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Mössbauer Spectroscopy

Mössbauer spectroscopy is concerned with absorption in the high-energy portion of the spectrum, the γ-ray region. The energy is higher than that encountered in atomic spectroscopic techniques because the source of electromagnetic radiation is an excited nucleus. This relatively recent and simple absorption spectroscopy is named after R. L. Mössbauer, who, in 1958, reported an enhanced resonance absorption of *γ* rays at low temperature. An acoustic analogue of this resonance phenomenon is the transference of energy via sound waves in air from one tuning fork to another. If the tuning forks have the same vibrating frequency, or pitch, one vibrating tuning fork can induce sympathetic vibrations in another nearby. Similarly, in Mössbauer spectroscopy, an excited nucleus can excite a nearby nucleus in its ground state, by transferring energy via a quantum of high-energy light, a *γ*-ray photon. However, the recoiling nucleus lowers the energy of the photon during emission, which can easily suppress subsequent resonance absorption. Mössbauer discovered that recoilless emissions occur at low temperatures as the entire solid absorbs the recoiling momentum rather than the emitting nucleus, thereby resulting in a recoil energy approaching zero for the nucleus.

The ratio of the width of the emission energy line (related to the Heisenberg uncertainty principle) to the energy of the line determines resolution. Resolutions of the order of 10^{-12} are obtained easily and energy changes of 10^{-14} to 10^{-16} can be measured. Therefore, it is possible to observe extremely small changes within a given material. Only recently has the potential of

