local atomic structure or electronic structure around the resonant Mossbauer atom. The important hyperfine interactions originate with the electron density at the nucleus, the gradient of the electric field at the nucleus, or the unpaired electron spins at the nucleus. These three hyperfine interactions are called the "isomer shift" (IS), "electric quadrupole splitting" (EQS), and "hyperfine magnetic field" (HMF), respectively.

Over the past five decades there has been considerable effort to learn how the three hyperfine interactions respond to the environment around the nucleus. In general, it is found that Mossbauer spectrometry is best for identifying the electronic or magnetic structure at the Mossbauer atom itself, such as its valence, spin state, or magnetic moment. The Mossbauer effect is sensitive to the arrangements of surrounding atoms, however, because the local crystal structure alters the electronic or magnetic structure at the resonant nucleus. Different chemical and structural environments around the nucleus can often be assigned to specific hyperfine interactions.

In such cases, measuring the fractions of nuclei with different hyperfine interactions is equivalent to measuring the fractions of the various chemical and structural environments in a material. Phase fractions and solute distributions, for example, can be determined in this way. The viewpoint from the nucleus is sometimes too small to address problems in the microstructure of materials, however.

Other applications of the Mossbauer effect utilize its sensitivity to vibrations in solids, its timescale for scattering, or its coherence. To date these phenomena have seen little use outside the international community of a few hundred Mossbauer spectroscopists. Nevertheless, some new applications for them have recently become possible with the advent of synchrotron sources for Mossbauer spectrometry.

This unit is not a review of the Mossbauer spectrometry, but an instructional reference that gives the working materials scientist a basis for evaluating whether or not Mossbauer spectrometry may be useful for a research problem. There have been a number of books written about the Mossbauer effect and its spectroscopies (see Key References). Most include reviews of materials research. These reviews typically demonstrate applications of the measurable quantities in Mossbauer spectrometry, and provide copious references.

Recent research publications on Mossbauer spectrometry of materials have involved, in descending order in the numbers of papers: oxides, metals and alloys, organometallics, glasses, and minerals. For some problems, materials characterization by Mossbauer spectrometry is now "routine." A few representative applications to materials studies are presented. These applications were chosen in part by the taste of the author, who makes no claim to have reviewed the literature of approximately 50,000 publications utilizing the Mossbauer effect.

PRINCIPLES OF MOSSBAUER SPECTROSCOPY
- Just as gun recoils when bullet is fired, conversation of momentum requires a free nucleus to recoil during emission or absorption of gamma rays
- If nucleus at rest emit gamma ray, the energy of the gamma ray is slightly less than the natural energy of the transition, but in order for a nucleus at rest to absorb a gamma ray, the gamma ray's energy must be slightly greater than the natural energy, because in both cases energy is lost to recoil
- Means nuclear resonance is unobservable with free nuclei because shift in energy is too large to have significant overlap of emission and absorption spectra.

THEORY
THE MOSSBAUER EFFECT
The Mossbauer effect (the recoil-free emission and absorption of gamma rays from nuclear transitions) and

use Mossbauer spectroscopy to examine the properties of recoil-free radiation processes and investigate the effects of environmental factors on the energy levels of the nucleus

In quantum mechanics, the nucleus can be treated in much the same way as the atom. Although the details of nuclear binding differ considerably from the Coulomb binding of the atom, both the atom and the nucleus are multiparticle systems subject to the same sort of quantum mechanical analysis. In particular, just like the atom, the nucleus has quantized energy levels. Although the nucleus generally occupies the ground state energy level, it can be excited to higher levels and make transitions back to lower levels, absorbing or emitting photons in the process. While atomic (electronic) transitions have energies in the eV to keV range, nuclear gamma rays have energies on the order of keV to MeV. Reminder: photons that originate from atomic deexcitations are called x-rays, and those from nuclear deexcitations are γ-rays.
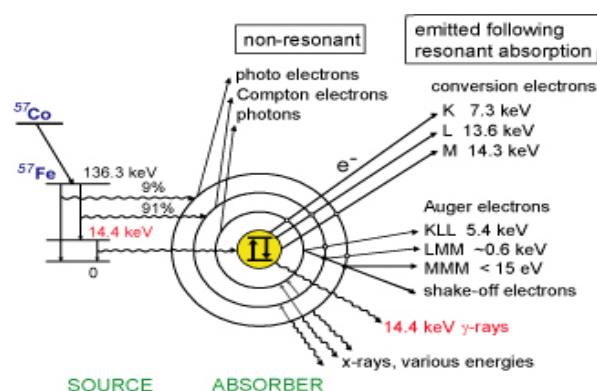

MOSSBAUER EFFECT ON ATOM
Transitions between nuclear states generally occur by radiation processes involving recoil. In recoil emission, conservation of momentum requires the nucleus to carry away momentum equal and opposite to that of the emitted gamma ray. The kinetic energy of the nucleus necessarily takes up some of the energy available from the transition. As a result, there is less energy left for the gamma, and its energy is lower than the energy released by the transition. Conversely, absorption with recoil requires a gamma ray of energy greater than the energy of the transition, as some of the energy is again taken up by the kinetic energy of the nucleus. The energy shifts of the gammas in emission and absorption are large compared to the width of the transition line (determined by the lifetime of the state according to the Heisenberg relation, $\Delta E \Delta t \geq \square \square$). You should calculate the value of the energy shift for some typical example(s). Because the overlap is minimal, a gamma emitted by a nucleus in a transition from state 2 to state 1 generally cannot excite the transition from state 1 to state 2 in another nucleus of the same element.

