Préhistoire, Problèmes et Tendances (Éditions du Centre National de la Recherche Scientifique, Paris, France, 1968), pp. 327–336; L. Pericard and S. Lwoff, *Bull. Soc. Préhist. Fr.* **37**, 155 (1940); L. Pradel, *Mém. Soc. Préhist. Fr.* **5**, 170 (1958).
14. S. Lwoff, *Bull. Soc. Préhist. Fr.* **39**, 51 (1942), figure 3.
15. The bone was examined in 1967, 1968, and 1970, each time after work with other engraved materials had revealed additional aspects of the symbolic engraving tradition. The results of the first analyses appear in (*5*). In this article I correct that version with the microscopic data concerning the use and reuse of the La Marche bone.
16. There is considerable microscopic documentation for basic right-handedness in the engraving of the extremely fine Upper Paleolithic compositions and notations, the left hand having served as the retainer and aligner. The evidence for an alternation in the direction of engraving and, at times, of reading images and notations is one of the unexpected findings of the microscopic method and is among the clues that have made possible the sequential analysis of complex compositions (*2–6*).
17. Two traditional Aurignacian "plaques," reinterpreted by microscopy as pressure flakers used for fine retouch and also engraved with cumulative notations on both faces, are analyzed in (*4*) and (*5*).
18. A. Marshack, in *Prehistoric and Roman Studies*, G. de G. Sieveking, Ed. (Trustees of the British Museum, London, England, 1970), pp. 137–145.
19. Two eagle bones from a single site and level (Le Placard, Charentes, France, Magdalenian IV) each engraved with notations in the same style and perhaps by the same hand, have offered the only other evidence for rigidly contemporaneous comparison (*4, 5*).
20. The use of signs and cue marks with notations is common in the historical period (*8–11*) and has been extensively documented for the Upper Paleolithic in (*4*) and (*5*).
21. See (*4*), figure 2, p. 10 and figure 27, p. 43, and (*5*), figure 24, p. 93.
22. The differentiation of stallion, mare, and colt in a single composition by nonsexual dimorphic characteristics is documented in (*5*), chapter 11. The depiction of seasonal, sexual, and age differences is common and is documented for many species in (*3*) and (*5*).
23. The Upper Paleolithic tradition of reusing or renewing an animal image by the addition of parts of the animal, documented for the mobiliary materials in (*2*), has been verified by microscopy for the cave images by M. Lorblanchet. In a memoir now in press (M. Lorblanchet, preprint) he documents the addition of engraved eyes, ears, and manes and also the addition of muzzles, legs, and other parts as described in (*2*).
24. R. Vega del Sella, *El Paleolítico de la Cueto de la Mina* (Comisión de Investigaciones paleontológicas y Prehistóricas, Madrid, Spain, 1916), plate XXXIX: 2, a and b, and plate XL.
25. An abstract of the analysis of this example appears in (*5*), pp. 213–218, and its cognitive contents in (*6*). A complete documentation is in preparation.
26. K. Absolon, *Artibus Asiae* **20**, 123 (1957).
27. B. Frolov, in *Actes du Symposium International d'Art Préhistorique*, E. Anati, Ed. (Centro Camuno di Studi Preistorici, Capo di Ponte, Val Camonica, Italy, 1970), pp. 475–478.
28. The National Science Foundation is presently supporting the development of spectroscopic techniques for analysis of the painted cave compositions.
29. A. Marshack, in *Proceedings of the Symposium on Mesoamerican Archeology*, Cambridge, England, 1972, in press.
30. L. Cope, *Univ. Calif. Publ. Amer. Archaeol. Ethnogr.* **16**, 119 (1919). Cope documents the widespread tradition of lunar and seasonal naming sequences for the North American Indian, which is comparable to the Siberian tradition documented in Orlova (*9*) and Delaby (*10*). See also L. Spier (*31*).
31. L. Spier, *Bull. Mus. N. Ariz.* **28**, 16 (1955).
32. W. R. Goldschmidt, *Amer. Anthropol.* **42**, 176 (1940).
33. A model based on images from Upper Paleolithic compositions with notations that have been published (*4, 5*) might be: Moon of the Thaw (April); Moon of the Spring Salmon Run (May); Moon of the Calving (June); Moon of the Flowers (July); Moon of the Moulting (August); Moon of the Rutting Bison (September); Moon of the Nut (October); Moon of the First Frost (November).
34. See (*5*), figure 101b, p. 213.
35. The research was funded by the National Science Foundation and the Wenner-Gren Foundation. Special thanks to H. L. Movius, Jr., curator of Old World Archaeology, Harvard University, who supported the research and supervised the research and helped make the development of the methodologies possible.

Mössbauer Spectroscopy: Recent Developments

The current status of Mössbauer spectroscopy is reviewed, emphasizing materials science applications.

R. L. Cohen

The Mössbauer effect (*1*), more formally known as "recoil-free gamma-ray resonance absorption," was first reported in 1958, and was, just 2 years later, the subject of a topical conference. Experimental research with the use of the Mössbauer effect has diffused so rapidly into the diverse fields of solid-state physics, metallurgy, chemistry, and biochemistry that it has become impossible to follow as a united field. One participant leaving the 1964 conference on the Mössbauer effect remarked that "this was not simply the Third International Conference on the Mössbauer effect, but the *last* such conference." This prophecy has turned out to be correct—although many conferences have been held since that time in which research involving the use of Mössbauer spectroscopy has been the main subject (*2, 3*), there has been no attempt to reunite all workers using the technique. Approximately 15 research papers involving the Mössbauer effect are published each week, and it is virtually impossible to keep up with the literature of the entire field.

