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Hyperfine Interactions

ISSN 0304-3843
Volume 224
Combined 1-3

Hyperfine Interact (2014) 224:43-50
DOI 10.1007/s10751-013-0814-9

Springer

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Design of an Auger Electron Mössbauer Spectrometer (AEMS) using a modified cylindrical mirror analyzer

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Received: 3 December 2012 / Accepted: 21 January 2013 / Published online: 19 February 2013

Abstract We have designed and built an Auger Electron Mössbauer Spectrometer (AEMS) for the detection of resonant ^{57}Fe Auger electrons using a modified commercial cylindrical mirror analyzer (CMA). The CMA final aperture was modified intentionally in order to increase electron transmission at the expense of reducing its energy resolution, from an original value of 0.5 % to a value of 11 % after the modification. The Channeltron detector electronics and the pre-amplifier were also modified in order to increase the counting efficiency. The electron energy analyzer is selective in energy in the 30 eV–3000 eV range, so the spectrometer can be used to detect MNN (45 eV) and LMM (600–700 eV) Fe Auger signals, what gives it a high surface sensitivity for Fe containing samples. We have used it to acquire the Fe LMM Auger signals generated from the de-excitation process after γ-Ray resonant nuclear absorption. The spectrometer can be used to study samples non-enriched in ^{57}Fe, with acquisition times from 5 to 7 days, what is a big advantage. From electron trajectory Monte Carlo simulations in metallic iron, the mean-escape-depth of the detected Auger signals has been estimated in approximately 1 nm. Fe K conversion electrons and KLL Auger electrons with mean escape depths of 129 nm and 78 nm respectively also contribute to the detected signal although in a lesser proportion.

Keywords AEMS · Surface sensitivity · Energy resolution · Mean escape depth

Proceedings of the Thirteenth Latin American Conference on the Applications of the Mössbauer Effect, (LACAME 2012), Medellín, Columbia, 11–16 November 2012.

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1 Introduction

Mössbauer Spectroscopy analysis can be carried out in either of two modes: transmission or backscattering; being the electron backscattering mode [1, 3] the best choice for the study of phenomena associated to the surface region like, for instance, the oxidation and corrosion of steels. In the backscattering mode where Mössbauer resonant electrons are detected, there are different techniques or variants that can be applied, which differ mainly in their depth resolution or sensitivity to the surface region. Techniques like; Depth Selective Conversion Electron Mössbauer Spectroscopy (DCEMS) and Auger Electron Mössbauer Spectroscopy (AEMS) are selective in energy by the use of electron analyzers tuned around an energy center value (E) with a given energy resolution (R). By choosing to detect electrons with low enough characteristic kinetic energies, one can guarantee that the majority of the detected signal comes from the surface region of the sample. In the present work the AEMS technique is used.

Mössbauer surface analysis of metallic samples using AEMS can provide results with a very high surface sensitivity due to the shorter inelastic mean free path (IMFP) of the 600–700 eV Fe LMM Auger electrons (1–2 nm), compared with the IMFP of the 7.3 keV Fe K conversion electrons (5 nm) [1]. In AEMS the mean escape depth of the detected signal can be close to the IMFP [1] of the electron signal while in integral CEMS (ICEMS) it can reach values as high as 80 nm [3]. However the use of the AEMS technique is not so common due to the complexity and high cost that implies the use of an electron energy analyzer, an ultra-high vacuum chamber, high activity sources and ^{57}Fe-enriched samples. Surface sensitivity refers to the relative proportion of surface and bulk signals but even if a technique has a high surface sensitivity it can give a very small signal due to the small absolute number of atoms characteristic of the surface region. In order to diminish acquisition times ^{57}Fe sample enrichment and/or high activity sources are usually required to increase the intensity of resonant signal available.

Some authors [4, 5] were able to perform AEMS spectroscopy using a gamma source (^{57}Co) of 20–50 mCi, high transmission electron analyzers and samples enriched in ^{57}Fe. Our contribution here is to construct an instrument able to perform Mössbauer surface analysis with the big advantage of using a conventional 50 mCi gamma source to study non enriched ^{57}Fe samples and with acceptable acquisition times from 5 to 7 days. We used an Auger Electron Spectrometer installed in an ultra-high vacuum chamber and converted it to an Auger Electron Mössbauer Spectrometer with a very low cost, modifying an old Cylindrical Mirror Analyzer (CMA) [2] specifically for this Mössbauer application.