In 1957 Rudolf Mossbauer, a graduate student at the Max-Planck Institute in Heidelberg, discovered the

recoil-free emission and absorption of gamma rays from nuclear transitions, a discovery for which he was awarded the Nobel Prize three years later at the age of thirty-two. The essence of the Mossbauer effect is the absorption of recoil momentum by the entire lattice of the solid. Since the lattice is much more massive than the nucleus, its recoil kinetic energy is effectively zero. In this case the gamma ray carries away exactly the energy of the transition, and the emission and absorption lines overlap, centred about the transition energy. Suppose a nucleus emits a gamma ray (without recoil) of energy $E\gamma$ in making the transition from state 2 to state 1. The overlap between emission and absorption lines allows another nucleus to absorb that gamma ray in going from state 1 to state 2. Such resonant absorption is the key to Mossbauer spectroscopy. The probability of recoil free emission/absorption can be calculated using quantum mechanics.
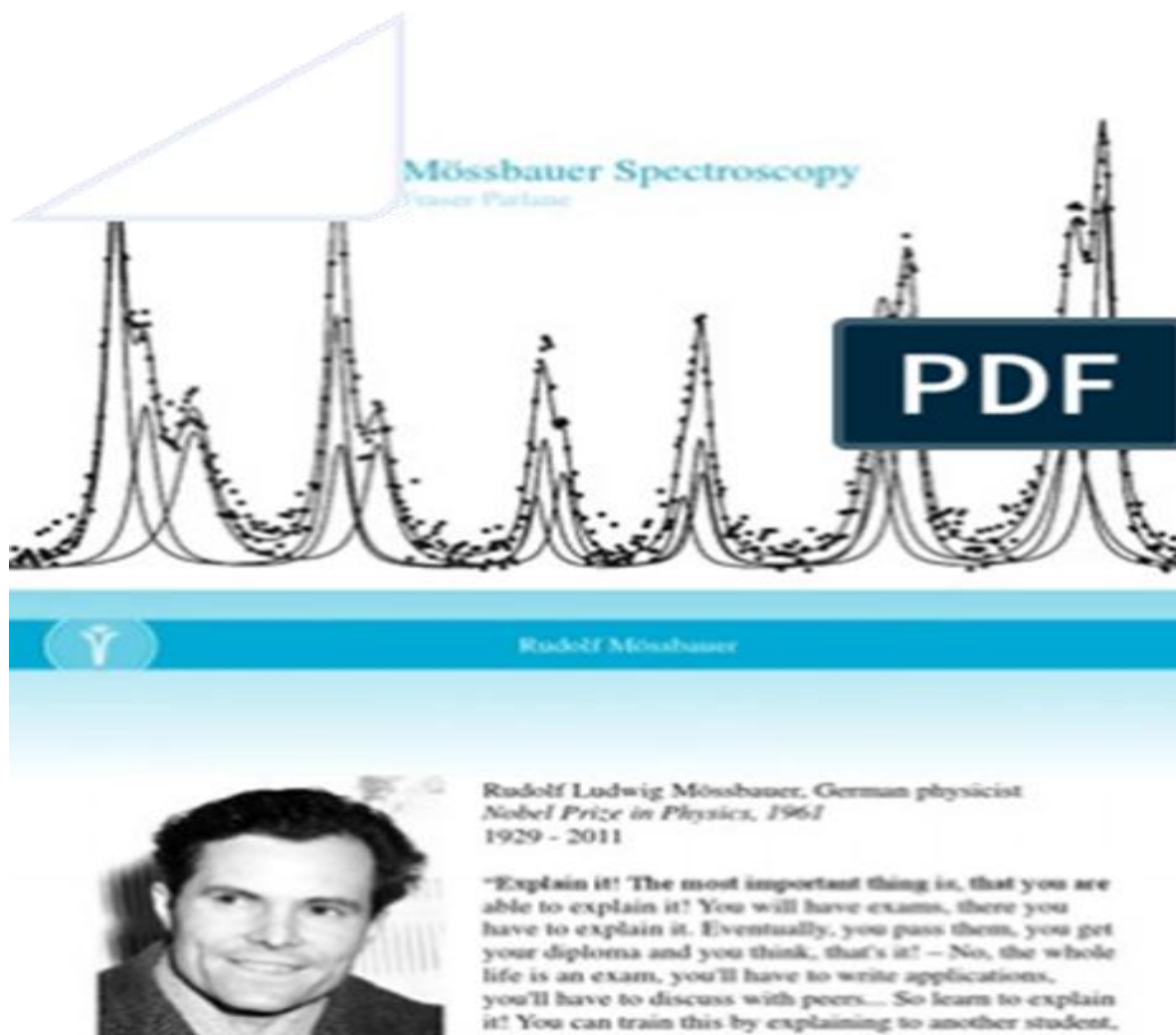

Given the possibility of recoil-free emission and absorption, one can use resonant absorption to examine energy profiles of nuclear transitions. The range of energies incident on an absorber can be precisely shifted by one part in 10 or so (energies on the order of μeV or neV) using the Doppler effect: radiation emitted by a source moving with velocity v has an energy shift $\Delta E = (v/c)E\gamma$, where $E\gamma$ is the unshifted gamma-ray energy. By varying the velocity, and thus the energy shift, it is possible to scan through a range of energies on the order of those for natural line widths of nuclear processes, for temperature shifts in the nuclear transition lines, and for hyperfine structure in the energy levels. The shifted gamma rays are absorbed in proportion to the overlap of the shifted emission line with the absorption line. Thus the relative absorption at different energy shifts reveals much information about the details of the nuclear energy levels. Even more importantly, for solid-state physics, it serves to test lattice vibrational models predicting the fraction of recoil-free processes, as well as to provide data on the environment of the nucleus in the lattice -- e.g., internal magnetic fields, Coulomb interactions with atomic electrons, and quadrupole interactions with field gradients, among many other.

