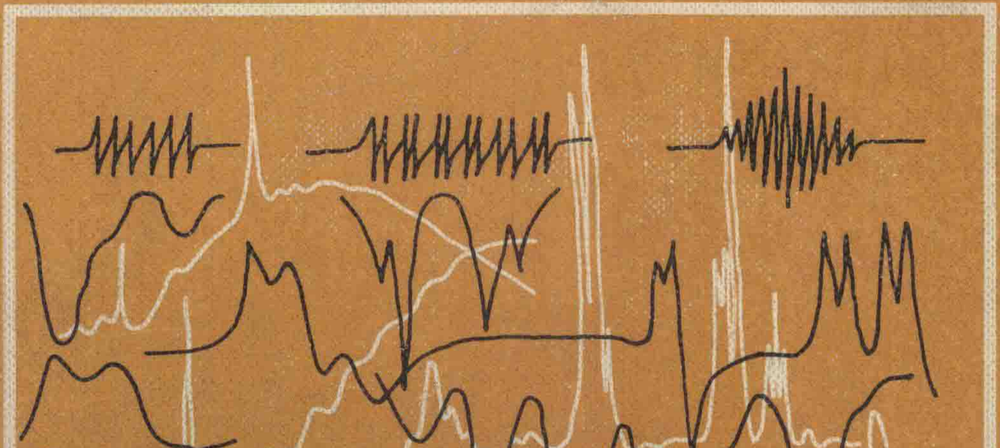
A.S. Marfunin

Spectroscopy, Luminescence and Radiation Centers in Minerals



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Spectroscopy, Luminescence and Radiation Centers in Minerals

Translated by V. V. Schiffer

With 170 Figures

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Preface

The development of mineralogy, the evolutionary changes in comprehending the mineral substance of the earth are closely associated with the progress of research methods.

Over a space of more than two and half centuries, from the goniometry of the mineral crystals to microscopic petrography and optical mineralogy, to crystal structure determinations, electron microscopy and electron diffraction and finally investigations into their electrical, magnetic and mechanical properties, all this has led to the formation of the existing system of mineralogy, its notions, theories and to a proper description of minerals.

However, no matter how great the variety of methods employed in mineralogy, they all come to a few aspects of substance characteristics. These are methods of determining the composition, structure and properties of the minerals. Thus the X-ray microanalyzer, the atom-absorption, neutron-activation, chromatographic and other analyses open up new opportunities for determining nothing else but the elementary composition of minerals.

In the last 10 to 15 years the scope of these analytical possibilities has been considerably enlarged by an addition of the spectroscopy of solids methods which help expose a new facet in the cognition of the substance in general and of the mineral one, in particular. The spectroscopy of solids includes electron paramagnetic resonance, nuclear magnetic and nuclear quadrupole resonance, Mössbauer (γ-resonance) spectroscopy (all of them owing their origin to the discovery of new physical phenomena), X-ray and electron spectroscopy (that began developing after construction and improvement of new spectrometer types), optical spectroscopy and luminescence (which have assumed quite a new significance due to use of crystal field theory).

Embracing all regions of the spectrum, from the gamma and X-ray and throughout the ultraviolet, visible, infrared, to the superhigh-frequency and radio-frequency, being based on the nuclear, electron, vibrational and spin transitions and making use of radically different types of spectrometers, these methods have one major common feature that distinguishes them from all other research procedures.

The salient feature common to all branches of the spectroscopy of solids is the observation of atoms in a state of chemical bonding within concrete crystals and compounds. This gives a complete characterization of crystals and compounds, viz. their composition, the arrangement of atoms in the structure, properties of the atoms in a given crystal structure (electronic structure), and properties of the crystal as a whole, determined by the composition, atomic and electronic structure.

Spectroscopic parameters present the only direct possibility to measure and define the actual states of chemical bonding, a natural experimental groundwork forming a basis for the current theories of chemical bonding, such as the crystal field, molecular orbitals, and energy band theories which, in their turn, are at the same time the spectroscopic theories.

