eMIL: emission Mössbauer spectrometer

Author: Alice Kern
Supervisors: Juliana Schell, Karl Johnston
CERN, Geneva, Switzerland

Abstract
The advanced emission Mössbauer spectrometer eMil was built for the emission Mössbauer (eMS) collaboration at ISOLDE/CERN. The set-up combines on-line and off-line isotope implantation used to measure hyperfine interactions in solids. The specific design of each lid-sample-holder makes it possible to perform measurements under versatile conditions. The set-up allows fast changes between different sample holders without having to realign, which makes eMIL extremely flexible.
Within the scope of my CERN Summer Student Programme, I joined the Solid State Physics (SSP) Group at ISOLDE. During this time at CERN I prepared the set-up for Beam Time. The set-up was modified so that it complies to the electrical and mechanical standards in order to be moved to the experimental hall where the experiments were performed. Furthermore, I was able to participate in the Beam Time during which multiple experiments where conducted using emission Mössbauer spectroscopy by the emission Mössbauer collaboration at ISOLDE/CERN.

Keywords
nuclear solid state physics, Mössbauer spectroscopy, Mössbauer effect

Acknowledgements

I would like to express my gratitude to my supervisors Juliana Schell and Karl Johnston for giving me the opportunity to work within the Solid State Physics (SSP) Group at ISOLDE.
Furthermore, I want to emphasize that I am extremely grateful to Juliana Schell, for her guidance and commitment to making this a fruitful summer and for giving me the opportunity to continue my work with the SSP Group at ISOLDE/ CERN after finishing my Summer Student Programme.
I am also thankful to Ian Chang Jie Yap for his support with theoretical questions, his helping hands in the laboratory and his friendship. Thanks should also go to Dmitry, who generously provided knowledge and expertise.
Lastly, I want to thank Hannes Gürlich for all the entertainment in the office and his emotional support.

Contents

1 Introduction

Emission Mössbauer spectroscopy is one of the most powerful analytical techniques to study local probe structure and electronic properties in condensed matter. It is based on the Mössbauer effect, which describes the recoilless nuclear emission and resonant absorption of γ-rays. This method allows us to analyze the electronic and magnetic structure as well as the geometry of the studied materials on an atomic scale.
eMil is an emission Mössbauer spectrometer which was build for the emission Mössbauer collaboration at ISOLDE/CERN [10] [3].
When I joined the Solid State Physics Group as a Summer Student in July 2023 eMil has never been used for a Beamrun before and needed to be approved by CERN's electrical Safety and Mechanical Safety officers to be moved to the Isolde experimental hall. During my time at CERN I prepared the set up to be moved to the GLM area where later the experiments were conducted. In the following chapters I will first provide an overview of the theoretical background, secondly, I will introduce the experimental set-up and third give an outlook on further plans. My tasks involved mechanical and electrical work on the set-up. I was also able to take part in Beam Time with the eMS collaboration and conduct experiments. It should be noted that this report will not present experimental data, since the week of Beam Time was also the last week of my contract, therefore, there was no time to analyze the data. However, since I am joining CERN as a USER within the Mössbauer collaboration I am sure there will be more Beam Times and experimental data which will be reported in the future.

2 Background

2.1 Mößbauereffect

In 1958 Rudolf Ludwig Mössbauer a German physicist published the paper "Gammastrahlung in Ir^{191} (Gamma Ray Nuclear Resonant in Fluorescence Spectroscopy)" in the 'Zeitschrift für Physik'. In the same year he performed experiments where he used the Doppler Effect to scan resonant lines. The experimental data he published laid the foundation for a new experimental technique the Mössbauer Spectroscopy often also referred to as nuclear gamma resonance (NGR). Ludwig Mössbauer was awarded the Nobel Prize in physics in 1961 for his discovery and the theoretical basis of this phenomenon was called the Mößbauer effect. [1]
The Mössbauer effect is the phenomenon of recoilless emission and recoilless resonant absorption of γ-rays by the nucleus. The effect is of quantum nature and results are obtained from hyperfine interactions: the electric monopole, quadrupole and magnetic dipole interactions.

