Philipp Gütlich
Eckhard Bill
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Mössbauer Spectroscopy and Transition Metal Chemistry

Fundamentals and Applications

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Cover image: The picture shows a roman mask after restoration at the Roman-German Museum of Mainz. The mask originates from the roman aera and had fallen into many fragments which were found mixed together with fragments from other iron-containing items such as weapons. With the help of Mössbauer spectroscopy (^{57}Fe) the fragments belonging to the mask could be identified for successful restoration (P. Gütlich, G. Klingelhöfer, P. de Souza, unpublished).

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Preface

More than five decades have passed since the young German physicist Rudolf L. Mössbauer discovered the *recoilless nuclear resonance (absorption) fluorescence of γ-radiation*. The spectroscopic method based on this resonance effect – referred to as Mössbauer spectroscopy – has subsequently developed into a powerful tool in solid-state research. The users are chemists, physicists, biologists, geologists, and scientists from other disciplines, and the spectrum of problems amenable to this method has become extraordinarily broad. Up to now, more than 60,000 reports have appeared in the literature dealing with applications of the Mössbauer effect in the characterization of a vast variety of materials. Besides many workshops, seminars, and symposia, a biannual conference series called The International Conference on the Applications of the Mössbauer Effect (ICAME) started in 1960 (Urbana, USA) and regularly brings together scientists who are actively working on fundamental – as well as industrial – applications of the Mössbauer effect. Undoubtedly, Mössbauer spectroscopy has taken its place as an important analytical tool among other physical methods of solid-state research. By the same token, high-level education in solid-state physics, chemistry, and materials science in the broadest sense is strongly encouraged to dedicate sufficient space in the curriculum to this versatile method. The main objective of this book is to assist the fulfillment of this purpose.

Many monographs and review articles on the principles and applications of Mössbauer spectroscopy have appeared in the literature in the past. However, significant developments regarding instrumentation, methodology, and theory related to Mössbauer spectroscopy, have been communicated recently, which have widened the applicability and thus, merit in our opinion, the necessity of updating the introductory literature. We have tried to present a state-of-the-art book which concentrates on teaching the fundamentals, using theory as much as needed and as little as possible, and on practical applications. Some parts of the book are based on the first edition published in 1978 in the Springer series “Inorganic Chemistry Concepts” by P. Gütlich, R. Link, and A.X. Trautwein. Major updates have been included on practical aspects of measurements, on the computation of Mössbauer parameters with modern quantum chemical techniques (special chapter by guest-authors F. Neese and T. Petrenko), on treating magnetic relaxation phenomena (special chapter by guest-author S. Morup), selected applications in coordination chemistry, the use of synchrotron radiation to observe nuclear forward scattering (NFS) and inelastic scattering (NIS), and on the miniaturization of a Mössbauer spectrometer for mobile spectroscopy in space and on earth (by guest-authors G. Klingelhöfer and Iris Fleischer).

The first five chapters are directed to the reader who is not familiar with the technique and deal with the basic principles of the recoilless nuclear resonance and essential aspects concerning measurements and the hyperfine interactions between nuclear moments and electric and magnetic fields. Chapter 5 by guest-authors F. Neese and T. Petrenko focuses on the computation and interpretation of Mössbauer parameters such as isomer shift, electric quadrupole splitting, and magnetic dipole splitting using modern DFT methods. Chapter 6, written by guest-author S. Morup, describes how magnetic relaxation phenomena can influence the shape of (mainly ^{57}Fe) Mössbauer spectra. Chapter 7 presents an up-to-date summary of the work on all Mössbauer-active transition metal elements in accordance with the title of this book. This chapter will be particularly useful for those who are actively concerned with Mössbauer work on noniron transition elements. We are certainly aware of the large amount of excellent Mössbauer spectroscopy involving other Mössbauer isotopes, for example, ^{119}Sn, ^{121}Sb, and many of the rare earth elements, but the scope of this volume precludes such extensive coverage. We have, however, decided to describe and discuss some special applications of ^{57}Fe Mössbauer spectroscopy in Chap. 8. This is mainly based on work from our own laboratories and we include these to give the reader an impression of the kind of problems that can be examined by Mössbauer spectroscopy. In Chap. 8, we give examples from studies of spin crossover compounds, systems with biological relevance, and the application of a miniaturized Mössbauer spectrometer in NASA missions to the planet Mars as well as mobile Mössbauer spectroscopy on earth. Finally, Chap. 9 is devoted to the most recent developments in the use of synchrotron radiation for nuclear resonance scattering (NRS), both in forward scattering (NFS) for measuring hyperfine interactions and inelastic scattering (NIS) for recording the density of local vibrational states.