The considering determines the depth and width of the Mossbauer effect absorption line. This is followedby brief discussions of the various phenomena affecting the absorption line 1. Isomer shift 2. Nuclear Zeeman effect 3. Quadrupole splitting due to hyperfine interactions 4. Temperature shift is a relativistic effect.
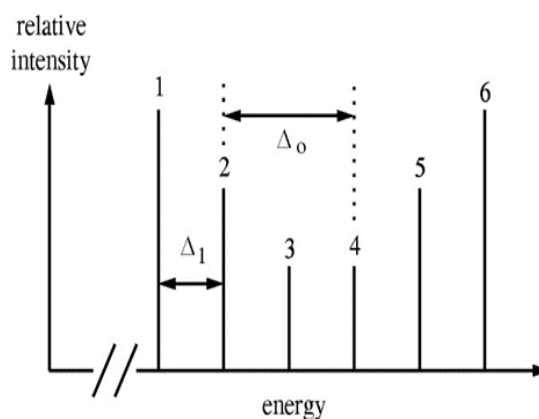
1. **Isomer shift (chemical shift)**

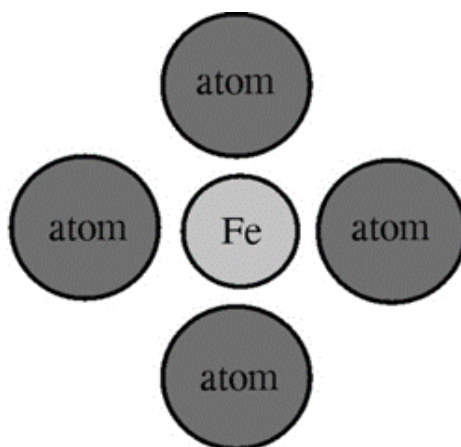origin of the chemical shift
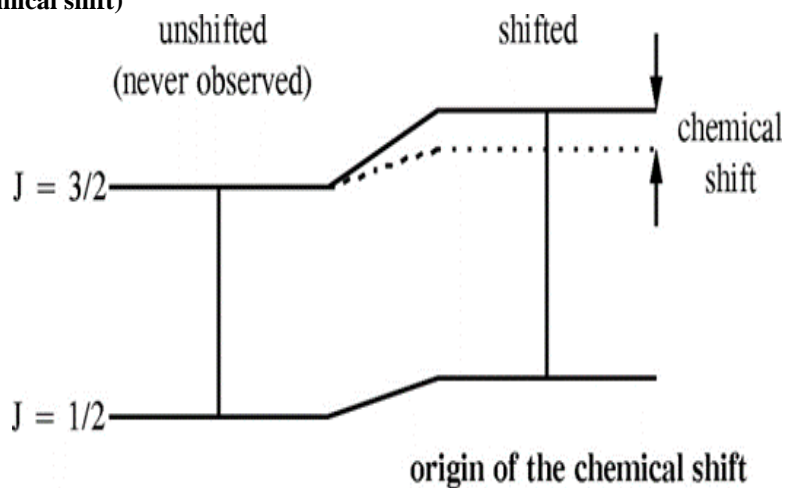
2. **Nuclear Zeeman effect**
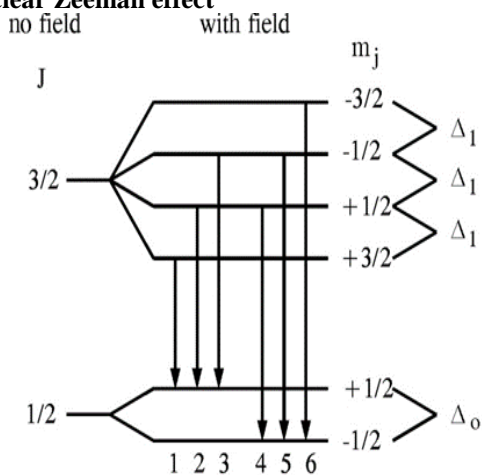
allowed transitions between Zeeman
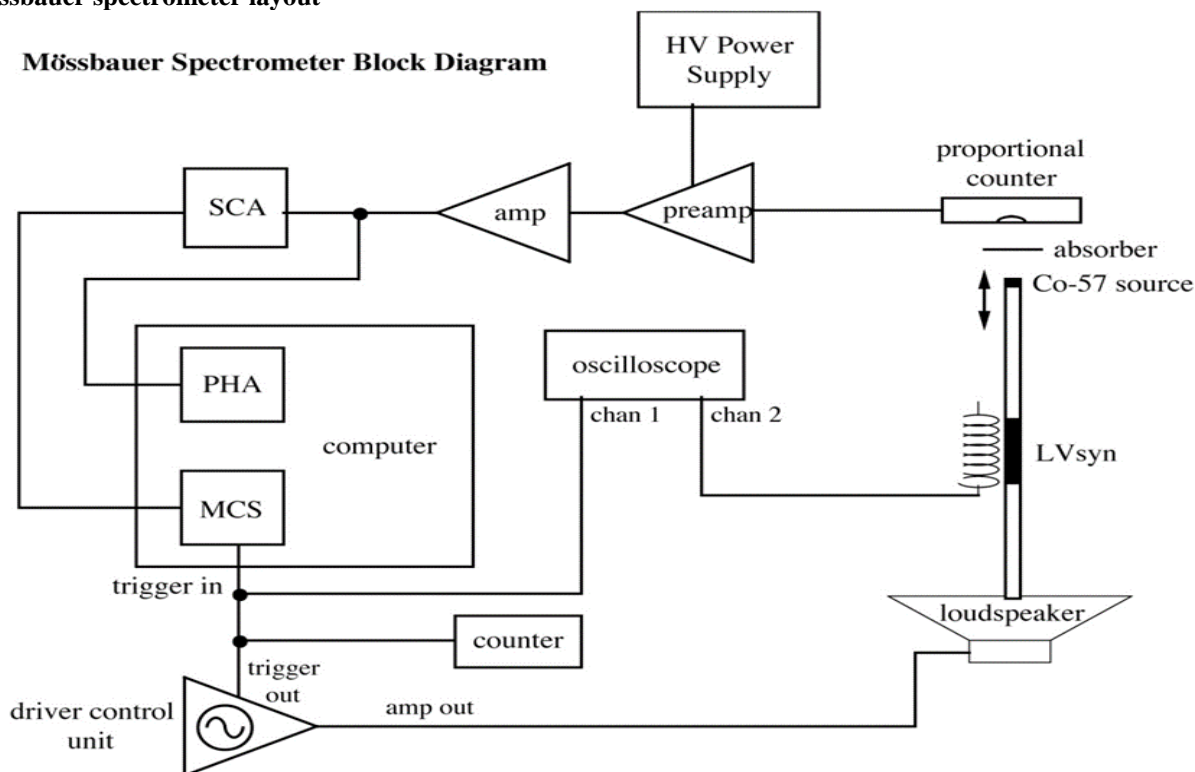split J=3/2 and J=1/2 levels

