

The Mössbauer effect

(*Laboratory course*)

Márton Nagy, Spring 2020

1 Introduction

The *Mössbauer effect* is an interesting phenomenon lying in between solid state physics and nuclear physics. *Mössbauer spectroscopy*, the method based on it, is in a sense one of the most sensitive methods of investigation: for some gamma rays it can achieve a precision of up to 10^{-15} in the measurement of the change of their energies. Gamma rays are emitted by transitions of atomic nuclei between excited states (and/or their ground state); their energy carries the difference of the nuclear energy levels. Energy changes on the level of the mentioned accuracy, however, are so small that such fine differences in the nuclear energy levels can be caused by a number of „external” factors (e.g. the structure of the atomic shell configuration, thus in turn the chemical bond of the atom, as well as electric or magnetic field in the material, etc). For this reason Mössbauer spectroscopy can unveil such material science informations, by measuring the nuclear energy levels of some atoms in the sample with said precision.

The effect is interesting on its own, from a purely fundamental physical point of view. It makes possible e.g. to determine the natural line width of gamma transitions, as well as the changes in photon energies caused by the presence of gravitational field (called *gravitational redshift*); a prediction of general relativity being that photons lose energy (and frequency, in the spirit of $E = \hbar\omega$) when traveling against gravitational force.

Mössbauer spectroscopy is used routinely in applied research in chemistry and material science. On this laboratory course, we get familiarized with the basic phenomenon as well as study the properties of the Mössbauer spectra of some typical samples.

2 Resonant absorption: recoil, line width

The *emission spectrum* of matter in gas state can be observed by studying the electromagnetic radiation (light) emitted by heating the gas. The frequency distribution contains intensity maxima (=spectral lines; their frequency now known to be of characteristic of the various transitions between energy levels of the atom). The *absorption spectrum* is obtained by studying the frequency of the missing components of light with a continuous frequency distribution when transmitted through the gas.

The basic observation is that the emission and absorption spectral lines of gases are roughly the same: the lines can be identified as those ω frequencies where $\hbar\omega = E_2 - E_1$ holds, E_2 and E_1 being two energy levels of the atom (with $E_2 > E_1$). Transition between these levels emits radiation with the give frequency (leading to the emission spectrum), and the atom can absorb such frequency light by getting excited from the E_1 to the E_2 level, leading to the absorption spectrum. Generally speaking: gases *do* absorb their own light. In general, we speak of **resonant absorption** when radiation emitted by an energy level transition of a system (an atom, a molecule, or an atomic nucleus) is absorbed by an other instance of the same system in a reverse, excitation process between the same levels.

Recognizing the presence of spectral lines as well as the mentioned coincidence of emission and absorption lines was a first step towards the experimental basis of the discreteness of energy levels (and building on this, quantum mechanics). If, however, one got convinced that energy levels are *indeed* discrete, well-defined energy values, then at first thought it may seem paradoxical that resonant absorption can occur. Only part of the energy difference

between an excited state and the ground (or some lower excited) state gets carried away by the photon: a small but finite amount is carried away by the **recoil** of the emitting system (atom, nucleus, molecule), that was necessary because of momentum conservation. Similarly, for the absorption process: the photon energy needs to be a bit higher than the level difference, so that the „knock-on” energy of the the absorbing atom/molecule/nucleus gets covered.

The notations are: $\Delta \equiv E_2 - E_1$ is the difference of energy levels, E_γ is the energy of the emitted photon, R is the recoil energy, p is the recoil momentum of the atom or nucleus, M is its mass. Approximately $M \approx A \cdot 1 \text{ amu} \cdot c^2 = A \cdot 931.5 \text{ MeV}$, with amu being the atomic mass unit.¹ In all practical cases, i.e. transitions between nuclear as well as electronic energy levels (producing photons of a few MeV or a few eV energies, respectively) we have $\Delta \ll Mc^2$. The recoil motion is thus non-relativistic, and obviously $E_\gamma \ll Mc^2$ also holds. If the emitting atom is not bound and is at rest, then we have

$$p = \frac{E_\gamma}{c}, \quad R = \frac{p^2}{2M} \quad \Rightarrow \quad R = \frac{E_\gamma^2}{2Mc^2}. \quad \text{If } E_\gamma \ll Mc^2, \text{ then we indeed have } R \ll E_\gamma, \text{ and also } R \approx \frac{\Delta^2}{2Mc^2} \text{ can be written.} \quad (2.1)$$

So the R recoil energy is indeed a tiny fraction of Δ . With a similar reasoning one arrives at the result that during absorption, the energy needed for the knock-on of the resting target atom is expressed by the same $R = \frac{E_\gamma^2}{2Mc^2}$ formula.

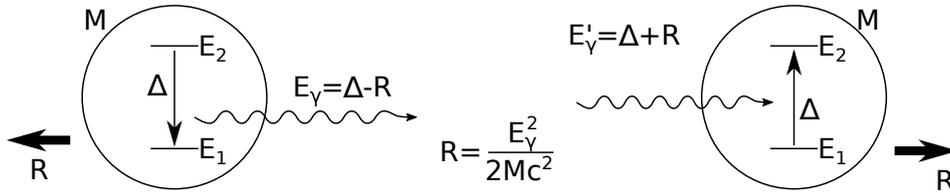


Figure 1: Illustration of the effect of recoil on resonant absorption: one might think at first that the photon does not have enough energy for the inverse process to occur.

If the atom has v velocity in the direction of the emission, then the energy (and frequency) of the emitted photon gets a **Doppler shift**. The modified photon energy E'_γ is:

$$\text{Doppler effect:} \quad E'_\gamma = \sqrt{\frac{c+v}{c-v}} E_\gamma. \quad \text{If } v \ll c, \text{ then the surplus energy is:} \quad \underline{\underline{\Delta E_\gamma = \frac{v}{c} E_\gamma.}} \quad (2.2)$$

We also have to consider that atoms are usually situated in a sample with finite temperature T , and thus have a thermal motion: some of the emitted photons gain and some of them lose energy because of the Doppler effect caused by the motion of the atoms. Practically, this has the result that the spectral line (photon energy distribution) from the $E_2 \rightarrow E_1$ transitions undergoes **Doppler broadening**. The line width Δ_{Doppler} corresponding to this is:²

$$\text{In gases:} \quad \underline{\underline{\Delta_{\text{Doppler}} = \sqrt{\frac{2k_B T}{Mc^2}}}}, \quad \text{since } \Delta_{\text{Doppler}} = \frac{\bar{v}}{c} E_\gamma, \quad \text{and } \bar{v} = \sqrt{\frac{2k_B T}{M}}. \quad (2.3)$$

In crystalline materials, where the quantum mechanical nature of the atomic motions comes in forefront, Doppler broadening has a different expression: approximately

$$\text{In solids:} \quad \Delta_{\text{Doppler}} = \sqrt{\frac{2k_B T_{\text{eff}}}{Mc^2}}, \quad T_{\text{eff}} \equiv \Theta f\left(\frac{T}{\Theta}\right). \quad \begin{array}{l} \text{for } x \gg 1, f(x) \approx x, \\ \text{for } x \approx 0, f(x) \neq 0. \end{array} \quad (2.4)$$

¹ The amu is approximately equal to the mass of a hydrogen atom or that of the proton; for order of magnitude estimations one needs only to remember that the corresponding energy is approximately 1 GeV.

² Only the component of the velocity that is parallel to the photon momentum has a role: the average of this component does not have a factor of 3.

The function f is a universal function (its exact form does not interest us here). The *Debye temperature* of the crystal, Θ , however, will come by again: this is the characteristic temperature of the quantum mechanical energy of crystal lattice vibrations. It is defined as:

$$\text{Debye temperature: } k_B\Theta = \hbar\bar{\omega}, \quad (2.5)$$

where $\bar{\omega}$ is some average frequency of crystal lattice vibrations.³

For resonant absorption, the bottom line is that the broadening of spectral lines can cover the recoil energy loss R . So:

$$\text{There can be resonant absorption, if } \Gamma \gtrsim 2R. \quad (2.6)$$

Roughly speaking, one has resonant absorption if the width of the lines is bigger than the recoil energy; in other words, the energy distribution of the emitted photons and of the absorption probability (which also broadens for the same reasons) sufficiently overlap.

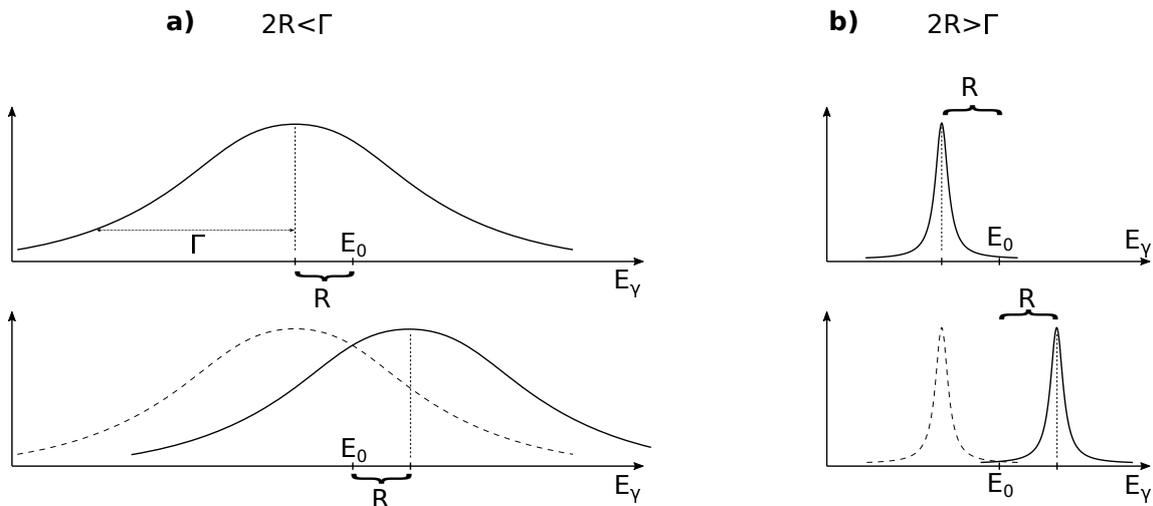


Figure 2: Illustration of the condition of resonant absorption (i.e. that the line width be bigger than the recoil energy loss). Photon energy distributions are on the top panels, while bottom panels show the absorption probabilities. On the left hand side, these overlap to a sufficient degree so resonant absorption may occur; on the right hand side they do not.