Why has the technique become so popular? What kind of research is being done? What are the future possibilities? In this review I will concentrate (after a brief introduction) on two basic points. First, I discuss a few recent results which exemplify the way in which "traditional" techniques of Mössbauer spectroscopy have provided useful information for those who are not Mössbauer spectroscopists. In keeping with the current enthusiasm for the application of pure research techniques to "relevant" problems, I emphasize the recent uses of Mössbauer spectroscopy to study problems apart from its uses in the determination of hyperfine structure and isomer shift (these terms are defined below). "Applications" of Mössbauer spectroscopy have usually consisted of analytical determinations, in which the spectrum of the sample is compared with that of standard materials, but I would like to use a somewhat broader definition here. Included in the sections on applications are a number of efforts in which the significant result has been qualitative information on the *existence* of multiple lattice sites, or information on a valence change of the ion being studied. This sort of result can be applied to biological and materials science problems in a much more direct way than the usual investigation of isomer shift and hyperfine structure (hfs), and gives people unfamiliar with the tech-

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The author is a member of the Technical Staff of Bell Laboratories, Murray Hill, New Jersey 07974.

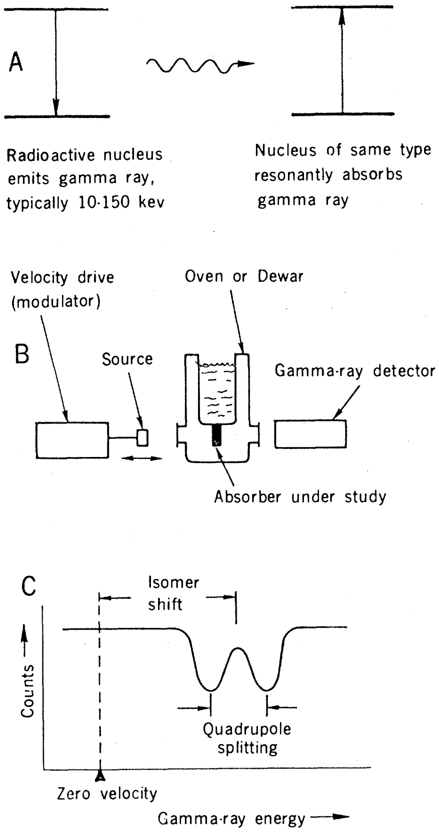


Fig. 1. (A) The Mössbauer effect is based on the resonant absorption of gamma rays emitted in the decay of a radioactive nucleus, which can be resonantly absorbed by a nucleus of the same kind in the ground state. (B) "Standard" configuration of a simple Mössbauer experiment. The source is moved with precisely controlled velocity to modulate the gamma-ray energy by means of the Doppler effect. When the gamma rays have the proper energy to be resonantly absorbed by nuclei in the absorber, fewer of them pass through to the detector and the counting rate decreases. (C) The result is normally plotted in terms of the transmission (or counting rate) versus the Doppler velocity applied to the source. The idealized spectrum shown would be obtained for a quadrupole-split doublet; for comparison, see, for example, Figs. 3, 4, and 6.

nique a much better idea of its utility and capabilities.

Second, I discuss developments in techniques of Mössbauer spectroscopy that have provided a continuing frontier for researchers who might be characterized as Mössbauer spectroscopists. No attempt is made to discuss any particular topic definitively, but a list of recent references is given (*2*, *3*).

The Mössbauer Effect

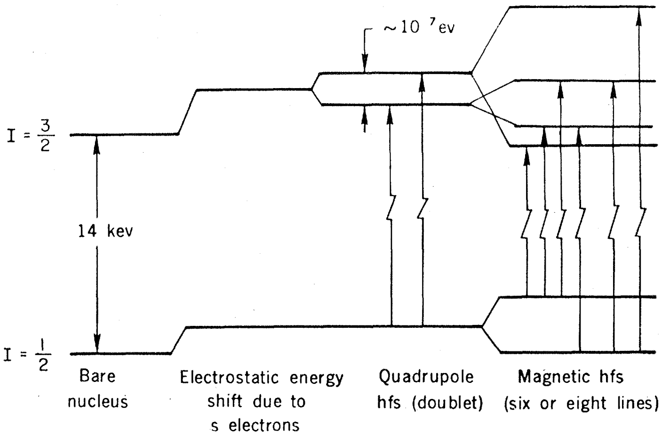
The simple process which is basic to all experiments involving the Mössbauer effect is shown in Fig. 1A, and can be briefly described as follows. An atomic nucleus makes a transition from an excited state to its ground state, emitting a gamma ray. This gamma ray has approximately the right energy (*4*) to be resonantly absorbed by a nucleus of the same kind in its ground state. Small perturbations in the energy of nuclear levels in the absorber can be measured by observing the change in gamma-ray energy required for the gamma ray to be resonantly absorbed. These measurements are usually performed (Fig. 1B) by scanning the gamma-ray energy, using the Doppler shift produced by moving the source with known velocities. The nuclear absorption at resonance is detected in terms of the decreased transmission of gamma rays through the sample containing the absorber nuclei. The result of the experiment is normally displayed (Fig. 1C) as a spectrum of transmission versus gamma-ray energy shift. The energy shifts at which resonant absorption occurs, as well as the relative line intensities, are the principal measured parameters in most Mössbauer spectroscopy experiments. These energy shifts arise from the interactions of electrons with the nuclei, and these measurements allow various inferences to be drawn about the electronic structure of the material being studied. This is the goal of most Mössbauer spectroscopy experiments.

Although research involving the use of the Mössbauer effect still has much of the prestige and mystique customarily associated with a new hot technique, one of the reasons for its popularity as an investigatory tool is that many experiments may be carried out with ease and with relatively little equipment. In fact, it is perfectly possible to demonstrate the existence of the effect with a Geiger tube radiation survey meter as the radiation detector, moving the source by hand to scan the Doppler velocity.

An index of the scope and applications of Mössbauer spectroscopy can be gotten from the fact that there are about 40 elements that have nuclear transitions that can be studied by this technique. Of these, there are six elements (iron, tin, antimony, iodine, europium, and dysprosium) that are easy to work with and yield interesting results. These elements show strong Mössbauer effect resonance and have hyperfine splittings and a range of isomer shifts large as compared to the observed resonance line width. The radioactive sources needed are either commercially available or easy to prepare.

