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Mössbauer Effect in Chemistry and Solid-State Physics

Recoil-free emission and resonant scattering of nuclear gamma rays provide a new tool for the study of solids.

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Nuclear physicists have a strong and understandable tendency to ignore the chemical binding of the atoms whose nuclei they investigate. This tendency is based on the fundamentally sound precept that the energies involved in nuclear reactions are so much larger than the energies of chemical binding that the atom may well be thought of as a free atom when one is analyzing nuclear events. Conversely, nuclear properties, except for the mass and the ground-state moments, are of little import to the chemist or solid-state physicist. Occasionally discoveries are made which bridge these disciplines and make contributions in both fields. Disturbed angular correlations and positron annihilation in solids fall into this category. A recent example of particular interest is the recoil-free emission and resonant absorption of nuclear gamma rays in solids, which were discovered by Rudolf L. Mössbauer during his graduate work at Heidelberg in 1957 (*1*).

The discovery rests on the simple realization that some of the energies associated with nuclear events are not necessarily larger than those of chemical binding, 1 to 10 electron volts, or even those characteristic of lattice vibrations, 10^{-2} to 10^{-1} electron volt. The energies in question are those associated with the recoil imparted to a nucleus by the emission of a low-energy gamma ray.

For a *free atom* this energy is readily computed from the requirement of momentum conservation, yielding the expression $E^2/2Mc^2$, where E is the energy of the emitted quantum, M is the mass of the emitting atom, and c is the velocity of light. For the range of gamma-ray energies shown in Fig. 1, this expression yields a range of values from 10^{-5} to 10^3 electron volts for the recoil energy. It is important to note that the free-atom recoil energies are greater than the natural widths of low-lying nuclear levels. As a result of energy conservation the energy of a gamma ray emitted by a freely recoiling nucleus is reduced by the amount of the recoil energy below that of the nuclear transition. This amount is greater than the line width, and consequently the gamma ray has insufficient energy to be resonantly reabsorbed by another nucleus of the same isotope unless the gamma ray is artificially broadened or shifted (*2*).

In solids the most energetic gamma rays ($E > 1$ Mev) impart sufficient recoil energy to the nucleus to break the chemical bonds of its atom and cause it to be torn out of its molecule or to be displaced from its lattice site. Such events are of no further interest to the present discussion. Gamma rays of intermediate energy (150 kev to 1 Mev) invariably excite lattice vibrations and thus are similarly unable to be resonantly reabsorbed. Below 150 kev a new type of event becomes possible. It is the emission of a gamma ray without excitation of the lattice, a process in which the whole energy of the nuclear transition goes into the gamma ray. The resulting gamma rays then have the proper energy to be resonantly absorbed in an analogous recoil-free process. These two recoil-free events, emission and absorption, are the essential processes of the Mössbauer effect, which may be concisely defined as the resonant scattering of gamma rays emitted without recoil by nuclei of atoms bound in solids.

The existence of recoil-free events is best understood when it is realized that the lattice is a quantized vibrational system which cannot be excited in an arbitrary manner (*3*). Changes in the state of the lattice must correspond to the emission or absorption of one or more phonons. Events in which the quantum state of the lattice does not change are possible and may become dominant when the free-atom recoil energy is small as compared to the characteristic phonon energy. Momentum conservation is satisfied in this case by the "simultaneous" recoil of the solid as a whole, a process which requires negligible energy.

The property of the zero-phonon gamma rays which has raised the Mössbauer effect from a laboratory curiosity to a valuable and respected tool is to be found in their line widths. When the lattice is excited, the effective line width will be of the order of the phonon energies; when the lattice is not excited, so that the whole energy of the nuclear transition appears in the gamma ray, the width of the nuclear levels involved in the transitions alone will determine the line width. According to the uncertainty principle, a nuclear lifetime of 10^{-7} second corresponds to a width of 10^{-8} electron volt; this is less by six orders of magnitude than the width when the lattice is excited. More important, however, is the

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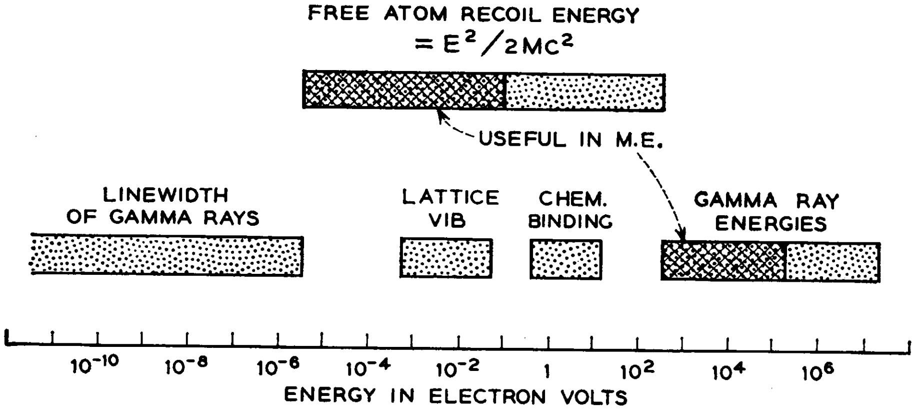