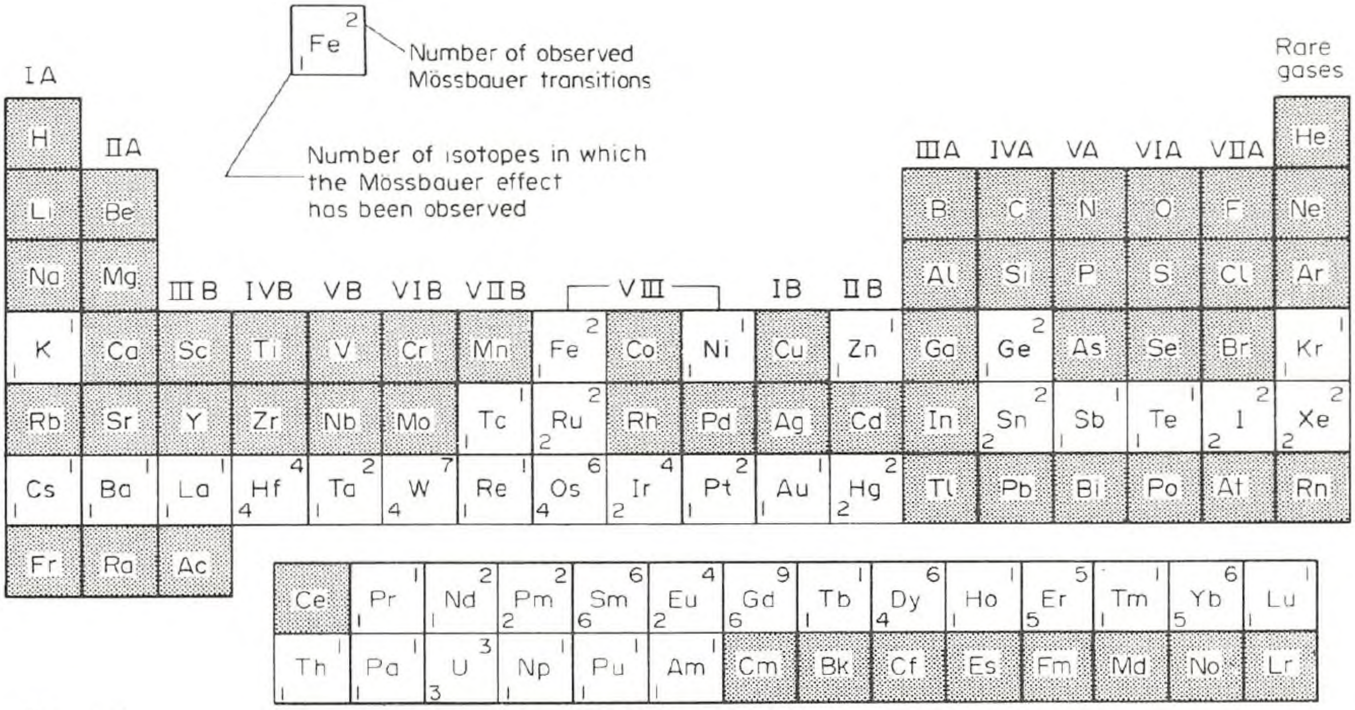

Figure 1
Mössbauer effect periodic table

Mössbauer spectroscopy, for providing insights into the understanding of materials and answers to questions encountered in industrial processes, been realized. The technique is very selective and only one isotope is studied at a time, the most common being ^{57}Fe , followed by ^{119}Sn. Although there are over 80 isotopes (representative of more than 40 elements) in which the Mössbauer effect has been observed (Fig. 1), ^{57}Fe and ^{119}Sn constitute the vast majority of current studies due to the relative ease in obtaining Mössbauer spectra for them.

1. Experimental Arrangement

For any kind of spectroscopic technique, it is necessary to have a source, a sample, a detector for the radiation, a method of varying the energy of the radiation, and the necessary electronics for recording the data. Most unique to Mössbauer spectroscopy is the method employed to vary the energy of the radiation. Small changes in energy are controlled by Doppler shifting the extremely monoenergetic γ rays. This is achieved by moving either the source or the absorber (sample) relative to the other. This results in a γ-ray energy shift of $(v/c)E\gamma$, where $E\gamma$ is the unperturbed γ-ray energy, v is the relative velocity between the source and sample, and c is the speed of light. The relative velocity is typically a few millimeters per second and Mössbauer spectra are reported expressing the energy axis in these units (Fig. 2).

Several commercial Mössbauer spectrometers are currently available, and almost all are electromechanical drive units which can scan a range of velocities during a very short period of time. The accumulated data from a large number of scans results in a Mössbauer spectrum.

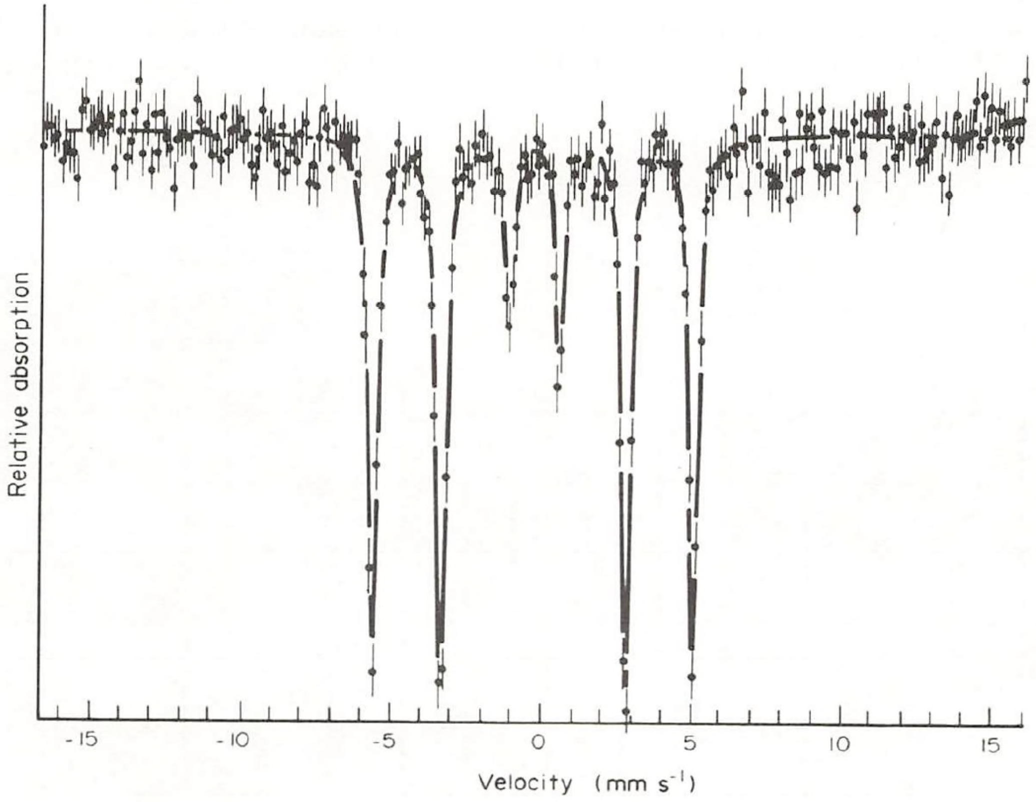

Figure 2
Six-line Mössbauer spectrum for α-Fe at room temperature

There are two other experimental arrangements for Mössbauer spectroscopy besides the usual absorption arrangement. The sample material under investigation can be used as the source of radiation with the absorber serving as the reference material, or resonantly scattered γ rays, characteristic x rays or even conversion electrons can be counted. Conversion-electron Mössbauer spectroscopy has a number of important industrial applications.