2.1.1 Recoil and Dopplershift

Assume a free excited nucleus at rest. If a γ-ray is emitted from a free excited nucleus with a Mass m, due to the conservation of momentum, if an impulse acts on the nucleus, it will cause it to move in the appropriate direction. This is observed as the recoil of the nucleus. Therefore, the energy of the emitted electromagnetic radiation is equal to the transition Energy E_0 minus the recoil Energy E_R. The recoil of the nucleus causes a shift of the emission line E_0 by an amount of E_R. This shift of emission lines prevents the subsequent resonant absorption of the γ-rays.

If we look at a monoatomic gas, then the energy of the excited nucleus is given by

$$E_{pre} = E_a + \frac{\vec{p}^2}{2M}. \tag{1}$$

with E_a denoting the excited state. After the emission the energy is given by

$$E_{pre} - E_{post} = E_g + \frac{(\vec{p} - \hbar\vec{k}^2)^2}{2M}. \tag{2}$$

with E_g denoting the ground state. The energy difference can now be calculated as follows

$$E_{pre} - E_{post} = \hbar\omega_0 + \hbar(\vec{k} \cdot \vec{v}) - \frac{\hbar^2\vec{k}^2}{2M} \tag{3}$$

where $\hbar(\vec{k} \cdot \vec{v})$ describes the Doppler effect and $\frac{\hbar^2\vec{k}^2}{2M}$ is the recoil term. The emission spectrum of a monoatomic gas is shown in Fig. 1.

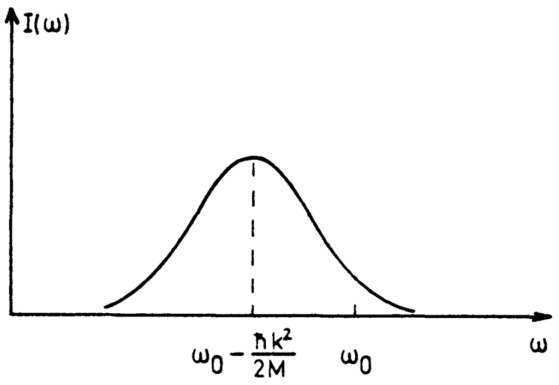

Figure 1: Emission γ-spectrum of a monoatomic gas in thermal equilibrium. [4]

The emission spectrum is shifted by $\frac{\hbar^2\vec{k}^2}{2M}$ compared to ω_0. In the absorber the conditions are reversed, the absorption line is moved to higher frequencies, therefore a higher energy is needed than the excitation energy [4].

However, if the nucleus is bound in a lattice instead of being a free nucleus then the recoil will be transferred via linear momentum to the lattice. Energy can still be lost but this will occur in form of discrete vibrations called phonons. The lattice as a whole acts as recoiling body and the conservation of momentum is satisfied by the momentum of the lattice which results in a practically recoilless emission. If the event is recoilless then the resonant emission and absorption by another nucleus which is also bound to the lattice is possible [2] [3].
To explain further, in a solid the atoms are bound with a typical energy of $20\,eV$ needed to displace an atom. The recoil energy is in an order of $10^{-3}\,eV$ which will only set the atom in a vibrational mode at most. If there are no phonons produced the whole lattice takes up the recoil. The mass of the whole lattice is 10^{20} times bigger than the mass of one Atom, hence the recoil and the thermic movement of the solid is negligible.

2.1.2 Debye-Waller-Factor

The ratio of the unshifted $\gamma-$emission to the total $\gamma-$emissions or the ratio of recoil-free to total nuclear resonant absorption is called the $Debye - Waller$ factor f_D. f_D is temperature dependent and the highest at $T = 0$. [4] The $Debye - Waller\,factor$ is a measure of how effective the Mössbauer source works, since the shifted γ- emission will not have enough overlap to produce a significant peak in the resonance spectrum.
In the simple classical model, a nucleus is considered, which continuously emits electromagnetic radiation with an angular frequency of $\omega_0 = \frac{E_\gamma}{\hbar}$ (Hertzscher Dipol) and also oscillates around the equilibrium position. The recoil effect is of quantum nature therefore it does not occur in the classical radiation theory because the radiation pressure has to be 0 on a hertz dipole due symmetry considerations.
The analysis can first be limited to one vibrational frequency Ω which corresponds to the Einstein model of vibrations in a solid. The electrical field of the emitted radiation is given by

$$E(t) = E_0 exp(-i[\omega_0 t + kx(t)]) \tag{4}$$

with the vibration of the nucleus $x(t) = asin\Omega t$, a denoting the amplitude of the vibration. Substituting x(t) and expanding the exponential function gives

