

## DESIGN AND CONSTRUCTION OF A $^{57}\text{Fe}$ MÖSSBAUER SPECTROMETER FOR STUDIES IN SURFACE PHYSICS

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### ABSTRACT

In this work we describe the design and construction of a Mössbauer spectrometer based in the use of a Channel Electron Multiplier to detect the electrons emitted as a consequence of the resonant nuclear absorption of  $\gamma$ -Rays by  $^{57}\text{Fe}$  containing samples. The main resonant signals being detected are the Fe(K), Fe(L) and Fe(M) conversion electrons as well as the Fe(KLM), Fe(KLL) and Fe(LMM) Auger electrons. The design is compact since all the components of the spectrometer are mounted into a single flange, so it can be easily installed in any conventional vacuum chamber dedicated to the study of surfaces. Its performance was tested by acquiring Mössbauer spectra from a pure iron metal sheet and from an iron metal thin film deposited onto a stainless steel plate.

*Keywords:* Mössbauer-Spectroscopy, Surfaces, CEMS, ICEMS, Channel-electron-multiplier.

## DISEÑO Y CONSTRUCCIÓN DE UN ESPECTRÓMETRO MÖSSBAUER DE $^{57}\text{Fe}$ PARA ESTUDIOS EN FÍSICA DE SUPERFICIES

### RESUMEN

En el presente trabajo se describe el diseño y construcción de un espectrómetro Mössbauer basado en el uso de un multiplicador de electrones tipo canal para detectar los electrones emitidos como consecuencia de la absorción resonante de Rayos  $\gamma$  por muestras que contengan el isótopo  $^{57}\text{Fe}$ . Las principales señales resonantes que se detectan son las de electrones de conversión Fe(K), Fe(L) y Fe(M), así como las de electrones Auger Fe(KLM), Fe(KLL) y Fe(LMM). El diseño es compacto ya que todos los componentes del espectrómetro están montados en una sola brida, la cual puede ser fácilmente instalada en cualquier cámara de vacío convencional dedicada al estudio de superficies. Se probó su desempeño mediante la adquisición de espectros Mössbauer de una lámina de hierro metálico puro y de una película delgada de hierro metálico depositada sobre una placa de acero inoxidable.

*Palabras clave:* Espectroscopía Mössbauer, Superficies, CEMS, ICEMS, Multiplicador de electrones.

### INTRODUCTION

Mössbauer Spectroscopy is a well established nuclear analytical technique based on the Mössbauer effect (Ovchinnikov, 2006), characterized by its extremely high energy resolution in comparison with atomic spectroscopies. It is used in the characterization of solids containing the so called "Mössbauer isotopes", like  $^{57}\text{Fe}$ ,  $^{119}\text{Sn}$  and  $^{151}\text{Eu}$ . Mössbauer Spectroscopy of the iron isotope  $^{57}\text{Fe}$  is by large the most widely used because of the relatively high natural abundance of this isotope (2%), the possibility of working over a wide range of temperatures ( $\sim 2\text{K}$ - $1000\text{K}$ ) and the great importance of iron as a chemical component in samples studied in fields as diverse as Geology, Metallurgy, Magnetism, Biology and Archeology (Desimoni et al. 2009).

The Mössbauer effect consists in the emission of characteristic  $\gamma$ -Rays photons by nuclei of a given species (source) and its resonant absorption by nuclei of the same species (absorber). Given the small width of the nuclear levels, for this resonant absorption to occur it is necessary that the nuclei do not recoil neither in the emission nor in the absorption processes, conditions that are achieved if they are bound to the structure of a solid state substance. In  $^{57}\text{Fe}$  Mössbauer Spectroscopy the source typically consists of radioactive  $^{57}\text{Co}$  nuclei embedded into a Rh or Pd matrix and the absorber is the iron containing solid under study. The  $^{57}\text{Co}$  nuclei decay by electron capture into excited  $^{57}\text{Fe}^*$  nuclei that have a half life of 270 days. Upon de-excitation, these  $^{57}\text{Fe}^*$  nuclei emit characteristic  $\gamma$ -Rays with well defined energies  $E_1 = 122.0$  keV,  $E_2 = 136.4$  keV and  $E_3 =$

14.4 keV. The  $\gamma$ -Ray photons of energy  $E_3$  are the ones used in  $^{57}\text{Fe}$  Mössbauer Spectroscopy. They are produced when the excited nuclei suffer transitions from the first excited state ( $I = 3/2$ ) to the ground state ( $I = 1/2$ ).