Fig. 1. The energy scale for nuclear and atomic events pertinent to the Mössbauer effect.

fact that this energy is less than characteristic hyperfine-coupling energies in solids, so that it becomes possible to resolve the hyperfine splitting of nuclear levels by observing their gamma-ray transitions.

Detection of Recoil-Free Gamma Rays

The conventional techniques of gamma-ray spectroscopy are inadequate for resolving the energy difference between zero-phonon and multiphonon gamma rays and offer no hope of reaching the resolution required to measure the natural line widths of low-lying states. Mössbauer realized that the inverse of the recoil-free emission process—namely, recoil-free resonant absorption—constitutes an ideal detector, tuned to the full energy of the nuclear gamma ray. In fact, recoil-free resonant absorption makes it possible to compare the nuclear transition energy in a source with that in an absorber with unprecedented precision.

An experiment is typically carried out with a setup similar to that shown in Fig. 2. One major problem remains: to provide a means of modulating the energy of the source gamma rays in order to be able to sweep through the resonance. The method used by Mössbauer, and one which has found almost universal acceptance, is based on the Doppler effect. The energy of a photon (gamma ray) emitted by a moving source, when viewed by a stationary observer (here the absorber), is changed by Ev/c, where v is the component of velocity along the source-to-absorber direction. A determination of the absorption as a function of the Doppler velocity results in an absorption spectrum like that shown in Fig. 3.

In general one must spend a relatively long time in scanning at each velocity in order to obtain statistically significant data. To accumulate a spectrum may take many hours. To overcome the limitation arising from the lack of long-term stability of the counting system, it is necessary to scan repeatedly through the spectrum, adding successive determinations. In practice this is most conveniently accomplished by scanning the Doppler velocity many times per second over the desired spectral range, while synchronously sorting the gamma-ray counts into a multichannel time analyzer. The scanning and sorting are accomplished with a device shown schematically in Fig. 4, which may well be called a Mössbauer-effect spectrometer (*4*).

A major restriction on the isotopes available for Mössbauer experiments is introduced by the use of an absorber, since it must of necessity be made of a stable (or very long lived) isotope. A requirement that the gamma ray be the result of a transition to the ground state is also imposed. Fortunately many such low-lying first-excited states are known. A list of isotopes which have been used successfully in Mössbauer experiments (Table 1) shows many elements of interest to the chemist and to the solid-state physicist.

Atomic Motion

Although the natural line width of gamma rays is much less than typical phonon energies, it is reasonable briefly to consider the spectrum of the gamma ray on a scale comparable to that of phonon energies. This spectrum (Fig. 5) consists of a narrow recoil-free component at the energy of the nuclear transition plus a broad "phonon wing," to borrow a term that has gained acceptance in optical spectroscopy, where analogous effects are observed (*5*). Strictly speaking, Mössbauer experiments are concerned only with the recoil-free line; however, attempts are being made to observe inelastically scattered gamma rays in certain favorable cases where local mode or optical mode vibrations may give rise to sharp peaks in the phonon wing, or in other special cases, such as that of He^4, where the fundamental excitation spectrum may be amenable to examination (*6*).

The recoil-free gamma-ray line is not devoid of information concerning the vibrational properties of the solid. It was found quite early that the exact energy of the emitted line is temperature dependent (*7*): the higher the temperature, the lower the gamma-ray energy, hence the terminology "thermal red-shift." The effect arises from the mean square thermal velocity of the atoms and may be thought of either as a second-order Doppler effect or as a relativistic slowing down of a clock on a moving reference frame, here the emitting atom. Further information is provided by the proportion of the total spectrum contained in the zero-phonon line, usually called the recoil-free fraction. This fraction depends on the ratio