The spectroscopy of solids not only opens up a new chapter in the understanding of the substance, but within the framework of the visible "physical oecumen", if one may put it this way, it appears as conclusive, synthetizing, and unique in describing causal relationships among the composition, structure, and properties, and enables it to comprehend and assess these properties. The crystals themselves and compounds are a product subsequent to self-consistency of the electronic properties of the atoms, the one that has led to a given arrangement of the atoms in the crystal structure and has imparted specific features to them in the crystal, as well as shaped the properties of the crystals themselves.

In all directions of these spectroscopic methods, the detailed and thorough investigations have been effected in mineralogy at the most advanced technical and theoretical level. Both fundamental data and those relevant to individual rock-forming and ore minerals have been already obtained.

Thus, in addition to a change in the general approach to the chemical binding in minerals, X-ray and electron spectroscopy helped trace molecular orbital diagrams for rock-forming silicates.

The nuclear-magnetic resonance spectra furnished a basis for measuring intracrystalline fields, while from the electron paramagnetic resonance spectra the degree of ionicity – covalency – has been determined. In the case of sulfides, the bonding states have been estimated according to the Mössbauer and optical reflectance spectra and for the arsenic, antimony, bismuth sulfosalts – on the ground of the nuclear quadrupole resonance data.

Spectroscopic methods are of aid in establishing the distribution of cations in nonequivalent positions within the structures of olivines, amphiboles, mica, and other minerals, with some of these serving as a means for setting apart geothermometers, determining types and localization of water in minerals, obtaining all the information about the impurity elements, interpreting causes accounting for colors and luminescence of minerals and helping describe in great detail the state of iron (its valent states, magnetic properties, supermagnetism of ultra-fine particles, properties of diamond and apatite with implanted iron, etc.).

The results thus made available are used in subdividing intrusive massifs, sedimentary and metamorphic complexes, separating facial rock varieties, determining relative ages, temperature conditions attending their formation and educing prospective indications for exploration.

It was the electron paramagnetic resonance alone that helped discover in minerals an abundance and a great variety of radiation electron-hole centers and to interpret their models. By this time such centers have been shown to be of geological and prospective value, to influence flotation of minerals, determine the photochromatism of some crystals (of sodalites in particular), utilized in T.V. screens, to define the mechanism of thermoluminescent dosimetry, specify the choice of radiation-stable lasers, piezoelectrics, the service-life of reactor materials, to intensify and change the coloration of gems. The entire complex of spectroscopic methods occupies a place of prime importance in continuing investigations of lunar rocks and minerals.

In many branches of the spectroscopy of solids, natural minerals and their synthetic analogs represent the best-studied systems, such, for instance, as those of fluorite, scheelite, apatite, ruby in the electron paramagnetic resonance and luminescence, spinels-chromites-ferrites in the Mössbauer spectroscopy.

The introduction of new methods into mineralogy pre-supposes each time their adaptation conformably to features specific for mineral matter and to problems of mineralogy, petrology, lithology, ore deposits geology, prospecting and enrichment of raw mineral materials. In the past decade the potentialities and trends of each one of the spectroscopic methods in this cycle of research have taken their main shape; the notions, methods of measurement and interpretation have been selected and data covering major mineral groups accumulated. An attempts at systematic presentation of all this material has been made in this book.

A general theoretical introduction to all sections of the book is the crystal field theory and molecular orbital theory, discussed in the preceding book of the author[1], where subject to consideration was also the optical absorption spectroscopy of minerals.

The bibliography includes selected works which, however, reflect all the principal trends of research in the domain of spectroscopy of the minerals. References to works cited in *Physics of Minerals and Inorganic Materials* are almost omitted here and, therefore, one should look there for literature sources touching upon related problems (spectroscopy and chemical bonding, spectroscopy and crystal field, molecular orbital theories, etc.).

The author wishes to express his indebtness and gratitude to L.V. Bershov, V.M. Vinokurov, I.N. Penkov, A.N. Platonov, A.N. Taraschan, S.A. Altshuler, M.M. Zaripov, M.I. Samoilovich, V.I. Nefedov, A.M. Bondar, V.O. Martirosyan, M.L. Meilman, R.M. Mineeva, A.R. Mkrtchyan, M.Ya. Scherbakova, A.V. Speransky for fruitful discussions of many issues concerned with the spectroscopy of minerals which proved of great help to the author in writing this book.

Moscow, April 1979 A.S. MARFUNIN

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[1] A.S. Marfunin: Physics of minerals and inorganic materials. An introduction. Berlin, Heidelberg, New York: Springer 1979.