2 Design and building of the spectrometer

2.1 The source-sample-detector system

The first part of this project was to design the source-sample-detector system. In order to locate the gamma source close to the sample, which is at the center of the chamber, a stainless steel tube was connected to a 70 mm chamber port. The tube was lead lined and finishes in an aluminized Mylar window. The final pressure achieved

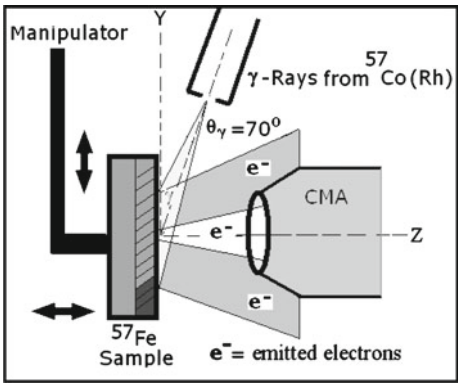

Fig. 1 Source-sample-detector array in the spectrometer

with this condition is 10^{-6} mbar. For ultra-high vacuum condition a welded beryllium window is required.

The lead collimator tube has one side attached to a lead disk of 3 mm thick with a 5 mm diameter centered hole. Also a Plexiglas filter of 1 mm thick has been added to reduce the 6.3 keV X-rays from the source. An aluminum rod, joined to the motor fixed in the outside of the chamber allows the gamma source to be very close of the sample without breaking the vacuum. The collimator design let us to illuminate just a centered region of the sample at the working distance and minimizes the noise from the X-rays. The distance from source to sample is ∼3.5 cm and from sample to face of the CMA∼3 cm. The source-sample-detector configuration is shown the Fig. 1.

2.2 The modified CMA

The second part consisted in modifying a small commercial CMA electron energy analyzer in order to increase its transmission at the expense of reducing its resolution, what was possible by altering its optics. This CMA had an annular entrance window that defines an angle of acceptance for the electrons between 40° and 60°. This electron energy analyzer is selective in energy in the 30 eV–3000 eV range. After studying its operation it was found that the original resolution for a focused electron beam (0.5 %) is controlled by a third slit (slit 3) placed at the back of this analyzer. This slit acts as an energy filter of the dispersed electrons on their path from the inner cylinder of the CMA to the Channeltron detector. This slit was completely removed and the position of the detector was adjusted. The resolution was measured, using a broad electron beam in order to simulate the area shone by the gamma source. It was found that the resolution changes from 0.5 % to 4 % on defocussing the electron beam and then to 11 % on removing slit 3, what is convenient for our purposes since in that way the three Fe LMM Auger peaks, at approximately 600 eV, 650 eV and 700 eV, can be merged into a single, more intense, peak. Figure 2 shows the schematics for the function of slit 3 and a picture of it.

Figure 3 shows the elastic peak spectra used to determine the analyzer resolution, defined as the ratio of ΔE/E where E is the peak energy and ΔE is the full width at half maximum, obtained with the defocussed electron beam: 3(a) with the slit in position and 3(b) without the slit.

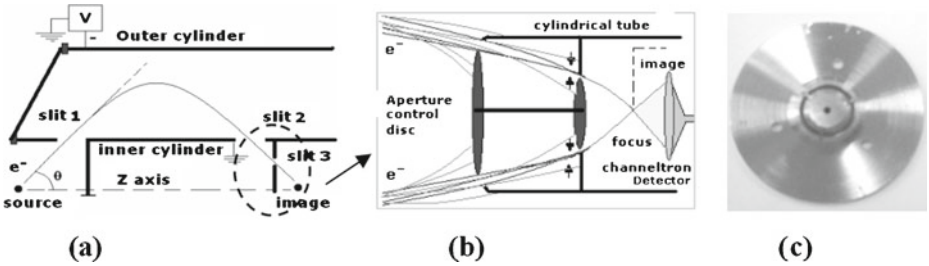

Fig. 2 **a** Main trajectory of electrons through the inner cylinder and the slit 3 of the CMA. **b** Schematic for the function of the slit 3 in the CMA. **c** Picture of the Slit 3

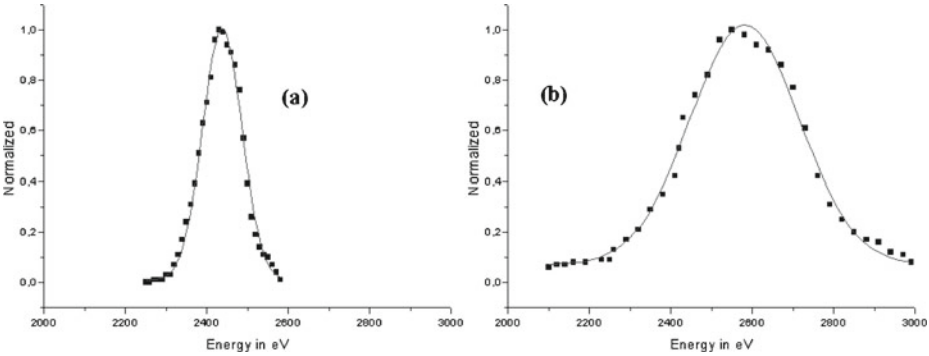

Fig. 3 **a** Resolution with the slit in position (4 %). **b** Resolution with the removed slit (11 %)