Apart from Doppler broadening, there is a purely quantum mechanical contribution to the width of spectral lines, which is of fundamental importance from the point of view of Mössbauer spectroscopy. This is the so called *natural line width*, denoted here by Γ_0 . If an excited state has a mean life time of τ , then⁴ the photon emitted by the de-excitation will not have a definite energy. The energy uncertainty will be $\Gamma_0 = \frac{\hbar}{\tau}$, and the energy distribution becomes a *Lorentzian distribution* (also called *Cauchy distribution*) around its mean value:

$$\Gamma_0 = \frac{\hbar}{\tau}, \quad p(E) = \frac{2}{\pi\Gamma_0} \cdot \frac{1}{1 + \left(\frac{E-E_0}{\Gamma_0/2}\right)^2}, \quad (2.7)$$

with E_0 being the expectation value corresponding to the nominal energy difference of the levels (minus recoil energy). The above formula is basically a realization of the *energy-time*

³ In the Debye model of the vibrational frequency spectrum one has $\bar{\omega} = \bar{c}_s \cdot \sqrt[3]{6\pi^2 N/V}$, where N/V is the number density of atoms, and \bar{c}_s is the average speed of sound. The meaning of $\bar{\omega}$ is more or less that of the frequency of sound waves whose wavelength is the average distance between atoms. Remember, in solids the speed of sound is usually different for longitudinal and transversal waves (c_l and c_t , respectively); the density of states will be properly accounted for if one defines \bar{c}_s to be $3/\bar{c}_s^3 = 2/c_l^3 + 1/c_t^3$.

⁴ Life time (τ) and half-life ($T_{1/2}$) are related as $T_{1/2} = \tau \cdot \ln 2$. Remember: $\ln 2 < 1$; actually $\ln 2 \approx 0.693$.

uncertainty relation of quantum mechanics. According to it, $\Delta E \cdot \Delta t \approx \hbar$, meaning that if one measures the energy of a closed system at different times Δt apart, energy conservation will only hold up to $\Delta E \approx \frac{\hbar}{\Delta t}$ deviations: because of the measurements themselves, such amount of energy transfer necessarily happens between the system and the surroundings.⁵

This also has an effect on absorption and emission as well. For one thing, we can think of the photons generated in the $E_2 \rightarrow E_1$ transition as having energies „smeared” at least by this Γ_0 amount (meaning that it has the distribution given above). On the other hand, we may think that when trying to make the opposite transition, the $E_1 \rightarrow E_2$ excitation happens by letting a photon be absorbed, we do not have to exactly hit the corresponding energy: we can „miss” by Γ_0 (and the absorption probability will follow the distribution given above).⁶

In the case of optical photons (of a few eV energy from atomic shell transitions) the typical magnitude of natural line width is $\Gamma_0 \sim 10^{-6}$ eV, and the recoil energy is $R \lesssim 10^{-7}$ eV. So the condition for resonant absorption almost always holds: materials absorb their own *light*. In case of nuclear **gamma rays, however**, (E_γ being much higher, 10-100 keV, or even a few MeV, and R depends quadratically on E_γ) one has R values from $\sim 10^{-3}$ eV to a few hundred eV. The condition (2.6) is thus less likely to be fulfilled here, so in nuclear physics for some time it was deemed harder if not impossible to observe resonant absorption.

P. B. Moon successfully observed resonant absorption with ^{198}Hg isotope in 1951, using the Doppler effect to account for the missing $2R$ energy. (An ultracentrifuge was used to move the gamma source with high velocity.) When reaching the appropriate velocity, the observed absorption increased sharply. Malmfors used another technique (in the same year): by heating the source (that emits gamma rays) and the sample (meant to absorb gamma rays by the level transition in the opposite direction) to high temperatures, the fraction of nuclei capable of resonant absorption increased. The principle is that by increasing thermal Doppler broadening, Δ_{Doppler} , the overlap of the energy distributions of the emitted photons and of the absorption probability increases, so the situation depicted on panel a.) on Fig. 2 emerges.

3 The Mössbauer effect

In 1958, R. L. Mössbauer investigated the mentioned temperature dependence of resonant absorption using the 129 keV gamma rays emitted by an excited state of the iridium isotope ^{191}Ir .⁷ Contrary to the expectation based on the T -dependence of Doppler broadening, he observed that *lowering* the temperature led to an *increase* in resonant absorption. This phenomenon and its interpretation came to be known as the *Mössbauer effect*. In a nutshell, the lower the temperatures, the higher fraction of nuclei bound in a crystal become capable of **recoil-free** absorption and emission. [1].

An attempt at a classical explanation could be to observe that if in the denominator for the expression of R , Eq. (2.1), instead of the M mass of the absorbing or emitting nucleus, we

⁵ *Side note:* a model of a decaying state with life time τ is e.g. a particle that by means of tunneling can escape with a small but finite probability from between a pair of high but finite potential walls. The probability of decay not having been happened yet is proportional to the average value of the square of the wave function between the walls. Requiring outgoing waves, the time dependent Schrödinger equation admits only *complex*, $E \equiv E_0 - i\frac{\Gamma_0}{2}$ energy eigenvalues. At time t we then have $|\psi(t)|^2 = |\psi(t=0)|^2 \cdot \exp(-\frac{\Gamma_0}{\hbar}t)$: one reads off from the exponent that $\tau = \frac{\hbar}{\Gamma_0}$. The formula (2.7) for the energy distribution follows by Fourier decomposing the $\exp(-\frac{\Gamma_0}{2\hbar}t - \frac{i}{\hbar}E_0t)$ time dependence into components of different frequency (and energy).

⁶ The reason for speaking somewhat vaguely („we can think of...”) is that there are deeper and more fundamental questions at play here, needing much more thorough investigation. However, for the sake of understanding resonant absorption, it might be enough to know the things said so far.

⁷ The recoil energy here, according to Eq. (2.1), is 0.047 eV. At room temperature, Doppler broadening (taking $T_{\text{eff}} \approx T$) amounts to approx. 0.07 eV: there is thus overlap even at room temperature. The life time of the excited state here is $\tau = 89.9 \cdot 10^{-12}$ s, and from this, the natural line width is $\Gamma_0 = 7.3 \cdot 10^{-6}$ eV.

write the total mass of the crystal (i.e. we think of the nuclei as infinitely tightly bound), then indeed R becomes totally negligibly small, and E_γ becomes $E_2 - E_1$. If the same holds true for the absorption process (meaning that R is also zero there because of the fixed positions of the absorbing nuclei in the sample crystal), then natural line width will make resonant absorption possible: the nuclei can get excited by a photon coming from the same type of de-excitation event.

This simple picture does not offer any hints at temperature dependence, let alone at the fact that only a fraction of the nuclei do not recoil. A first clarification is that nuclei are not tightly bound in the sense that they very much can and do vibrate around their equilibrium position. Recoil momentum could be carried away by crystal lattice vibrations, leading to energy loss. The task thus becomes to explain how it is possible in a certain fraction of events that during the emission of a gamma photon (and also during absorption), lattice vibrations *do not get excited*, and in this way indeed the whole crystal mass appears in R , rendering it negligibly small. To this end, a quantum mechanical description is needed.

In a crystal, nuclei are ordered into a lattice. The nature and strength of the bonds between them determine the distribution (=spectrum) of the vibrational frequencies as well as the configuration of the vibrational motions (the normal modes). The motions of solids (among others, the one resulting from the push of one atom) are treated as excitations of the harmonic oscillators corresponding to the normal modes. Recall that an oscillator of frequency ω can only take up an integer multiple of the energy $\hbar\omega$; such elementary excitations of the normal modes are called *phonons*. The vibrational spectrum necessarily has an upper frequency limit: ω_m ; it is on the same order of magnitude as (=a few times as much as) the „average frequency” introduced above (for defining the Θ Debye temperature). Recall that

$$k_B\Theta = \hbar\bar{\omega}, \quad \bar{\omega} \sim \omega_m. \quad (3.1)$$

The vibrational spectrum of real solids is complicated; an historically important model is the *Einstein model*, where all the $3N$ vibrational degrees of freedom (N meaning the number of atoms in the crystal) oscillate with the same $\omega = \omega_m$ frequency.⁸ In this picture we can say that if $R < \hbar\omega_m$, the recoil energy is not enough to excite vibrations, so all such photons can and will cause resonant absorption. The quantized nature of oscillators can thus explain why vibrations do not get excited sometimes; however, a more accurate description needs a realistic model of crystal vibrations.

A real phonon frequency spectrum fills the whole $0 < \omega < \omega_m$ domain, i.e. in principle, an arbitrarily small recoil energy can excite phonons that have lower energy. Nevertheless, it is still possible that in some fraction of events, no phonon creation will occur at all. If the gamma photon emission and the absorption both happen without the excitation of phonons (meaning no recoil energy loss), then natural line width makes resonant absorption possible. The fraction of gamma emission events (or the fraction of absorption events in the opposite transition) that happen without phonon creation, f , is called *Lamb-Mössbauer factor*. This depends on crystal structure, gamma energy and T . For a thorough treatment, see Ref. [2] (with further explanations given in [3]); a sort of result is the following:

$$\text{Lamb-Mössbauer factor:} \quad f = \exp\left(-\frac{1}{2}k^2\langle x^2 \rangle_T\right). \quad (3.2)$$

Here k means the wave number of the emitted photon: $\hbar kc = E_\gamma$, so k is proportional to the photon energy E_γ , and k^2 to the (2.1) classical recoil energy: $R = \frac{\hbar^2}{2Mc^2}k^2$. The quantity $\langle x^2 \rangle_T$ denotes the average squared displacement of atoms in the crystal at temperature T . The cited formula is not an *end result* in the sense that it does not give f from first principles

⁸ This simple „model” is important historically for first predicting a changing specific heat of solids versus temperature based on quantum mechanics; a feat that was unexplainable classically.

(i.e. from the crystal structure); $\langle x^2 \rangle_T$ is still a quantity to be inferred from somewhere else. Nevertheless, the equation is suited for some simple considerations.

It seems a natural expectation, and is indeed true that lower photon energy (meaning smaller k ; this is the classical thought that the recoil energy is the smaller the better) leads to bigger f , meaning more probability for recoilless absorption and emission. (The „intensity” of the Mössbauer effect is clearly f^2 if we assume the gamma source and the absorbing sample to be at the same temperature and of the same material type, since this f factor appears both at emission and at absorption.) Another thing to observe is that the smaller $\langle x^2 \rangle_T$, the bigger is f , meaning larger effect. Because of zero point fluctuations, $\langle x^2 \rangle_T \neq 0$ even at $T = 0\text{K}$, however, it is clear that $\langle x^2 \rangle_T$ decreases with decreasing temperature. This leads to a increasing f with decreasing T , the phenomenon observed by Mössbauer. A simple additional reasoning: at lower T , the average phonon numbers (i.e. occupation numbers) are smaller in each mode. Phonons are bosons: the more of them are in a given state, the more probable for another one to appear there (similar argument goes by *induced emission* when explaining laser light). So higher occupation numbers (i.e. higher T) means less probability for a phonon *not* to be created by an external perturbation (in our case, this is the back-effect of the gamma photon emission).