For a number of other elements (including nickel, ruthenium, tellurium, xenon, samarium, tungsten, iridium, and gold) one particular factor, such as the difficulty of preparing the radioactive source, complicates the research, but useful information can still be obtained with moderate effort. Other

Fig. 2. Nuclear energy level scheme showing the perturbations most frequently observed with the Mössbauer effect. The nuclear level scheme shown is that of ^{57}Fe, the isotope most commonly used in Mössbauer spectroscopy, and the "probe" in most of the examples shown here. Several other isotopes (including ^{119}Sn) also have the combination of nuclear states with spin 1/2 and spin 3/2, giving a quadrupole-split doublet under the quadrupolar interaction and six (or eight) lines under the magnetic hyperfine interaction. The hyperfine splittings, and isomer shift, indicated by the spacing of the nuclear energy levels, tend to be different for different solid surroundings. Measurements of these parameters are the primary experimental results in most Mössbauer experiments.

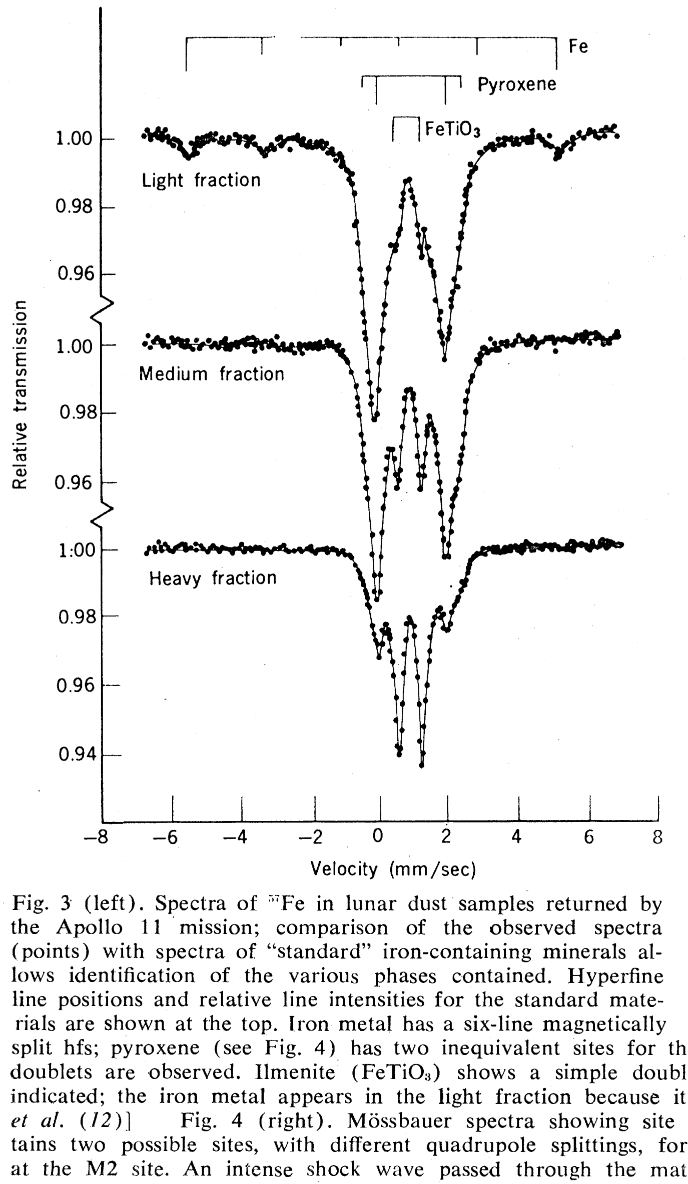


isotopes either are experimentally more difficult to study or provide only limited information.

Since the Mössbauer effect is based on a nuclear resonance absorption, the absorption cross section is not greatly affected by changes in electronic form factors or site symmetry about the ion being studied. Thus, all the "Mössbauer" atoms in a given sample will show roughly (*4*) the same total absorption cross section, and will be seen with roughly the same efficiency. Although this may not appear to be an unusual feature, it is not automatically true of other spectroscopic techniques; for example, nuclear magnetic resonance (NMR) spectra in ferromagnetic metals come primarily from atoms in magnetic domain boundaries, and the interpretation of infrared or optical absorption spectra in solids may be hampered by transitions which may be unobservable as a result of symmetry considerations. Another feature of Mössbauer spectroscopy which enhances its utility in some situations is that the splittings of the nuclear energy levels observed are normally substantially smaller than 100 times the natural width of the resonance. Although this factor limits somewhat the ultimate resolution that can be achieved, one always knows approximately where to look for the resonance line. A corollary of this rule is that the resonance will not normally be broadened to the point of being unobservable by variations in the environment (caused by, for example, stoichiometry variations, impurities, or lattice strain) of the atoms under study, or by time-dependent effects (see below).

The perturbations of the nuclear energy levels observed by means of Mössbauer spectroscopy are almost completely dominated by the effects of the nearest neighbors and next nearest neighbors to the atom being studied. Thus, in systems such as glasses and disordered alloys (*5*), where a fair amount of short-range order exists but where there is very little long-range order, reasonably sharp spectra characteristic of the local atomic environment can be obtained. In fact, one of the major active areas of Mössbauer effect research recently has been the study of order-disorder transitions in alloys (*5*, *6*).