$$\begin{aligned} E(t) &= E_0 exp(i\omega_0 t) exp(-ikasin\Omega t) = \\ &= E_0 exp(-i\omega_0 t)(1 - ikasin\Omega t - \frac{k^2 a^2}{2} sin^2 \Omega t + \cdots) \end{aligned} \tag{5}$$

using the relation

$$sin^n \Omega t = \frac{1}{(2i)^n} [exp(i\Omega t) - exp(-i\Omega t)]^n \tag{6}$$

which leads to

$$\begin{aligned} E(t) &= E_0 exp(-i\omega_0 t) exp[-ikx(t)] = \\ &= \left(1 - \frac{k^2 a^2}{4} + \cdots\right) exp(-i\omega_0 t) \\ &+ \left(-\frac{ka}{2} + \cdots\right) (exp[-i(\omega_0 - \Omega)t] - exp[-i(\omega_0 + \Omega)t]) \\ &+ \left(\frac{k^2 a^2}{8}\right) (exp[-i(\omega_0 - 2\Omega)t] - exp[-i(\omega_0 + 2\Omega)t]) + \cdots]. \end{aligned} \tag{7}$$

It can be seen that the main frequency ω_0 is shifted by the factor of $(1 - \frac{k^2 a^2}{4} + \cdots)$ and the side-lines with the frequencies $\omega_0 \pm \Omega$, $\omega - 0 \pm 2\Omega$ arise. This means that the oscillations of the nucleus reduces the intensity by $(1 - \frac{k^2 a^2}{4} + \cdots)$, this is called the Debye-Waller Factor. [4] To get the amplitude of the unshifted frequency all terms of the series expansion have to be summed up

$$A(\omega_0) = 1 - \frac{k^2 a^2}{4} + \cdots = exp\left(-\frac{k^2 a^2}{4}\right). \tag{8}$$

The Debye-Waller Factor is the absolute square of $A(\omega_0)$,

$$f_D = |A(\omega_0)|^2 = exp\left(-\frac{k^2 a^2}{4}\right) = exp(-k^2 < x^2 >) = J_0^2(ka). \tag{9}$$

Here the relation of the mean square deflection for a $1D$ harmonic oscillator $< x^2 >= \frac{a^2}{2}$ was used. The classical model however differs from the correct quantum mechanical model quite a bit as seen in 2. In the classical model at $T = 0$ there are no vibrational modes and $f = 1$. In the quantum mechanical model at $T = 0$ it can be seen that $f < 1$, due to zero point oscillations which are non equal to zero. At $T = 0$ there are no emission lines for $\omega > \omega_0$ because at this temperature the γ particles cannot have enough energy to create vibrations. To calculate $< x^2 >$ the Einstein Model can be used where only one oscillation frequency Ω is assumed. The total Energy of a harmonic oscillator with n oscillation modes is given by

$$E_n = \hbar\Omega(n + \frac{1}{2}). \tag{10}$$

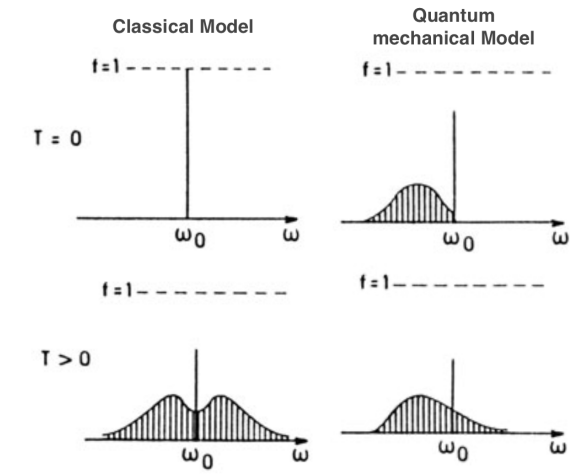

Figure 2: Comparison of the classical and quantum mechanical Theory of the Mößbauer effect. Adapted from [4]

The probability to find the oscillator in the state n is given by

$$P_n = \frac{exp(-n\hbar\Omega)/k_BT)}{\sum_{n=0}^{\infty} exp(-n\hbar\Omega/k_BT}). \tag{11}$$

By equating the mean potential energy with the half of the total energy the time averaged squared deflection $\overline{x_n^2}$ in state n can be calculated. Taking into account the occupation probability and averaging over all possible states n

$$< \overline{x^2} >_E = \frac{\hbar}{M\Omega}\left(\frac{1}{2} + \sum_{n=0}^{\infty} nP_n\right). \tag{12}$$