On Fig. 3 the calculated value of the Lamb-Mössbauer factor f is plotted as a function of crystal temperature T , Debye temperature Θ and recoil energy R is plotted. The real values are well reproduced, although the plot was made using the Debye model of vibrations: here the ratios Θ/T and R/Θ are that matter.⁹

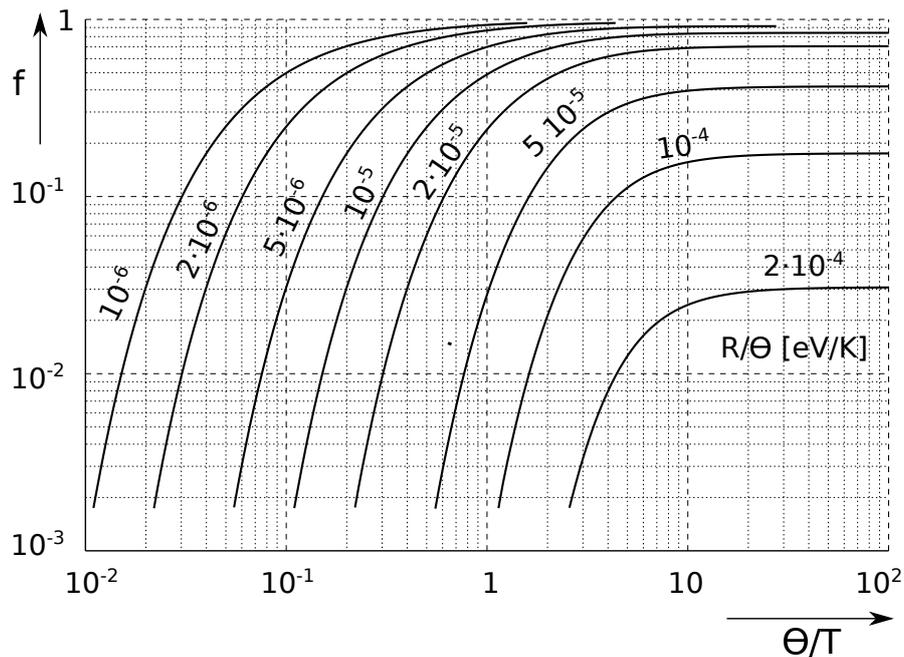


Figure 3: The strength of Mössbauer effect (i.e. the f Lamb-Mössbauer factor) as a function of recoil energy (R), sample temperature (T) and the Debye temperature Θ of the crystal. The parameter of the curves is R/Θ , its unit is eV/K.

We highlight three important materials (and the gamma energies relevant to the Mössbauer effect). One is the most frequently used *Mössbauer nucleus* (used also by us, in this class),

⁹ I made the plot myself using formulas from Ref. [2]. The physical meaning of R/Θ is that how does the classical recoil energy compare to the characteristic quantum mechanical energy of lattice vibrations (which is $\sim \hbar\bar{\omega}$, and Θ is proportional to $\bar{\omega}$). The meaning of Θ/T is something like „to what extent are the vibrations quantum mechanical”: the bigger this ratio, the more, since the less it is true that average occupancy numbers are high. As expected f increases with increasing Θ/T .

the iron isotope ^{57}Fe . Another important Mössbauer nucleus is an isotope of tin, ^{119}Sn . The original experiment by Mössbauer used iridium, ^{191}Ir . Table 1 shows the properties of these isotopes.

Isotope	E_γ	R	$T_{1/2}$	Θ	R/Θ
^{57}Fe	14.413 keV	$1.958833 \cdot 10^{-3}$ eV	98.3 ns	460 K	$4.258 \cdot 10^{-6}$ eV/K
^{119}Sn	23.880 keV	$2.57423 \cdot 10^{-3}$ eV	18.03 ns	170 K	$1.514 \cdot 10^{-5}$ eV/K
^{191}Ir	129.415 keV	$4.7077 \cdot 10^{-2}$ eV	0.123 ns	430 K	$1.095 \cdot 10^{-4}$ eV/K

Table 1: Some important Mössbauer nuclei: nuclear properties (the half life, gamma energy and recoil energy corresponding to the level used for Mössbauer effect) as well as the Debye temperature Θ of the metallic crystal.

From these, we can read off the value of the Lamb-Mössbauer factor f (the fraction of recoilless gamma emissions) from Fig. 3. One observes that at room temperature ($T = 300$ K), the magnitude of the effect can reach as high as 80% for the gamma radiation from the 14.4 keV excited state of ^{57}Fe . It is also possible to do room temperature measurements with ^{119}Sn , however, in case of ^{191}Ir , it is advisable to cool the sample well below room temperature.

4 Characteristics of Mössbauer spectra

The Mössbauer effect, in a nutshell: an f fraction of gamma photons is emitted without energy loss to recoil, and in the sample, an f fraction of them is absorbed without „knock-on” energy loss and causes a transition in the same type of nucleus from the ground state into the excited state. The energy distribution of such photons is like Eq. (2.7), a Lorentzian whose width is the Γ_0 natural line width, the most probable energy (denoted there by E_0) is the exact $E_2 - E_1$ energy difference of the levels. Also the energy dependent probability distribution for knock-on-free absorption is the same Lorentzian, with the same Γ_0 width. So resonant absorption is possible for recoilless and knock-on-free emission and absorption, thanks to natural line width, and consequently, the overlapping of the probability curves. On the other hand, natural line width is usually very small: for example for the most widely used Mössbauer nucleus (which we used on this course as well):

$$\text{For the 14.4 keV excited state of the } ^{57}\text{Fe} \text{ nucleus:} \quad \tau = 141.8 \text{ ns} \quad \Rightarrow \quad \Gamma_0 = \frac{\hbar}{\tau} \approx \underline{\underline{4.65 \cdot 10^{-9} \text{ eV}}}.$$

So if a small effect causes a shift of this magnitude e.g. in the energy of the photons emitted by the source w.r.t. the $E_2 - E_1$ difference in the nuclei in the sample, overlap is destroyed. This is the reason why one can reach the accuracy mentioned in the introduction: a Γ_0 change in the 14.4 keV photon energy is recognizable since it causes recoil-free resonant absorption to cease and makes the sample absorb a smaller number of photons.

Put otherwise: if for any reason the $E_2 - E_1$ value for the ^{57}Fe nuclei in the sample is different but only by Γ_0 from that in the source, one needs to compensate for this difference in order resonant absorption to happen. This „compensation” will be exactly the difference looked for. *Mössbauer spectroscopy* is to investigate the appearance of resonant absorption (which means an increase in the photon attenuation of the sample) as a function of the energy compensation. The E_γ photon energy can be changed with such accuracy by using Doppler effect: if we make the source move against the sample with velocity v , then

$$\Delta E_\gamma = \frac{v}{c} E_\gamma. \quad \text{E.g. in case of } ^{57}\text{Fe}, \text{ for } v = 1 \text{ mm/s:} \quad \Delta E_\gamma = 4.8 \cdot 10^{-8} \text{ eV}.$$

We thus make the source move w.r.t. to the sample (the absorber), and scan the interesting energy range by means of changing the velocity: the energy change is $\frac{v}{c}E_\gamma$. The spectrum value at a given v will mean the magnitude of absorption.

What spectrum shape is expected by investigating absorption as a function of v ? Assume first that for whatever reason (Doppler shift or a difference in the E_2-E_1 values that is genuinely present) the most probable photon energy and the maximum point of the absorption probability do not coincide, but are shifted by ΔE . In this case, the probability P of resonant absorption can be given as an integral over all possible E_γ photon energies:

$$P_{\text{res.abs.}}(\Delta E) = \int dE_\gamma \underbrace{p(E_\gamma - \Delta E)}_{\text{emission}} \cdot \underbrace{p(E_\gamma)}_{\text{absorption}},$$

where we assumed that both probability distributions are similar Lorentzian curves, shifted by ΔE . $P(\Delta E)$ is thus essentially the *convolution* of the emission and absorption distributions;¹⁰ this is what we can scan by continuously changing the v velocity (and in turn the ΔE energy difference). Recall here that *a convolution of two Lorentzians is again a Lorentzian*, and their widths are added up.¹¹ So the $P(\Delta E)$ distribution *as a function of ΔE* will be a Lorentz curve of $2\Gamma_0$ width: if we change v (thus: ΔE) uniformly, this is the line shape describing the v dependence of resonant absorption.

If the E_2-E_1 energy level differences are the same for the nuclei in the source and the sample, then resonant absorption will be maximal at $v=0$. If they are not exactly the same, then the absorption maximum will be at $v \neq 0$ since the missing energy needs to be compensated for by the Doppler effect; we can determine the compensatory energy value from the deviation of v from zero. Fig. 4 tries to show these features.

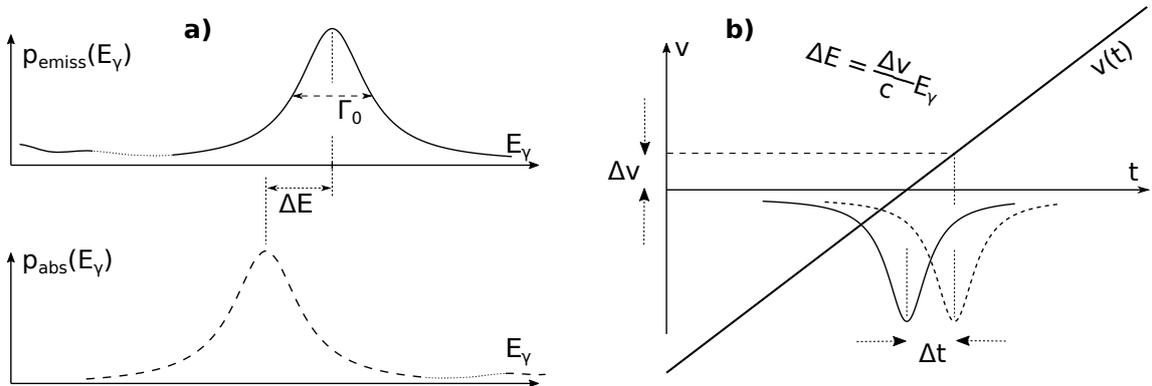


Figure 4: a.) The Mössbauer resonant absorption strength vs ΔE is the convolution of the two distributions. I plotted the *not recoil-free* events farther away (with distorted horizontal scale). b.) Changing v as a function of time, the shift of the peak position from $v=0$ translates into the *difference of the* level differences in the sample and the source.

Since the velocity v of the source can be known to one hundredth of a mm/s precision, we can infer the change of the 14.4 keV photon energy of ^{57}Fe to $\sim 10^{-10}$ eV precision. It is interesting that E_γ itself (meaning the energy difference E_2-E_1 between the ground and excited state) is known much less precisely. This will get no better, but the *difference in E_2-E_1 between*

¹⁰ The convolution $f*g$ of the f and g functions is defined usually as $(f*g)(y) = \int dx f(y-x)g(x)$. In our case $p(E)$ is an even function; does not matter that we wrote the subtraction in the opposite order.

¹¹ One can calculate this by means of the residue theorem. Or knowing the properties of Fourier transformation, namely if $f(x) = \int \frac{d\omega}{2\pi} e^{i\omega x} \tilde{f}(\omega)$ and $g(x) = \int \frac{d\omega}{2\pi} e^{i\omega x} \tilde{g}(\omega)$, then $(f*g)(y) = \int \frac{d\omega}{2\pi} e^{i\omega y} \tilde{f}(\omega) \tilde{g}(\omega)$, and knowing that a Lorentzian is the Fourier transform of $\tilde{p}(\omega) = e^{-\Gamma|\omega|/2}$, we get the result.

the source and sample is what the mentioned high accuracy refers to.¹² If, on the other hand, we agree that the source that produces the excited ^{57}Fe nuclei and thus the needed gamma photons must always be the same well defined material type, then we can compare energy level shifts measured in other material samples to this type of source.