The sensitivity of the hfs to the local environment means that, in most cases, accretions of just a few molecules of a compound yield a Mössbauer spectrum similar to that of the bulk compounds. Thus it is quite feasible to



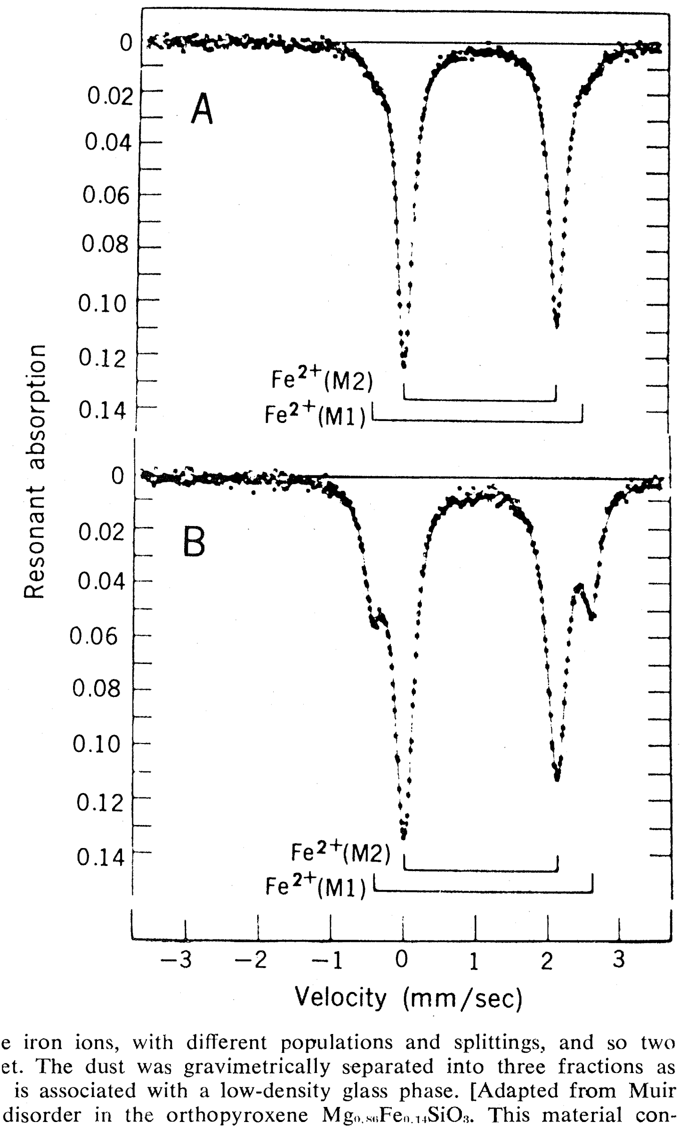


Fig. 3 (left). Spectra of ^{57}Fe in lunar dust samples returned by the Apollo 11 mission; comparison of the observed spectra (points) with spectra of "standard" iron-containing minerals allows identification of the various phases contained. Hyperfine line positions and relative line intensities for the standard materials are shown at the top. Iron metal has a six-line magnetically split hfs; pyroxene (see Fig. 4) has two inequivalent sites for the iron ions, with different populations and splittings, and so two doublets are observed. Ilmenite ($FeTiO_3$) shows a simple doublet. The dust was gravimetrically separated into three fractions as indicated; the iron metal appears in the light fraction because it is associated with a low-density glass phase. [Adapted from Muir *et al.* (*12*)] Fig. 4 (right). Mössbauer spectra showing site disorder in the orthopyroxene $Mg_{0.86}Fe_{0.14}SiO_3$. This material contains two possible sites, with different quadrupole splittings, for the Fe^{2+} ions. The normal material (A) has almost all the iron at the M2 site. An intense shock wave passed through the material creates local disorder, putting (B) some Fe^{2+} at the M1 sites. [Adapted from (*13*)] study the early stages in the nucleation of a colloid (*7*), the details of the adsorption of atoms on active surfaces (*8*), the chemical makeup of corrosion products at a metal surface (*9*), or the intermediates produced in a chemical transformation taking place in a solid (*10*). Under favorable conditions, intermediate products can be identified on the basis of a comparison of their hyperfine spectra with those of known compounds. The ability to determine (by means of the isomer shift) the valence of the Mössbauer ion being studied is very important for technical and analytical applications.

Origins of the Isomer Shift and Hyperfine Structure

The perturbations of the nuclear energy levels (Fig. 2) studied by means of the Mössbauer effect arise primarily from two sources. The first, called the "isomer shift" or "chemical shift" is an effective change in the nuclear transition energy arising from the presence of electronic charge inside the volume of the nucleus (*11*). After one has studied an isotope somewhat, it is normally possible to use the measured energy shift to determine the electronic density at the nucleus; in favorable cases this measurement provides enough information to permit one to determine the valence state of the ion.

The isomer shift alters the energy of the transition but does not split the levels. The hyperfine interaction, the other principal perturbation studied by means of the Mössbauer effect, splits the nuclear energy levels and gives rise to hfs but does not normally change the center of gravity of the transition. There are two sources of hfs: (i) electric (quadrupolar), produced by the interaction of the nuclear quadrupole moment with electric field gradients, and (ii) magnetic (nuclear Zeeman effect), arising from the interaction of the nuclear magnetic moment with an effective magnetic field at the nucleus.

Electric field gradients can arise either from asymmetrically disposed ligand ions or from partly filled electronic shells of the ion being studied; magnetic fields arise from partly filled electronic shells, from the presence of spin-polarized conduction electrons in metals, from superexchange in ionic crystals, and from fields applied by external magnets. The research significance of hfs measurements is that one is able to use the measured hyperfine fields to draw conclusions about the electronic structure, magnetic properties, or crystal structure of the material being studied. In analytical applications, the measured hfs splittings can be compared with those of known compounds to identify the material being studied.