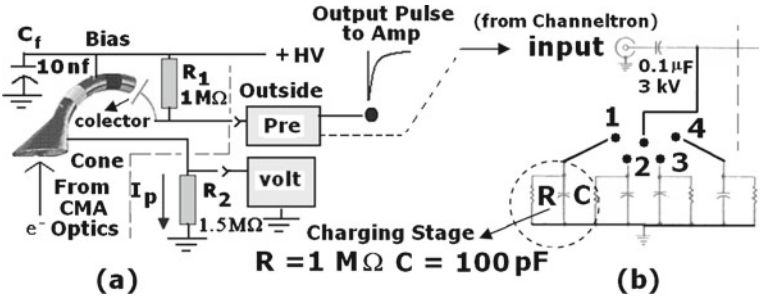

Fig. 4 **a** Electronic Arrangement made in the Channeltron detector connected to the pre-amplifier and multimeter. **b** Modified section in the Pre-amplifier ORTEC-113

The analyzer was reassembled positioning the Channeltron detector closer to the CMA body in order to maximize the signal at the detector.

2.3 Detector and modified electronics

The electronics associated to detection was also modified to enhance its response to pulse counting, especially for low pulse count rates. Changes were made both

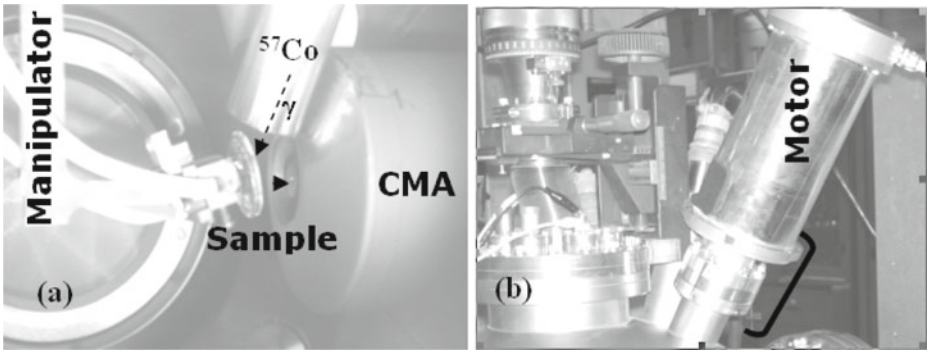

Fig. 5 **a** Internal view. **b** External part showing motor coupling

in the Channeltron detector and in the pre-amplifier (ORTEC-113), increasing the sensitivity of the analyzer in a noticeable fashion. Figure 4 shows these arrangements.

Figure 5a and b show the internal and external view of the AEMS spectrometer that has been constructed.

3 Experimental results

Initially we tested the equipment with a very low activity (1 mCi) ^{57}Co/Rh source, and an enriched (>90 %) ^{57}Fe sample using an acquisition time of 7 days. We also changed the center of the analyzer pass energy in order to observe possible changes in the sensitivity to the detected signal. The results are shown in Fig. 6. In this experiment it was observed that the pass energy in the range of 580–650 eV produces the highest sensitivity, so for the rest of the experiments the pass energy was fixed at 650 eV, what coincides with the central peak of the Fe LMM Auger spectrum. This Fe LMM Auger spectrum consists of three peaks of comparable intensity located approximately at 600 eV, 650 eV and 700 eV. With the pass energy centered at 650 eV and the quoted 11 % resolution, the three Auger peaks located from 590 eV to 710 eV can be merged into a single peak, what increases the amount of detected signal without varying much its escape depth.

The second experiment was performed using a 50 mCi ^{57}Co/Rh source and a non-enriched iron metallic foil as the sample. Figure 7 shows the spectrum obtained after a 7-day acquisition time.

The spectrum of Fig. 7 shows an emission of 0.6 %. Despite that the effect measured is very low, the spectrum can be well detected, and confirm the possibility of using iron samples with a natural isotopic composition.