In the usual absorption arrangement, a radioactive source is chosen that decays to the excited level of the isotope in the sample material for which a Mössbauer spectrum is desired. For a sample of ^{57}Fe, ^{57}Co is chosen as the source since it decays by electron capture to an excited level of ^{57}Fe. This decay is illustrated in Fig. 3. If the ^{57}Fe sample is replaced with any other isotope, the sample will be transparent to γ resonance absorption. This characteristic allows for the study of very specific elements within a material, and consequently a large range of applications.

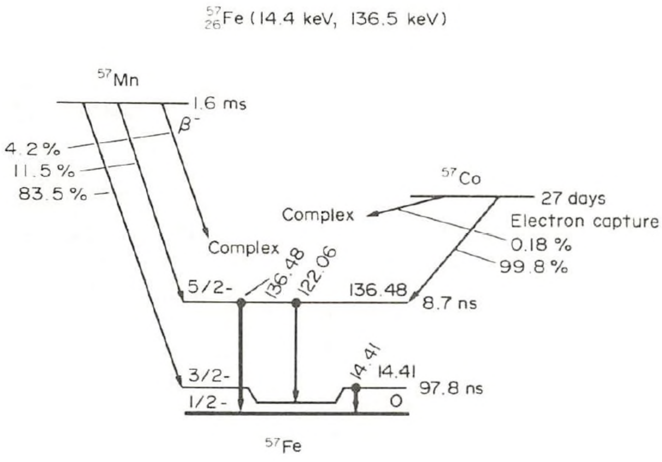

Figure 3
Simplified decay diagram for ^{57}Fe. Here, 5/2-, 3/2- and 1/2- are the nuclear spin quantum numbers and their parities for a particular energy level

Solids must be studied in Mössbauer spectroscopy so that the bulk material can absorb the recoil energy as a result of γ emission or absorption. For a large number of isotopes, the recoil energy is too large for solid samples at room temperatures. Therefore, in many instances, the sample must be cooled to liquid-nitrogen or liquid-helium temperatures in order to make the material stiff enough to minimize the effect of recoil at the nuclear emitting site.

Samples are usually ground into fine powders, although there are many examples of studies with single crystals or some other form of bulk material. For normal absorption spectroscopy, 50 mg of sample material is usually required.

Detection devices employed are the same as those used for detecting x rays. The γ rays of Mössbauer spectroscopy are of low energy. Higher-energy γ rays result in recoil energies that are too high to allow resonance absorption to occur. Two of the most common detectors are proportional counters and scintillation counters. The digital data is handled by computers which provide for the necessary data analysis. Electronic devices associated with the Mössbauer spectrometer are: preamps and amplifiers for the detectors, a single-channel analyzer, a multichannel analyzer, and data output devices. The data output device may be a plotter or a direct input into a computer. The main instrument is the multichannel analyzer, which controls the operation of the spectrometer and its data collection.

Accessory equipment is available for extending the capability of a normal spectrometer. ^{3}He-^{4}He dilution refrigerators can be used to study materials down to mK temperatures. It is also possible to reach temperatures higher than 1000 K. Electromagnets assist in the investigation of magnetic materials. Magnets are available that can supply large magnetic fields parallel or perpendicular to the source-absorber direction. Large magnets using superconducting solenoids resulting in fields as high as 10 T are being routinely used in a number of laboratories. The orientation of these fields is important for gathering data which can provide much information about the internal structure of the sample.

2. Physical Principles

Most of the valuable information gathered in Mössbauer spectroscopy is due to interactions between the nucleus and its electronic environment, called hyperfine interactions. Measurements of these hyperfine interactions give direct insight into the properties of the electronic environments of various materials, since the nuclear properties of the sample isotope are constants in Mössbauer spectroscopy. This supplies information about a variety of processes, such as corrosion at the surface of the material or various stages of catalytic transformations. The three principal interactions are the electrostatic monopole interaction, the magnetic dipole interaction and the electric quadrupole interaction. The three respective experimental parameters associated with these hyperfine interactions are the isomer shift δ, the magnetic hyperfine field H and the quadrupole splitting Δ.