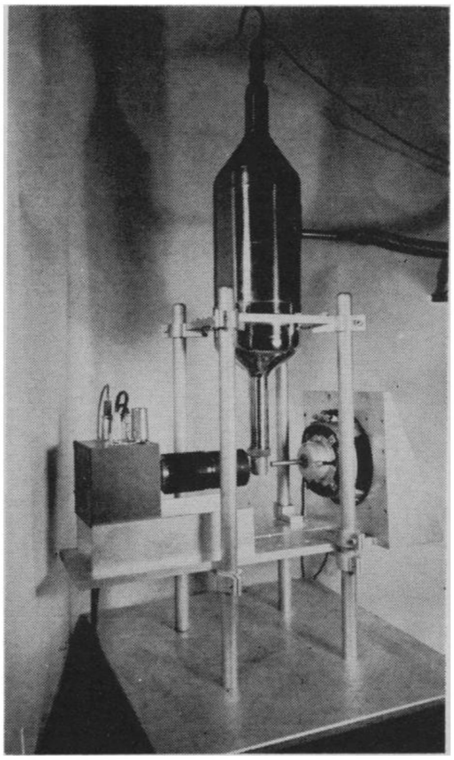


Fig. 2. A typical setup for investigating Mössbauer-effect absorption. The radioactive source is attached to the rod emerging from the velocity transducer at right. The absorber is mounted in the Dewar flask. The detector is a scintillation probe containing a thin NaI(Tl) crystal.

of the mean square vibrational amplitude, $\langle X^2 \rangle$, of the emitting or scattering atom to the square of the wavelength, λ, of the scattered radiation. The reason for this dependence can be understood in a nonrigorous way on the basis of classical radiation theory as follows: If the emitting atom moves over distances comparable to a wavelength during the emitting process, then the phase coherence will be destroyed and parts of the emitting wave will interfere destructively with one another, weakening the component at the natural frequency of the emitter. At the same time the Fourier components of the disturbance will result in broadening (or in the production of side bands if the motion is harmonic) (*8*).

The recoil-free fraction, f, may be written

$$f = \exp - \frac{4\pi^2 \langle X^2 \rangle}{\lambda^2} \quad (1)$$

where $\langle X^2 \rangle$ is the mean square amplitude of the vibration in the direction of emission of the gamma ray, averaged over an interval equal to the lifetime of the nuclear level involved in the gamma-ray emission process. A number of simple conclusions may be drawn from an inspection of Eq. 1. For example, if $\langle X^2 \rangle$ is not bounded, as would be the case in a liquid, the recoil-free fraction will vanish. The diffusive motion which reduces the recoil-free fraction has also been observed in metallic tin very close to, but below, its melting point (*9*). In the case of a solution of a salt of the resonant isotope in glycerine, however, the attenuation of the recoil-free fraction with increasing temperature as the material passed from a viscous state (*10*) of 10^5 poises to one of 10 poises was relatively slight, indicating that $\langle X^2 \rangle$ remained small.

Table 1. Isotopes in which the Mössbauer effect has been observed.

Isotope	Gamma-ray energy (kev)	Half-life of excited state (in nanoseconds*)
Fe^{57}	14.4	100
Ni^{61}	71	51
Zn^{67}	93	10,000
Kr^{83}	9	
Ru^{99}	89	
Sn^{119}	24	18
Te^{125}	35.5	2.2
I^{129}	27	
Xe^{129}	40	1
Sm^{149}	22	~1
Eu^{151}	22	3
Sm^{152}	122	1.4
Gd^{155}	87	0.6
Tb^{159}	58	
Dy^{160}	84	2.5
Dy^{161}	26	28
Er^{166}	81	1.8
Tm^{169}	8	4
Yb^{170}	84	1.6
Hf^{177}	113	0.6
Ta^{181}	6.25	9,800
W^{182}	100	1.3
W^{183}	46	0.15
W^{183}	99	.57
Re^{187}	134	2
Ir^{191}	129	0.13
Ir^{193}	73	
Pt^{195}	99	.16
Au^{197}	77	1.9

* One nanosecond = 10^{-9} second.

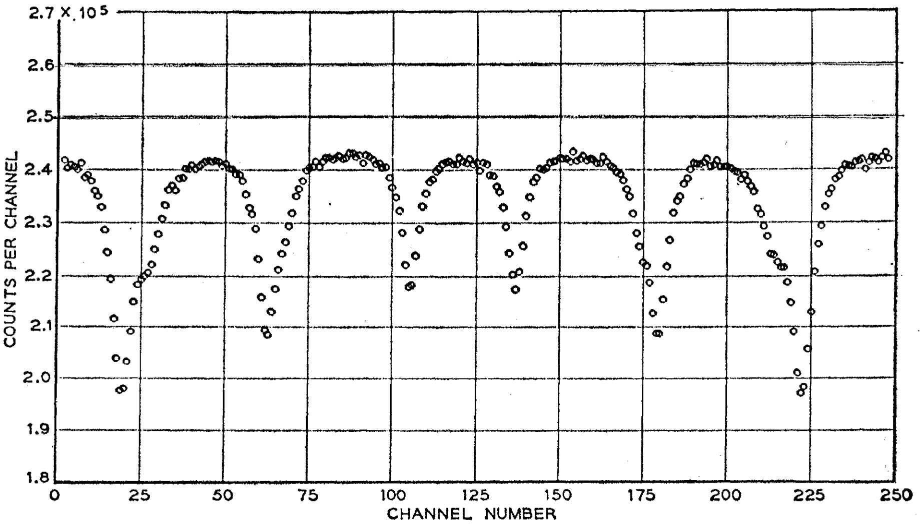


Fig. 3. A typical absorption spectrum as plotted by a computer. The source consists of Co^{57} dissolved in metallic copper; the absorber is a dilute alloy consisting of 2-percent chromium in metallic iron. The six major Fe^{57} absorption lines show satellite structure attributable to iron atoms with chromium atom neighbors.