4 Monte Carlo simulations

We used David Joy Monte Carlo simulation programs [6] for electron trajectories in solids to estimate the mean escape depth of the signals detected by our spectrometer when an iron metal sample is analyzed. For this purpose we obtained the energy distribution of the electrons emerging from a face of a thin iron film when a beam of

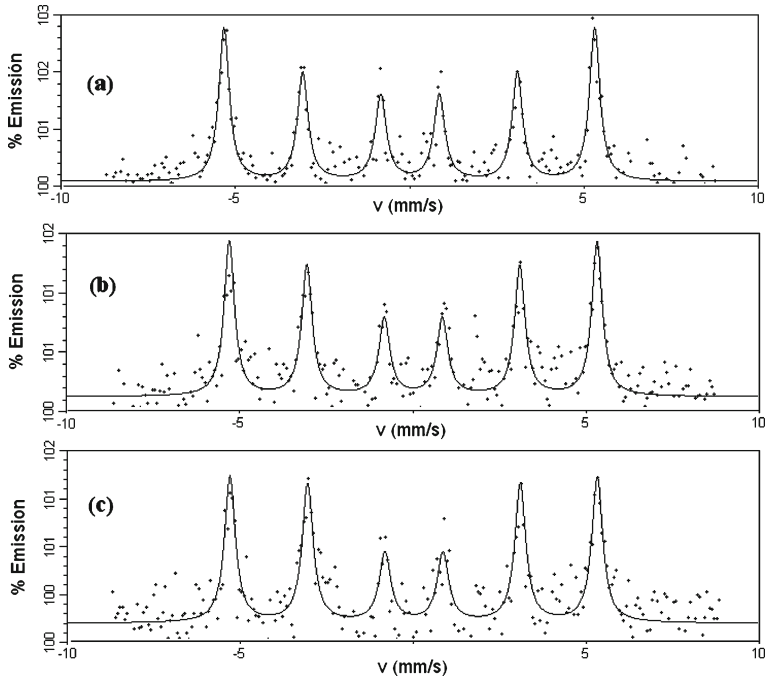

Fig. 6 AEMS spectra of an enriched ^{57}Fe sample with a 1 mCi ^{57}Co/Rh source acquired in 7 days. **a** Pass energy at 580 eV, 3 % of emission, **b** 650 eV, 2 %, **c** 700 eV, 1.5 %

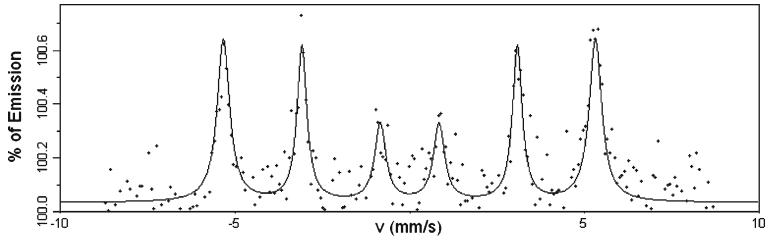

Fig. 7 AEMS spectrum of a non-enriched metallic iron sample, using a 50 mCi ^{57}Co/Rh source acquired in 7 days. Pass energy at 650 eV, 0.6 % of emission

10^5 electrons impinges on the other face. Film thicknesses were varied from 0.25 nm to 230 nm and beam energies of 7.3 keV, 5.4 keV, 600 eV, 650 eV and 700 eV were used with an incidence angle corresponding to the acceptance window of the CMA analyzer. These energy values correspond respectively to the K conversion electrons, to the KLL Auger electrons and to the triplet LMM Auger electrons. The combined LMM triplet, with a low 9 % emission probability, was chosen because of its high surface sensitivity. The more energetic K and KLL electronic emissions were included in the simulation because of their high emission probabilities that amount to 81 % and 43 % respectively. Figure 8a shows the electron energy distributions obtained when a 7.3 keV conversion electron beam traverses iron films of 50 nm,

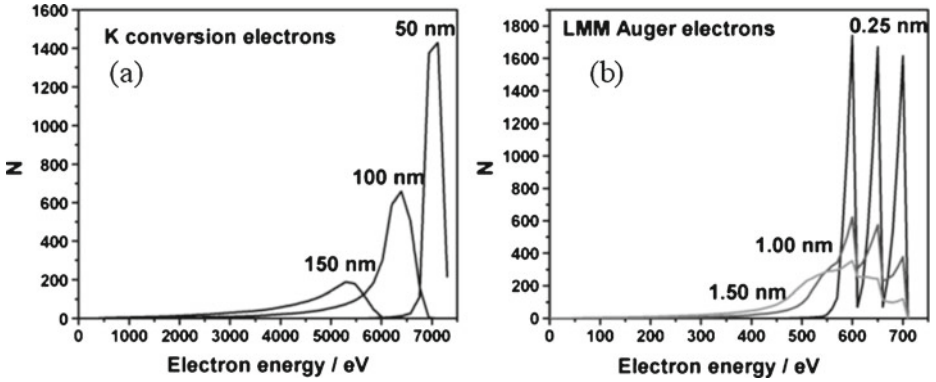

Fig. 8 Electron energy distributions as a function of iron slab thickness for **a** 7.3 keV K conversion electrons. **b** Triplet (600, 650, 700) eV LMM Auger electrons