relative energies and intensities
for allowed transitions

3. **Quadrupole splitting**

possible condition for quadrupole splitting

Mossbauer spectrometer layout

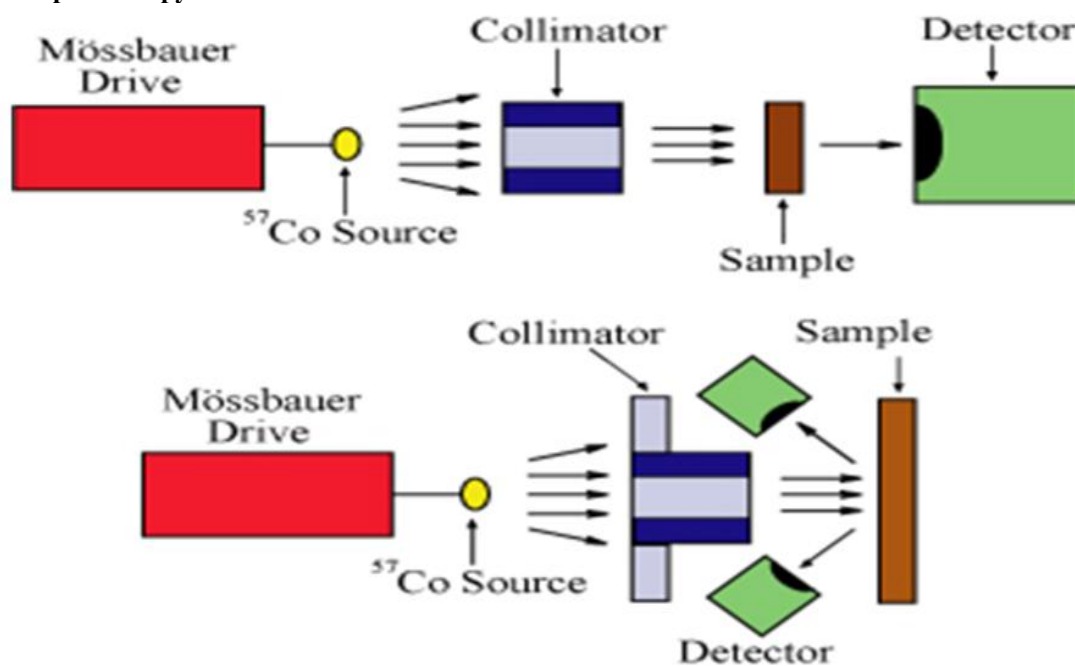Mössbauer Spectrometer Block Diagram

INSTRUMENTATION

The basic elements of a Mossbauer spectrometer are a source, sample, detector, and a drive to move the source or absorber. Most commonly, this is done by moving the source toward and away from the sample, while varying velocity linearly with time. For example, for 57Fe, moving the source at a velocity of 1 mm/ sec toward the sample increases the energy of the emitted photons by about ten natural