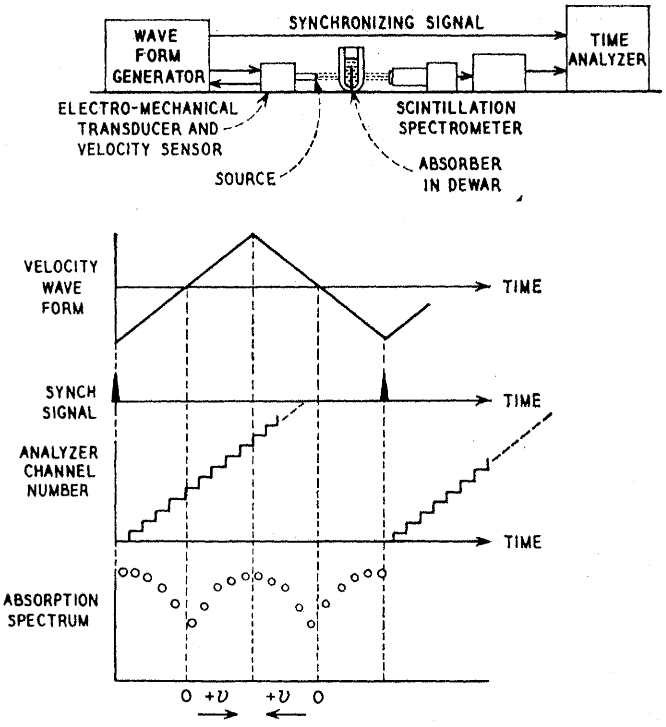
Note also that Eq. 1 gives no indication that crystal structure is required for recoil-free emission. It is not surprising, then, that the Mössbauer effect is readily observed in glasses. It has been demonstrated with Fe^{57} in fused quartz and silicate glass (*11*), with iron pentacarbonyl frozen in an organic solvent (*12*), and with Sn^{119} in polymethyl methacrylate (*13*). Serious work with glasses is in an early stage, but encouraging results have been obtained, especially in silicate glasses containing small amounts of Fe^{57} introduced as a separated isotope (*14*).

Another experiment which can be interpreted in terms of Eq. 1 concerns the recoil-free fraction for iron dissolved in metallic indium, a fraction which was found to be almost independent of temperature (*15*). According to Eq. 1, this finding implies that $\langle X^2 \rangle$ is also temperature independent, a condition which obtains trivially if the binding potential can be represented by a square well. Intuitively one finds this conclusion satisfactory, since an iron atom is smaller than an indium atom and fits into a substitutional site with room to spare.

If the binding of the atom is noticeably anisotropic, the mean square amplitude of its motion will be different in different principal directions, resulting in an anisotropic recoil-free fraction. While this effect could be best demonstrated with oriented single-crystal samples, Goldanskii and others have recently pointed out (*16*) that it does not disappear even in a randomly oriented polycrystalline specimen provided the hyperfine structure is resolved.

This comes about from the fact that the various hyperfine components themselves have intensities which are a function of the direction of emission relative to the crystallographic axes, and therefore provide means of taking spatially weighted averages of the recoil-free fraction.

In spite of the attractive simplicity of Eq. 1, it is often desirable to use the Debye approximation to determine the recoil-free fraction. This leads to the familiar Debye-Waller factor, which, however, is strictly applicable only to an atom in a monatomic lattice of identical atoms. It has been shown that an impurity atom acts as though the host lattice atoms had the same mass as the impurity, provided the binding forces between host lattice and impurity and between the host lattice atoms themselves are the same (*17*).