* * *

There are many nuclei that fulfill the conditions necessary for Mössbauer effect (such as the ability to be inserted into a solid carrying material and a gamma transition relatively of low energy): presently there are more than 30 Mössbauer nuclei known. The most widely used ones are the mentioned ^{57}Fe and ^{119}Sn isotopes: as seen earlier (on Fig. 3, based on Table 1), there is a considerable effect at and above room temperature. In the following, we restrict ourselves to measurements using the ^{57}Fe nucleus (as this is used in this lab course). Ground state ^{57}Fe nuclei make up 2.12% of naturally occurring iron (besides the more abundant ^{56}Fe isotope). So any material is suited for absorbing material (i.e. sample to measure) that contains iron as chemical element.

The excited state ^{57}Fe nuclei that emit the gamma ray to be resonantly absorbed can be supplied by the decay of the ^{57}Co cobalt isotope. ^{57}Co decays by electron capture (with a half life of 271.8 days), the daughter ^{57}Fe nucleus is produced in a highly excited state, and reaches ground state by emitting a cascade of gamma photons. Among these in a small (approx. 9%) fraction of events we find the photon emitted by the decay of the 14.4 keV state into the ground state. On Fig. 5 the relevant level structure and decay scheme of the ^{57}Fe and ^{57}Co nuclei are shown. The spin 3/2 excited state with 14.4 keV energy has a life time of 141.8 ns (half life: 98.3 ns), and a precise energy of 14413 eV.

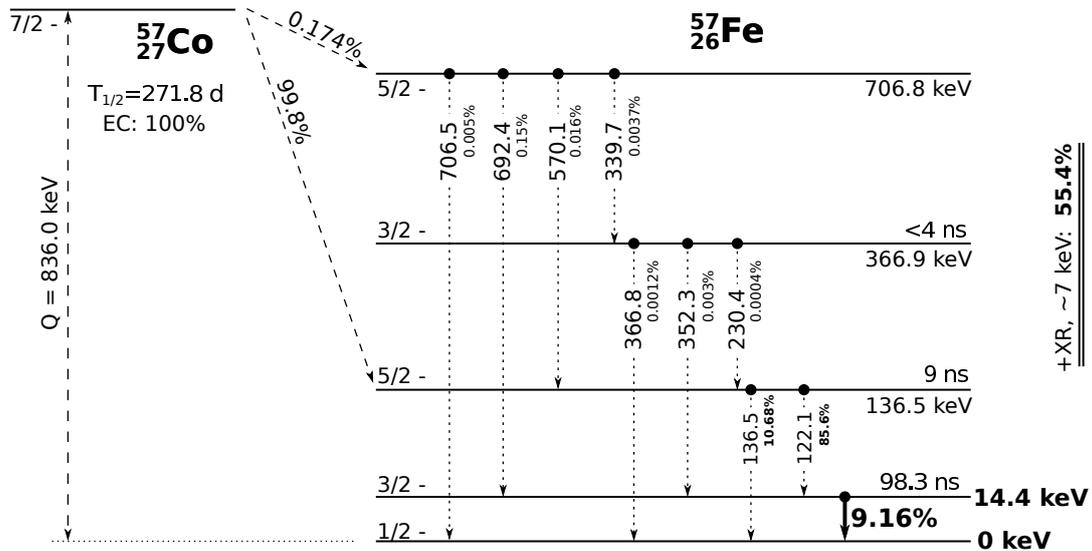


Figure 5: Decay scheme of ^{57}Co and the levels of ^{57}Fe that play a role (with somewhat distorted scale), with parity and angular momentum quantum numbers as well as half lives. The gamma energies and relative intensities are denoted as well. The 14.4 keV gamma photon (useful for the Mössbauer measurement) is highlighted. There are X-ray photons also produced by the decay of ^{57}Co . Many level transitions can emit *conversion electrons* instead of gamma photons; these make up the „missing” probabilities. (For example, for the 14.4 keV state decaying into ground state, this is more probable: $\sim 78\%$, while the gamma photon emission (useful for Mössbauer spectroscopy) is only $\sim 9\%$.)

¹² As if one could know the mass of a 100000 ton aircraft carrier with an accuracy of a few tons, but be able to compare *two aircraft carriers* down to 100 micrograms precision.

We can tell very fine changes in the energy levels form a Mössbauer spectrum. These changes mirror what effect the environment of the nucleus exerts on it *at the place of the nucleus*. For example, energy level (i.e. spectrum peak) split is caused by the interaction of the nuclear magnetic moment with a magnetic field, or the interaction of nuclear quadrupole moment and an inhomogeneous electric field. Line shift is caused by the Coulomb interaction of the nucleus and the electron shell. Even if there is only one line, one has to investigate it thoroughly, since it is possible that one has a multiplet of lines in very close proximity. Of course, interpreting the results is hindered by the fact that many different environmental effects can lead to very similar Mössbauer spectra, so these spectra are not in one to one correspondence with the crystal structure and/or electronic (chemical) properties of the material. In such cases one might do additional measurements with additional external fields applied, or compare to results from other measurements.

For measurements with the ^{57}Fe isotope we need ^{57}Co as radioactive isotope. One widely used setup is the „Co-Rh source”, where the ^{57}Co nuclei are embedded in the surface layer of a thin foil made of rhodium (Rh, a rare transition metal): in this type of source, the energy levels of the daughter ^{57}Fe nucleus have no splitting, and are well determined (but as said, known only to $\sim\text{eV}$ accuracy). This energy is the reference then for line shifts of other samples. In the following, we briefly overview some typical Mössbauer spectrum profiles (to be met in this lab course) of samples containing iron (i.e. the ^{57}Fe isotope).

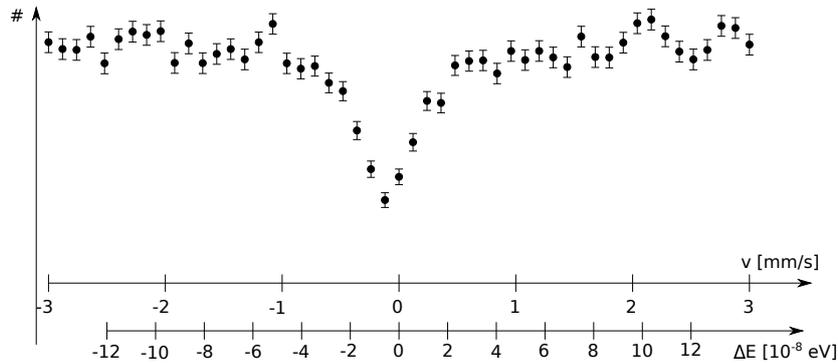


Figure 6: Example Mössbauer spectrum of a steel sample; horizontal axis labelled with the source velocity and the corresponding $\frac{v}{c}E_\gamma$ energy shift. Vertical axis: the number of photons that go through the sample (in arbitrary units): where there is a dip, there is resonant absorption.

Change in peak position:

We speak of (chemical) *isomeric shift* if the energy levels of the nucleus get modified by the interaction of the nucleus with the electric field of the electron shell. In different chemical compounds or crystals, where the electron structure is different, the density of s -orbit electrons is different at the nucleus, so the mentioned interaction also changes. So the Mössbauer spectra (the resonant absorption peaks) also shift compared to each other. The shift is expressed as (taken from relevant literature):

$$\Delta E \simeq Zq_e^2(|\Psi_s(0)|_A^2 - |\Psi_s(0)|_S^2)(\langle r^2 \rangle_E - \langle r^2 \rangle_G), \quad (4.1)$$

where Z is atomic number, q_e is the elementary charge, $\Psi_s(0)$ is the s -electron wave function in the absorber (A) and in the source (S), $\langle r^2 \rangle$ is the average value of squared nuclear radius in the excited (E) and ground (G) states. Eq. (4.1) shows that the energy shift depends on the electron density at the nucleus, which is influenced by the total electron structure. So one can conclude at the latter. It is customary to call isomer shift other types of line shifts that are caused not by interaction with the orbital electrons but other effects, like gravitationa

field or temperature change (through change in crystal structure). When speaking of isomer shift of a sample as of itself, it is understood as the shift with respect to the energy level difference of the nuclei in the radioactive source.

Fig. 6 above shows a typical singlet spectrum: the detector setup that gives such spectrum is where the number of photons penetrating the sample is measured (as a function of source velocity). Resonant absorption will lead to a decrease in the number of such photons; the position of the peak (with respect to $v = 0$) gives the isomer shift readily.

Quadrupole splitting:

If a nucleus with quadrupole moment Q sits in an **inhomogeneous** electric field with gradient $\frac{\partial^2 V}{\partial z^2}$ (where V is the electrostatic potential), nuclear levels shift according to the formula below. Here I is the total angular momentum quantum number („nuclear spin”) of the level, m_I is the magnetic quantum number (the z component of the angular momentum), η is the so-called asymmetry factor; here it is zero, owing to axial symmetry of the nuclear states.

$$\Delta E = \frac{q_e Q}{4I(2I-1)} \frac{\partial^2 V}{\partial z^2} [3m_I^2 - I(I+1)] \sqrt{1 + \frac{\eta^2}{3}}. \quad (4.2)$$

The shift can be different for different m_I quantum numbers: this causes the degenerate energy level to split. It is interesting to observe that the shift is same for $+m_I$ and $-m_I$, meaning these states remain degenerate. The most apparent reason for electric field gradient is usually an asymmetry of the surrounding electron cloud, of which we thus can get information. Fig. 7 shows the structure of the iron-containing part of the *sodium nitroprusside* molecule (to be investigated during the lab course). In one of the vertices there is NO⁻ (nitrous oxide) group, in the others, CN (cyanide), leading to a non-spherically symmetric electron cloud around the Fe nucleus. Fig. 7 also shows a quadrupole split Mössbauer spectrum, typical to such cases.

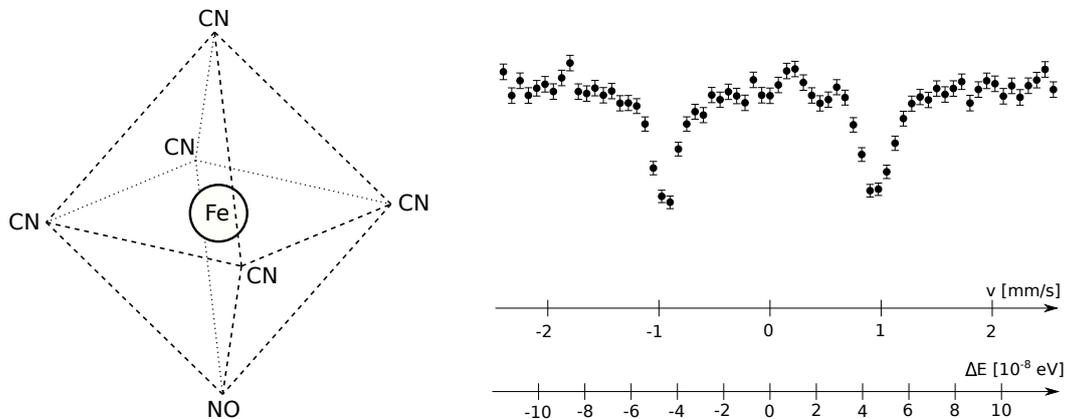


Figure 7: Left: structure of the Fe-containing part of the sodium nitroprusside molecule. Right: quadrupole split Mössbauer spectrum (illustration).