A CD-ROM is attached containing a teaching course of Mössbauer spectroscopy (ca. 300 ppt frames), a selection of examples of applications of Mössbauer spectroscopy in various fields (ca. 500 ppt frames), review articles on computation and interpretation of Mössbauer parameters using modern quantum-mechanical methods, list of properties of isotopes relevant to Mössbauer spectroscopy, appendices refering to book chapters, and the first edition of this book which appeared in 1978. In subsequent printruns files are available via springer.extra.com (see imprint page).

The authors wish to express their thanks to the *Deutsche Forschungsgemeinschaft*, the *Bundesministerium für Forschung und Technologie, the Max Planck-Gesellschaft*

and the *Fonds der Chemischen Industrie* for continued financial support of their research work in the field of Mössbauer spectroscopy. We are very much indebted to Dr. M. Seredyuk, Dr. H. Paulsen, and Mrs. P. Lipp, for technical assistance, and to Professor Frank Berry, for critical reading of the manuscript, and to Dr. B.W. Fitzsimmons for assistance in the proof-reading.

Mainz, Mülheim, Lübeck, November 2010 Philipp Gütlich, Eckhard Bill,
Alfred X. Trautwein

Contents

Chapter 1
Introduction

Some 50 years ago, Rudolf L. Mössbauer, while working on his doctoral thesis under Professor Maier-Leibnitz at Heidelberg/Munich, discovered *the recoilless nuclear resonance absorption (fluorescence) of γ rays*, which subsequently became known as the *Mössbauer effect* [1–3]. Some three decades before this successful discovery, Kuhn had speculated on the possible observation of the nuclear resonance absorption of γ-rays [4] similar to the analogous optical resonance absorption which had been known since the middle of the nineteenth century. The reason that nuclear resonance absorption (or fluorescence) was so difficult to observe was clear. The relatively high nuclear transition energies on the order of 100 keV impart an enormous recoil effect on the emitting and absorbing nuclei, such recoil energies being up to five orders of magnitude larger than the γ-ray line width. As a consequence, the emission and absorption lines are shifted away from each other by a very large distance, that is, some 10^5 times the line width, and the resonance overlap between the emission and absorption line is therefore no longer possible. In optical resonance absorption, the electronic transition energies are much smaller, typically of only a few electron volts, and hence the resultant recoil energy loss is negligibly small such that the emission and absorption lines are hardly shifted and can readily overlap. Several research groups had tried to compensate for the nuclear recoil energy loss by making use of the Doppler effect. Moon mounted the radioactive source on a centrifuge and moved it with suitably high velocity towards the absorber [5]. Malmfors heated both the source and the absorber in order to broaden the line widths, leading to a higher degree of overlap of emission and absorption lines [6]. In both cases, a very small but measurable resonance effect was observed. Mössbauer's procedure, in order "to attack the problem of recoil-energy loss at its root in a manner which, in general, ensures the complete elimination of this energy loss," as he said [7], was fundamentally different from the methods described by Moon and Malmfors. The basic feature of his method was that the resonating nuclei in the source and absorber were bound in crystals. He employed radioactive sources which emitted 129 keV γ-quanta leading to the ground state of ^{191}Ir. His first experiment aimed at measuring the lifetime of the 129 keV state of ^{191}Ir using an experimental arrangement similar to that of Malmfors. However, instead of

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increasing the temperature as in the Malmfors experiment, Mössbauer decided to decrease the temperature because he believed that chemical binding in the crystal could play a decisive role in absorbing the recoil effect, particularly at lower temperatures. The results of his experiments were most spectacular: the nuclear resonance effect increased tremendously on lowering the temperature [1–3]. Not only was the *recoilless nuclear resonance absorption (fluorescence)* experimentally established but also theoretically rationalized on quantum mechanical grounds. The key features in his interpretation are twofold: (1) part of the nuclear recoil energy is imparted onto the whole crystal instead of a freely emitting and absorbing atom; this part becomes negligibly small because of the huge mass of a crystal in comparison to a single atom; (2) the other part of the recoil energy is converted into vibrational energy. Due to the quantization of the lattice phonon system, there is a certain probability, which is high for hard materials such as metals and lower for soft materials such as chemical compounds, that lattice oscillators do not change in vibrational energy (*zero-phonon-processes*) on the emission and absorption of γ-rays. For this probability, known as the Lamb–Mössbauer factor, the emission and absorption of γ-rays takes place entirely radiationless. Rudolf Mössbauer received the Nobel Prize in Physics at the age of 32 for this brilliant achievement.