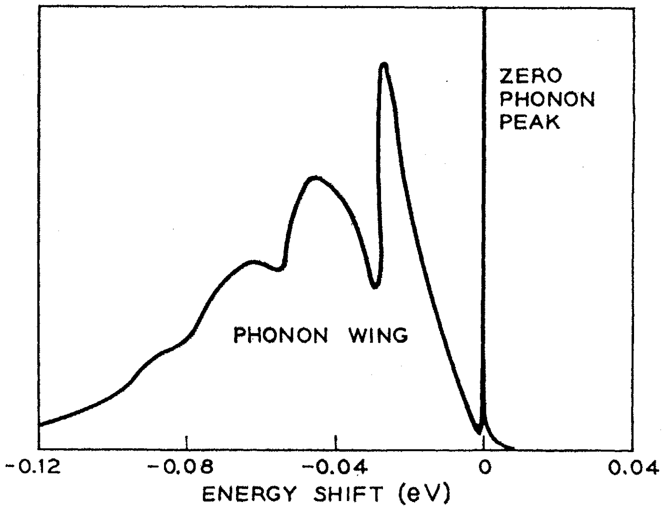


Fig. 4 (left). Schematic diagram of the complete Mössbauer-effect spectrometer.

Fig. 5 (above). The theoretical spectrum of the 129-kev gamma ray of Ir^{191} emitted by an atom in a solid at low temperature. The Mössbauer spectrometer is sensitive only to the narrow, recoil-free line at zero energy shift. [W. M. Visscher, *Ann. Phys. N.Y.* **9**, 194 (1960)]

In more complicated solids—for example, molecular crystals—the presence of optical as well as acoustic modes complicates matters considerably. In general, optical modes of high energy will have little effect on the recoil-free fraction (*18*). The low-temperature behavior will almost inevitably be dominated by the acoustic modes.

The Isomer Shift

We have seen that the Mössbauer effect makes it possible to compare the nuclear transition energies in two materials with high precision. At first thought this does not appear to be a particularly valuable accomplishment, because one tends to believe that nuclear levels are fixed in position. This view overlooks the fact that the nucleus is surrounded and penetrated by electronic charge with which it interacts electrostatically (*19*). The energy of interaction can be computed classically by considering a uniformly charged spherical nucleus imbedded in its *s*-electron charge cloud. A change in the *s*-electron density such as might arise from a change in valence will result in a change in the coulombic interaction, which manifests itself as a shift of the nuclear levels (Fig. 6). This effect is properly considered a part of the electric hyperfine structure and could be called the "electric monopole interaction," in analogy with the electric quadrupole splitting. However, the term *isomer shift* (I.S.) has been almost uniformly adopted, because the effect depends on the difference in the nuclear radii of the ground (gd) and isomeric (is) states. The nonrelativistic expression for the shift is (*20*)

$$\text{I.S.} = \frac{2\pi}{5} Ze^2 \left[\underset{\text{abs}}{|\psi(O)|^2} - \underset{\text{source}}{|\psi(O)|^2} \right] \times \left[R_{is}^2 - R_{gd}^2 \right] \quad (2)$$

where Z is the atomic number, $e|\psi(O)|^2$ is the electronic charge density at the nucleus, and R is the radius of the nucleus represented by a uniformly charged sphere (*21*).

To the chemist the isomer shift is without doubt the most important parameter which can be derived from a Mössbauer spectrum. It yields information which is not available from other experiments—information which bears directly on the chemical binding. Since it measures the electronic charge density at the nucleus, it is directly sensitive to the *s*-electrons and indirectly sensitive to the other electrons which may be involved in chemical bonds.

The effects of *d*-electrons or of electrons of other inner, unfilled shells, such as are found in the lanthanides and actinides, arise indirectly by way of the outer *s*-electrons. The wave functions of these *s*-electrons are sensitive to the filling of the inner shells because the electrons in the inner shells shield the nuclear charge and thus alter the Coulomb potential, which determines the wave function. Inner *s*-electrons are also affected because they spend a small fraction of their time outside the 3*d*-electron charge cloud.