A. S. Marfunin

Physics of Minerals and Inorganic Materials

An Introduction
Translated from the Russian by G. Egorova,
A. G. Mishchenko

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Contents: Quantum Theory and the Structure of Atoms. – Crystal Field Theory. – Molecular Orbital Theory. – Energy Band Theory and Reflectance Spectra of Minerals. – Spectroscopy and the Chemical Bond. – Optical Absorption Spectra and Nature of Colors of Minerals. – Structure and the Chemical Bond. – Chemical Bond in Some Classes and Groups of Minerals. – References. – Subject Index.

Solid-state theories and spectroscopy account for the third crucial change within this century in our concept of the basis of mineralogy and the inorganic materials sciences. This book is a revised, updated, and supplemented translation from the Russian edition, providing a complete system of recent theories of solids as they apply to minerals and inorganic materials. Both basic principles and sophisticated new theories are presented with the mineralogist and materials researchers in mind. The book contains extensive references for further study and will be a valuable reference work since each chapter is self-contained.

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Physics and Chemistry of Minerals is an international journal that publishes articles and short communications about physical and chemical studies on minerals, as well as solids related to minerals.
The journal supports competent interdisciplinary work in mineralogy as it relates to physics or chemistry. Emphasis is placed on the application of modern techniques and theories, and the use of models to interpret atomic structures and physical or chemical properties of minerals.
Subjects of interest include:
Relationships between atomic structure and crystalline state (structures of various states, crystal energies, crystal growth, thermodynamic studies, phase transformations, solid solution, exsolution phenomena, etc.)
General solid state spectroscopy (ultraviolet, visible, infrared, Raman, ESCA, luminescence, X-ray, electron paramagnetic resonance, nuclear magnetic resonance, gamma ray resonance, etc.)
Experimental and theoretical analysis of chemical bonding in minerals (application of crystal field, molecular orbital, band theories, etc.)
Physical properties (magnetic, mechanical, electric, optical, thermodynamic, etc.)
Relations between thermal expansion, compressibility, elastic constants, and fundamental properties of atomic structure, particularly as applied to geophysical problems.
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2 X-Ray and X-Ray Electron Spectroscopy

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7 Radiation Electron-Hole Centers (Free Radicals) in Minerals

1. Mössbauer (Nuclear Gamma-Resonance) Spectroscopy

1.1 Basic Principles and Experimental Arrangement

1.1.1 Isomer Nuclear Transitions and Gamma-Ray Emission

A nucleus, like an atom, has discreet (quantized) ground and excited levels, the transition from the upper to the lower level being accompanied by gamma-ray emission. Nuclear gamma emission line spectrum is similar in this respect to atomic optical emission spectrum occurring as a result of the transition from the upper to the lower electronic level.

The period during which the nucleus continues to stay in any excited state determines its mean lifetime. This is the time necessary for the transition from a given to the ground, or some other lower-lying excited level.

Two nuclei with equal charge and mass number, but in different excitation states with easily measurable lifetimes, are called isomer nuclei. By isomer states are understood excited states of a nucleus with a fairly long lifetime (typical values of the mean lifetimes of the isomer states of the nuclei used in the Mössbauer spectroscopy are 10^{-6}–10^{-10} s).

The isomer transitions that are used in Mössbauer spectroscopy are shown in Figure 1 for nuclei of iron, iridium and tin. Thus, gamma-emission of a Fe^{57} nucleus with energy of 14,400 eV occurs as a result of an isomer transition from the excited state of the Fe^{57} nucleus with a nuclear spin $I = 3/2$ (for this excited state), mean lifetime $\tau = 1.4 \cdot 10^{-7}$, and energy $E = 14{,}400$ eV to the ground state of a Fe^{57} nucleus with a nuclear spin $I = 1/2$. The nuclear spins of the ground and excited states determine the splitting of nuclear levels in crystalline fields, as well as in external electric and magnetic fields; the lifetimes determine the natural width of the lines.

Since in the case of Fe^{57} an isomer with energy of 14,400 eV has a lifetime of only about 10^{-7} s, in practice a radioactive cobalt isotope Co^{57} with a half-life of 270 days is taken as a source of gamma radiation; then through electron capture, Co^{57} transforms into an excited isomer Fe^{57}. Thus, following the cobalt decay, an iron isomer emitting gamma-rays emerges directly in the spectrometer.