The interaction of the  $^{57}\text{Fe}$  nuclei with the surrounding atoms in the particular sample under study can cause level shifts and/or splits that impede the resonant absorption of the 14.4 keV  $\gamma$ -Rays emitted by the source. However, the resonance condition can be recovered if the energy of the emitted  $\gamma$ -Rays is modulated by Doppler effect. This can be done by mounting the source on an oscillatory mechanical device or velocity transducer which moves the source to and fro with constant acceleration up to a maximum speed  $v_M$  in each sense. In this way the energy of the  $\gamma$ -Rays is modulated continuously within the interval  $E_3(1 \pm v_M/c)$  and the resonant absorption is obtained when the photon energy coincides with an allowed transition between two nuclear levels in the absorber. In each motion cycle the condition for a given resonant absorption is achieved twice; one when the source moves forward and the other when it moves backward.

Conventional Mössbauer Spectroscopy deals with  $\gamma$ -Rays absorption spectra, but one can also obtain Mössbauer emission spectra if one detects the  $\gamma$ -Rays, the X-rays or the electrons emitted from the sample as a consequence of the de-excitation of the  $^{57}\text{Fe}$  nuclei which have been excited by the resonant absorption. In the present work we describe the installation of an electron emission Mössbauer spectrometer in an ultra-high vacuum (UHV) chamber used for analysis of surfaces with conventional surface sensitive techniques.

## THE EMISSION SPECTROMETER

It is useful to compare the performance of the Mössbauer Emission Spectrometer with that of a conventional Mössbauer Absorption Spectrometer. The absorption detection system used in conventional spectrometers consists of a simple transmission arrangement composed of the velocity transducer holding the  $\gamma$ -Ray source, followed by the absorber and then by a proportional counter. Absorption Mössbauer spectra are obtained by plotting the intensity of the transmitted  $\gamma$ -Ray signal as a function of the relative velocity between source and absorber. The spectra show an absorption baseline caused mainly by photoelectric effect in all types of atoms present in the sample region traversed by the  $\gamma$ -Rays, superimposed on which there are Mössbauer absorption resonances due only to the presence of  $^{57}\text{Fe}$  isotopes. The statistical quality of the spectra depends mainly on the activity of

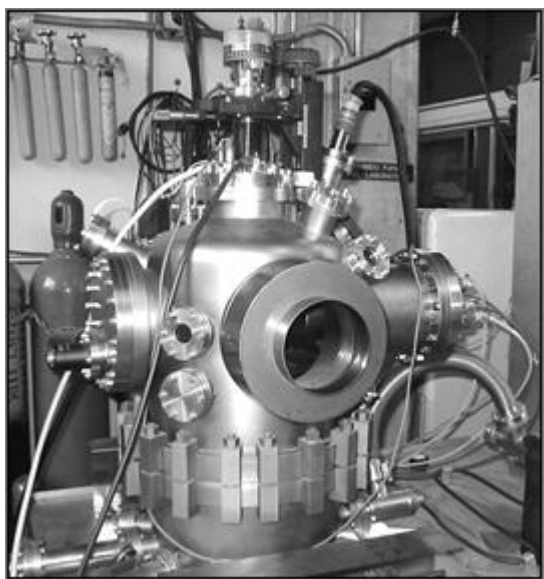
the source, on the acquisition time used and on the ratio of  $^{57}\text{Fe}$  isotopic mass to the total mass of the absorber. The absorption structure observed in the spectra corresponds to the interaction of the absorbing nuclei with the surrounding atoms, structure that is evaluated by the so called "hyperfine parameters" IS, QS and H. The isomer shift (IS) measures the electrostatic interaction between the absorbent nucleus and the surrounding electrons; it is characterized by a shift of the spectrum relative to that of a reference material, usually  $\alpha$ -iron. The quadrupole splitting (QS) arises from the interaction of the nuclear quadrupole moment with the local electric field gradient. When an asymmetry in the electric charge distribution around the  $^{57}\text{Fe}$  nuclei produces an electric field gradient, this interaction causes a splitting of the  $I=3/2$  nuclear state into two levels, resulting in two distinct spectral lines. The hyperfine magnetic field (H) measures the splitting caused by the interaction of the nuclear magnetic moment with the local magnetic field at the nucleus site. When this internal magnetic field is present, this interaction lifts all degeneracy between nuclear levels allowing six spectral lines to be observed. Through a fitting procedure of the experimental data one obtains the hyperfine parameters which are characteristic of the particular iron phase under study. For  $\alpha$ -iron the Mössbauer spectrum is a sextet with the following values of hyperfine parameters: IS=0 mm/s, QS=0 mm/s and H=330 kOe.