Magnetic splitting:

Nuclear states with nonzero spin usually have magnetic moment as well. A magnetic field of B strength at the place of the nucleus leads to a modification of the energy levels:

$$\Delta E = -g \cdot \mu_N \cdot B \cdot m_I, \quad (4.3)$$

g being the *gyromagnetic ratio* of the state, different in ground and excited states. Also its sign may be arbitrary. $\mu_N = \frac{q_e \hbar}{2m_p} \simeq 5 \cdot 10^{-27} \text{ J/T} = 3.15238 \cdot 10^{-11} \text{ keV/T}$ is the *nuclear magneton*, m_I is the nuclear spin component quantum number in the B direction. The minus sign means that if $g > 0$ (the magnetic moment pointing in the direction of the spin, not oppositely), then the spin pointing in the B direction has lower energy (a more favorable configuration).

In case of iron (meaning pure, normal, body centered cubic crystalline iron) the magnetic field at the place of the ^{57}Fe nucleus (the same that causes hyperfine splitting) causes three doublet lines to occur, because a spin $3/2$ excited state decays into a spin $1/2$ ground state and a spin one photon is emitted: in this case angular momentum conservation stipulates that m_I can change either by 0 or by 1. There will be six possible transitions: $\pm\frac{3}{2} \rightarrow \pm\frac{1}{2}$, $\pm\frac{1}{2} \rightarrow \pm\frac{1}{2}$, és $\pm\frac{1}{2} \rightarrow \mp\frac{1}{2}$. The energies of these will be slightly shifted compared to each other, because states with different m_I have different energies in a B field. Fig. 8 shows the typical Mössbauer spectrum of pure iron.

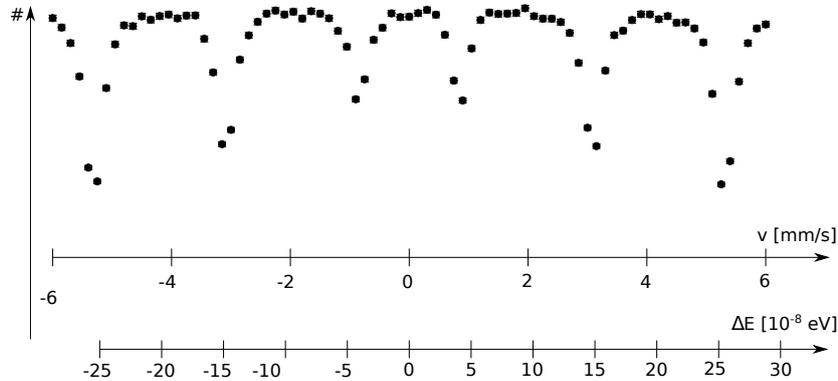


Figure 8: Illusztráció mágneseesen felhasadt Mössbauer-spektrumra (^{57}Fe mag esetén).

Line widths in the spectrum and effective thickness of the sample:

If the *effective thickness* (the thickness compared to the photon mean path without resonant absorption) of the source or the sample is not small, the shape of the absorption curve in the Mössbauer spectrum ceases to be exactly Lorentzian, as assumed so far. This is because the probability of a photon getting through a given thickness decreases no longer linearly with the thickness, one has to treat it with the exponential decay law instead. This results in that the peak gets „flatter”: where the absorption would have been bigger, it will be not so big, because it will be less probable for such photons to reach the latter parts of the sample (so that they could „use” it for absorption).¹³ In the end, if we still do fits using Lorentz curves, the flatter peak curves lead to the Γ observed line width to be bigger than expected (which would be twice the natural line width). If we are interested in the „real” width (meaning the Γ_0 natural line width), we must correct for this effect. This is somewhat complicated if we are to use exact formulas, especially in the case of split lines. In practice, the following approximation can be used, that is good for not very thick foils:

$$\frac{\Gamma_i^{(exp)}}{\Gamma_0} = 2 + \frac{w_i T_A + T_S}{4} - \frac{(w_i T_A + T_S)^2}{625}. \quad (4.4)$$

In fact even the quadratic term may be neglected for thin samples. Here w_i is the relative intensity of the given (i th) line in the spectrum ($\sum w_i = 1$), Γ_0 is the natural line width, $\Gamma_i^{(exp)}$ is the measured (i.e. fitted) line width of the i th line. As seen earlier, the factor of 2 at the beginning comes from the fact that the convolution of the absorption and emission Lorentz curves is a Lorentz curve with twice the width of the original (same) ones. The other terms describe the effect of finite thicknesses: T_A and T_S are the (dimensionless) *effective thicknesses* of the absorber (sample) and the source; i.e. the thickness divided by the mean free path pertaining to resonant absorption. The definition is (although we will not need it

¹³ Photons are „lost” to the beam not only by resonant absorption but also by photoelectric effect or Compton scattering. These, however, act similarly on all the photons (differing in energy only by a few times of Γ_0) so they do not influence the shape of the Mössbauer spectrum.

here): $T = f \cdot n \cdot \sigma_0 \cdot d$, with f being the Lamb-Mössbauer factor, n the number density of absorbing nuclei, σ_0 the cross section of absorption at the exact („resonant”) energy (for ^{57}Fe , this is $2.56 \cdot 10^{-22} \text{ m}^2$), and d the actual thickness.

For the effective width of the ^{57}Co source to be used in this laboratory class, we can take $T_S \approx 0.5$.¹⁴ If there is no line split in the sample, then in the above formula $w_i = 1$. If there is splitting, the sample seems „thinner” to the separate lines. For example, in the spectrum of iron that has six lines, the fitted widths of the lines with different intensity will also be different. (We could get the intensities and their ratios from the measurement by calculating the area of the absorption peaks, this area being proportional to the product of the peak amplitude and width. Nevertheless, we will see the exact values for the w_i s; these do not exactly match those so got from the fits, right because of the distortion introduced by the thickness of the sample.)

5 The measurement device

We measure Mössbauer spectra in the laboratory course in the way already mentioned: we make the gamma source move with respect to the absorber (the sample containing iron nuclei), so we can create energy changes of such magnitude by the Doppler effect whose measurement is our end. The setup is: the gamma photons from the source are let through the (not very thick) sample, and are detected by a gamma detector placed behind the sample. Resonant absorption will manifest itself through an observed decrease of photons reaching the detector.¹⁵ (When photons get absorbed, the resulting excited states emit them in random directions, meaning that they are „lost” to the beam.) We can see the block diagram of our measurement apparatus on Fig. 10 below.

We use a source of the type mentioned above, where ^{57}Co is embedded into a rhodium metal matrix. There is no splitting in the 14.4 keV photon energy. The change in the photon energy is $\Delta E = \frac{v}{c} E_\gamma$ when the source moves with velocity v ; recording the intensity at many different velocity values we essentially get the spectrum, i.e. the absorption of the sample as a function of such energy change.

It is most convenient to move the source with a constant acceleration back and forth, changing the sign of the acceleration in every half period. In this way, v changes between a positive and negative maximal value during a period. So we can group the photon hits (that made through the sample) according to the actual source velocity by grouping them with respect to *arrival time*: by plotting the number of hits vs. arrival time, we get the Mössbauer spectrum itself. A peak (intensity minimum) will be visible where the velocity is exactly what is needed for the condition of resonant absorption to hold.

¹⁴ The effective width of new Co-Rh source (meaning all ^{57}Co and no daughter ^{57}Fe) is zero. In time ^{57}Fe is produced by the decay, the effective thickness increases. The sources used in our laboratory class are weak, almost totally decayed away. The given T_S value is got by calculating the mean free path with the assumption that the original ^{57}Co content is totally replaced by ^{57}Fe .

¹⁵ It is worth noting that this is not the only possible measurement setup. The drawback of the mentioned methodology is that it can be applied only for not very thick samples. In thin film physics, a widespread method is the use of conversion electrons: here resonant absorption is not inferred from the number of photons passing through but by observing the decay of the excited states *created by* the absorption. It is made possible by the fact that this back-decay in most of the cases does not happen by the re-emission of the absorbed gamma photons but by an emission of a conversion electron (whose energy is the photon energy minus the original binding energy in the atomic shell), followed by emission of characteristic X-rays or Auger electrons. So the detection of any of these also tells about the occurrence of the resonant absorption. Because it is not necessary here that the gamma rays pass through the material, only the detection of conversion electrons emitted backwards from the thin surface layer of the sample is necessary, this *conversion electron Mössbauer spectroscopy* (CEMS) is very much suited for the material scientific investigation of thin layers and other nanostructures.

Such type of data taking can be performed by a special type of multichannel analyzer. The magnitude (i.e. voltage amplitude) of the pulses coming from the gamma ray detector is proportional to the energy deposit: firstly we group the pulses into channels according to their magnitude, in 512 equidistant classes between zero and a maximal value. So when we plot the number of hits as a function of channel number, we get the measured energy spectrum. By investigating this, we can single out the photon hits that correspond to the 14.4 keV transition, the one interesting for the Mössbauer effect. Many other types of photons (such as lower energy X-ray photons from the source, higher energy gamma photons (see Fig. 5 above), secondary X-ray photons produced by the absorption of the higher energy photons in the shielding material, as well as electronic noise) also leave signals in our detector. It is of utmost importance to get rid of these: if we included photons into our Mössbauer spectrum that surely do not cause resonant absorption, it would decrease the statistical significance (signal to background ratio) of our measurement.

After selecting the photon hits pertaining to the transition relevant to the Mössbauer effect, the binning of hits in time is also performed by the multichannel analyzer. In our setup, the source movement is governed by a triangle wave of $T = 41.2 \pm 0.2$ ms period. Binning of hits according to arrival time is done by gating the successive channels of the data buffer of the multichannel analyzer by a counting signal in every $40 \mu\text{s}$, thus sending the coming signal into the appropriate channel. In this way a hit arriving at a definite time goes to the channel corresponding to that time bin. In accordance with the given time values, one has 1024 channels.¹⁶ In a half period there is a linear relation between velocity and time (see Fig. 9 right below), meaning that sampling in time means sampling w.r.t. velocity.