Similarly, upon decay of radioactive osmium-191, iridium isomers emerge. In the case of tin, its isomer with a long lifetime (250 days) is used.

1.1.2 Resonance Fluorescence

1. Atomic (optical) resonance fluorescence. Should a vessel containing Na vapors under low pressure be irradiated by the light of the yellow line of the spectrum of

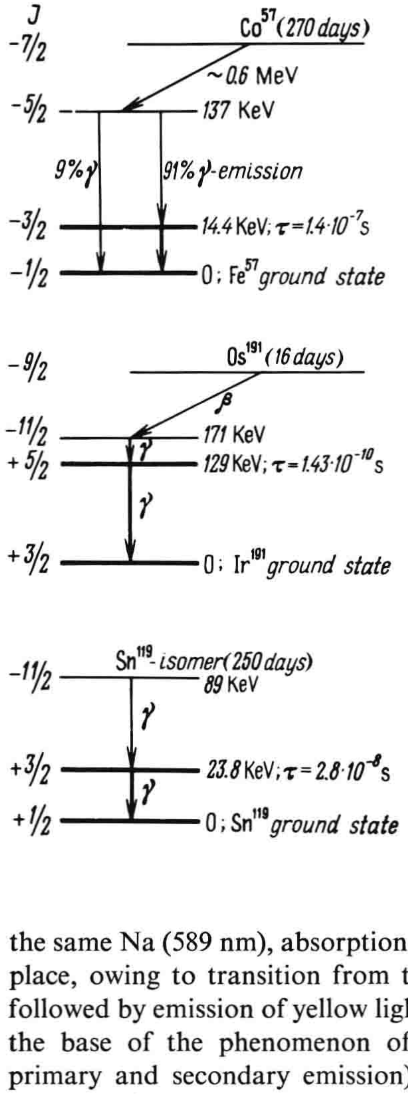

Fig. 1. Isomer transitions of the Fe^{57}, Ir^{191}, Sn^{119} nuclei. Shown are transitions whose gamma-emission is used in the Mössbauer spectroscopy: for $Fe^{57} = 14.4$ keV, for $Ir^{191} = 129.0$ keV and for $Sn^{119} = 23.8$ keV; τ is transition time determining the natural line width; I is nuclear spins in ground and excited states

the same Na (589 nm), absorption of this radiation by the Na vapors will then take place, owing to transition from the lower level $^2S_{1/2}$ to the upper one $^2P_{1/2,3/2}$, followed by emission of yellow light as a result of the reverse transition. This lies at the base of the phenomenon of resonance fluorescence (equal frequencies of primary and secondary emission).

2. Nuclear gamma-resonance fluorescence in the case of free atom nuclei. If Fe^{57} gamma emission, occurring as a result of an isomer transition from the level 3/2 with energy of 14,400 eV to the level 1/2 of the ground state (see Fig. 1), is directed against the free atom nuclei of the same Fe^{57}, there should then be observed the resonance fluorescence, due to transition from the ground state 1/2 to the same level of 3/2. This, however, does not happen.

3. The reason for the difference in conditions under which atomic (optical) and nuclear (gamma) resonance fluorescence are observed is as follows. The emission of a gamma quantum by the nucleus is followed by a nuclear recoil (as a barrel recoil after a shot), in which a part of the energy of the transition of the nucleus from the excitation to the ground level is spent. An equal amount of energy is spent in accelerating the absorption nucleus (absorber). Hence, the gamma-quantum energy fails to equal the difference between the absorption nucleus levels, but is lesser by

the amount of double energy of recoil. The latter is much greater than the width of the line, which is determined by the diffuseness of the excited level and, for this reason, conditions for resonance (equal energy difference between levels of the emitting and absorbing nuclei) are not complied with, and in this case no resonance gamma fluorescence is observed.

Thus for a Fe^{57} nucleus with emission energy of $E = 14{,}400$ eV, the recoil energy R is $0.19 \cdot 10^{-2}$ eV, and the line width[1] $\Gamma = 4.6 \cdot 10^{-9}$ eV.