Once the Mössbauer resonant absorption has occurred, the excited  $^{57}\text{Fe}$  nuclei return rapidly to their ground states by two possible mechanisms: the re-emission of  $\gamma$ -Rays or the radiationless emission of atomic core electrons, a process known as Internal Conversion (Krane, 1988). The probability of de-excitation by  $\gamma$ -Ray re-emission is of only 9%, so most of the  $^{57}\text{Fe}$  excited nuclei (91%) de-excite themselves by the emission of conversion electrons; 81% of them emit K electrons (7.3 keV kinetic energy), 9% L electrons (13.6 keV) and 1% M electrons (14.3 keV). The emission of conversion electrons leaves the atoms with a hole in a core level, so there is a further de-excitation of these atoms through the emission of either characteristic X-rays or Auger electrons. The main Auger electron signals being produced are the KLM (6.3 keV kinetic energy), the KLL (5.4 keV), the LMM (0.65 keV) and the MVV (0.047 keV). Secondary, low energy, electrons are also produced in the process. We see that there is an important amount of electronic signals that are consequence of the resonant absorption of  $\gamma$ -Rays which then could be used to perform Mössbauer Spectroscopy if these signals are properly detected. The spectra obtained in this fashion are emission spectra and the technique is known as Conversion Electron Mössbauer Spectroscopy (CEMS) [Nomura et al. 1996]. Superimposed to the mentioned Mössbauer

electron signals there are also non resonant electron signals contributing to the spectrum background, produced mainly by photoelectric and Compton effects due to the interaction with the sample of the  $\gamma$  and X-rays emitted by the source. As electrons are particles with electric charge, in general they interact with matter more strongly than  $\gamma$  or X-Rays do, so one expects that the electrons that escape from the sample in Conversion Electron Mössbauer Spectroscopy come from a region close enough to the sample surface that they could be used in the characterization of surfaces, interfaces and thin films.

## EXPERIMENTAL TECHNIQUES

The chamber where the spectrometer was installed is shown in Figure 1. It is a cylindrical stainless steel UHV chamber used for the characterization of metal surfaces by Auger Electron Spectroscopy and Low Energy Electron Diffraction. It has a front glass viewport, several ports of different sizes and a sample manipulator, located at the top, with capacity for x, y and z displacements, 360° rotation around a vertical axis and  $\pm 50^\circ$  tilt around a horizontal axis.

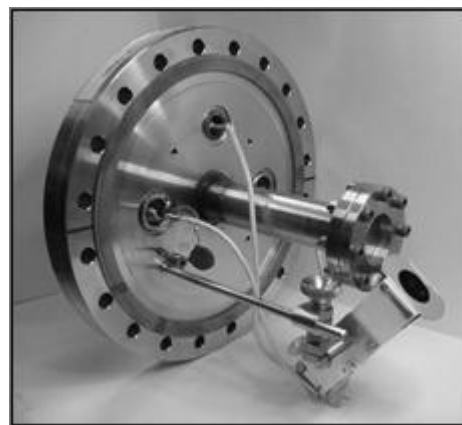


*Figure 1. UHV chamber where the CEMS analyzer was installed*

It is convenient that the different parts of the spectrometer be assembled onto a single flange in order to facilitate its installation in this chamber or in similar ones. For this purpose the 20 cm flange located at the left in Figure 1 was chosen. The sample could be positioned as usual in the manipulator in order to face this spectrometer and other ones installed in the chamber simply by rotating it around the vertical axis. It is also desirable that the radioactive source be kept outside the chamber in order to avoid heating it when the chamber is baked out and to be able

to use it in another experimental set up, if needed, without breaking the vacuum. This can be done by using a Beryllium window, capable of sustaining UHV conditions and being transparent to the 14.4 keV  $\gamma$ -Rays. Given the dimensions of the chamber, it was difficult to place the source close to the sample in order to irradiate it with sufficient intensity, so it was necessary to include in the design a stainless steel tube, 25 mm diameter and 115 mm long, welded to the flange at the central position, that extends itself into the chamber and is closed at the end by a 550  $\mu\text{m}$  thick Beryllium window. This tube was lined with a lead foil for shielding purposes and had at the end a 3 mm thick lead disk with a 9 mm diameter circular aperture that acts as a collimator of the  $\gamma$ -Rays. Additionally it contains a 1.5 mm thick Plexiglas® disk that acts as a filter for attenuating the parasitic X-Rays produced by the radioactive source.