Until now, it was assumed that there was only one phonon frequency, if there are more possible frequencies a distribution function $Z(Q)$ for all phonon frequencies can be used. The distribution is normalized $\int Z(\Omega)d\Omega = 3N$ where N is the number of the lattice elements. Eq. 12 can be rewritten as follows

$$< x^2 >= \frac{1}{3N}\int_0^{\infty} Z(\Omega) < x^2 >_E d\Omega = \frac{\hbar}{6MN}\int_0^{\infty} \frac{Z(\Omega)}{\Omega}\left[1 + \frac{2}{exp\hbar\Omega/k_BT - 1}\right] d\Omega, \tag{13}$$

plugging $< x^2 >=< u^2 > /3$ into equation 9 gives for the Debye-Waller factor

$$f(T) = exp\left(-\frac{\hbar k^2}{6MN}\int_0^{\infty} \frac{Z(\Omega)}{\Omega}\left[1 + \frac{2}{exp(\hbar\Omega/k_BT) - 1)}\right] d\Omega\right). \tag{14}$$

To calculate $f(T)$ the phonon state density, $Z(\Omega)$ has to be known. The Debye-Modell is a good approximation in which the phonon density is given as

$$Z(\Omega) = \frac{9N\hbar^3}{k_b^3}\frac{\Omega}{\Theta} \qquad for \quad \Omega < \Omega_D \tag{15}$$

$\Omega_D = k_B\Theta/\hbar$ is the Debye frequency and Θ the Debye Temperature. Plugging this into equation 13 gives

$$< x^2 >= \frac{3\hbar^2}{4Mk_B\Theta}\left[1 + 4\left(\frac{T}{\Theta}\right)^2 \int_0^{\Theta/T} \frac{y}{e^y - 1} dy\right]. \tag{16}$$

For temperatures $(T >> \Theta)$, $< x^2 >$ depends linearly on the temperature for $(T << \Theta)$ it is quadratic dependency on T. Therefore for low temperatures the Debye- Waller factor in Debye-Modell is

$$f_D(T) = exp\left(-\frac{\hbar k^2}{2M}\frac{3}{2k_B\Theta}\left[1 + n\frac{2\pi^2}{3}\left(\frac{T}{\Theta}\right)^2\right]\right) \tag{17}$$

From this it is apparent that the phonon frequency density $Z(\Omega)$ can be determined by calculation of the Debye-Waller factor. If the recoil energy $\hbar k/2M$ grows, the Debye-Waller factor becomes smaller, hence a larger atomic mass M leads to a higher $f_D(T)$. Furthermore the energy of the $\gamma-$emission should not be too high since $E_\gamma \hbar k = E_\gamma/c$, typical values are $E_\gamma < 100\, keV$. In other words the energy level difference between the excited state and the ground state of the atom should be in the order of $100\, keV$. The Temperature should be low so high values for $f_D(t)$ can be archived, which leads to a more efficient Mössbauer source. Furthermore $T < \Theta$ should apply and the maximum Debye-value is obtained at $T = 0$. High Debye temperatures Θ are preferred, thus high Debye cut off frequencies Ω_D. High Debye temperatures correlate with materials with high binding energies which are preferred for Mössbauer Spectroscopy. [4]

2.2 Emission Mössbauer Spectroscopy

Emission Mössbauer spectroscopy (eMS) technique uses the implantation of radioactive isotopes as probe atoms into solids. The emission spectrum is measured by measuring the resonant absorption of the γ- radiation emitted during the ground state transition of the radioactive probe nucleus by a stable nucleus of this isotope in a suitable sample material.
While absorption spectra measurements in conventional Mössbauer spectroscopy are measured in transmission geometry, eMS is based on emission geometry. The central principle of this technique is based on the recording of the emitted radiation of an absorbing nucleus after a resonant absorption and de-excitation (Fig. 4). The excited state decays by mean of internal conversion followed by the emission of conversion electrons, followed by the emission of Auger electrons or X-ray, when the vacancy is refilled. Alternatively, a γ- photon of $14,4\, kEv$ might be re-emitted. [3]