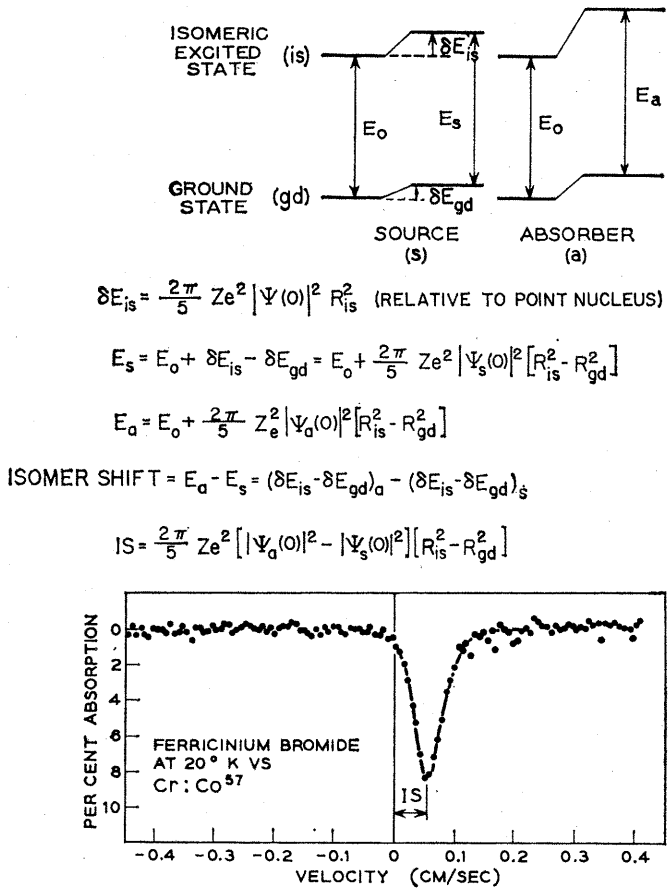
The isomer-shift systematics have been observed for a large number of isotopes, including Fe^{57} (*22*), Sn^{119} (*23*), I^{129} (*24*), Eu^{151} (*25*), and Au^{197} (*26*). The most extensive chemical investigations have been concerned with iron and tin compounds. In both cases a change in valance—that is, of Fe^{++} to Fe^{3+} or of Sn^{++} to Sn^{4+}—has a dramatic effect on the isomer shift, and this finding was the first conclusive indication that the shift would be a useful chemical tool. In the case of Sn^{4+} it has been shown that the electronegativity of the halides and other compounds is linearly related to the isomer shift (*27*). Tin-organic compounds have also been widely studied (*13, 28*).

The isomer shift has also given valuable information on bonding in iron-organic compounds (*29*), especially in π-bonded systems—for example, cyclopentadienyl-iron and cyclo-octatetraene-iron compounds. In zero-oxidation-state compounds of iron it has been possible to assign additive partial isomer shifts to ligands such as NO, terminal CO, bridging CO, $P(C_6H_5)_3$, and $P[N(CH_3)_2]_3$, among others. The bonding in covalent complexes has recently received attention (*12, 30*).

Electric Hyperfine Splitting

The line widths of many isotopes suitable for Mössbauer effect experiments are sufficiently small to make it possible to resolve the hyperfine splitting of nuclear levels.

The nuclear electric quadrupole splitting results from the interaction of the nuclear quadrupole moment with the gradient of the electric field due to extranuclear charge (Fig. 7). The splitting has been of primary concern to the nuclear physicist because ground-state and excited-state quadrupole moments are of great value in testing the predictions of nuclear models. However, to deduce the moment from the splitting, the electric field gradient (EFG) must be known. This calls for a detailed examination of the sources



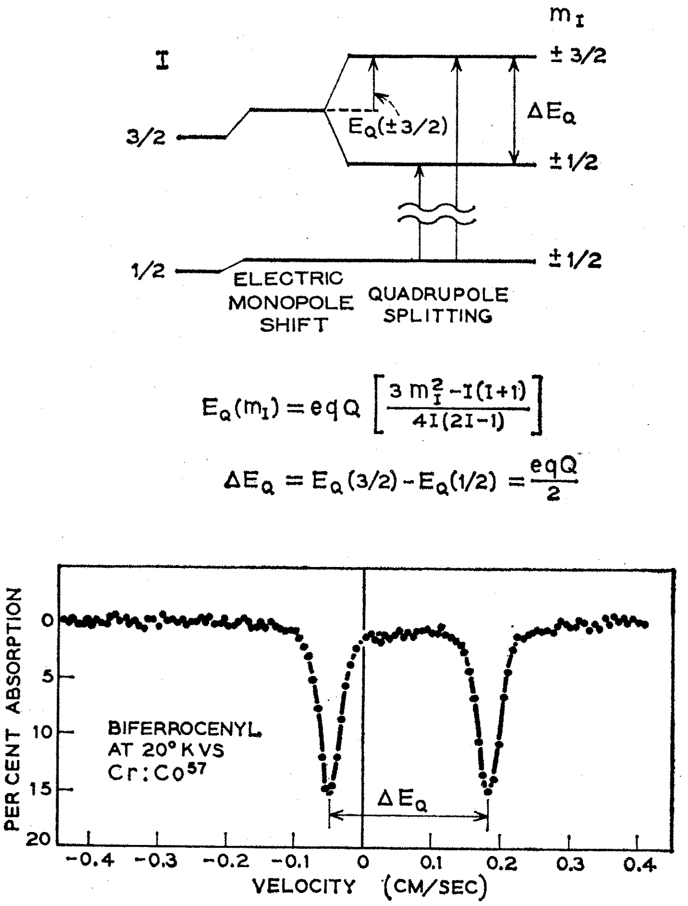
$$\delta E_{is} = \frac{2\pi}{5} Ze^2 |\Psi(0)|^2 R_{is}^2 \quad \text{(RELATIVE TO POINT NUCLEUS)}$$