The electron detector was fixed to a stainless steel rod, welded to the internal part of the 20 cm flange, through a sliding support that allows moving it close to the sample and tilting it in order to face the sample surface. On the same flange were also welded three electrical feedthroughs in order to make the electrical connections needed for the electron multiplier operation. Figure 2 shows a picture of the assembled parts onto the 20 cm diameter flange.

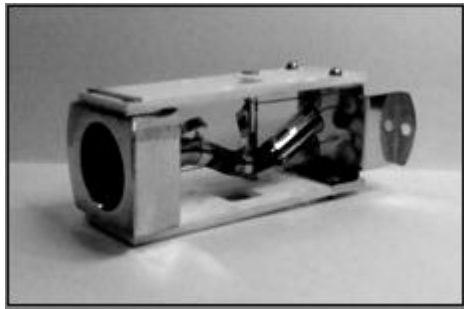


*Figure 2. Assembly of the CEMS spectrometer onto the 20 cm diameter flange*

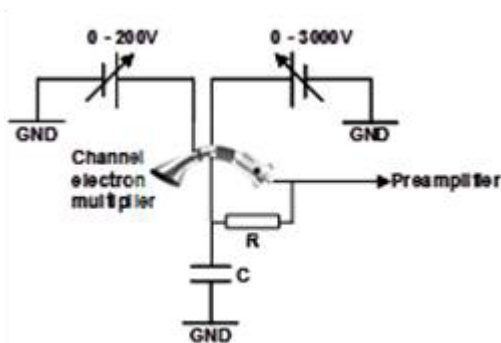
The electron detector used, shown in Figure 3, was a DeTech 512 Channel-electron-multiplier, operated in the pulse counting mode although it was originally designed to operate in the current mode as part of an Auger Electron Spectrometer. This device has a 19 mm input aperture and requires electrical connections for high voltage bias, input cone bias and signal collector (BURLE, 2009). This electron multiplier is bakeable and normally works under high or ultra-high vacuum conditions, giving a maximum gain of  $10^6$ . The circuit diagram of Figure 4 shows the connections used for its operation. The graph of Figure 5 shows its

detection efficiency as a function of the kinetic energy of the electrons impinging on the surface of its entrance cone; it acts as a high-pass filter whose efficiency drops abruptly for kinetic energies below 500 eV.

The radioactive source used was a 10 mm diameter disc of  $^{57}\text{Co}$  in a Rh matrix which was placed at the end of an extension rod, connected to the velocity transducer and inserted into the lead-lined tube at approximately 15 mm from the collimator aperture.



**Figure 3.** DeTech 512 channel electron multiplier used as electron detector

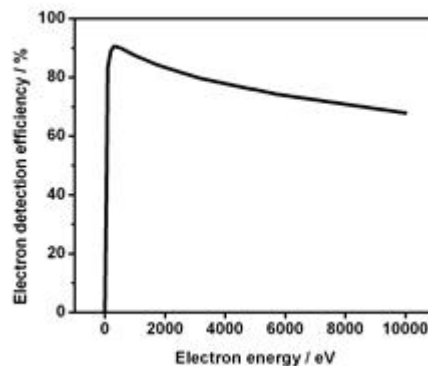


**Figure 4.** Circuit diagram used to operate the channel electron multiplier.  $R = 1\text{ M}\Omega$ ,  $C = 1.5\text{ nF}$

In order to get the maximum electron signal, the sample was positioned opposite to the Beryllium window but tilted  $45^\circ$  downwards and the electron multiplier was tilted  $45^\circ$  upwards in order to face the sample. The distances window to sample and sample to electron multiplier were about 5 cm.