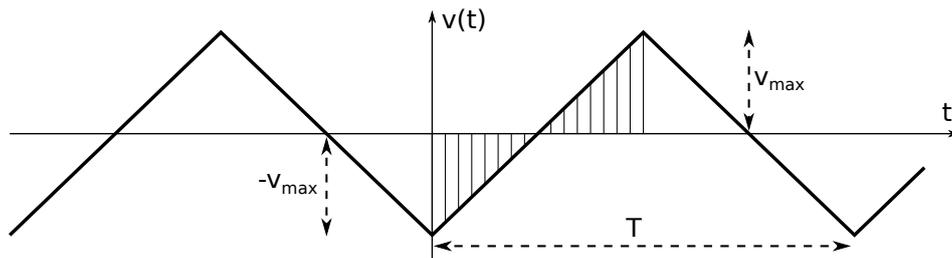


Figure 9: The triangular waveform describing the source motion. Vertical lines illustrate the time sampling by the multichannel analyzer. The period begins at $t=0$, with channel #0.

In a full time period, we have two time instants corresponding to the same velocity, the photon hits of whose are fully equivalent for Mössbauer spectra (meaning having the same velocity and thus Doppler shift). Because of this, when analyzing the spectrum, we need to „fold” it by adding up the contents of channels situated symmetrically to the center line. Our analyzer card does this automatically, so we are left with a spectrum in 512 channels.

Time sampling is started by a signal at the start of the triangular wave. After looping through all 1024 channels, the analyzer card sends back a synchronizing signal to end the triangle wave. In this way it can be enforced that the movement and the sampling run strictly together. Since Doppler effect is proportional to velocity, we can write

$$v(t) = v_0 + a't \quad \Rightarrow \quad \Delta E \sim v \sim t \sim \text{channel number.}$$

Thus at the end of data taking, the Mössbauer spectrum of the sample is obtained by plotting the channel contents against the channel number.

¹⁶ Because of the acceleration, the velocity does change even in the small time interval. To avoid the distortion of the spectrum by this, it is (was) necessary to choose the channel width to be at least a few times smaller than the natural line width of the transition (expressed in velocity).

The source is mounted on a metal rod on a loudspeaker (movement apparatus). A „sampling” coil accurately senses the movement of the rod via electric induction. The signal from this is brought on a differential amplifier, and gets also visualized on an oscilloscope. On the other input of the differential amplifier, we bring the triangular signal coming from the control unit (seen on Fig. 9). The amplified difference then gets to the voice coil of the loudspeaker unit: this is the so-called signal-following regulation, that approximates the reference signal (in our case, the triangular signal) the better, the bigger the amplification of the differential amplifier. The start signal of the period as well as the channel-changing signals for the time sampling are sent to the multichannel analyzer from the control unit.

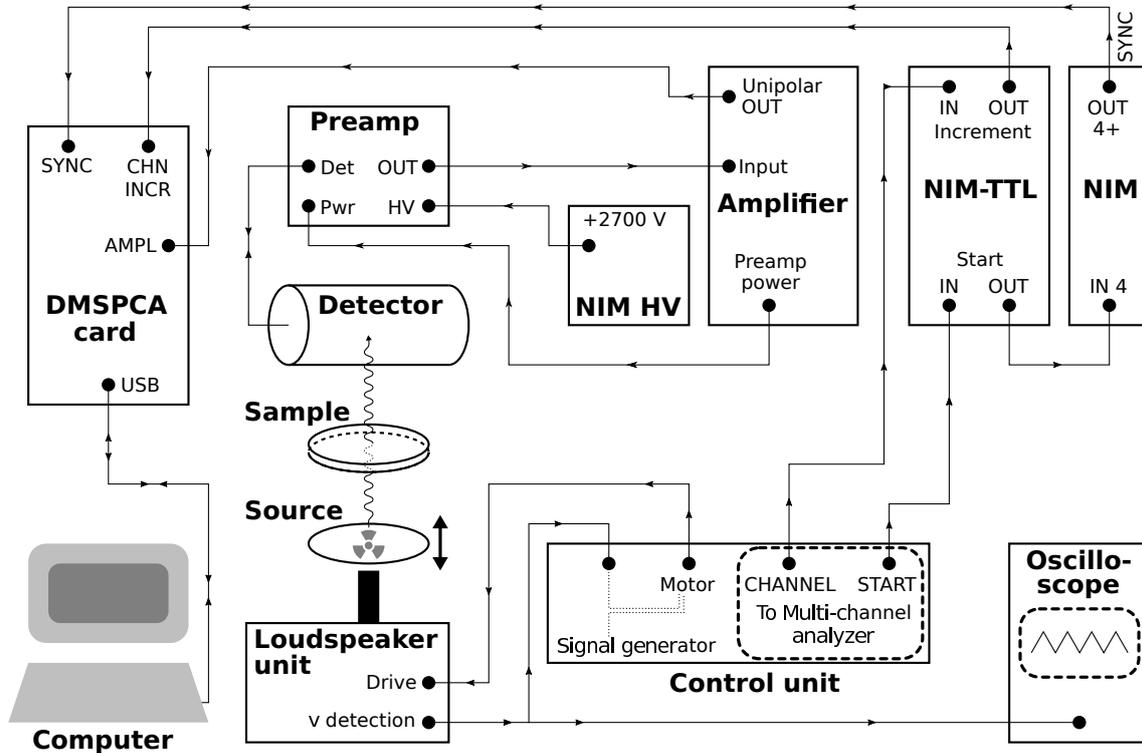


Figure 10: A sketch of the measurement setup, roughly using the actual layout, with directions of communication indicated by arrows. The DMSPCA analyzer card gets the amplified detector signal, and the signals from the movement control unit necessary for the time sampling (the start signal of a time period as well as the signals for changing between channels).

We detect the photons that are of 14.4 keV energy (so are from the excited state of the ^{57}Fe nucleus interesting to us, produced by the electron capture decay of ^{57}Co), and pass through the sample. The source is enclosed in lead shielding, with a hole (=collimator) in the appropriate direction, leaving the photons out towards the sample and the detector behind it. The detector is a proportional counter: a metal cylinder with a thin anode wire at the center, the cathode being the wall of the cylinder. The filling gas is Xe + CO₂ mixture at 1.5 bar pressure. We put a high positive voltage (+2700 V) onto the anode wire (taken from a NIM high voltage power supply unit). Photons get into the gas volume of the detector through a „window” made of beryllium metal (Be), and interact with the xenon gas via photoelectric effect (or Compton scattering),¹⁷ giving off their energy to an electron. This electron will in

¹⁷ *Photoelectric effect*: the gamma photon disappears, its energy given to a (usually strongly bound) electron in the atomic shell. *Compton scattering*: the photon goes further away after pushing an electron; the energy given off to it changes between zero and a maximum value (less than the total photon energy). Xenon atom has high atomic number ($Z=54$) and thus has high cross section for photoelectric absorption: the 14.4 keV photons give off their full energy with high probability. Beryllium ($Z=4$), however, almost does not get into any interaction with photons, that is why it is a good window material here.

turn create other ions. Because the cross section of photoelectric absorption falls off rapidly with increasing photon energy, our detector is much less sensitive to the higher energy photons (they might give off part of their energy through Compton scattering). This makes the 14.4 keV gamma energy even more convenient (beyond the fact, of course, that this is needed for the Mössbauer effect). Low energy hits in the detector are mainly from secondary X-rays and electronic noise.

The electron hit by the deposited photon energy ionizes the gas further, and the electrons set free start to move towards the anode. Close to it, high field strength makes electrons get enough energy during one mean free path so that they are able to ionize and set one additional electron free by a collision with another atom: an *electron avalanche* is formed.¹⁸ In this the number of electrons gets thus multiplied, but it remains proportional to the number of the primary electron-ion pairs, which is proportional to the deposited photon energy.¹⁹ Electrons gathered around the wire screen the high voltage electric field a little bit: this small decrease of the high voltage will be the electronic signal that tells about energy deposit and thus photon detection. From the wire, the signal goes to the preamplifier and then to a spectroscopic amplifier, the output of which goes directly to the multichannel analyzer that does all further processing, and feeds the output through a USB cable into the computer, where the appropriate driver program handles it. From this program terminal we can also set the discriminator, i.e. the lower and upper energy (signal magnitude) limits between which we accept the photon signals as ones belonging to the 14.4 keV gamma radiation (to be used for Mössbauer measurement). Because of the statistical fluctuation of the number of multiplied electrons, the energy resolution of the detector is only 10-15%; nevertheless, this is enough to differentiate between 14.4 keV photons and the others (e.g. the ~ 7 keV X-rays).

The other operating mode of the analyzer card is suited for recording Mössbauer spectra: here we group photons into channels not by signal strength but their arrival time (measured from the beginning time of the actual triangular signal period). As we have seen, this basically corresponds to a classification by actual source velocity, and in turn, by the scanned Doppler energy surplus of the photons. The signal generator and the timing of the channels need to be synchronized to this end. The signal of the start of a new time period as well as those pulses signalling the steps between channels (in every $40 \mu\text{s}$) are produced by the control unit of the signal generator, and sent to the analyzer card via a chain of different types (NIM, TTL) of customary nuclear electronics modules.

A remark: besides the 14.4 keV gamma photons (these are already absorbed by a thin metal plate, and do not get far in air as well), the ^{57}Co source also emits higher energy photons. The radioactive source is shielded by a lead enclosing, except for the upwards going collimator window for the outgoing gamma rays. Although the source can safely be said to be harmless, we ought to observe the ALARA principle, and not tamper above the collimator if unnecessary. The activity of the source changes from time to time (it decays; sometimes we get a newer source); the typical value is between 10 MBq and 100 MBq (the original factory-line value is 1.8-2.0 GBq). Of course, with higher activity there is less time needed for a measurement of a given accuracy.

¹⁸ In the mixture, xenon is a noble gas, and carbon dioxide is also chemically inert. Even a little number of oxygen or water molecules would hinder operation by trapping free electrons. This is the reason why overpressure is needed in the so that no outer air may diffuse in at pores and welds. In gaseous detectors used in particle physics, overpressure is unfeasible because of the necessarily light and thin walls, so continuous replacement of the filling gas is required.

¹⁹ This is the proportionality that gave the detector type its name. Higher anode voltage would yield a detector like a Geiger-Müller counter: here the greater electron multiplication and the surplus ionization by secondary X-ray photons produced along the path of the electron avalanche would lead to a continuous electric breakdown, whatever the number of initial electrons.

6 Measurement procedure

Turning on the apparatus:

The measurement apparatus is to be used under the supervision of the lab instructor. First we turn on the oscilloscope, the main switch of the control unit (*netz*), and the electronic circuitry of the gamma detector (on the rightmost NIM module). The oscilloscope will show the source velocity versus time (the triangular signal shape). Before turning on the high voltage power supply, verify that it is set to zero, then turn it on, then set the voltage to 2700 volts in a measured pace, **slowly**, waiting 3 to 5 seconds after each step! Under normal circumstances the red LED light on the amplifier module starts to glow, showing that pulses caused by gamma events are indeed detected. Turn on the DMSPCA analyzer card (at the back of the box). Start the driver program (`DMSPCA1.exe`) on the computer. It soon connects to the device; now our apparatus is ready for measurement.