linewidths. For simplicity, "mm/sec" is the conventional "energy" unit in Mossbauer spectroscopy. It is also possible to leave the source stationary and oscillate the sample, as is done with synchrotron Mossbauer. The location of the detector relative to the source and the sample defines the geometry of the experiment (Figure 5); most commonly, either transmission or backscatter modes are used.
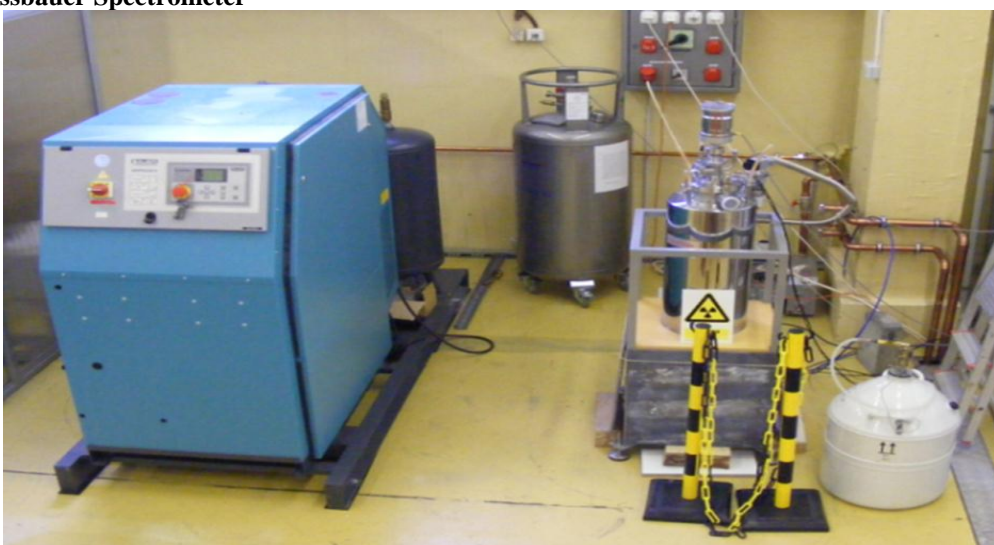
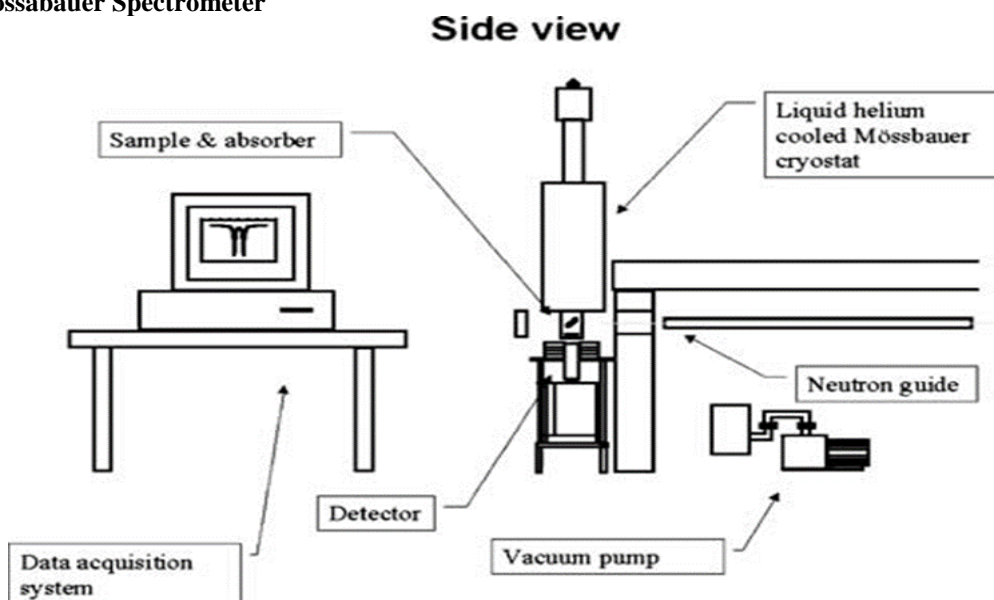**Mossbauer Spectroscopy Instrumentation**

INSTRUMENTATION IN MOSSBAUER SPECTROSCOPY
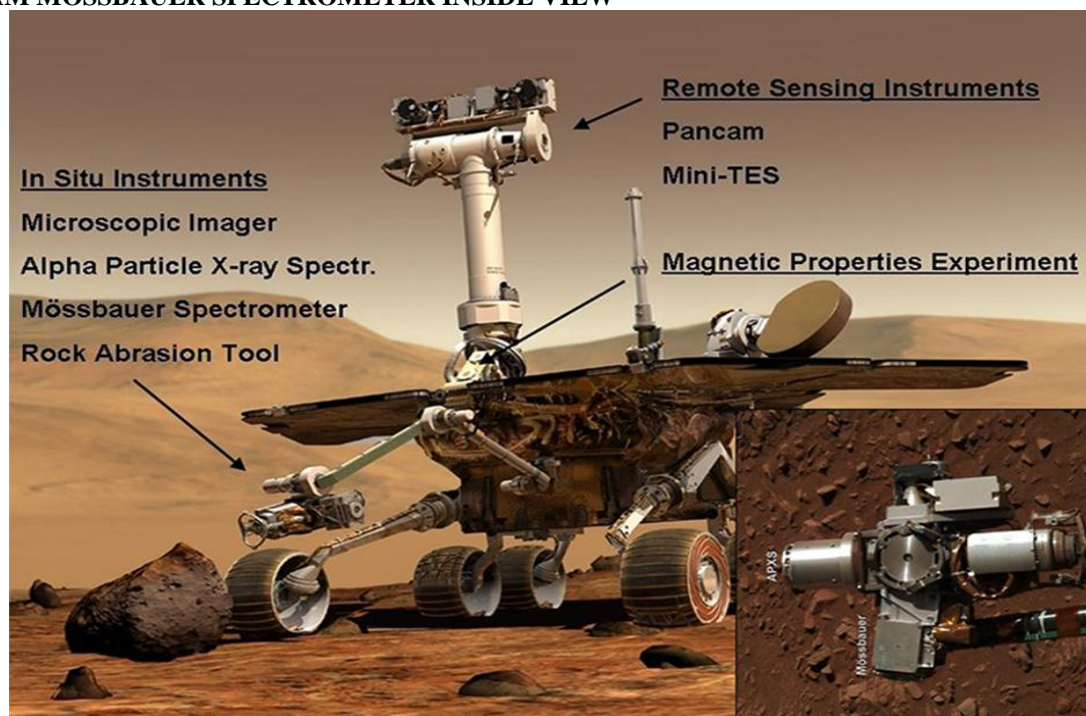**Modern Techniques of Mossbauer Spectroscopy**