The external system required for spectra acquisition consists of the following components:

- a) A drive unit for the control of the velocity transducer.
- b) A 2000-3000 V high voltage power supply for biasing the electron multiplier.
- c) A 0-200 V power supply for biasing the entrance cone of the electron multiplier.
- d) A preamplifier for decoupling the output pulses of the electron multiplier from the high voltage bias, converting the charge into a proportional voltage signal.
- e) An amplifier for pulse shaping and amplifying the output pulses.
- f) A single channel analyzer for transforming output pulses of the amplifier into logical pulses after discriminating them by the use of a selecting window.
- g) A multichannel analyzer for accumulating the Mössbauer spectra as histograms of number of counts as a function of channel number, by receiving the pulses from the single channel analyzer and synchronizing the repetitive signal from the drive unit. We used the multichannel scaling data acquisition module CMCA-550 from WISSEL.
- h) A personal computer for receiving, storing and processing the spectra.



**Figure 5.** Typical channel electron multiplier efficiency curve for electron detection. Plotted from data given in (BURLE, 2009)

The processing of the Mössbauer spectra includes a folding of the experimental data corresponding to the positive and negative velocity ramps and a least-squares fitting of the folded spectra with Lorentzian peaks. As a result of the fitting procedure the hyperfine parameters that characterize the sample are determined. In our case the spectra processing was carried out with the program “Recoil”® 1.0 (Lagarec & Rancourt, 1998).

## RESULTS AND DISCUSSION

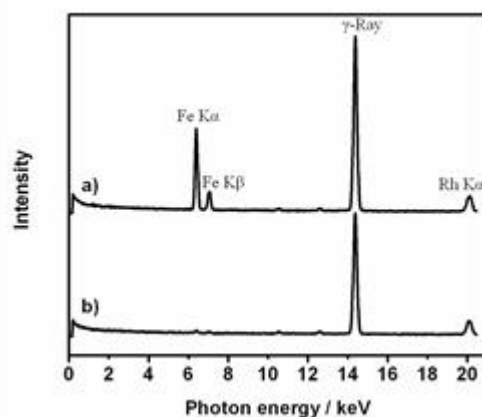
The  $^{57}\text{Co}/\text{Rh}$  radioactive source used is shielded at the back so the  $\gamma$  radiation is emitted mainly in the forward direction. One advantage of the conventional absorption mode is that the  $\gamma$  absorption process is detected in the direction of the emission of the  $\gamma$ -Rays by the radioactive source, so in principle all the transmitted signal is detected. On the other hand, the signals emitted by the atoms in the absorber as a consequence of the desexcitation process of their excited nuclei, travel with equal probability in all directions; the detected signal in this case is only a fraction of the emitted one since it is proportional to the solid angle subtended by the detector entrance.

Given the geometry of our Mössbauer Emission Spectrometer, it is important to know the area irradiated on the sample position in order to determine the optimum size of the sample to be used. This was determined using an X-Ray dental film to measure the exposed area. Figure 6 shows a picture of the exposed film in which one observes a dark shadow corresponding to the irradiated area; it is elliptical since the film was placed on the sample holder, tilted  $45^\circ$ . The clear disk superposed on the dark shadow corresponds to the 25 mm diameter circular sample used in our measurements, placed on top of the exposed film. One observes that the whole sample area is irradiated by the  $\gamma$ -Rays.

The effect of the Plexiglas filter can be appreciated in Figure 7, where we show energy dispersive spectra of the source obtained both without the filter (7a) and with the filter (7b) covering it. Besides the 14.4 keV  $\gamma$ -Ray signal, we observe in Figure 7a the presence of the 6.40 keV Fe  $K\alpha$ , the 7.06 keV Fe  $K\beta$  and the 20.21 keV Rh  $K\alpha$  X-Ray signals. The Fe K signal is the result of the de-excitation of the iron atoms produced in the  $^{57}\text{Co}$  electron capture process, while the Rh K signal is the result of fluorescence caused by the high energy  $\gamma$ -Rays on the Rh matrix. With the Plexiglas filter, we see in Figure 7b that the Fe K signal disappears without reducing much the 14.4 keV  $\gamma$ -Ray signal. According to these spectra, the use of the filter reduces the intensity of the 14.4 keV  $\gamma$ -Rays to 72% of its original value. However, in this case 86% of the photons that irradiate the sample are the 14.4 keV  $\gamma$ -Ray photons and only 14% are X-Ray photons; while without the filter, 60% of photons that irradiate the sample are the 14.4 keV  $\gamma$ -Ray photons and 40% are the X-Rays photons, which contribute to the spectrum noise by generating photoelectrons. The use of the Plexiglas filter reduces the non-resonant electron signals by eliminating the Fe K X-Rays generated by the radioactive source.