Measuring the energy spectrum, setting the discriminator:

Our multichannel analyzer can be used in two operational modes: to measure the energy spectrum (PHA), and to measure Mössbauer spectra (MCS). First we measure the energy spectrum so that we know where to set the discriminator. To this end, we switch into the PHA (**P**ulse **H**eight **A**nalyzer) mode. On the graphic interface, using the **On/Off** buttons we can start and stop data taking. For the sake of better visibility, we can adjust the vertical axis range during the data taking, as well as change to logarithmic scale if we want to. In case of normal operation we will see a more or less continuous „background” (coming mainly from Compton scattering events of higher energy gamma rays), as well as two well pronounced peaks: one corresponds to photons of 14.4 keV energy (the ones we need), the other to smaller (~ 7 keV) energy X-ray photons.²⁰ We can try out if we place a thin aluminium or iron foil (both to be found scattered around the sample holder box on the table) in the pathway of the gamma ray between the source and the detector, then the aluminium foil ($Z = 13$) blocks the lower energy X-ray photons but transmits the 14.4 keV ones, while the iron foil blocks both of them. Fig. 11 shows a typical energy spectrum measured with our detector.

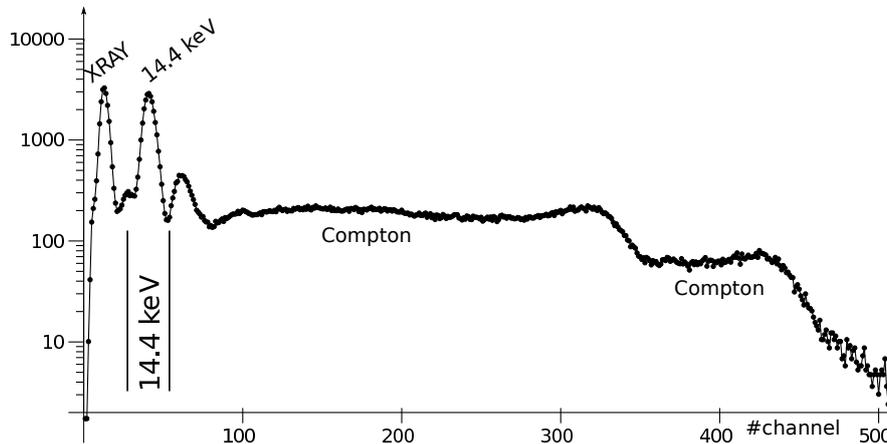


Figure 11: A typical energy spectrum (as a function of channel number) obtained with our measurement apparatus; some features highlighted (such as X-ray photons and higher energy hits, to get rid of, as well as the interesting 14.4 keV peak). Note the logarithmic scale.

Having observed the peaks in the energy spectrum, we turn on the discriminator on the graphic interface (in the *Discriminator* field, using the *Enable* button): this will only allow through photon signals with signal magnitude (i.e. energy) in a given range. The limits are,

²⁰ Actually, there are four slightly different energy X-ray photons coming around ~ 7 keV energy; the energy resolution of our detector is incapable of disentangle these.

not surprisingly, set by the *Set Upper* and *Set Lower* buttons. Guided by the eye, choose an appropriate range that encloses the 14.4 keV peak. (Remember, Mössbauer effect is caused only by these photons, other ones would only serve to increase background.)

A side note: if the moving apparatus of the source is turned on, electronic noise from it causes many fake „hits” at the lower energy end of the energy spectrum. Nevertheless, these also can be got rid off by setting the discriminator limits in an appropriate way.

Placing in the samples, measuring spectra:

Erase all remnant spectra, then change the operating mode of the card (in the *Mode* field) to the one necessary for Mössbauer spectrum measurement: MCS (**M**ulti-**C**hannel **S**caler). In this case the different channels sample different time instants of the velocity profile (i.e. the different velocities), as explained above to be necessary.

First put the stainless steel sample in the path of the gamma beam (with the purpose-fabricated sample holder). After starting data taking, the first impression is that channels are filled at a uniform speed (since photons are emitted randomly in time), but a few minutes later a clear absorption peak should be visible around the center. After collecting sufficiently many hits, we stop data taking and save the spectrum. The file name should always be telling about the sample (steel, iron or sodium nitroprusside) as well as measurement time. **After saving it** we erase the spectrum and insert the sodium nitroprusside sample, and start data taking again. Again, save the data, erase it, and finally do this same for the iron sample. After saving all three spectra, we can send them to ourselves from the computer (the files are ~6 kB each). After this we can turn off the apparatus; again do it carefully, the high voltage should be slowly set to zero. At the end do a check again on all the components if they are indeed turned off.

Remark: In case of the stainless steel sample, it is enough to have a few hundred hits per channel in order to be able to perform the calculations related to this at the desired level. In case of sodium nitroprusside, it is advisable to have a few thousand hits in each channel. In case of the iron sample, the peak *positions* can be fitted reasonably well with a couple thousand hits per channel, however, in order that the *line widths* to be properly determined (needed for calculating the effective thickness of the sample as well as the natural line width of the 14.4 keV level, see above, and also below), we might need a few ten (if not hundred) thousand hits per channel. Such a measurement usually cannot be done under the duration of the lab course (because of the low activity of the source); for this one task we usually use an existing high statistics spectrum.

Evaluating the spectra (each of you by your own):

The files containing the spectra are 512 rows of numbers (the numbers of hits in the respective channels) for all three samples. (This corresponds to dividing the time period of the triangular velocity-time signal into 1024 channels; the driver program of the card does the „folding” of the spectrum already, meaning that the contents of the channels lying symmetrically to the middle line are added up into one value (as the hits in two such channels correspond to the same velocity value). For fitting and plotting, we can use any program that is capable of reading and plotting numbers from such simple text files as well as fitting them with any pre-given functional form. (We should scan the file by eye nevertheless, to determine if there are indeed only hit numbers that we are after!) In all three cases, the functional form to be fitted is a baseline minus a combination of Lorentzians.

Preliminary remarks:

1. When typing in the functions to be fitted, *pay attention to the parentheses!* Soon we will see why it is necessary to call attention to this...
2. When fitting such a complicated function, it is necessary for virtually all fitting programs that one quite accurately *guesses* the parameter values by eye; we may try to compare the

fit function with the parameter guesses and the measured dataset by plotting them on top of each other. If there agreement between them is already satisfactory, then the fitting algorithm can be trusted to find the precise values of the parameters. *After* the fitting one should always plot the data and the fit (and also put it into the lab report) so that one sees if the fit is indeed properly done.

3. The data files do not contain the uncertainties of the channel contents; we can assume them to be the square roots of the channel contents (hit numbers), as in case of Poissonian distributions. In this way the fit algorithm will be better at finding the accurate uncertainty estimation of the final parameter values.
4. All answers to questions about the measured values should be given with uncertainty estimations. We should use the rules of *error propagation* whenever applicable.

Stainless steel:

The Mössbauer spectrum of steel is one with a singlet line. The probability of resonant absorption as a function of velocity is described by a Lorentzian curve (that is, as we have seen, the convolution of the gamma energy distribution and the absorption probability): this is the shape of the yield decrease where there is resonant absorption. The fit function is thus

$$\text{Steel: } f(x) = B - \frac{A}{1 + \left(\frac{x-x_0}{\Gamma/2}\right)^2},$$

where the four parameters to be fitted are: the B baseline, the peak height A , the position x_0 and the width Γ . (B and A have units of *hit number*, x_0 and Γ have that of *channel number*.) The most interesting here is carried by x_0 : if this is not exactly 256, then there is an isomer shift w.r.t. the gamma line of the source.

Sodium nitroprusside:

The spectrum of sodium nitroprusside shows quadrupole splitting (see also Fig. 7 above): there are two peaks, of whom it is however known that they have the same amplitude and width. Thus we have five parameters here: baseline (B), amplitude (A), width (Γ), and two peak positions: knowing already what type of information we want to extract, it is recommended to take the two corresponding parameters to be the average position (x_0) and the distance („splitting”, s):

$$\text{Sodium nitroprusside: } f(x) = B - \frac{A}{1 + \left(\frac{x - \left(x_0 - \frac{s}{2}\right)}{\Gamma/2}\right)^2} - \frac{A}{1 + \left(\frac{x - \left(x_0 + \frac{s}{2}\right)}{\Gamma/2}\right)^2}.$$

The most interesting parameter here is the value of the splitting.

Iron:

Here we have magnetic splitting (see Fig. 12), causing six peaks. Symmetrically positioned pairs of them have the same characteristics (of course their distance, i.e. splitting, is different). We have 13 fit parameters: the B baseline and a „package” like above for every pair of peaks: $A_1, \Gamma_1, x_1, s_1, A_2, \Gamma_2, x_2, s_2, A_3, \Gamma_3, x_3, s_3$. The average positions x_1, x_2 , and x_3 do not differ much in principle, nevertheless consider them as separate parameters! The function is

$$\text{Iron: } f(x) = B - \frac{A_1}{1 + \left(\frac{x - \left[x_1 - s_1/2\right]}{\Gamma_1/2}\right)^2} - \frac{A_1}{1 + \left(\frac{x - \left[x_1 + s_1/2\right]}{\Gamma_1/2}\right)^2} -$$

– twice more the same, for the two other peak pairs.

Here the peak positions carry information about the magnetic field, and the peak widths about the thickness of the sample and about the natural line width.

7 Measurement tasks

1. Calibrate the energy and the velocity vs. the channel number using the spectrum of the iron sample (already fitted). The velocity difference between the two farthest absorption peaks is known to be $\delta_6 - \delta_1 = 10.6162$ mm/s, and the photon energy is 14413 eV.
2. Determine the isomer shift of stainless steel and that of $\text{Na}_2\text{Fe}^{\text{II}}(\text{CN}_5)\text{NO}$ (sodium nitroprusside) compared to that of iron.
3. Determine the value of the electric field gradient $\frac{\partial^2 V}{\partial z^2}$ in the sodium nitroprusside sample according to Eq. (4.2). The value of the quadrupole moment of the excited state of ^{57}Fe is known to be $Q_{3/2} = 0.21$ barn (1 barn = 10^{-28} m²) from other measurements. We can use $\eta = 0$. Remember, the ground state of ^{57}Fe has $I = \frac{1}{2}$ nuclear spin, the 14.4 keV excited state has $I = \frac{3}{2}$.
4. In a magnetic field B , the Zeeman split (shift) of the nuclear energy levels is given by $\Delta E_m = -\frac{m}{I}\mu_I B$, where $\mu_I = g\mu_N I$. Determine the magnetic moment of the ^{57}Fe nucleus in its first excited state ($\mu_{3/2}$). Determine the value of B in the iron sample. (The ground state magnetic moment of ^{57}Fe is known: $\mu_{1/2} = +0.090604 \mu_N$.) To identify the levels belonging to the lines, it might help that the relative intensities \mathcal{I} of transitions between different sub-levels obey the following:²¹

$$\mathcal{I}_{\pm\frac{3}{2} \rightarrow \pm\frac{1}{2}} : \mathcal{I}_{\pm\frac{1}{2} \rightarrow \pm\frac{1}{2}} : \mathcal{I}_{\pm\frac{1}{2} \rightarrow \mp\frac{1}{2}} = 3 : 2 : 1.$$