Modern Mossbauer Spectrometer

In Beam Mossabauer Spectrometer

**IN BEAM MOSSBAUER SPECTROMETER INSIDE VIEW**

MOSSBAUER SPECTROMETR IN SOLID STATE REASEARCH INDISPENSIBLE Artist's impression of the Athena payload of the two NASA Mars Exploration Rovers, Spirit and Opportunity. Inset is an image of the instruments on the robotic arm obtained with Spirit's Pan camera on sol 287 of her mission: The Alpha Particle X-ray Spectrometer (pointing to the left), the Mossbauer spectrometer (down), the Rock Abrasion Tool (right) and the Microscopic Imager (up). A sol is a day on Mars, slightly longer than 24 h. The two Panoramic Camera -pan "eyes" on top of the mast are at a height of approximately 1.5 m. Images: NASA/JPL/Cornell

MOSSBAUER SPECTROSCOPY WITH A MINITRAUISED PORTAL SPECTROMETER
Efforts to miniaturise Mossbauer instrumentation, which were started by Egbert Kankeleit in Darmstadt and continued by Gostarklingelhofer in Mainz, were driven by the desire to utilise Mossbauer spectroscopy for the exploration of the planet Mars. Space mission constraints of limited mass, volume and power resulted in the miniaturised Mossbauer spectrometer MIMOS II. It is set up in backscattering geometry, originally to eliminate the need for a complicated sample preparation mechanism on a Mars lander. Without the need to prepare powders or thin slices of samples for measurements and, together with its easy portability, MIMOS II allows for true non-destructive in situ analyses. Below we give a few examples of the new applications which are now possible. The instrument is under continuous development. The latest version, MIMOS, has the additional capability of acquiring X-ray fluorescence spectra.
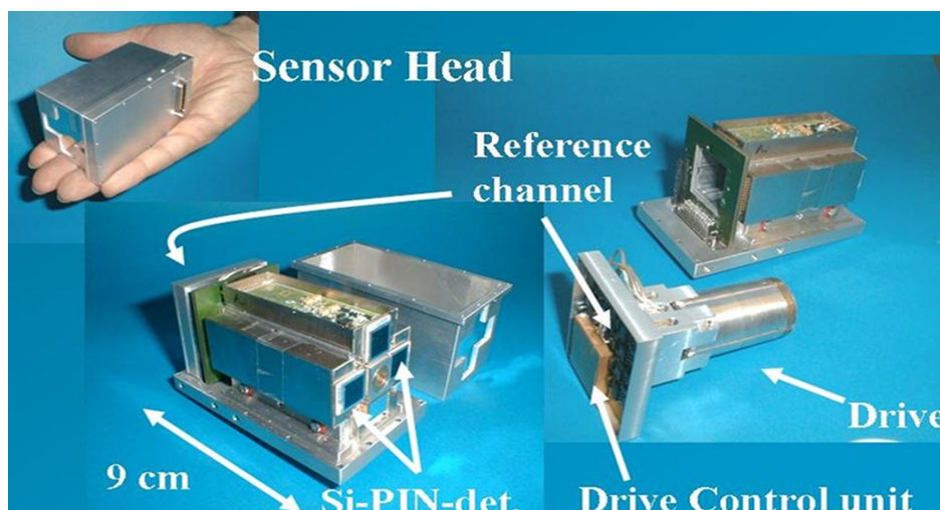
The sensorhead of the miniaturised Mossbauer spectrometer, MIMOS II, contains the drive unit, the Mossbauer source and the detectors and amplification electronics

Mossbauer spectroscopy with synchrotron radiation

Mossbauer spectroscopy with synchrotron radiation has an advantage over the conventional technique because the synchrotron beam can be conveniently focused. The high brilliance and the extremely collimated beam thus allow the measuring of samples with diameters of a few micrometres in less than one hour. Also, experiments on interfaces and surfaces with sub-monolayer coverage of Mossbauer-active Fe atoms are, nowadays, almost routine at third generation synchrotron sources such as ESRF (Grenoble, France), APS (Argonne National Laboratory, USA), SPRING-8 (Hyogu Prefecture, Japan) and PETRA III (DESY, Germany).

Nuclear forward scattering

Coherent nuclear resonant forward scattering (NFS) can be regarded as Mossbauer spectroscopy in the time domain. A pulse of monochromatised synchrotron radiation is used to excite the Fe nuclei in the sample. Due to the long lifetime (141 ns) of the 14.4 keV excited state the radiation is re-emitted with a delay which is sufficient to discriminate it from the promptly scattered quanta by time-gated detectors. The time dependence of the coherently forward scattered radiation is determined by the hyperfine parameters (isomer shift, electric field gradient and hyperfine field) and the dynamics of the iron. NFS allows the direct determination of these parameters including the Lamb–Mossbauer factor.
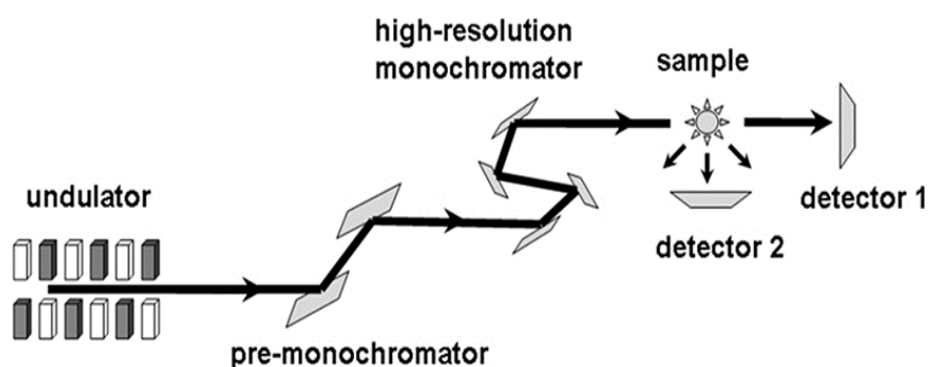

Set-up for Nuclear Forward Scattering (NFS) and Nuclear Inelastic Scattering (NIS). For NFS coherent scattering is detected by detector and for NIS incoherent scattering is detected by detector.