In the case of the Na atom for the D line with $\lambda = 589$ nm (16.978 cm^{-1}) $E = 2.1$ eV, $R = 10^{-10}$ eV, $\Gamma = 4.4\ 10^{-8}$. Accordingly, here the line width is much smaller than the recoil energy ($2R \ll \Gamma$), and recoil does not stand in the way of resonance fluorescence. For the Fe^{57} nucleus that yields emission of a far greater energy, the recoil energy $2R$ is accordingly much higher than for Na atom (though it constitutes only a negligent part of the total emission energy), being by far in excess of the line width, i.e., $2R \gg \Gamma$. For this reason no resonance fluorescence occurs here.

1.1.3 Mössbauer Effect: a Recoilless Gamma-Fluorescence

It has been possible to eliminate nuclear recoil during emission and absorption of gamma quanta. The essence of the Mössbauer effect consists in placing a nucleus in a crystal, when the recoil impulse is borne not by a single nucleus but by the whole of the crystal lattice, the emission and absorption of gamma-quanta by nuclei thus fixed taking place with practically no energy losses in recoil. This permits it to obtain resonance gamma fluorescence as mentioned above and as exemplified in the case of Fe^{57}. To this end it suffices for the emitting nucleus (Fe^{57}, Os^{191}, Sn^{119} and others) and the absorber of the same composition to form only part of a solids.

Here, a major property of recoilless gamma emission becomes manifest, i.e., an extremely small width of the line by comparison with emission energy. Thus for Fe^{57} $\Gamma = 4.6 \cdot 10^{-9}$eV with gamma-emission energy $E = 14{,}400$ eV. The Γ/E ratio equals $3.2 \cdot 10^{-13}$. This means that the energy of the emission can be determined to an accuracy of the order of 10^{-13}. Because of this, recoilless gamma emission can be measured most exactly of all regions of the electromagnetic spectrum.

Doppler Velocity. Owing to the apparent difference in the energy of emitting and absorbing nuclei and disturbed resonance conditions, it is possible to record the slightest deviations in the chemical state of absorbers. The conditions of resonance have to be re-established in order to assess and measure all these deviations. This is accomplished by using the Doppler effect, whose essence consists in the emission source moving toward the observer at a velocity of v, and the emission energy increasing, while with the source moving away from the observer it diminishes by a value of $\Delta E = \pm v/c \cdot E$.

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[1] Conformable to Heisenberg's uncertainty relation $\tau\Gamma = h$, where τ is mean lifetime of the state; Γ is uncertainty of the excitation state energy that determines the width of the excitation state energy that determines the width of the excitation level, and consequently that of the line; $\hbar = h/2\pi$, where h is Planck's constant. For Fe^{57} $\tau = 1.4 \cdot 10^{-7}$ s (Fig. 1); $\hbar = 1.05 \cdot 10^{-27}$ erg. Hence $\Gamma = \hbar / \tau = 0.75 \cdot 10^{-20}$ erg $= 4.6 \cdot 10^{-9}$eV.

The difference in the emission and absorption nuclear energy can be offset by displacing the specimen (absorber) with varying speed relative to the source.

For the Fe^{57} nucleus, the speed of the relative motion of the absorber and the source $v = 1$ mm s^{-1} corresponds to an energy difference:

$$\Delta E = \pm \frac{1 \text{ mm s}^{-1}}{3 \cdot 10^{11} \text{ mm s}^{-1}} \cdot 14{,}400 \text{ eV} = 4.8 \cdot 10^{-8} \text{ eV}.$$

For Sn^{119} ($E = 23{,}800$ eV) 1 mm s^{-1} = $7.9 \cdot 10^{-8}$ eV; for I^{191} ($E = 129{,}000$ eV) 1 mm s^{-1} = $4.3 \cdot 10^{-7}$ eV.

1.1.4 Experimental Arrangement for Observing the Nuclear Gamma-Resonance (Mössbauer Spectrometer)

As with any other spectra, Mössbauer spectra are measured by using spectrometers consisting of an emission source, a specimen (absorber), and a detector of the resonant gamma-rays transmitted through (or emitted, or scattered by) the specimen (absorber). A necessary component for the Mössbauer effect is a system capable of moving the specimen (absorber) relative to the source (Fig. 2).