The isomer shift is proportional to the electron density of the *s* electrons at the nucleus of the isotope. Experimentally, it is observed as the shift of a single peak or the center of several peaks from a standard reference point. The isomer shift is sensitive to the oxidation state of the atom, to the number of ligands bonded to the atom, to the type of ligand bonding to the atom, and to the electronegativity of the ligands that are attached. The isomer shift can often identify a particular chemical species or indicate that there is more than one environmental site for the atom under investigation.

The magnetic hyperfine interaction (see *Nuclear Magnetic Resonance Spectroscopy*) is observed as a multiple number of peaks in a Mössbauer spectrum. In the case of the common isotopes ^{57}Fe and ^{119}Sn, six lines appear (Fig. 2). Magnetic hyperfine data indicate the nature of the magnetic field at the nucleus of an atom in the sample material. Large magnetic fields are observed in the spectra as large splittings between the peaks (for α-Fe, the field strength is 33 T). However, it should be emphasized that these measured properties are local properties of the material at the atomic sites rather than bulk properties. Complex magnetic hyperfine interactions result in unresolved spectra. This not only occurs in magnetic ordered compounds (ferromagnetic, antiferromagnetic, ferrimagnetic), but also in paramagnets if the paramagnetic relaxation frequency is small compared with the Larmor frequency. For example, a number of simple iron oxides such as Fe_2O_3 and Fe_3O_4 will give six-line spectra.

Quadrupole-type interaction spectra are much simpler than magnetic hyperfine spectra. In the cases with ^{57}Fe and ^{119}Sn, two peaks are observed. The separation between the two peaks is called the quadrupole splitting parameter. This energy splitting is proportional to the electric field gradient at the nuclear site. It represents a measure of the deviation of the electron density from spherical symmetry. Consequently, the quadrupole splitting provides information about the electronic structure surrounding the isotope. Often, its value can be used to distinguish the chemical state. In particular, high-spin Fe^{3+} and low-spin Fe^{2+} have small values of quadrupole splitting, which are temperature independent, whereas high-spin Fe^{2+} compounds have much larger temperature-dependent quadrupole splittings.

Often, all three of the hyperfine parameters are used to determine the chemical state of a particular atom in a material. The isomer shift is present and measurable in all Mössbauer spectra; however, the quadrupole splitting and the magnetic hyperfine interaction may or may not be present. All three parameters are usually temperature dependent, which provides information about a sample material as a function of temperature.

Two experimental parameters easily observed in a Mössbauer spectrum are linewidth and line intensity. Since the spectral lines are usually not broadened much by experimental control factors, they are close to their theoretical values predicted by the Heisenberg uncertainty principle. Consequently, broadening of lines provides additional information about the sample material. Line intensity not only provides information related to isotope concentration, but also provides clues to the strength of the bonding of the isotope to its environment.

3. *Applications*

Mössbauer spectroscopy is of great use to scientists in many different fields because of the information that it is possible to obtain by measuring the hyperfine interactions. Biologists use Mössbauer spectroscopy to study a particular biological process in detail. Geologists use it to assist in identifying a particular mineral, and, in some cases, something about its history. Physicists use Mössbauer spectroscopy to test theories of relativity.

Mössbauer spectroscopy has several advantages over other experimental techniques for investigating catalysts. The main advantage is that catalysts can be examined as the reaction proceeds. Another advantage is the ability to study the bulk of the catalyst in addition to studying surface properties. Numerous catalyst systems have been studied, including alloy catalysts, ammonia catalysts, partial-oxidation catalysts, Fischer-Tropsch catalysts and electroless electrocatalysts. Many studies of catalysts are difficult using other techniques, because of the presence of small particles, but with Mössbauer spectroscopy this is not a problem. In fact, it is possible to determine an average particle size by the line shape of the resulting Mössbauer spectrum. It is not always necessary that a catalyst has as one of its major constituents the Mössbauer atom. It is possible to perform studies in which the Mössbauer atom is introduced in to the catalyst as a probe. Although most of the studies have been on heterogeneous catalysts, more studies on homogeneous catalysts will, no doubt, be reported in the future. The ability to measure the Mössbauer parameters and the catalytic behavior simultaneously makes the use of Mössbauer spectroscopy extremely valuable in these studies.