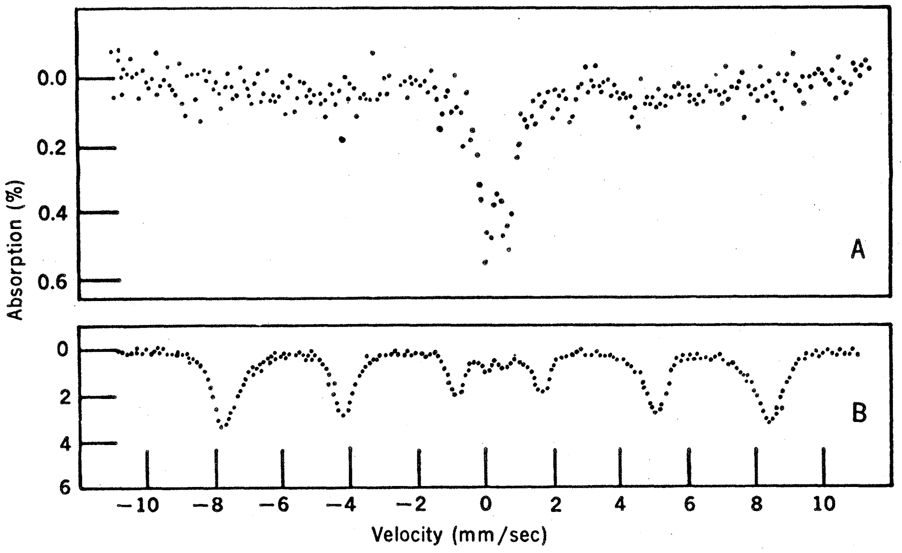


Fig. 5. The ^{57}Fe Mössbauer spectra of dried material (A) from a normal human lung and (B) from the lung of a hemosiderosis victim (*14*). The spectrum in (A) could arise from a small amount of Fe^{3+} in a hemoglobin compound. The spectrum in (B) (note the change in the absorption scale) shows a large amount of an additional iron-containing phase, split by paramagnetic hfs (see Figs. 7 and 8). The particular hfs observed suggests that the iron is in the form of Fe^{3+} in a finely divided, low-molecular-weight compound. [Courtesy of the American Institute of Physics, New York]

Hyperfine structure patterns can be extremely complex since, in general, two nuclear spin states and two interactions are involved. For clarity of presentation, I have chosen examples only from ^{57}Fe and ^{119}Sn spectra; in both of these (see Fig. 2) a doublet is produced by the quadrupole interaction alone, and (usually) a six-line pattern is produced by the magnetic hyperfine interaction.

Applications

I would like to discuss here three recent applications of Mössbauer spectroscopy, demonstrating the range of problems considered and the type of result obtained. The first (see Fig. 3) shows a straightforward decomposition of a complex spectrum from a sample of lunar dust returned by the Apollo 11 mission (*12*). The second, also mineralogically oriented, shows (Fig. 4) the result of pressure shock in changing the site population in an orthopyroxene (*13*). The significant result here is that one is able to distinguish, by virtue of different quadrupole splitting of the two inequivalent cation sites, how the Fe^{2+} population of the two sites has been changed by the shock wave. The spectral lines obtained are

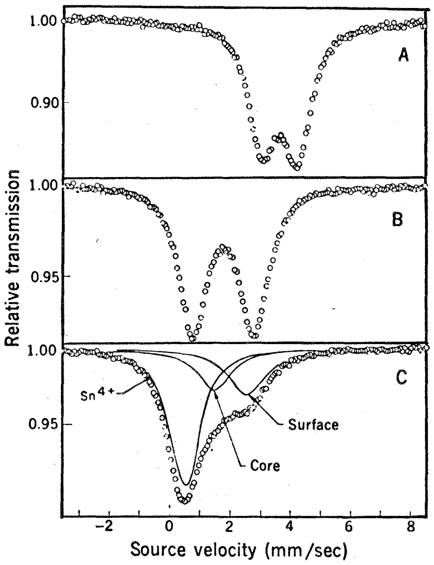
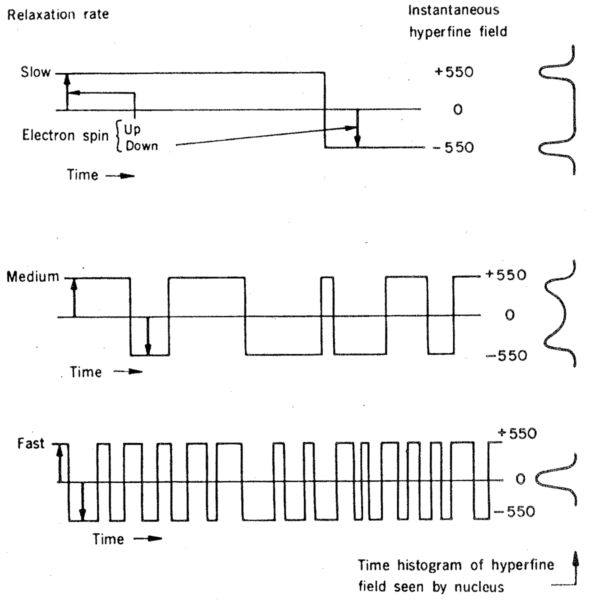


Fig. 6. A chemical reaction in aqueous hydrochloric acid observed by Mössbauer spectroscopy of the ^{119}Sn in frozen samples of the solution. (A) Spectrum of Sn^{2+}, Cl$^-$ complexed in hydrochloric acid (quadrupole doublet). (B) Spectrum of the tin-palladium complex after the addition of Pd^{2+} ions. This complex spontaneously decomposes (C), rejecting Sn^{4+} to the solution, and producing a tin-palladium alloy sol, stabilized by a layer of Sn^{2+} [see (*7*)]

Fig. 7. Origin of magnetic hfs in paramagnetic materials with slow and medium relaxation. If the electron spin relaxation time is very long, the nucleus "sees" a magnetic field of well-defined absolute value and produces a sharp hyperfine pattern (see Fig. 8). As the electronic relaxation becomes more rapid, the effective field "seen" by the nucleus has a distribution of values; at very high relaxation rates, this distribution becomes narrow and lies about zero field, and the hyperfine spectrum is a single line.



sharp even in the highly disordered "shocked" material.

The third example is chosen from the rapidly growing literature (*2*) on the use of Mössbauer spectroscopy in the study of biological materials, many of which contain ^{57}Fe (*14*). Figure 5 shows the spectra of lung material from a normal person and from a victim of hemosiderosis, an occupational disease of coal miners. The abnormal spectrum (Fig. 5B) shows a large amount of extra iron; from the size of the magnetic hyperfine splitting and the temperature dependence (not shown) of the spectrum, the extra iron can be identified as Fe^{3+} in small clusters. By a similar technique it has been possible to study hemoglobin from persons suffering from sickle cell anemia (*15*).