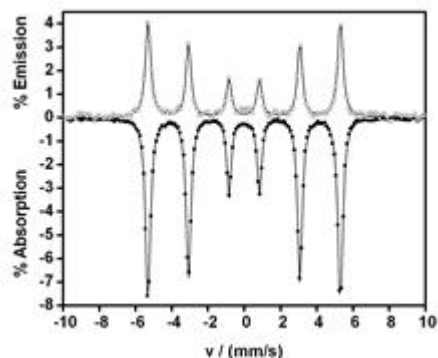


**Figure 6.** Image of an X-Ray film exposed to the collimated  $\gamma$  radiation, with a 25 mm diameter sample superimposed on it

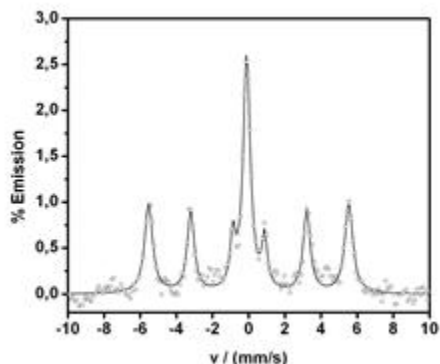


**Figure 7.** Energy dispersive emission spectra of the  $^{57}\text{Co}(\text{Rh})$  radioactive source. a) without the Plexiglas filter, b) with the Plexiglas filter

Figure 8 compares an emission conversion electron Mössbauer spectrum from an iron plate with a conventional absorption Mössbauer spectrum from a  $6.4\ \mu\text{m}$  thick iron foil. The acquisition time was about 24 hours for both spectra, although the source activity was 30 mCi in the emission experiment and 6 mCi in the absorption one. As expected, both spectra consist of a sextet whose hyperfine parameters agree with those corresponding to  $\alpha$ -iron. The signal to noise ratio is clearly smaller in the CEMS spectrum despite the larger source activity that was used. In the case of the absorption spectrum the sample region generating the Mössbauer signals corresponds to the whole thickness, i.e.  $6.4\ \mu\text{m}$ . In the case of the emission spectrum the mean-escape-depth of the signals from metallic iron detected by our spectrometer has been calculated to correspond to approximately only 80 nm, taking into account both the conversion electrons and the Auger electrons, as well as the coincidence effects in their detection (Moutinho et al. 2010).



**Figure 8.** CEMS Emission ( $\circ$ ) and Conventional Absorption ( $\bullet$ ) Mössbauer spectra from  $\alpha$ -iron



**Figure 9.** CEMS spectrum corresponding to a 100 nm Fe film deposited on a 304 stainless steel plate

Figure 9 shows a conversion electron Mössbauer spectrum, obtained with the designed CEMS spectrometer, corresponding to a 100 nm Fe thin film deposited on a 304 stainless steel plate. One observes the superposition of two sub-spectra; the sextet characteristic of the  $\alpha$ -iron from the film and the central singlet characteristic of the non-magnetic stainless steel substrate. The main contribution to the total detected signal comes from the Fe(K) conversion electrons, which provide information from a surface region of about 200 nm thick. Thus, although the mean-escape-depth of the CEMS signal in  $\alpha$ -iron is smaller than the iron film thickness, the contribution of Fe(K) conversion electrons provides information about the underlying substrate, what explains the comparable importance in the spectrum of both the  $\alpha$ -iron film and the stainless steel substrate components. The Auger electrons resonant signals are in principle more surface sensitive than the conversion electrons signals, but our spectrometer cannot discriminate between them as it adds or integrates all these different electron signals. This type of spectrometer is known as an Integral Conversion Electron Mössbauer Spectrometer (ICEMS). An energy selective Mössbauer spectrometer, or Differential Conversion Electron Mössbauer Spectrometer (DCEMS), capable of differentiate each type electron signal, tuning in this way its surface sensitivity, is under construction.

## CONCLUSIONS

An ICEMS Mössbauer spectrometer for surface studies in iron containing samples was designed and successfully constructed. It is based in the use of a channel electron multiplier for the detection of the integrated conversion and Auger electron signals emitted by the  $^{57}\text{Fe}$  isotopes as a consequence of the resonant nuclear absorption of  $\gamma$ -Rays. As this spectrometer is contained within a single flange it can be easily installed in any conventional ultra-

high vacuum chamber dedicated to surface physics studies, enhancing in this way its analytical capability.

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