The nuclear resonance phenomenon rapidly developed into a new spectroscopic technique, called Mössbauer spectroscopy, of high sensitivity to energy changes on the order of 10^{-8} eV (ca. 10^{-4} cm^{-1}) and extreme sharpness of tuning (ca. 10^{-13}). In the early stages, Mössbauer spectroscopy was restricted to low-energy nuclear physics (e.g., determination of excited state lifetimes and nuclear magnetic moments). After Kistner and Sunyar's report on the observation of a "chemical shift" in the quadrupolar perturbed magnetic Mössbauer spectrum of α-Fe_2O_3 [8], it was immediately realized that the new spectroscopic method could be particularly useful in solid state research, solving problems in physics, chemistry, metallurgy, material- and geo-sciences, biology, archeology, to name a few disciplines. It now transpires that the largest portion of the more than 60,000 papers on Mössbauer spectroscopic studies published to date deal with various kinds of problems arising from, or directly related to, the electronic shell of Mössbauer active atoms in metals and nonconducting materials, for example, magnetism, electronic fluctuations, relaxation processes, electronic and molecular structure, and bond properties. Such properties are characteristic of different materials (compounds, metals, alloys, etc.) and are the basis for nondestructive chemical analysis. The method, therefore, serves as a kind of "fingerprint" technique.

Up to the present time, the Mössbauer effect has been observed with nearly 100 nuclear transitions in about 80 nuclides distributed over 43 elements (cf. Fig. 1.1). Of course, as with many other spectroscopic methods, not all of these transitions are suitable for actual studies, for reasons which we shall discuss later. Nearly 20 elements have proved to be suitable for practical applications. It is the purpose of the present book to deal only with Mössbauer active transition elements (Fe, Ni, Zn, Tc, Ru, Hf, Ta, W, (Re), Os, Ir, Pt, Au, Hg). A great deal of space will be devoted to the spectroscopy of ^{57}Fe, which is by far the most extensively used Mössbauer nuclide of all. We will not discuss the many thousands of reports on ^{57}Fe

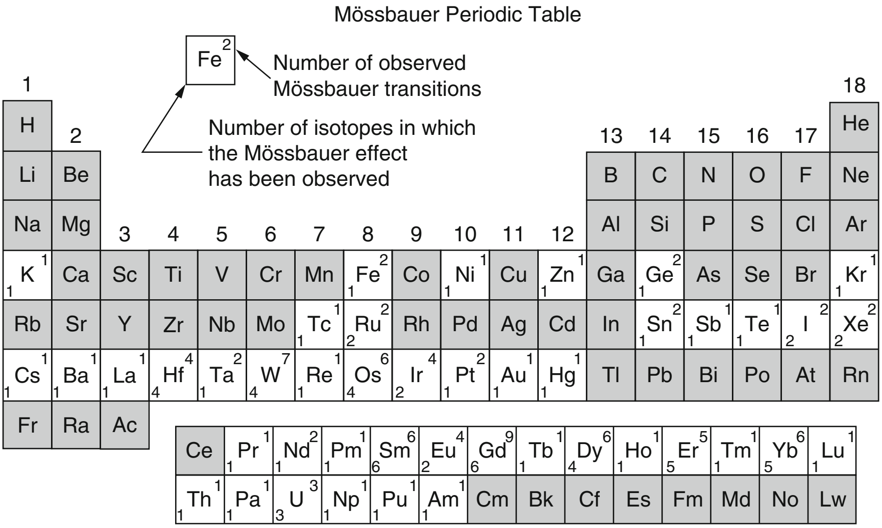

Fig. 1.1 Periodic table of the elements; those in which the Mössbauer effect has been observed are marked appropriately. (Taken from the 1974 issue of [10])

spectroscopy that have been published so far. Instead, we endeavor to introduce the reader to the various kinds of chemical information one can extract from the electric and magnetic hyperfine interactions reflected in the Mössbauer spectra. Particular emphasis will be put on the interpretation of bonding and structural properties in connection with electronic structure theories.

A CD-ROM (arranged in power-point format) is attached to the book. The first part of it contains lecture notes by one of the authors (P.G.) covering the fundamentals of Mössbauer spectroscopy, the hyperfine interactions and selected applications in various fields. This part of the CD (ca. 300 frames) is primarily arranged for teaching purposes. The second part of the CD (nearly 500 frames) contains examples of the applications of Mössbauer spectroscopy in physics, chemistry, biology, geoscience, archeology, and industrial applications. These examples are contributions from different laboratories and describe Mössbauer effect studies which, from our point of view, demonstrate the usefulness of the relatively new method. Those who are further interested in using Mössbauer spectroscopy in their research work may consult the many original reports as compiled in the Mössbauer Effect Data Index [9, 10], the Mössbauer Effect Reference and Data Journal [11], and relevant books [12–44].