Nuclear inelastic scattering

Nuclear inelastic scattering (NIS) of synchrotron radiation can be regarded as an extension of the site conventional, energy-resolved Mossbauer spectroscopy to energies of phonons or molecular vibrations. Therefore, this technique is also called nuclear resonance vibrational spectroscopy (NRVS). In contrast to a NFS-experiment, the energy of the incoming radiation $E\gamma$ is varied within an interval of up to ± 100 meV around the resonance energy, E = 14.4 keV, of the Mossbauer nucleus (see Figure 16 for a typical spectrum). In a NIS experiment, the absorption probability is measured as a function of the energy difference $E - E\gamma$. An advantage of the NIS technique, when compared to other vibrational spectroscopies, is that it is a site-selective method, which solely detects the dynamics of the active iron: the intensity of individual peaks in a spectrum is roughly proportional to the mean-square displacement of the Mossbauer nucleus arising from the corresponding molecular vibration. Different from infrared or Raman spectroscopy, NIS spectra depend solely on mechanical properties, i.e. the eigenfrequencies and eigenvectors of the vibrations, but not on electrical properties such as the polarising ability of the molecule.[37] For this reason, NIS can be calculated by theoretical methods with good reliability.
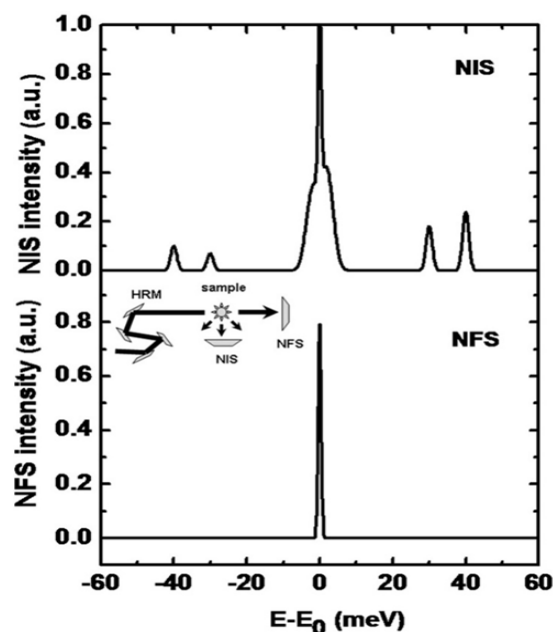
A sketch of a typical NIS spectrum. A high-resolution monochromator (HRM, see inset) is tuned around the nuclear resonance. The scattered intensity in forward direction (NFS) and perpendicular to the incoming beam (NIS) is monitored as a function of energy relative to $E\gamma$

(14.4 keV in case of 57Fe). Around $E = E\gamma$, the elastic peak is overlaying the corresponding energy sidebands which are caused by phonon creation ($E > E\gamma$) and phonon annihilation ($E < E\gamma$).

The spectrum shows the intensity of the forward scattered radiation which is called the instrumental function

DATA ANALYSIS AND INITIAL INTERPRETATION

Mossbauer spectra are often presented for publication with little or no processing. An obvious correction that can be applied to most transmission spectra is a correction for thickness distortion (see Sample Preparation).

This correction is rarely performed, however, in large part because the thickness of the specimen is usually not known or the thickness is not uniform. The specimen is typically prepared to be thin, or at least this is assumed, and the spectrum is assumed to be representative of the Mossbauer absorption cross-section.

A typical goal of data analysis is to find individual hyperfine parameters, or more typically a distribution of hyperfine parameters, that characterize a measured spectrum.

SAMPLE PREPARATION

A central concern for transmission Mossbauer spectrometry is the choice and control of specimen thickness. The natural thickness of a specimen is t is, t = (fa na σa)–1 owing to the hyperfine magnetic field in bcc Fe. The strongest of these comprises 1/4 of the total absorption. that was acquired with a sample of natural bcc Fe 25 μm in thickness. The linewidths of the inner two peaks are 0.235 mm/s whereas the outer two are 0.291 mm/s. Although the outer two peaks are broadened by thickness distortion, effects of impurity atoms in the Fe were also important. The widths of the inner two lines are probably a better of the spectrometer resolution.