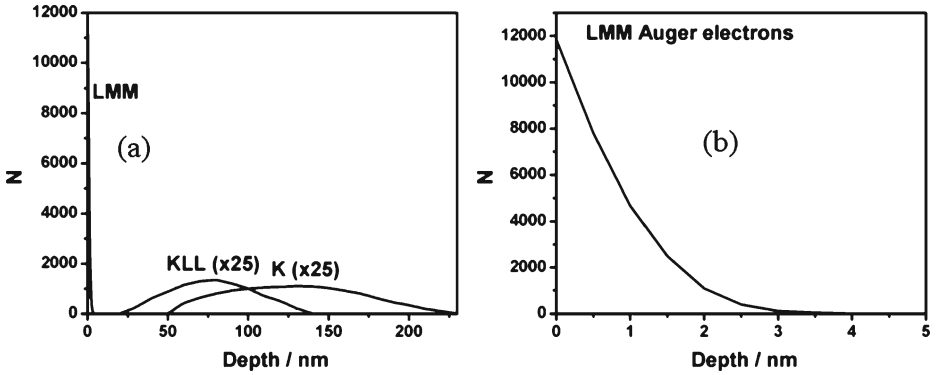

Fig. 9 **a** Depth distribution for the detected LMM, KLL and K electron signals from metallic iron. **b** LMM depth distribution zoomed from **a**

100 nm and 150 nm. As can be observed, the thicker the film the smaller the peak maximum and the broader the tail toward lower energies. After suffering inelastic scattering a significant number of these resonant electrons can reduce its energy to reach the (590 eV–710 eV) energy window defined by the CMA. The number of K, KLL and KLM electrons within this energy window, weighted by their corresponding emission probabilities, were evaluated using the results of the Monte Carlo simulation. Figure 8b shows the electron energy distributions corresponding to the triplet LMM Auger signal, obtained after traversing very thin iron slabs. This time, the reduction in intensity within the (590 eV–710 eV) CMA energy window occurs more rapidly with increasing iron thickness, an indication of the high surface sensitivity of these signals.

By counting the number of K, KLL and LMM electrons within the (590 eV–710 eV) CMA energy window, weighted by their emission probabilities, one can obtain the depth distribution functions for these three kinds of signals, detected by the analyzer in AEMS. Figure 9a shows the three separated contributions. The detected LMM signals are originated in a very thin surface layer that can be better

appreciated in Fig. 9b, where one observes a monotonic decrease with depth that disappears after 5 nm. From this depth distribution one obtains a value of 0.75 nm, less than 3 iron monolayers, for the mean-escape-depth of the Fe LMM signals, what amounts for the 62 % of the total Mössbauer electron signal. The depth distributions for the K and KLL contributions can be observed in Fig. 9a, where their intensities have been amplified 25 times to be able to appreciate them. The KLL distribution forms a broad band from 20 nm to 140 nm, giving a mean-escape-depth of 78 nm for this signal, which represents a 16 % of the total. The K distribution forms an even broader band, from 50 nm to 230 nm, giving a 129 nm mean-escape-depth for this signal, which represents a 22 % of the total.

5 Conclusions

We have constructed an AEMS spectrometer which offers the advantage of acquiring Mössbauer spectra from non-enriched samples, using 50–25 mCi sources and acquisition times from 5 to 7 days.

Monte Carlo electron trajectory simulations allowed us to calculate the mean-escape-depth of the detected Fe LMM Auger signals in metallic iron, taking into account the energy resolution of the analyzer. The main Mössbauer ^{57}Fe electron signals that are being detected in this spectrometer are the LMM Auger signal, the KLL Auger signal and the K conversion electron signal, being the LMM Auger signal the one which contributes to the surface sensitivity of the technique.

Acknowledgements Financial support from CDCH-UCV under Project PG 03-8216-2011/1 and from FONACIT under Project PEII 3896 are gratefully acknowledged.

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