$$E_s = E_o + \delta E_{is} - \delta E_{gd} = E_o + \frac{2\pi}{5} Ze^2 |\Psi_s(0)|^2 [R_{is}^2 - R_{gd}^2]$$

$$E_a = E_o + \frac{2\pi}{5} Z_e^2 |\Psi_a(0)|^2 [R_{is}^2 - R_{gd}^2]$$

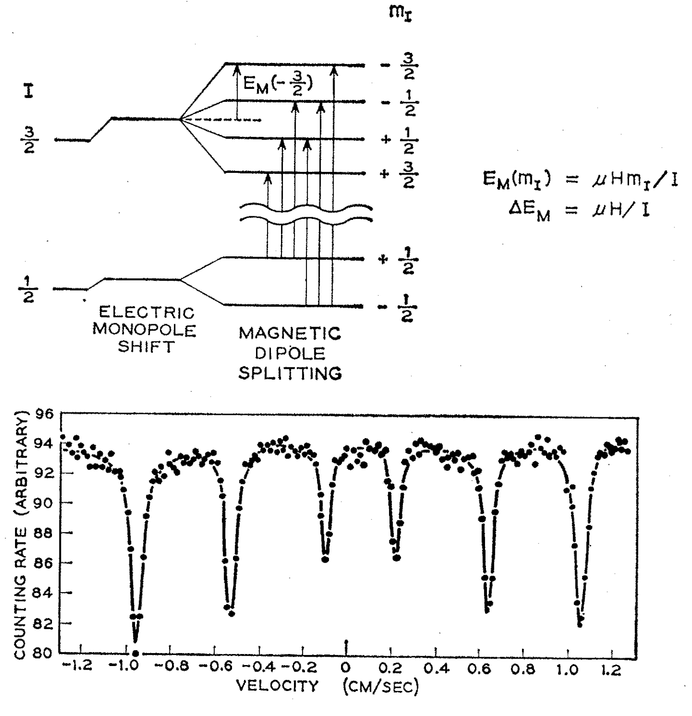
$$\text{ISOMER SHIFT} = E_a - E_s = (\delta E_{is} - \delta E_{gd})_a - (\delta E_{is} - \delta E_{gd})_s$$

$$IS = \frac{2\pi}{5} Ze^2 [|\Psi_a(0)|^2 - |\Psi_s(0)|^2][R_{is}^2 - R_{gd}^2]$$



$$E_Q(m_I) = eqQ \left[\frac{3m_I^2 - I(I+1)}{4I(2I-1)}\right]$$

$$\Delta E_Q = E_Q(3/2) - E_Q(1/2) = \frac{eqQ}{2}$$



$$E_M(m_I) = \mu H m_I / I$$

$$\Delta E_M = \mu H / I$$

Fig. 6 (left above). Isomer shift. The effect of the electric monopole interaction is to shift nuclear levels without separating the magnetic sublevels. The shifts are very small as compared to the total energy of the gamma ray, 10^{-12} E_γ.

Fig. 7 (top right). Quadrupole splitting. The interaction of the nuclear quadrupole moment, Q, with the gradient of the electric field, eq, is illustrated for nuclear ground-state spin $I_{gd} = 1/2$ and for isomeric-state spin $I_{is} = 3/2$; the diagrams are applicable to Fe^{57}, Sn^{119}, and Tm^{169}, among other isotopes. For the ground state, or any state with $I = 1/2$, Q is inherently zero. An example of a pure quadrupole Mössbauer absorption spectrum is shown at bottom.

Fig. 8 (bottom right). Magnetic hyperfine splitting for $I_{gd} = 1/2$, $I_{is} = 3/2$. As a result of the selection rule, $\Delta m = 0 \pm 1$, only six of the possible eight lines are observed. The graph at bottom shows the Fe^{57} hyperfine splitting of FeF_3, which corresponds to a field of 620,000 oersteds.

of the EFG, a problem of solid-state physics.

The two fundamental sources are the charges on distant ions and the electrons in incompletely filled shells of the atom itself. Distant ions contribute, provided their symmetry is lower than cubic. If the crystal structure is known to a high degree of precision, and if an ionic charge can be assigned to the lattice sites, then the value of the EFG at the *atomic* site can be obtained from a straightforward electrostatic calculation. This is not, however, the EFG at the *nuclear* site. The latter is usually greatly modified by the atom's own electrons; their wave functions are distorted by interaction with the external EFG, and as a result they create an EFG of their own (*31*). Usually this serves to amplify the EFG attributable to the distant charges; this phenomenon is called antishielding, and the magnitude of the effect can be calculated. The EFG due to the electrons in partially filled, nonspherical shells, when it is present, dominates that due to distant charges. This field gradient is also influenced by shielding or antishielding of calculable magnitude.