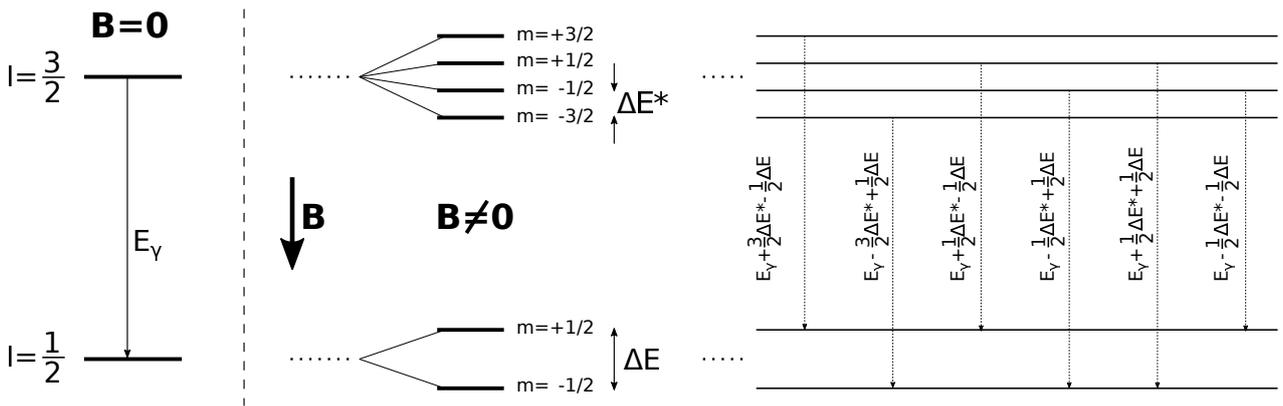


Figure 12: Magnetic splitting in the iron sample (levels and transitions shown). Of course the nominal E_γ energy is several orders of magnitude higher than the split caused by the magnetic field. In the ground state, μ is positive, so the energy shift has the sign as plotted. However, in the excited state, at first sight, $g_{3/2}$ could be positive as well as negative (one will see): the plot was made assuming that $g_{3/2} > 0$.

From the difference of positions of split peaks (i.e. from the s_i values) the energy difference of the ground state and the excited state apparently cancels (which is approximately 14.4 keV, but is known to far less precision than the split between the levels). Using the s_i values obtained from the fit of the spectrum we can determine ΔE and ΔE^* with a simple linear fit (to three points). From this we can get to B and $g_{3/2}$.

5. Compare the measured electric field gradient (Problem 4) and the magnetic field (Problem 5) to that calculated in the Bohr model of the hydrogen atom (where the electron that causes these fields at the place of the proton orbits it at a fixed distance with a fixed velocity.)
6. Plot the measured Γ_i^{exp} widths of the lines in the spectrum of iron versus the relative line

²¹ The spin 3/2 state decays into a spin one photon and a spin 1/2 ground state. The ratios given here are the modulus squares of the corresponding Clebsch-Gordan coefficients (owing to the Wigner-Eckart theorem).

intensities w_i (see above), and fit it with a linear function. Using Eq. (4.4), and the obtained linear fit parameters calculate the life time of the excited state, its uncertainty, and compare it to the value found in the literature (141.8 ns). Determine also the effective thickness of the sample (T_A), and check if it is indeed justified to neglect the quadratic term in Eq. (4.4). As mentioned around there, we can use $T_S = 0.5$ for the radioactive source.

7. From the calibrated velocity-time correspondence, determine the maximum spatial offset of the radioactive source in motion. Assuming a distance of 5 cm between the source and the anode wire of the detector, what percentage distance fluctuation does one have? (Does this cause significant distortion of the line shapes in the Mössbauer spectrum?)

8. (optional, see material below) Contemplate on a measurement setup that can be used to detect gravitational redshift. (What would be the necessary height of the sample, what source activity should be used, for how long a data taking time, in order the effect to be observable?)

8 Overview questions

1. What is resonant absorption?
2. Why it is more difficult to observe resonant absorption in nuclear transitions than it is for transitions between atomic shell energy levels?
3. What is Mössbauer effect?
4. How does the strength of Mössbauer effect depend on temperature, and why was this a surprise?
5. Why exactly do we use ^{57}Co as radiation source in the experiment?
6. How does ^{57}Co decay into ^{57}Fe , and what particles are produced in this decay?
7. How many split levels do we observe in the spin 1/2 ground state and in the spin 3/2 excited state of the ^{57}Fe nucleus in a homogeneous external magnetic field (and for what reason)? How many allowed transitions are between these levels, and why only so many?
8. What is the unit of electric quadrupole moment?
9. What causes quadrupole splitting?
10. What factors can cause isomer shift?
11. How many split levels of the 14.4 keV excited state of the ^{57}Fe nucleus are caused by a homogeneous external electric field?
12. What is the polarity of the high voltage of the gamma detector? (Where is the anode and where is the cathode?)
13. How does the photon detecting instrument work in our setup?
14. What types of interactions are possible between the photons and the detector material? What has the highest probability in our measurement setup?
15. How does the position, velocity and acceleration of the radioactive sample change as a function of time? What would happen to the measured spectrum in case of another functional form?
16. Is our detector sensitive to 137 keV gamma photons coming from the ^{57}Co source? Why?
17. What is the energy resolution of our photon detector; where do the limitations to it come from?
18. What is the role of the discriminator in the measurement, why is it necessary to use it?
19. How can one determine the life time of the spin 3/2 excited state from our measurements?
20. What makes it possible for us to be able to change the energy of the gamma photons with a relative accuracy of 10^{-14} ?
21. Why does one occasionally apply external fields in Mössbauer spectroscopy?

9 Additional material: gravitational redshift

Gravitational redshift was a prediction of general relativity: according to this, photons going „upwards” in a gravitational field lose energy, their frequency decreases (thus the name *redshift*). In a homogeneous field of g strength and H height difference this energy loss is

$$\text{(A mnemonic:)} \quad \begin{array}{l} \Delta E_\gamma = m_\gamma g H, \\ E_\gamma = m_\gamma c^2 \end{array} \quad \Rightarrow \quad \underline{\underline{\Delta E_\gamma = \frac{gH}{c^2} E_\gamma.}}$$

The resulting formula is **true**. This short mnemonic might help to memorize it; nevertheless, photons of course do not have m_γ mass, let alone so that $E_\gamma = m_\gamma c^2$ holds. On top of all: in the inhomogeneous case, in weak gravitational fields (i.e. everywhere with the exception of close vicinity of neutron stars and black holes) we have

$$\Delta E_\gamma = \frac{\Phi_2 - \Phi_1}{c^2} E_\gamma,$$

where $\Phi_2 - \Phi_1$ is the change of the (Newtonian) gravitational potential.²² The above formula is a special case, since in a homogeneous field, $\Phi = gz$ at a height of z .

One can try to verify this prediction in optical spectroscopy e.g. by studying the difference of positions of well-known (hydrogen or helium) spectral lines found in starlight (coming from the Sun or from a denser star, like a white dwarf) and that coming from a terrestrial gas discharge lamp. For example, the energy lost to a photon when „climbing out” from the surface of the Sun is

$$\Delta E_\gamma = \frac{1}{c^2} \frac{GM_\odot}{R_\odot} E_\gamma \approx 2.1 \cdot 10^{-6} \cdot E_\gamma.$$

Here $M_\odot = 2 \cdot 10^{30}$ kg and $R_\odot \approx 700000$ km are the solar mass and radius. If E_γ is taken as the well-known visible $H\alpha$ spectral line of hydrogen from the Balmer series ($\lambda = 656$ nm), then $E_\gamma = 1.9$ eV, and $\Delta E_\gamma \approx 4 \cdot 10^{-6}$ eV. It is not inconceivable to observe this shift with a high-resolution spectrograph,²³ however, spectral lines in sunlight undergo Doppler broadening (owing to the high temperature and thus high average atomic velocity). Up to the 1960s there were no convincing experimental verification of gravitational redshift in starlight.

By means of the precision offered by Mössbauer spectroscopy, however, Pound and Rebka managed to measure it in a terrestrial experiment in 1960 [4]. They observed the energy change of the 14.4 keV gamma photon emitted by the ^{57}Fe nucleus: firstly they measured a (simple, preferably singlet) Mössbauer spectrum of a given sample and then did the same with the sample (and the detector) raised to a given height (they had $H = 22.5$ m in the original experiment), and looked for a change in the position of the absorption line. This shift could and did reveal the energy loss of the photon suffered by traveling the height difference.

The change is $\Delta E_\gamma = \frac{gH}{c^2} E_\gamma$, substituting the numbers, the result is $3.52 \cdot 10^{-11}$ eV. Remembering the natural line width of the 14.4 keV photons, $\Gamma_0 = 4.7 \cdot 10^{-9}$ eV (with the width of the Mössbauer line being circa twice that value) this means that one has to observe the shift of the Mössbauer line by an amount that is 1/300th of its width. This is not at

²² This can be derived in general relativity by knowing that weak gravitational fields ($\Phi \ll c^2$) enter the space-time metric by modifying the g_{00} component as $g_{00} \approx 1 + \frac{2\Phi}{c^2}$, and that the proper time interval $\Delta\tau$ and the coordinate time interval Δt relate to each other as $\Delta\tau = \sqrt{g_{00}} \Delta t$. If we invoke the fact that the wave number four-vector of a photon gets parallel transported along the world line (this means practically that the frequency of the photon is constant if measured with respect to the proper time, whose lapse depends on the position), we are ready: the change in the frequency *with respect to the coordinate time* (the outside observer) will be written as $\Delta\omega = \frac{\Phi_2 - \Phi_1}{c^2} \omega$.

²³ As a comparison, the fine structure of the $H\beta$ hydrogen line contains lines with an $0.94 \cdot 10^{-6}$ eV energy difference, observable with good instrumentation.

all impossible if enough data is collected (and the spectrum is precise enough) so that the uncertainty in the peak position becomes so small.

To contemplate over the number of hits necessary for this (and try to compare to the accuracy of our fits performed on spectra with known number of hits), we can assume that if one has N^2 times as many hits, the uncertainty of the peak position from the fit becomes N times smaller; this is to be somewhat expected (knowing the Poissonian distribution), and indeed holds quite accurately.

It might be interesting to point out that if one changes the H height by a factor of, say, 2, then the accuracy of the peak position necessary to observe the effect can be twice as bad (i.e. twice big uncertainties would be allowed). But by placing the sample twice as far, only quarter as much of the (isotropically produced) photons from the source reach the sample, which means four times less hits (thus exactly two times less accurate peak position fit) for a given data taking time. It seems thus that if the source activity and the measurement time are taken as fixed (i.e. limiting factors for the measurement), then the height H cancels (at a first approximation) from the „figure of merit” of the measurement setup.

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<http://www.medc.dicp.ac.cn/Resources.php>