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Chapter 2
Basic Physical Concepts

Mössbauer spectroscopy is based on recoilless emission and resonant absorption of γ-radiation by atomic nuclei. The aim of this chapter is to familiarize the reader with the concepts of nuclear γ-resonance and the Mössbauer effect, before we describe the experiments and relevant electric and magnetic hyperfine interactions in Chaps. 3 and 4. We prefer doing this by collecting formulae without deriving them; comprehensive and instructive descriptions have already been given at length in a number of introductory books ([7–39] in Chap. 1). Readers who are primarily interested in understanding their Mössbauer spectra without too much physical ballast may skip this chapter at first reading and proceed directly to Chap. 4. However, for the understanding of some aspects of line broadening and the preparation of optimized samples discussed in Chap. 3, the principles described here might be necessary.

2.1 Nuclear γ-Resonance

Most readers are familiar with the phenomenon of resonant absorption of electromagnetic radiation from the observation of light-induced electronic transitions. Visible light from a white incident beam is absorbed at exactly the energies of the splitting of *d*-electrons in transition metal ions or at the energies corresponding to metal-to-ligand charge transfer transitions in coordination compounds. These are the most common causes of color in inorganic complexes. Only when the quantum energy of the light matches the energy gap between the electronic states involved does such resonant absorption occur.

An analogous process is possible for γ-radiation, for which nuclear states are involved as emitters and absorbers. In such experiments, the emission of the γ-rays is mostly triggered by a preceding decay of a radioactive precursor of the resonance nuclei with Z protons and N neutrons (Fig. 2.1). The nuclear reaction (α-, or β-decay, or K-capture) yields the isotope (Z, N) in the excited state (e) with energy E_e. The excited nucleus has a limited mean lifetime τ and will undergo a transition to its ground state (g) of energy E_g, according to the exponential law of decay. This leads,

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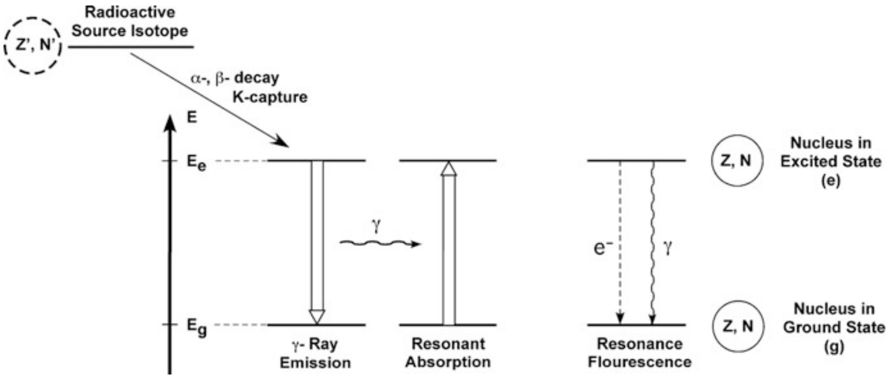

Fig. 2.1 Nuclear resonance absorption of γ-rays (Mössbauer effect) for nuclei with Z protons and N neutrons. The top left part shows the population of the excited state of the emitter by the radioactive decay of a mother isotope (Z', N') via α- or β-emission, or K-capture (depending on the isotope). The right part shows the de-excitation of the absorber by re-emission of a γ-photon or by radiationless emission of a conversion electron (thin arrows labeled "γ" and "e^-", respectively)

with a certain probability, to the emission of a γ-photon,[1] which has the quantum energy $E_0 = E_e – E_g$ if the process occurs without recoil. Under this, and certain other conditions which we shall discuss below, the γ-photon may be reabsorbed by a nucleus of the same kind in its ground state, whereby a transition to the excited state of energy E_e takes place. The phenomenon, called *nuclear resonance absorption of γ-rays*, or *Mössbauer effect*, is described schematically in Fig. 2.1.

Resonant γ-ray absorption is directly connected with *nuclear resonance fluorescence*. This is the re-emission of a (second) γ-ray from the excited state of the absorber nucleus after resonance absorption. The transition back to the ground state occurs with the same mean lifetime τ by the emission of a γ-ray in an arbitrary direction, or by energy transfer from the nucleus to the K-shell via internal conversion and the ejection of conversion electrons (see footnote 1). *Nuclear resonance fluorescence* was the basis for the experiments that finally led to R. L. Mössbauer's discovery of nuclear γ-resonance in ^{191}Ir ([1–3] in Chap. 1) and is the basis of Mössbauer experiments with synchrotron radiation which can be used instead of γ-radiation from classical sources (see Chap. 9).