Mössbauer Spectroscopy in Frozen Solutions

Now I would like to summarize a few of the new developments on the frontier of the research in Mössbauer spectroscopy. In recent years, the Mössbauer spectroscopy of dissolved atoms has been a research area of growing importance. Experiments on these systems can be carried out if the solution is frozen [to inhibit molecular motion (*4*)] during the measurement. Such experiments, called "frozen solution" experiments, have been conducted for a number of isotopes in both ionizing and nonionizing (*16*) solvents. (Aqueous solutions containing ^{57}Fe and ^{119}Sn have been the most popular for this work.) There are five phenomena which can be studied by this technique:

1) If an aqueous solution crystallizes as it is frozen, hydrated salts are usually formed. These salts can be identified as distinct phases on the basis of their Mössbauer spectra, and the results can be used (especially in conjunction with specific heat measurements) to determine (*17*) the phase diagram of the water-salt system.

2) If the solution is maintained at a temperature at which the solid component is metastable, the phase transformations, grain-boundary motion, and diffusion of ions through the "ice" phase can be monitored (*18*).

3) If the solution does not crystallize as it solidifies, the surrounding of the Mössbauer ion is similar (*19*) to that in the liquid phase; the spectra of the frozen solution can then be used to study the complexing of the dissolved ion. This information can be used either in fundamental chemical studies of complexing and solution mechanisms or in analytical studies of chemical reactions in solution. An example of the utility of this approach is shown in Fig. 6, in which the intermediate reactions involved in the formation of a tin-palladium sol have been elucidated (*7*).

4) The "frozen solution" technique can readily be applied to the study of formation and stabilization mechanisms of colloidal systems, without the necessity of precipitating or otherwise altering the colloid (*7, 20*).

5) In systems which freeze into a "glassy" phase, the devitrification and precipitation of crystalline phases can be readily observed (*21*).

In all of the applications listed above, the fact that Mössbauer spectroscopy makes possible the detection of distinctive spectra of accretions as small as a single complexed ion is fundamental to the success of the investigations.

Dynamic Effects: Paramagnetic Hyperfine Structure

Since about 1963, probably the most extensively studied new topic in Mössbauer spectroscopy has been that of paramagnetic hfs (*22*) and spin relaxation effects. These phenomena are most frequently observed in those trivalent iron compounds in which the distance between iron ions is relatively large

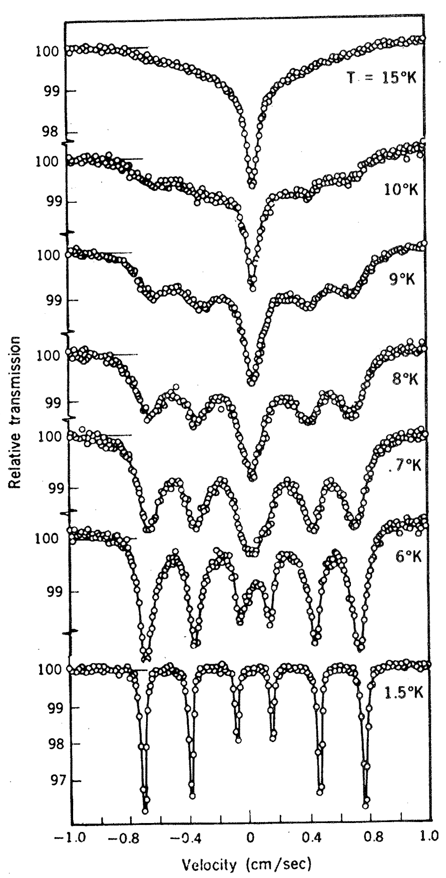


Fig. 8. Spectra of ^{57}Fe at low temperatures in an iron dithiocarbamate. At 1.5°K, the electronic relaxation is slow, and a sharp hyperfine pattern with large splitting is obtained. As the temperature is increased, the electronic relaxation speeds up and the lines become broadened and collapse into a single line for fast electronic relaxation. [Adapted from (*23*)]

(the large distance reduces the strength of the spin-spin interaction between iron ions that is one of the mechanisms contributing to rapid relaxation), and in compounds containing the rare-earth elements. Many materials of biochemical interest (*14*), such as cytochrome, hemoglobin, and other porphyrin-based compounds contain widely spaced iron atoms, and exhibit paramagnetic hfs in their Mössbauer spectra. The proper interpretation of these complex spectra is vital if any information is to be gained about the structure of the material being studied.

Paramagnetic hfs arises in much the same way as the magnetic hfs described earlier, that is, from the interaction of the nuclear moments with fields from the ion's electrons (in partly filled shells). Whereas in the above descriptions of the origins of hfs it has been implicitly assumed that the electrons producing the hyperfine field remained in the same spin position, so that the hyperfine field was constant, this is not always the case. Figure 7 shows a representation of a case in which the hyperfine field is time-dependent. The simplest case is that of "slow relaxation," in which the electrons remain in the spin up (or spin down) state for a time which is, on the average, long as compared to the hyperfine (or Larmour precession) period of the nucleus. Thus, the nucleus "sees" an effectively static hyperfine field, of essentially the same size as it would experience in the same material in the magnetically staturated state. It is not normally possible to tell from the low-temperature hyperfine spectrum alone whether the substance is paramagnetic (with a long relaxation time) or magnetically ordered.

In the limit of short relaxation time, the electron spin flips so frequently between the possible configurations that the hyperfine field "seen" by the nucleus is averaged to nearly zero, and only a slight broadening of the transition can be observed. This averaging out of the field as a result of fast relaxation is the same process as the "motional narrowing" process in resonance experiments. In the "intermediate" relaxation time region (relaxation rate approximately equal to the hyperfine frequency), the nucleus "sees" a distribution of hyperfine fields which can be calculated from the stochastic time dependence of the electron spin.