The understanding of the corrosion process has been aided by the use of conversion-electron Mössbauer spectroscopy. The oxidation process has been studied under a variety of conditions, varying temperature, environment and coatings. It is possible not only to identify various phases that are formed during the corrosion process as a function of time, but also by a depth-selection method to follow the corrosion process at various layers on the surface. These experiments are often tedious, but the data that can be obtained are quite valuable. Of special importance is the possibility of obtaining kinetic parameters for the oxidation process from a measurement of the total oxide thickness. If the corrosion layer becomes too thick for study by conversion-electron Mössbauer spectroscopy, then either the backscattered x rays or the resonance-scattered Mössbauer γ rays can be detected, and then a spectrum obtained. In most corrosion processes, the spectra are very complex, due to the number of iron sites and iron phases that are being formed during the process. A wide variety of environmental situations has been investigated. Such studies include all kinds of aqueous solutions in which the pH varies, the solution contains dissolved salts, the temperature of the aqueous solution varies or special additives are present. Mössbauer spectroscopy then allows a careful examination of the formation of any phases on the surface created by the oxidation process. Because of the wide variety of oxides and the variety of particle sizes that can be formed, it is often necessary to obtain Mössbauer spectra at various temperatures to assist in identification of the phases that are formed. The effect of surface treatments of steels can be studied by examining these materials before the treatment, after the treatment, and some time after the exposure to the corrosive environment. It is obvious that there are a number of very practical corrosion-type problems that can be studied effectively using Mössbauer spectroscopy.

Amorphous materials can be investigated by Mössbauer spectroscopy. Since these materials lack long-range ordering, it is not possible to use a number of other standard instrumental techniques. The advantage of Mössbauer spectroscopy here is that it is only concerned with the local environment around the Mössbauer isotope. There are four areas in which Mössbauer spectroscopy can provide valuable information: electronic processes, structure and bonding, phase transitions and magnetism. Although most of the information that is available on the electronic processes for Mössbauer spectroscopy is minimal, it is possible to obtain valuable information on the various kinds of charge-transfer processes, such as Fe^{2+}–Fe^{3+}, which are known to occur in some oxide glasses. The quadrupole-coupling and isomer-shift data should be able to give information on the bonding and the configuration surrounding the Mössbauer isotope. It is difficult to identify the precise bonding and structure: this is not possible in general with Mössbauer spectroscopy, and certainly not possible in the cases of its applications to amorphous substances. Using the intensity of the Mössbauer absorption, it is possible to determine glass transitions. Also, by measuring any one of the Mössbauer parameters as a function of temperature, it is quite easy to observe phase transitions. Certainly, the most interesting and fruitful application of Mössbauer spectroscopy to amorphous solids is the study of their magnetic properties. Often, it is possible to determine the distribution of magnetic fields which exist in such materials. As has been mentioned previously in the studies of other materials, a Mössbauer isotope probe can also often provide valuable information. Since the number of experimental techniques available for studying these amorphous substances is limited, Mössbauer spectroscopy is proving to be quite valuable in obtaining the necessary information to understand the properties associated with these materials.

Another application of Mössbauer spectroscopy is its use to characterize coal. Because of the presence of iron in a large percentage of the minerals that are dissolved in coal, Mössbauer spectroscopy is very effective in identifying substances. Besides the capability of identifying most of the minerals that are present in coal, with careful procedures it can also be used to obtain quantitative information. This is especially important, since many of these iron-bearing materials contain sulfur. Some of the consequences of these dissolved minerals are atmospheric pollution due to the sulfur, and the resulting ash and slag from combustion. Mössbauer studies of coke can investigate how the iron-bearing minerals transform during carbonization and, likewise, Mössbauer spectra can be used to obtain quantitative information on the amount of sulfur that is in the coke and the form of the iron sulfides. In this way the ash, which is a result of coal combustion, can be characterized. The disposal or potential use of this ash is a major problem. Understanding more about its phase makeup using Mössbauer spectroscopy can assist in solving this problem. Other processes can be studied that are related to coal, such as the weathering that the coal undergoes upon atmospheric exposure.

The major limitation of Mössbauer spectroscopy is the number of elements which will give Mössbauer spectra. Although there are over 40 elements in which spectra have been obtained, only about 15 of these are relatively easily obtained and provide the useful information that makes the technique worthwhile. It is unfortunate that among these 15 some of the more common low-atomic-weight elements, such as carbon, oxygen, nitrogen, sulfur or hydrogen, are not included. On the other hand, for those elements for which the effect is observable, unique information about materials can be obtained. Processes can be investigated in careful detail, and the structure and bonding at the electronic level can be studied.

See also: Investigation and Characterization of Materials: An Overview; Mössbauer Techniques in Nondestructive Evaluation

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