ADVANTAGES
- Bulk and surface analysis and high resolution
- Particle size (volume) measurement and low maintenance
- Microscopic magnetic measurements and ion sensitive
- In-situ measurement and non-destructive
- Fingerprint technique

DISADVANTAGES
- Long data acquisition time
- Difficult analysis
- Vibration sensitive
- Cryogenic requirements
- Limited isotopes

APPLICATIONS
1. Quadrupole splitting (along with the hyperfine field, in the case of magnetic phases) is used to identify the valence state and site occupancy of Fe in a given site and individual mineral.
2. If the phase is magnetically ordered, additional information in the form of a value for As an analytical tool Mossbauer spectroscopy has been especially useful in the field of geology for identifying the composition of iron-containing specimens including meteors and moon rocks.
3. In situ data collection of Mossbauer spectra has also been carried out on iron rich rocks on Mars.
4. In another application, Mossbauer spectroscopy is used to characterize phase transformations in iron catalysts, e.g., those used for Fischer-Tropsch synthesis. While initially consisting of hematite (Fe_2O_3), these catalysts transform into a mixture of magnetite (Fe_3O_4) and several iron carbides.
5. The formation of carbides appears to improve catalytic activity, however it can also lead to the mechanical break-up and attrition of the catalyst particles, which can cause difficulties in the final separation of catalyst from reaction products.
6. Mossbauer spectroscopy has also been used to determine the relative concentration change in the oxidation state of antimony (Sb)during the selective oxidation of olefins.
7. During calcination all the Sb ions in an antimony-containing tin dioxide catalyst transform into the +5 oxidation state. Following the catalytic reaction, almost all Sb ions revert from the +5 to the +3 oxidation state.
8. A significant change in the chemical environment surrounding the antimony nucleus occurs during the oxidation state change which can easily be monitored as an isomer shift in the Mossbauer spectrum.
9. The combination of isomer shift the magnetic field can help with identification of some phases.
10. In some cases, Mossbauer spectrometers are also used to identify minerals. This application is limited, however, by the fact that many different minerals can have site geometries that are the same, such that their Mossbauer spectra and the resultant peak parameters will also be the same.
11. For example, the spectra of amphibole and pyroxene group minerals are all very similar, so you could not tell these minerals apart by their Mossbauer spectra alone.
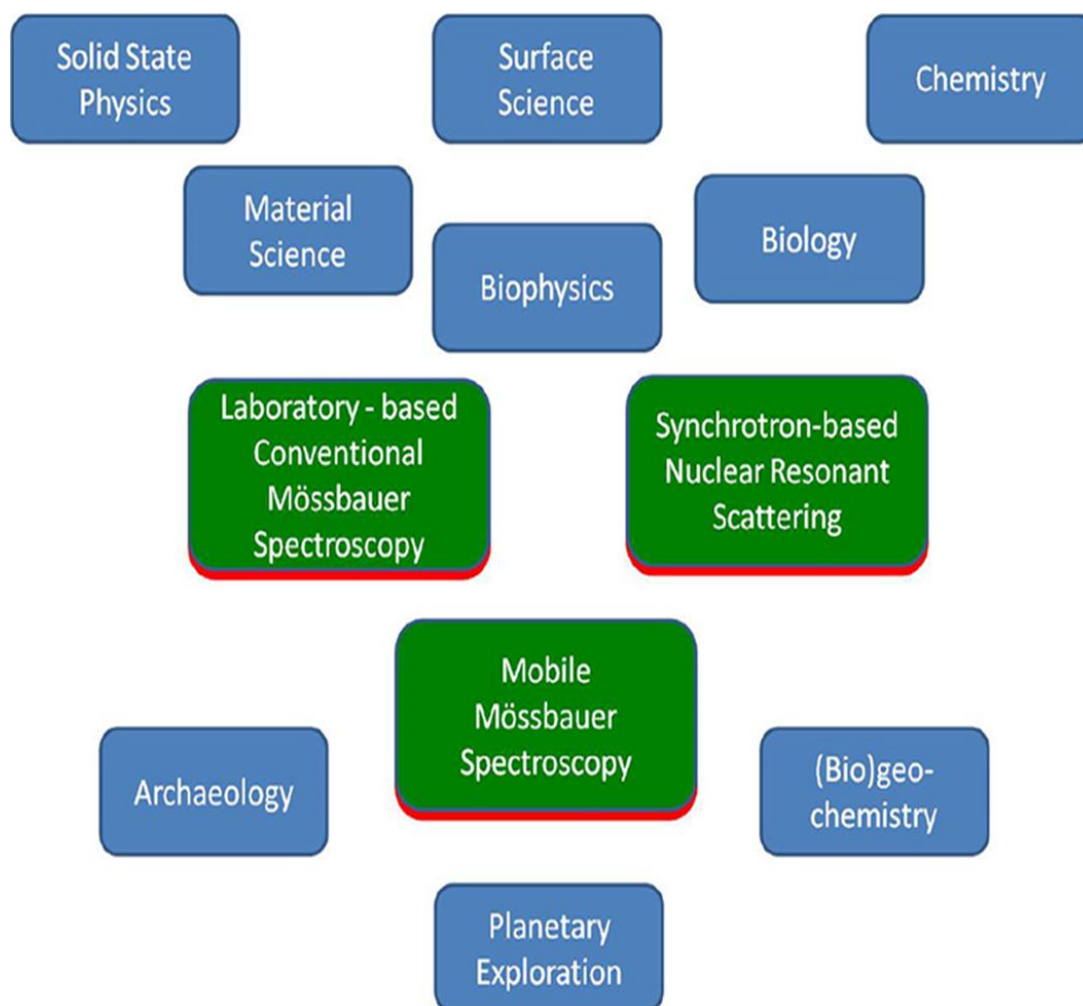
DIFFERENT STATES OF MOSSBAUER SPECTROSCPY

CONCLUSION

Mossbauer spectroscopy can contribute significantly to industrially related investigations and research. The major hurdle that needs to be overcome is the lack of communication between the Mossbauer community and the various industrial administrations and development committees. Industrial leaders and other personnel involved with research and development at the commercial level, need to be informed of the important contributions that Mossbauer spectroscopy can make to their productivity, monitoring and quality control. For the Mossbauer spectroscopist, case studies such as the example listed above for galvanneal, may help provide support to demonstrate the ability of the technique to be an important and perhaps necessary addition to the analytical facilities of many different industries.

ACKNOWLEDGEMENT

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