Since relaxation times usually decrease rapidly when the sample temperature is raised, it is possible to observe experimentally the effect of changes in the relaxation rate simply by measuring the spectrum at a number of different temperatures. An example of such a measurement (*23*) is given in Fig. 8, which shows the characteristic behavior of "relaxation spectra." At low temperature, the electrons are essentially "frozen into" their spin positions, and a spectrum of sharp lines, identical to that obtained in a magnetically ordered sample, is seen. As the temperature is raised and the relaxation rate increases, first the lines broaden, and then a sharp line starts to grow in the center. At 15°K, essentially all the intensity of the absorption is in the central peak, but this peak still has extremely broad and non-Lorentzian shoulders, which continue to narrow at higher temperatures. The presence of the weak broad lines (see especially the 8° and 9°K curves) near positions corresponding to the maximum field value is characteristic of "relaxation spectra." It should be emphasized that the sample is paramagnetic (that is, thermal agitation is strong enough to overcome the magnetic coupling of spins on adjacent ions) at *all* temperatures shown here. If the sample had been magnetically ordered at 1.5°K, and the relaxation rate had been fast, the sharp lines shown in the 1.5°K spectrum would simply have moved closer together (with a splitting proportional to the sublattice magnetization) with increasing temperature, suddenly collapsing into a single sharp line at the magnetic ordering temperature.

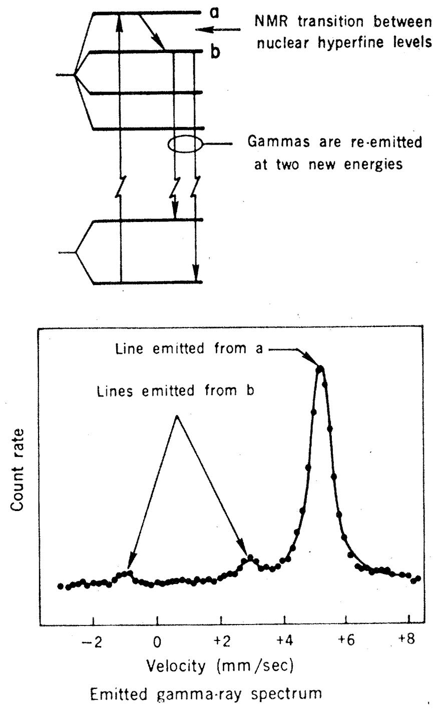


Fig. 9. Mössbauer-detected NMR experiment. A single hyperfine level, *a*, in the 14-kiloelectron volt state of the ^{57}Fe nucleus is excited by the resonant absorption of gamma rays. Application of a RF magnetic field at the hyperfine frequency (corresponding to the energy difference between levels *a* and *b*) produces NMR transitions which populate level *b*. When the nucleus decays out of its excited state, gamma rays originating from level *b* are observed in the spectrum. [Adapted from (*24*)]

Although the spectrum shown here is a relatively simple one, the frequent occurrence of paramagnetic hfs in interesting materials has led to a great deal of theoretical analysis of the much more complex cases that can arise (*22*). For this particular topic there has been an exemplary interaction between experimental work and theoretical modeling and analysis.

Dynamic Effects: Radio-Frequency Nuclear Magnetic Resonance

So far in this discussion I have not considered the effects of fields applied to the absorber. If, for example, a time-varying magnetic field is applied, does this affect the Mössbauer spectrum? Such experiments had already been conducted at the time of the first conference on Mössbauer spectroscopy in 1960, but they were difficult to interpret at the time and only in the past few years has this subject been intensively investigated. Work to date has involved a study of the isotope ^{57}Fe, in magnetically ordered materials which magnify the relatively small fields (tens of gauss) that can be readily produced at the radio frequencies (RF) (10 to 100 megahertz) of interest. In these situations, three effects can be observed: (i) transitions between nuclear substates (that is, NMR can be observed with the use of the Mössbauer effect as a detector); (ii) RF-induced electronic relaxation; and (iii) acoustic excitation.

Figure 9 shows a simple but realistic rendition of an experiment (*24*) which shows directly the RF-induced nuclear transition in the excited state. The experiment is simple in concept, but the overall result is very impressive in that

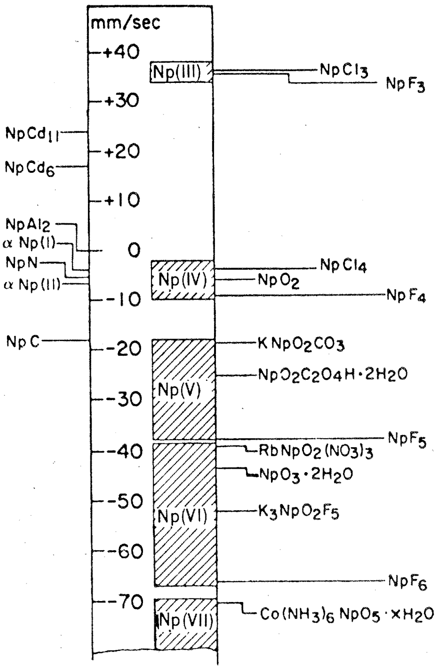


Fig. 10. Isomer shifts for a large number of neptunium compounds in different valence states (electronic density increasing toward the bottom). Materials on the right are insulators; the different valence states are produced by a change in the *5f* electronic configuration. Materials on the left are metallic, and the conduction electrons contribute to the electron density at the nucleus. The two different sites in α-Np have observably different shifts. [Adapted from (*27*)]

the NMR transitions are being produced in a state that has a lifetime of only 10^{-7} second (because of the natural decay out of the 14-kiloelectron volt level).

The second effect has only very recently been clearly observed. Normally in a magnetically ordered material, the direction of the hyperfine field is determined by that of the host magnetization, and, if the direction of the host magnetization is changed, the field at the nucleus will turn. If the host magnetization is periodically reversed by an applied RF field, the field at the nucleus will also reverse rapidly. This situation is very much like the "fast relaxation" case discussed above, except that the relaxation is induced periodically by an external field with a well-defined frequency. For ^{57}Fe, an applied frequency of about 100 megahertz provides rapid enough relaxation (*24*) to give a spectrum very much like the 15°K curve in Fig. 8.