In order to understand the Mössbauer effect and the importance of recoilless emission and absorption, one has to consider a few factors that are mainly related to the fact that the quantum energy of the γ-radiation used for Mössbauer spectroscopy ($E_0 \approx$ 10–100 keV) is much higher than the typical energies encountered, for instance, in optical spectroscopy (1–10 eV). Although the absolute widths of the

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[1] Not all nuclear transitions of this kind produce a detectable γ-ray; for a certain portion, the energy is dissipated by internal conversion to an electron of the K-shell which is ejected as a so-called conversion electron. For some Mössbauer isotopes, the total internal conversion coefficient α_T is rather high, as for the 14.4 keV transition of ^{57}Fe ($\alpha_T = 8.17$). α_T is defined as the ratio of the number of conversion electrons to the number of γ-photons.

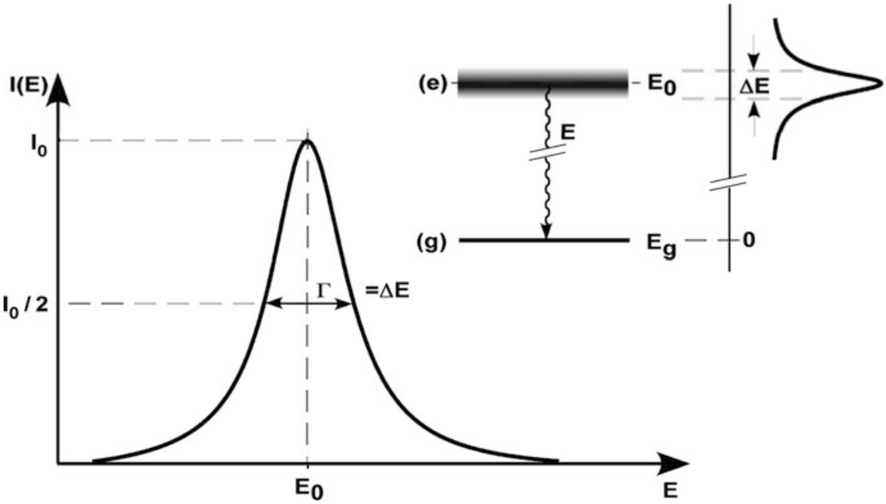

Fig. 2.2 Intensity distribution $I(E)$ for the emission of γ-rays with mean transition energy E_0. The Heisenberg natural line width of the distribution, $\varGamma = \hbar/\tau$, is determined by the mean lifetime τ of the excited state (e)

energy levels involved in both spectroscopies are rather similar ([15] in Chap. 1), the *relative* widths of the nuclear levels are very small because of the high mean energies ($\Delta E/E_0 \approx 10^{-13}$ or less, see Fig. 2.2). Consequently, the *recoil* connected with any emission or absorption of a photon is a particular problem for nuclear transitions in gases and liquids, because the energy loss for the γ-quanta is so large that emission and absorption lines do not overlap and nuclear γ-resonance is virtually impossible. Thermal motion and the resulting *Doppler* broadening of the γ-lines are another important aspect. R. L. Mössbauer showed that, for nuclei fixed in solid material, a substantial fraction *f* of photons, termed the Lamb–Mössbauer factor, are emitted and absorbed without measurable recoil. The corresponding γ-lines show natural line widths without thermal broadening.

2.2 Natural Line Width and Spectral Line Shape

The energy E_0 of a nuclear or electronic excited state of mean lifetime τ cannot be determined exactly because of the limited time interval Δt available for the measurement. Instead, E_0 can only be established with an inherent uncertainty, ΔE, which is given by the Heisenberg uncertainty relation in the form of the conjugate variables energy and time,

$$\Delta E \ \Delta t \geqslant \hbar, \tag{2.1}$$

where $h = 2\pi\hbar =$ Planck's constant.

The relevant time interval is on the order of the mean lifetime, $\Delta t \approx \tau$. Consequently, ground states of infinite lifetime have zero uncertainty in energy.

As a result, the energy E of photons emitted by an ensemble of identical nuclei, rigidly fixed in space, upon transition from their excited states (e) to their ground states (g), scatters around the mean energy $E_0 = E_e - E_g$. The intensity distribution of the radiation as a function of the energy E, the *emission line*, is a Lorentzian curve as given by the Breit–Wigner equation [1]:

$$I(E) = \frac{\Gamma/(2\pi)}{(E - E_0)^2 + (\Gamma/2)^2}. \tag{2.2}$$

The emission line is centered at the mean energy E_0 of the transition (Fig. 2.2). One can immediately see that $I(E) = 1/2\ I(E_0)$ for $E = E_0 \pm \Gamma/2$, which renders Γ the full width of the spectral line at half maximum. Γ is called the *natural width* of the nuclear excited state. The emission line is normalized so that the integral is one: $\int I(E)\mathrm{d}E = 1$. The probability distribution for the corresponding absorption process, the *absorption line,* has the same shape as the emission line for reasons of time-reversal invariance.