The quadrupole splitting due to atomic electrons is related to the concerns of the solid-state spectroscopists. The crystal-field states involved in optical transitions are the ones responsible for EFG observed in the quadrupole splitting (*32*). As a result, the nuclear quadrupole moment may be determined with the help of optical spectroscopy, provided the corrections for antishielding can be properly introduced. This approach has recently been used in the case of Tm^{169} in thulium ethyl sulfate (*33*) and has given results which are in good agreement with those obtained from an analysis of the splitting in the metal and in the intermetallic compound Fe_2TM. Such splitting is discussed later.

A more prosaic use of the quadrupole splitting has been its use to help define molecular structure. Absence of splitting is indicative of a cubic or near-cubic environment—for example, octahedral or tetrahedral. In $Fe_3(CO)_{12}$, the Mössbauer absorption spectrum indicates that one atom is in a nearly cubic environment and that two are in noncubic surroundings. This implication favors the linear $(CO)_3Fe(CO)_3Fe(CO)_3Fe(CO)_3$ structure, in which the central atom is octahedrally surrounded by bridging carbonyls (*34*).

Magnetic Hyperfine Splitting

Some of the most rewarding applications of the Mössbauer effect have been made in studies of magnetism. This is due both to the existence of the isotope Fe^{57} and to the large number of suitable rare-earth isotopes (Fig. 8). The ease with which Fe^{57} experiments can be made has led to a rapid filling-in of the essential picture of the magnetic hyperfine splittings in ionic compounds, but our understanding of metals and alloys remains rudimentary (*35*). Perhaps the most important finding here is the recent discovery that the effects of near-neighbor impurity atoms in dilute ferromagnetic alloys can be resolved (*36*). It has made possible a detailed investigation into the ferromagnetic exchange interaction in iron (*37*) and may lead to a better understanding of ferromagnetism itself.

The magnetic properties of iron impurities in *d*-group transition metals are of fundamental importance to a better understanding of both magnetism and superconductivity (*38*). In the case of the dilute ferromagnetic cobalt-palladium and iron-palladium alloys, where atomic moments as large as 12 Bohr magnetons have been found by means of susceptibility measurements, the Mössbauer effect has shown that the electronic structure of the Fe remains similar to that of the pure metallic form (*39*). In dilute paramagnetic alloys the moment associated with the iron atoms may be examined by applying external fields of approximately 50,000 oersteds, by means of Bitter solenoids or of superconducting magnets (*40*).

In the case of the rare-earth isotopes, the most interesting information has been obtained from the study of two classes of compounds: (i) the rare-earth iron garnets (*41*) and (ii) the cubic Laves phase compounds of rare earth and iron (*42*). The intermetallic compounds are ferrimagnetic and have a simple magnetic behavior which contrasts with that of the rare-earth metals themselves (*43*). The simplicity is due to the weak crystal-field splitting and the weak exchange coupling of the rare-earth ions. The magnetic behavior of the iron is almost entirely independent of the behavior of the rare earth, which acts almost like paramagnetic ions aligned by a static magnetic field provided by the iron sublattice.

In these intermetallic compounds the temperature dependence of the magnetization of both sublattices can be examined by means of the Mössbauer effect; such examination provides a more detailed picture of the magnetic behavior than can be obtained from magnetization measurements (*44*).

Other Recent Developments

The discovery of noble gas compounds was rapidly followed up with Mössbauer investigations of a variety of Xe^{129} compounds (*45*). The Mössbauer effect in clathrates of Kr^{83} had been previously reported (*46*). The isomer shift may be expected to make a significant contribution to the understanding of the bonding in these materials.

The spectra obtained from gamma rays emitted after the electron-capture decay of Co^{57} in dielectric environments have been variously interpreted. In a number of cases complex spectra have been attributed to the production of both Fe^{++} and Fe^{3+} as the result of an Auger effect (*47*) following the decay of the parent isotope. In other systems no evidence for this effect has been obtained; rather, it has been shown that a variety of spectra result from the association of impurity atoms with vacancies (*48*). It is likely that both effects do in fact occur, and that one or the other may dominate, depending on the nature of the host lattice and perhaps even on the method of preparation.

Conclusion

The Mössbauer effect is rapidly becoming an accepted spectroscopic tool. Initially it was almost entirely the province of nuclear physicists, perhaps because of their greater familiarity with the techniques which are required. It soon became apparent, however, that interpretation of the data usually requires considerable knowledge of chemistry and of solid-state physics. Now the tables have been turned and we find chemists and solid-state physicists acquiring the requisite knowledge of nuclear physics to perform resonant scattering experiments.

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