

Fine Detail: Three Decades of Mössbauer Spectroscopy

In 1957 a postgraduate working at the Max-Planck Institute was the first to observe a gamma-ray resonance effect in iridium. In 1961 that postgraduate, Rudolf Ludwig Mössbauer, received the Nobel Prize in physics for discovering this "recoil-free gamma-ray resonance absorption effect." In his own Nobel laureate address, Mössbauer said that he thought the discovery "makes possible new advances in the exciting world of unknown phenomena and effects."

In the three decades since the publication of Mössbauer's first paper describing his experiments and theory, Mössbauer spectroscopy has been used in gamma-absorption measurements to extremely high precision (up to one part in 1,015). Over 10,000 technical papers have been written on various aspects of the resonance phenomenon. Applications of the effect are diverse, from studies of Einstein's relativity theory, to solid-state physics, biology, chemistry, nuclear physics, metallurgy... even archaeology and the analysis and authentication of classic paintings.

Rudolf Ludwig Mössbauer was born January 31, 1929; he grew up and was educated in Munich, spent a year in industrial laboratories, then attended the Munich Technical University. He received an intermediate degree in 1952 and completed his thesis in 1954. He went to do postgraduate research at the Max-Planck Institute for Medical Research in Heidelberg, West Germany from 1955-1957, then received his PhD from the Munich Technical University in 1958.

Mössbauer's doctoral thesis described his experiments on the recoil-free emission of gamma rays. Five years previously he had begun to study gamma-ray absorption in matter, particularly nuclear resonance absorption.

Rayleigh had predicted optical resonance in the 19th century, and Wood actually discovered it with a sodium flame in 1904. As early as 1929 (the year Mössbauer was born!) other researchers

were attempting unsuccessfully to achieve gamma-ray fluorescence.

In 1946, Ya.I. Barit and M.I. Podgoret'skii pointed out that it was energy loss from the recoil of the emitting nucleus that destroyed the expected gamma resonance. Other researchers attempted to compensate for the recoil energy loss by thermal or kinetic means—in one instance by heating ^{198}Hg to 1100°C , in another by rapidly rotating the source in the direction of the target (trying to blueshift the emitted gamma rays back up to the resonance energy). These experiments were unsuccessful, though. They suffered from thermal Doppler broadening to an extent that ruined the high resolution they hoped to achieve. The experiments were difficult, and interest did not spread much beyond a few nuclear spectroscopy laboratories.

In 1957, while studying the 129 keV gamma ray from ^{191}Ir , Rudolf Mössbauer discovered that when he cooled his source from 300 K down to 88 K, the resonance absorption increased dramatically. He speculated that at a low enough temperature the atoms in a crystal effectively "freeze" into place, thus damping the recoil in the entire crystal lattice.

Firing a pistol provides a good analogy: If you hold the pistol loosely and pull the trigger, the pistol will recoil significantly—as a nucleus recoils when it "fires" a gamma ray. But if you anchor the pistol onto a concrete pier—or freeze the atoms in a crystalline lattice—the pistol/nucleus is unable to recoil. This has a negligible effect on the energy of the emitted gamma ray, which then has the correct wavelength to be absorbed by another nucleus.

Since the energy dependence of the cross section for absorption is so narrow, even a slight deviation in gamma energy makes a drastic difference. Mössbauer discovered that by moving his source relative to a target, even at velocities as low as 4 cm/s, the tiny

energy change from the Doppler effect is enough to destroy the resonance again.

Other researchers confirmed Mössbauer's work by the following summer. It became apparent that the effect was much more pronounced in ^{57}Fe than in the ^{191}Ir isotope Mössbauer had used. The Mössbauer effect has so far been observed in more than 100 isotopes, the most commonly used being ^{57}Fe and ^{119}Sn .

In 1960 the Mössbauer effect found its first major use in a direct test of Einstein's theory of general relativity. All previous tests of relativity had been astronomically based (the advance of Mercury's perihelion, Eddington's measurement of the bending of light around the Sun during the eclipse of 1919, and the gravitational red shift of the light from a white dwarf star, measured by Adams in 1925). Using the Mössbauer effect, though, experimenters could directly detect relativistic shifts under experimentally controlled conditions.

Pound and Rebka at Harvard performed an experiment sending a beam of gamma rays from the top of the 22.6 m high tower in the Jefferson Physical Laboratory down to its base. Since the bottom of a building is closer to the center of the Earth than the rooftop, the gravity field is infinitesimally greater, and the gamma rays experience a tiny gravitational redshift that can be measured with Mössbauer spectroscopy.

In the last 30 years, the Mössbauer effect has been applied in an enormous variety of fields. In the preface to an early textbook on Mössbauer spectroscopy, Gunther Wertheim stated in 1964 (only three years after Mössbauer's Nobel Prize), "[the Mössbauer effect] quickly captured the imagination of a sizeable group of scientists who used it to carry out experiments beyond the reach of previously known techniques." As early as 1968 some researchers were already overwhelmed: The editors of a summary volume, V.I. Goldanskii and R.H. Herber, remarked, "Indeed, this field has grown so rapidly in the past few years that it has become increasingly difficult, even for the Mössbauer spectroscopist, to say nothing of the 'outsider' to this field, to keep up with current developments."