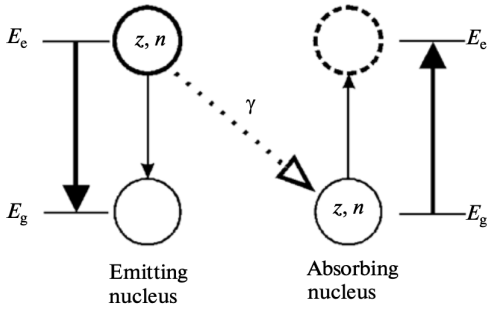

Figure 3: Nuclear transition an an emitting an absorbing nucleus. Taken from [5]

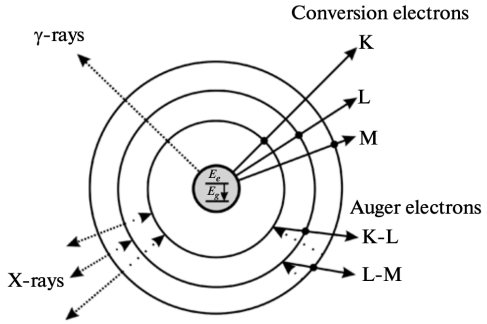

Figure 4: De-excitation of nucleus.Taken from [5]

2.3 Hyperfine Parameters

Hyperfine parameters describe the interaction between nuclei and their surrounding magnetic or electrical fields. These hyperfine interactions can be observed by Mössbauer spectroscopy and give information about the chemical, physical and crystallographic properties. For Mössbauer spectroscopy there are three hyperfine parameters which need to be considered, the isomer shift, quadrupole splitting and magnetic hyperfine splitting. [7]

2.3.1 Isomer shift

The isomer shift is an energy or frequency shift of the atomic spectra lines, which occurs when one nuclear isomer is replaced by another. It can be written as $\delta = \alpha_0[\rho_a(0) - \rho_s(0)]$, rho_a and ρ_s are the electron densities of the absorber and the source, respectively.
α_0 is a proportionality constant which solely depends on the nuclear parameters and has been determined for various Mössbauer sources. ρ_a is usually known and ρ_s can be determined from the measured isomer shift. The nuclear energy of the $\gamma-$ ray transition from one nuclear level in the source is comparable with the one in the absorber. In the absorber it might differ since the electronic and crystallographic environment is different. The isomer shift is sensitive to oxidation and therefore in ^{57}Fe Mössbauer spectroscopy able to identify Fe^{2+} and Fe^{3+}. For Nuclei with a smaller radius in the excited state than in the ground state δ_0 will decrease with increasing electron density at the ^{57}Fe nucleus. For nuclei with a larger radius in the excited state than in the ground state, the increase of electron density would lead to an increase of the isomer shift. [7] [8]

2.3.2 Quadrupole splitting

The interaction of nuclear energy levels with the surrounding electromagnetic field gradient with non-spherical symmetric field splits the excited state of ^{57}Fe into two states $m_I = \pm 1/2$ and $m_I \pm 3/2$ (see Fig. 5). Therefore, there are two possible transitions from the excited state to the ground which corresponds to two peaks shown by the Mössbauer spectrum. The magnitude of the quadrupole splitting depends on the asymmetrical electric field.

2.3.3 Magnetic hyperfine splitting

If the nucleus has a isospin quantum number I which is higher than 1 The coupling of a magnetic dipole moment μ with the surrounding magnetic field H results into the magnetic hyper fine splitting. For ^{57}Fe the excited state will split into 4 non-degenerate energy levels and the ground state into two non-degenerate energy levels (see Fig. 5). In this case the Mössbauer spectrum will show six peaks.