Weisskopf and Wigner [2] have shown that the natural width of the emission and the absorption line is readily determined by the mean lifetime τ of the excited state because of the relation (note the equal sign):

$$\Gamma\tau = \hbar. \tag{2.3}$$

The ratio Γ/E_0 of width Γ and the mean energy of the transition E_0 defines the precision necessary in nuclear γ-absorption for "tuning" emission and absorption into resonance. Lifetimes of excited nuclear states suitable for Mössbauer spectroscopy range from $\sim 10^{-6}$ s to $\sim 10^{-11}$ s. Lifetimes longer than 10^{-6} s produce too narrow emission and absorption lines such that in a Mössbauer experiment they cannot overlap sufficiently because of experimental difficulties (extremely small Doppler velocities of $<\mu\mathrm{m\ s}^{-1}$ are required). Lifetimes shorter than 10^{-11}s are connected with transition lines which are too broad such that the resonance overlap between them becomes smeared and no longer distinguishable from the base line of a spectrum. The first excited state of ^{57}Fe has a mean lifetime of $\tau = t_{1/2}/\ln 2 = 1.43 \cdot 10^{-7}$ s; and by substituting $\hbar = 6.5826 \cdot 10^{-16}$ eV s, the line width Γ evaluates to $4.55 \cdot 10^{-9}$ eV.

2.3 Recoil Energy Loss in Free Atoms and Thermal Broadening of Transition Lines

In the description of nuclear γ-resonance, we assume that the photon emitted by a nucleus of mean energy $E_0 = E_e - E_g$ carries the entire energy, $E_\gamma = E_0$. This is not true for nuclei located in free atoms or molecules, because the photon has

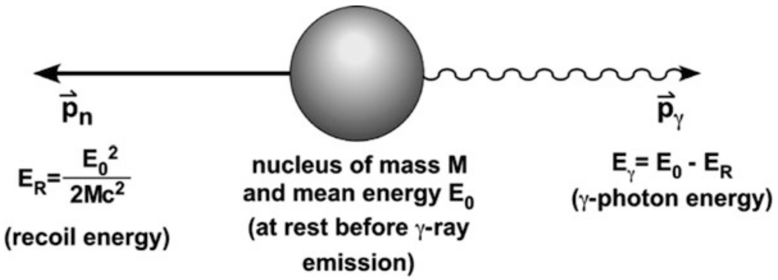

Fig. 2.3 Recoil momentum $\vec{p}_\mathrm{n}$ and energy E_R imparted to a free nucleus upon γ-ray emission

momentum. When a photon is emitted from a nucleus of mass M, recoil is imparted to the nucleus and consequently the nucleus moves with velocity υ in a direction opposite to that of the γ-ray propagation vector (see Fig. 2.3).

Suppose the nucleus was at rest before the decay, it takes up the recoil energy

$$E_\mathrm{R} = \frac{1}{2}M\upsilon^2. \tag{2.4}$$

Momentum conservation requires that

$$p_\mathrm{n} = -p_\gamma, \tag{2.5}$$

where p_n ($= M\upsilon$) and p_γ are the linear momenta of the nucleus and the γ-photon, respectively, and c is the velocity of light. The momentum p_γ of the (mass-less) photon is given by its quantum energy:

$$p_\gamma = -E_\gamma/c, \quad \text{with} \tag{2.6}$$

$$E_\gamma = E_0 - E_\mathrm{R}. \tag{2.7}$$

Because of the large mass of the nucleus and the low recoil velocity involved, we may use the nonrelativistic approximation

$$E_\mathrm{R} = \frac{1}{2}M\upsilon^2 = \frac{(M\upsilon)^2}{2M} = \frac{p_\mathrm{n}^2}{2M} = \frac{E_\gamma^2}{2Mc^2}. \tag{2.8}$$

Since E_R is very small compared to E_0, it is reasonable to assume that $E_\gamma \approx E_0$, so that we may use the following elementary formula for the recoil energy of a nucleus in an isolated atom or molecule:

$$E_\mathrm{R} = \frac{E_0^2}{2Mc^2}. \tag{2.9}$$

By substituting numerical values for c and $M = m_{\mathrm{n/p}} \cdot A$ one obtains

$$E_{\mathrm{R}} = 5.37 \cdot 10^{-4} \frac{E_0^2}{A}\ \mathrm{eV}, \tag{2.10}$$

where $m_{\mathrm{n/p}}$ is the mass of a nucleon (proton or neutron), A is the mass number of the Mössbauer isotope, and E_0 is the transition energy in keV. For example, for the Mössbauer transition between the first excited state and the ground state of ^{57}Fe ($E_0 = E_{\mathrm{e}}$–$E_{\mathrm{g}} = 14.4$ keV), E_{R} is found to be $1.95 \cdot 10^{-3}$ eV. This value is about six orders of magnitude larger than the natural width of the transition under consideration ($\Gamma = 4.55 \cdot 10^{-9}$ eV).