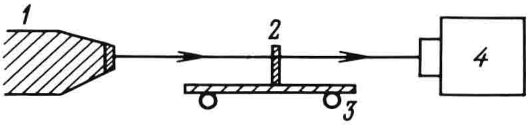

Fig. 2. Experimental arrangement for measuring the Mössbauer absorption spectrum. *1*, Source of gamma-emission; *2*, specimen containing the same nucleus as the source; 3, the motlon system; *4*, gammaquanta counter

The discovery of the Mössbauer effect has provided researchers with a source of monochromatic recoilless gamma emission. Radioactive isotopes, Co^{57}, for example, are embedded into metallic iron, stainless steel, platinum and other host matrices suitable for preparation of a given source of emission. According to patterns shown in Figure 1, they produce recoilless gamma emission.

A distinctive feature of Mössbauer spectra is the fact that a test specimen (absorber; in the form of powder or a monocrystal) reveals resonance fluorescence of the same nucleus (the same isotope) which is incorporated in the source and emits gamma-rays. Thus, by means of the Fe^{57} emission, it is possible to investigate only the ironmaking part of the specimen-absorber (Fe^{57} isotopic abundance is 2.17%), whereas to observe the spectrum of tin, a Sn^{119} source is needed, and so on.

The spectra of absorption, emission or scattering of gamma-rays by the specimen, can be measured but it is the absorption spectrum that is commonly measured.

Detecting is done by means of a gamma counter, whose basic component is usually NaI (Tl) scintillation crystal mounted on a photomultiplier tube, which converts weak light flashes into sufficiently strong electric pulses.

The specimen-absorber motion relative to the source (to equalize, by means of the Doppler effect, the energy of gamma quanta emitted by the source's nuclei and absorbed by the specimen), and the measurement of Doppler velocity of this motion are performed by using a carriage traveling at controlled speed. Depending on the latter, two types of spectrometer are distinguished: with constant velocity, and with constant acceleration. In the first the absorber moves with constant speed, and during displacement of the absorber, gamma quanta that enter the detector on traversing the absorber are counted. Thereupon, a new value for the velocity is recorded, the counting is repeated, and so on.

In the other type of spectrometer, the motion proceeds at a variable velocity, gradually and smoothly, increasing and decreasing in a set regularity. Special radio-technical devices—multichannel analyzers—accept the pulses and record the number of gamma quanta transmitted by the absorber during successive velocity intervals. Mechanical and electromechanical spectrometers are also distinguished, depending upon the mode of the motion.

Thus, the *Mössbauer spectrum is the velocity spectrum* and represents the number of gamma quanta recorded by the counter at different Doppler velocities of the absorber relative to the source.

The minimum of the gamma-quanta transmission and, accordingly, their maximum absorption by the specimen are in line with and correspond to the Doppler velocity at which the resonance absorption occurs. The velocity matching the maximum of absorption characterizes the degree of difference in the environment of the specimen's nucleus, and that of the source (when absorber and source nuclei are identical, the velocity at which maximum absorption is observed is nil). The values obtained for the maximum absorption shifts are relative and in this connection the source against which measurements are effected should be mentioned (for Fe^{57} in relation to a Fe^{57} source in stainless steel, for instance). The position of the absorption lines is usually indicated in terms of velocity in mm s^{-1}, or cm s^{-1}, but this can be easily rescaled in eV.

1.1.5 Development of the Method

The Mössbauer discovery was preceded by research into the possibilities offered by gamma-fluorescence of the free atom nuclei. First, gamma fluorescence could be obtained by means of Doppler acceleration of the emission source relative to the absorber, by centrifugation of the latter at a velocity of hundreds of m/s. Broadening of lines due to thermal vibrations (leading to Doppler shifting of the emission frequency and, consequently, to broadening of the lines) were also studied. Thus, the magnitude of nuclear recoil R with emission of a gamma quantum of Ir^{191} amounts to 0.05 eV, whereas the Doppler width of the line (due to thermal vibrations) is as great as 0.1 eV. Here, resonance fluorescence occurs in the case of free iridium atom nuclei.

While investigating resonant scattering of this isotope gamma emission, Mössbauer discovered in 1958 the phenomenon of nuclear recoilless gamma-resonance fluorescence, achieved by fixing the source and absorber nuclei in solids. Lamb's