The third effect, which is actually the easiest to observe (*24, 25*), results from the fact that the RF field normally moves the boundaries between magnetic domains in the crystals of which the absorber is made. Because of magnetostriction and defects, this motion results in small motions of the atoms themselves, synchronized with the oscillating field. This motion (which can be conveniently considered as producing a Doppler shift to modulate the gamma-ray energy) produces a series of side bands, spaced from the main line by multiples of the driving frequency. These side bands are so strong that they mask the first two effects described above, except in carefully chosen systems.

Studies with Radioactive Absorbers

The perpetual quest for new isotopes to study with the Mössbauer effect has led to research in which the *absorbing* nuclei are themselves radioactive. This is not difficult in cases where the isotope is very long-lived—for example, ^{129}I (half-life, 1.7×10^7 years) has been used in a number of studies of isomer shift and quadrupole splitting (*2*). One need only be a bit careful in carrying out the chemical procedures on the radioactive absorber materials. The shorter lived isotopes, however, are very difficult to use; the problems associated with carrying out the chemical procedures on the radioactive absorber atoms, the radiation damage in the absorber after it is prepared, and the extra radiation background that the absorber produces in the detector make the problem very challenging. Mössbauer measurements have already been made on ^{133}Ba (*26*) (half-life, 7.2 years) and ^{147}Pm (half-life, 2.6 years).

The most extensive work (*27*) with unstable isotopes has been done with the actinide elements (with these elements, of course, *any* research on the Mössbauer effect must be done with radioactive absorbers). The isotope ^{237}Np is undoubtedly the "star" of this series, having almost ideal properties for study with the techniques of Mössbauer spectroscopy, as well as an interesting chemistry and metallurgy. The only drawback is that one needs the facilities of a national laboratory to prepare the absorbers. Groups at both Argonne and Savannah River have been working with this isotope, and the isomer shifts of a large number of neptunium compounds are shown in Fig. 10. In this case the valence changes can be related to change in the number of *5f* electrons; this is the cause of the relatively constant spacing between valence states in the most ionic compounds (for example, the fluorides). The *5f* electrons in neptunium produce hyperfine fields as large as 6 megaoersteds, which give a very well resolved hyperfine spectrum. The size of the hyperfine field is strongly affected by the magnetic configuration of the *5f* electrons, and thus Mössbauer hfs measurements can show not just the number of *5f* electrons but also can tell something about how localized they are in the solid and what their magnetic moments are (*27*). For the actinides, this type of information is very difficult to get (because of the small amounts of material available, the difficulties of getting really pure samples, and the limited availability of single crystals) by the techniques normally used with stable elements, and the Mössbauer effect has made possible substantial additions to our knowledge of this series of elements and compounds.

Summary

In this review I have emphasized two basic points. First, Mössbauer spectroscopy has been widely used as a tool for basic research in solid-state physics, chemical structure, and magnetism. Second, the technique has been applied to many analytical and materials science problems where the nature of the sample prevents the use of more traditional approaches. Mössbauer spectroscopy research on frozen solutions, colloids, interface chemistry, and crystallographic transformations can be expected to increase rapidly in the next few years.

References and Notes

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and T. C. Gibb [*Mössbauer Spectroscopy* (Chapman & Hall, London, 1971)] contains an extensive discussion of the literature on the Mössbauer effect, emphasizing the chemical aspects. *Chemical Applications of Mössbauer Spectroscopy*, V. I. Gol'danskii and R. H. Herber, Eds. (Academic Press, New York, 1968) contains good review articles on most of the commonly used isotopes. An older book [G. K. Wertheim, *Mössbauer Effect: Principles and Applications* (Academic Press, New York, 1964)] is still very popular as an introductory text, but it predates the bulk of the literature. A brief review by C. E. Johnson [*Phys. Today* **24** (No. 2), 35 (1971)] summarizes applications of Mössbauer spectroscopy to biological systems. It is impossible to list here the review articles (more than 40 in just the past few years) involving Mössbauer spectroscopy.

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Metabolite Distribution in Cells

Two carbamyl phosphate gradients and their sources can be discerned in *Neurospora*.

Rowland H. Davis

Many small molecules are not uniformly distributed within cells in the course of their metabolism. Metabolic channeling, as this phenomenon is called, is hard to demonstrate with certainty or, once demonstrated, is hard to explain in terms of cell structure. The embryologist, the cell biologist, and the mitochondrial physiologist take it for granted that gradients exist in cells and influence cell function (*1*). Many biochemists fear metabolic channeling because it stultifies predictions of metabolic rates based on cellular metabolite concentrations. Sophisticated biochemists and bacterial physiologists contend with the reality of channeling with complex kinetic diagrams and equations (*2*). The disdain among the three groups continues because there is little common background or means of discourse.

In this article I describe the work done in my laboratory on the channeling of carbamyl phosphate (CAP) in *Neurospora*. My colleagues and I have proceeded with the conviction that the kinetics of channeling is secondary to a knowledge of the structures that make it possible. My goal here is to analyze this case of metabolic channeling in terms that biologists in all specialties can understand, enjoy, and possibly apply. The work is unique only in the clarity of the preliminary evidence, in the use of genetic techniques, and in the number of possible explanations for the channeling observed.

The CAP molecule is small in size and is used in the synthesis of the amino acid, arginine, and the pyrimidine nucleotide, uridylic acid. In the arginine pathway, ornithine transcarbamylase (OTC) (E.C. 2.1.3.3) uses CAP to form citrulline from ornithine. In the pyrimidine pathway, aspartate transcarbamylase (ATC) (E.C. 2.1.3.2) uses CAP to form ureidosuccinate from aspartic acid (Fig. 1). In *Neurospora*, two separate carbamyl phosphate synthetases (E.C. 2.7.2.5) catalyze the formation of CAP (*3*). Carbamyl phosphate synthetase A (CPS-A) provides a pool of CAP specifically for the arginine pathway, while carbamyl phosphate

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The author is professor in the department of botany at the University of Michigan, Ann Arbor 48104.