The recoil effect causes an energy shift of the emission line from E_0 to smaller energies by an amount E_{R}, whereby the γ-photon carries an energy of only $E_\gamma = E_0 - E_{\mathrm{R}}$. However, a recoil effect also occurs in the absorption process so that the photon, in order to be absorbed by a nucleus, requires the total energy $E_\gamma = E_0 + E_{\mathrm{R}}$ to make up for the transition from the ground to the excited state and the recoil effect (for which $\vec{p}_{\mathrm{n}}$ and $\vec{p}_\gamma$ will have the same direction).

Hence, nuclear resonance absorption of γ-photons (the Mössbauer effect) is not possible between free atoms (at rest) because of the energy loss by recoil. The deficiency in γ-energy is two times the recoil energy, $2E_{\mathrm{R}}$, which in the case of ^{57}Fe is about 10^6 times larger than the natural line width Γ of the nuclear levels involved (Fig. 2.4).

In real gases and liquids, however, atoms are never at rest. If γ-emission takes place while the nucleus (or atom) is moving at velocity υ_{n} in the direction of the γ-ray propagation, the γ-photon of energy E_γ is modulated by the Doppler energy E_{D} [3]:

$$E_{\mathrm{D}} = \frac{\upsilon_{\mathrm{n}}}{c} E_\gamma, \tag{2.11}$$

which adds to E_γ:

$$E_\gamma = E_0 - E_{\mathrm{R}} + E_{\mathrm{D}}. \tag{2.12}$$

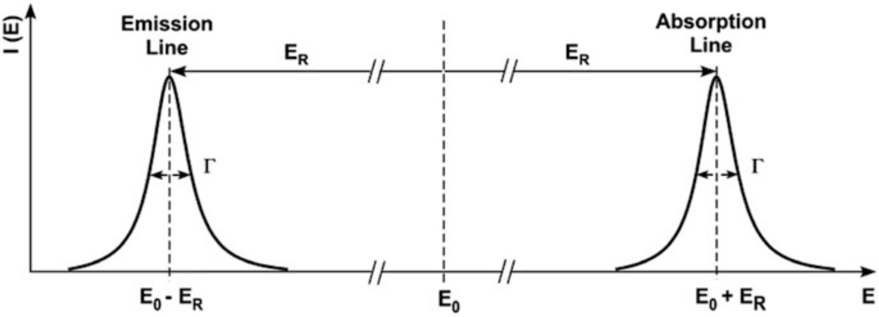

Fig. 2.4 Energy separation of γ-emission and absorption lines caused by recoil of resting free nuclei ($2E_{\mathrm{R}} \approx 10^6 \Gamma$, note the three separate sections of the energy scale). Since there is virtually no overlap between emission and absorption line, resonant absorption is not possible

Kinetic gas theory predicts a broad variation of velocities in gases, which for an ideal gas obeys the classical Maxwell distribution [3]. At normal temperature and pressure, the average time between collisions of the gas particles is so long (10^{-9}–10^{-10} s) that a typical Mössbauer isotope during its mean lifetime of about 10^{-9} s hardly experiences changes in motion. Relevant to the Doppler shift imparted to a certain γ-emission therefore is the component of the nuclear motion parallel or antiparallel to $\vec{p}_\gamma$. The large variety of possible results, with E_D possibly being positive or negative, leads to a wide statistical scattering of γ-energies, the so-called *Doppler broadening* of the transition line. The distribution has its maximum at $E_\mathrm{D} = 0$, which is plausible since all motions with a net velocity vector close to $\vec{\upsilon}_\mathrm{n} \perp \vec{p}_\gamma$ contribute virtually nothing to the energy of the photon, $E_\mathrm{D} \approx 0$. For sufficiently high γ-energies (large recoil energies) and fast kinetic motion, the shape of the recoil-shifted and Doppler-broadened emission and absorption lines for free atoms and molecules can be approximated by a Gaussian distribution. A derivation of the subject is given in ([15] in Chap. 1). There it is also shown that the width of the Doppler broadening can be given in terms of the recoil shift E_R of the γ-energy and the average kinetic energy ½kT of the gas particles at temperature T:

$$\Gamma_\mathrm{D} = 2\sqrt{E_\mathrm{R} \cdot kT}. \tag{2.13}$$

The Doppler broadening Γ_D is of the order of E_R or larger. For ^{57}Fe with $E_0 = 14.4$ keV and $E_\mathrm{R} = 1.95 \cdot 10^{-3}$ eV, for instance, it exceeds E_R by a factor of 5: $\Gamma_\mathrm{D} \approx 10^{-2}$ eV at 300 K. Thus, there must be a finite probability for nuclei in gases and liquids to compensate for the recoil loss E_R of the photon by the Doppler shift E_D. The strength of the absorption and the shape of the absorption line are mathematically obtained from folding the overlapping emission and absorption lines. Since the line amplitudes are very small (the area of the broadened lines is the same as that of the sharp natural lines), the absorption probability is very small. Experimentally, it is difficult to detect nuclear γ-resonance in gases and liquids at all, except for very viscous fluids. For practical applications, it is more important that the usual Doppler modulation of the γ-radiation, as it is used as the "drive" system in classical Mössbauer spectroscopy (see Fig. 2.6), does not affect γ-absorption in gases and liquids. Motions with velocities of a few millimeters per second are negligible because of the extreme line broadening in nonsolid samples, which is more than 10^6 times the natural width Γ.

2.4 Recoil-Free Emission and Absorption

The arguments seen in section 2.3 suggest that resonant γ-absorption should decrease at very low temperatures because the Doppler broadening of the γ-lines decreases and may even drop below the value of the recoil energy. In his experiments with solid sources and absorbers, however, R.L. Mössbauer ([1] in Chap. 1) observed on the contrary a dramatic increase in resonant absorption when the temperature approached that of liquid nitrogen. The correct explanation of this effect is found in the quantized nature of vibrations in solids ([1–3] in Chap. 1) [4]. In the following, we shall briefly illustrate the corresponding principles by means of a simple model. More information on this topic is found in Chap. 9 on Mössbauer spectroscopy with synchrotron radiation and nuclear inelastic scattering.

In the solid state, the Mössbauer active nucleus is more or less rigidly bound to its environment and not able to recoil freely, but it can vibrate within the framework of the chemical bonds of the Mössbauer atom. The effective vibration frequencies are of the order of $1/\tau_{\mathrm{vib}} \approx 10^{13}\mathrm{s}^{-1}$ ([15] in Chap. 1). Since, under this condition, the mean displacement of the nucleus essentially averages to zero during the time of the nuclear transitions, $\tau \approx 10^{-7}$ s, there is, firstly, no Doppler broadening of the γ-energy and, secondly, the recoil momentum can only be taken up by the "crystallite" as a whole: $p = M_{\mathrm{crystal}}\upsilon$. The induced velocity υ of the emitter in this case is vanishing because of the large mass of the system (even the finest "nano"-particles may contain 10^{14} atoms or molecules) and, hence, the corresponding recoil energy $E_{\mathrm{R}} = 1/2M_{\mathrm{crystal}}\upsilon^2$ of translational motion is negligible.

Instead, part of the energy E_0 of the nuclear transition can be transferred to the lattice vibrational system if the recoil excites a lattice vibration, a so-called phonon. Alternatively, a phonon can also be annihilated by the nuclear event. In either case, the corresponding energy deficit or excess of the emitted γ-quantum, E_{vib}, is again orders of magnitude larger than the natural line width Γ of the nuclear levels. Nuclear γ-resonance absorption is therefore not possible if phonon excitation or annihilation is involved. However, a quantum mechanical description of the nucleus and its vibrational environment includes a certain finite probability f for so-called zero-phonon processes. The factor f, also known as the Lamb–Mössbauer factor, denotes the fraction of γ-emissions or absorptions occurring without recoil, the *recoil-free fraction*. It is in fact equivalent to the Debye–Waller factor for Bragg X-ray scattering by periodic lattices.[2] Characteristic f-values are, e.g., 0.91 for the 14.4 keV transition of ^{57}Fe in metallic iron at room temperature, and 0.06 for the 129 keV transition of ^{191}Ir in metallic iridium.

Independent of specific theoretical models for the phonon spectrum of a solid matrix, the recoil-free fraction can be given in terms of the γ-energy E_γ and the mean *local* displacement of the nucleus from its equilibrium position ([2] in Chap. 1) [5]:

$$f = \exp\left[-\langle x^2\rangle E_\gamma^2/(\hbar c)^2\right], \tag{2.14}$$

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[2] The Bragg scattering of X-rays by a periodic lattice in contrast to a Mössbauer transition is a collective event which is short in time as compared to the typical lattice vibration frequencies. Therefore, the mean-square displacement $\langle x^2\rangle$ in the Debye–Waller factor is obtained from the average over the ensemble, whereas $\langle x^2\rangle$ in the Lamb–Mössbauer factor describes a time average. The results are equivalent.