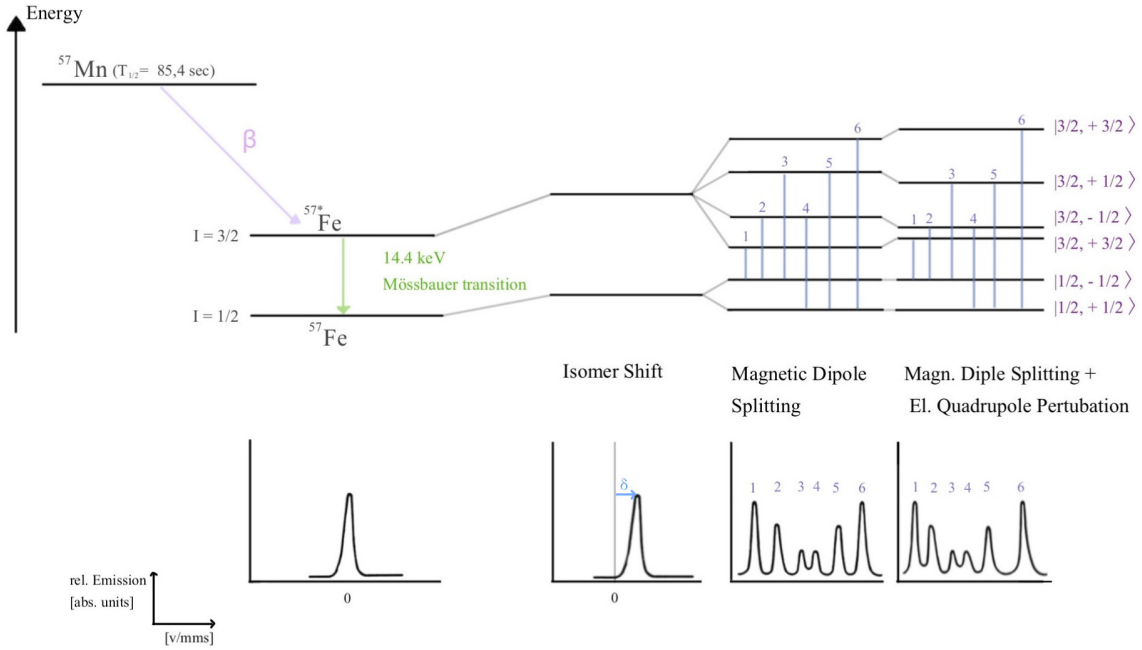

Figure 5: Schematic diagram of the hyperfine interactions between the electrons and the nucleus ^{57}Fe and the corresponding Mössbauer spectra.

3 Materials and Experimental Details

3.1 eMil

eMil is an advanced emission Mössbauer Spectrometer with a parallel-plate avalanche detector which was built for the Mössbauer collaboration at ISOLDE/CERN. This set-up, based on emission geometry, allows on-line and off-line measurements and has advantages over conversion electron and transmission Mössbauer spectroscopy. [3]
It was designed to measure hyperfine interactions in solids via which charge and spin states of the nucleus can be accurately determined. This can be related to the probe's environment and charge states of the implanted isotope of interest. The PPAC detector is placed at $90°$ to the incoming beam. A Beryllium filter is placed at the flange of the implantation chamber which blocks X-rays and high energetic electrons which are emitted during the β^- decay and allows $\gamma-$ray transmission of around 90%.
The detector is mounted on the transducer with a constant acceleration. The incoming signal is transferred to an amplifier and the oscilloscope, the signal will be amplified and then transmitted to the SCA (single channel analyzer). The SCA output is connected to a counter unit, the pulses shape and the count rate should be controlled since any unusual change can hint to vacuum leaks, sample absence ect.. The signal from the SCA is transferred to a MCA (multi channel analyzer), which allows multichannel scaling data acquisition. Furthermore, the MCA receives data from the transducer. The MCA will transfer the information to the PC after the evaluation process.

The pumping unit for eMIL is separated to eMIL to isolate it from vibrations. The whole pumping system is automatized and consists of a turbo pump, a fore pump, five valve gates and angle valves, Pfeiffer RPT 200 and CPT 200 gauges can be controlles by RS-485 serial communication with Siemense Simatic.
The versatility of the-set up is archived via different sample-holders (lids). Currently there are four lids (hot lid, cold lid, powder lid, rotation/magnetic lid). Each of these lids allow specific measurements and can be mounted on eMIL easily. This allows a remarkable flexibility of the set up. In Fig. 6 the implant-

ation chamber with the mounted hot lid can be seen, during Beam Time it is possible to dismount and mount any of the other lids without realigning the set-up. This allows for fast and diverse measurements during one Beam Time.