In materials research an experimenter can imbed the same kind of Mössbauer nuclei in two solids. One sample incorporates nuclei in the ground state (the target or absorber), while the other (the source) incorporates nuclei created in

the excited state through decay of a radioactive parent. The resonance effect between the source and the target is so sensitive that a motion as small as 1/10 cm/s is enough to measurably alter the results through Doppler distortion.

In solid-state physics, the Mössbauer effect has been used to study crystalline lattice dynamics. Researchers can determine motion along specific crystallographic directions, giving a detailed test of dynamical models. Also, Mössbauer spectroscopy has been used to study magnetic hyperfine interactions in magnetic materials such as ferromagnets, antiferromagnets, and ferrimagnets. The resolution of the technique gives details on the placement of magnetic ions in a lattice, as well as magnetic interactions and their pressure and temperature dependence. This is important for diagnostics of the metallurgy of iron-containing alloys (i.e., how the internal magnetic field depends on composition, pressure, and temperature) and has allowed materials researchers to develop useful high-pressure processes in preparative metallurgy.

One nondestructive variation on the technique uses conversion electron spectroscopy (where absorption is signaled by detection of an atomic electron emitted in the subsequent decay of the absorbing nucleus) to search for the Mössbauer effect in the surface layers of a substance to be investigated. The results allow for a better understanding of how surface layers of a material change in a reactive environment.

In chemistry, the Mössbauer effect's ability to study the isomer shift and quadrupole splitting is often useful. For instance, the isomer shift parameter as measured by Mössbauer spectroscopy can assign the oxidation state of tin in various compounds. The technique has also been used to analyze clathrates, catalysts, and even glass containing small quantities of Mössbauer isotopes.

The high resolution possible gives details on the structure of polymeric materials. Results have clarified the structures of many compounds of synthetic and industrial importance, such as stabilizers in the plastics industry and various compounds of ruthenium.

At extremely low temperatures, Mössbauer spectroscopy has been used to examine the superconductive transitions of some materials. The materials TaS₂:Sn, TaS₂:Sn_{1/3}, and Nb₃Sn (the last widely used in constructing superconducting magnets) have all been investi-



While reading his first published paper on the resonance in ¹⁹¹Ir, Mössbauer suddenly realized he could verify the lines of natural width directly by a Doppler shift experiment—an insight he was sure the competition would also reach. So he rushed back to Heidelberg and completed his measurements in less than two weeks. Then, knowing he had “hit upon a very exciting phenomenon,” Mössbauer tried “in an effort to gain more time for further exploration, to hide the results by publishing in the journal *Die Naturwissenschaften*, which I thought would not be very widely read. This turned out to be a tremendous mistake, which I quickly realized when I received more than 200 requests for reprints immediately after the publication.” (Photo and quote from *Hyperfine Interactions* 13 (1-3) 1983, p. 2, 4.)

gated using the Mössbauer isotope ¹¹⁹Sn.

As early as 1961, the Mössbauer effect was used to study biological materials containing iron, such as hemoproteins, iron-sulfur proteins, and iron storage and transport proteins. Almost 1,000 related technical papers have appeared since Gonzer, Grant, and Kregzde published “Mössbauer Effect in Blood” in 1963. Biological researchers used the technique to learn about the structure and bonding of iron into such complex systems, since Mössbauer isotopes (i.e., ⁵⁷Fe) act as “tracers” for biological processes. Researchers can cool materials containing paramagnetic iron compounds below the magnetic ordering temperature and determine the sign and magnitude of a magnetic field acting on a single iron atom in a giant biological molecule with a molecular weight as great as 50,000.

Archaeologists have applied Mössbauer spectroscopy to determine the geographic distribution of Greek pottery, using the characteristics and quantities of certain Mössbauer isotopes found naturally in clays as “fingerprints” of various regions. Archaeologists have also used nondestructive Mössbauer spectroscopy to identify physiochemical changes in the pottery, from the raw material (of the clay and of the various glazes used), through the

techniques of manufacture of the pottery, and finally through the centuries of deterioration and exposure to the environment. By analyzing these chemical changes, researchers can learn more about the exact firing processes and the materials used in ancient pottery making.

Many pigments used in old paintings also contain Mössbauer isotopes and have been similarly analyzed. In addition to simply identifying the materials used in paintings from early centuries, identifying the particular signature of pigments from specific regions and times offers a way to pinpoint probable forgeries.

On the twentieth anniversary of Mössbauer's Nobel Prize, a compendium volume stated that “straightforward investigations have not, however, exhausted the field, boredom had not set in, and unexpected applications continue to appear.” Indeed, the moon rocks have been analyzed in detail with the technique, as have deep core samples from the ocean. In 1968 one group of researchers even used the Mössbauer effect from ¹¹⁹Sn to detect tiny breathing motions in the abdomens of ants!

It goes to show that in only three decades the Mössbauer effect has proven to be one of the most important, and certainly one of the most versatile scientific discoveries of the 20th century.

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