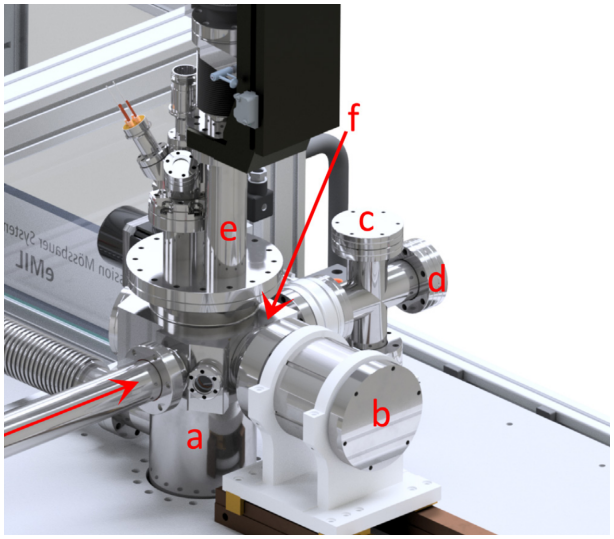

Figure 6: The implantation chamber(a) with the mounted hot lid (e). The arrow shows the path of the incoming beam. The beryllium window (f) is placed behind the transducer with the PPAC detector (b) the distribution cross can be used for chemical and magnetic extension (d) and a farraday cup can be mounted (c) [3].

3.2 Beam Time

At the CERN facility protons are being produced and accelerated up to 50 MeV by LINAC 4 (linear accelerator 4) then the protons are induced into the Synchrotron Booster. The synchrotron Booster possesses four superimposed rings with a radius of 25 m, where the protons get accelerated up to 1.4 GeV. The protons hit the ISOLDE target, which is made of Uranium Carbide (UCx) for producing the Mössbauer probe 57Mn with a yield of 3×10^8 ions per second. For this, the maximum available proton current is required (up to 2 micro-Ampere). The beam is ionized using LASER with the RILIS setup via stepwise resonance photo-ionization. The ISOLDE facility has two separation magnets the General Purpose Separator (GPS) and the High Resolution Separator (HRS). GPS allows the separation of three mass separated beams into two low mass-separated beams (GLM) and high mass-separated beams (GHM). The Mössbauer set-up is connected to the GLM beamline where the implantation of ions takes place [3]. During the Beamtime run in week 37 of 2023 three experiments were conducted by the eMS collaboration. The proposals for the experiments (IS-683, IS-681, IS-630) can be read on the eMS collaborations website, see [9].

4 Conclusion and Outlook

The emission Mössbauer spectrometer had some initial electrical problems, which were figured out and it could be proven that eMIL has the ability to become the new standard emission Mössbauer spectrometer for the eMS collaboration Beam Times. The data collected during the Beam Time will give additional experimental information for each sample. With the measured isomer shifts in solids together with theoretical approaches, semi-empirical models will be developed, which can be used to determine unknown charge and spin states of Fe in various materials.

Bibliography

[1] V.G: Semenov, Fifty Years since the Discovery of the Mössbauer EffectJ Anal Chem 64,1082–1084 (2009). https://doi.org/10.1134/S1061934809100190

[2] Wolfgang Sturhahn, Nuclear resonant spectroscopy,2004 J. Phys.: Condens. Matter 16 S497.

[3] Dmitry V. Zynabkin, Defect Complexes Interplay and its Influence on the Hyperfine Structure of Hydrogenated TiO_2, Doctoral Thesis, Technische Univeristät Ilmenau.

[4] G.Schatz, A.Weidinger, Nukleare Festkörperphysik: Kernphysikalische Meßmethoden und ihre Anwendung.- 2., neubearb. und erw. Aufl. - Stuttgart : Teubner, 1992. DOI 10.1007/978-3-322-93989-0

[5] Popov, V.V. Mössbauer spectroscopy of interfaces in metals. Phys. Metals Metallogr. 113, 1257–1289 (2012). DOI: 10.1134/S0031918X12130029

[6] Teke, A., Morkoç, H. (2006). Group III Nitrides. In: Kasap, S., Capper, P. (eds) Springer Handbook of Electronic and Photonic Materials. Springer Handbooks. Springer, Boston, MA. https://doi.org/10.1007/978-0-387-29185-7_32

[7] https://serc.carleton.edu/NAGTWorkshops/mineralogy/mineral_physics/mossbauer.html

[8] Jecong, J. F., Dingle, C., Hila, F., Lopez, G. E., Saligan, P., Guillermo, N. Conference Paper (2018). Determination of Fe ions in allanite from Ombo, Palawan through Mössbauer spectroscopy.

[9] https://e-ms.web.cern.ch/content/experiments

[10] Brent Fultz, “Mössbauer Spectrometry”, in Characterization of Materials. Elton Kaufmann, Editor (John Wiley, New York, 2011).