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DEPTH SENSITIVITY OF X-e⁻ COINCIDENCE MÖSSBAUER SCATTERING SPECTRA

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The performance of the X-ray - e⁻ coincidence technique
for recording depth selective ^{57}Fe CEMS spectra was
investigated. The technique proved useful for selection
of K-shell conversion electrons (7.3 keV) from a beam of
back scattered electrons. This makes it possible to
observe the depth sensitivity of CEMS spectra recorded
with an He/CH₄ flow proportional counter.

1.   INTRODUCTION

      In recent years there has been considerable interest in the
application of ^{57}Fe conversion electron Mössbauer spectroscopy
(CEMS) to surface studies. Both the depth integrated /1,2/ and the
depth sensitive /3-5/ techniques are being used in these studies.
      A depth integrated Mössbauer spectrum of the outer 300 nm of
the sample is usually recorded by detection of almost all back
scattered electrons with an He/CH₄ flow proportional counter. In
studies of thin oxide films on an iron substrate by the depth in-
tegrated technique all oxide layers and the iron substrate con-
tribute to the CEMS spectrum. From the percentage of the total
spectrum area contributed by each oxide layer the oxide-thickness
values can be approximately determined /1,2/. However, accuracy is
limited since the contribution of each layer to the depth inte-
grated CEMS spectrum originates from a few electron beams of dif-
ferent penetration depths. These are the K-shell conversion
electrons (7.3 keV), the L-shell conversion electrons (13.6 keV),
the K-LL Auger electrons (5.5 keV) and the L-MM Auger electrons
(0.53 keV). The intensity ratios and the energy distributions of
these originally monoenergetic beams of electrons are changed
during the electron interactions in the scatterer. Unfortunately,
those interactions are not very well known for low energy elec-
trons used in CEMS studies. This prevents detailed interpretation
of the depth integrated CEMS spectra.
      The depth sensitive technique is based on knowledge of an
electron energy distribution as a function of depth in the scat-
terer. In this technique the K-shell conversion-electron line is
usually selected by application of an electron spectrometer. The
correlation between electron energy loss and the electron depth of
the origin is utilized in the depth selective investigations.
A depth resolution in iron of the order of 5 nm can be obtained
/4/. However, the technique is time consuming due to the very low
transmission of electron spectrometers with good energy resolution.
      Thus, a search for a technique based on some sort of compro-
mise between the depth resolution and the spectra storage time is
necessary. The purpose of this paper is to present the depth
sensitivity of the X-e⁻ coincidence Mössbauer scattering spectra.

2.   THE X-e⁻ COINCIDENCE TECHNIQUE

An He/CH₄ proportional counter is an attractive detector for low energy electrons. It possess high counting efficiency and 2π (or even 4π) geometry for scattered electrons can be easily achieved. Its energy resolution (17.7% for the 6.36 keV electrons /6/) allows selecting at least four non-overlaping energy intervals within the 0 - 7.3 keV energy range. Moreover, by application of the X-e⁻ coincidence technique the ⁵⁷Fe K-shell electron contribution to a beam of back scattered electrons can be selected without a large decrease in the counting rate /6/. This contribution should possess depth sensitivity good enough for time-efficient preliminary surface studies. In order to show this property we used electronic circuits suitable for storing both the X-e⁻ coincidence electron pulse-height spectra and the X-e⁻ coincidence Mössbauer scattering spectra. The details of the X-e⁻ coincidence technique have been previously described elsewhere /6/.

The experiments were performed at room temperature using a Mössbauer spectrometer of the Polon type. The 6.47 keV X-rays emitted by a 50 mCi source were cut off by application of a thick plexiglass plate. A one-wire He/CH₄ flow conversion electron detector (2.5 cm thick) was used for detection of electrons emerging from a scatterer surface. The desired parts of the electron pulse-height spectrum, for which the Mössbauer spectra were simultaneously recorded, were selected by the single channel analyzers. A one-wire Ar/CH₄ proportional counter was used for detection of conversion X-rays (6.47 keV) produced inside the scatterer. It was placed just behind the conversion electron detector. The X-ray pulses were selected by the single channel analyzer and were used for coincidence purposes. The K-shell electrons are emitted simultaneously with the 6.47 keV X-rays. Thus, they can be selected from the beam of back scattered electrons by application of the X-e⁻ coincidence technique. We used them for storing depth selective CEMS spectra.

3.   RESULTS AND DISCUSSION

The experiments were performed both for a 90.7% ⁵⁷Fe enriched stainless steel scatterer and for 90.6% ⁵⁷Fe enriched hematite and magnetite layers on an iron substrate. A duplex layer of hematite and magnetite on the metallic iron substrate was produced by oxidizing an iron foil at 623 K in 1013 hPa of air for 3.5 hours. Hematite was the top layer, magnetite was the second layer and the effectively infinite iron substrate was the third layer of the investigated scatterer. The iron foil was neither polished no annealed prior to oxidizing.

For the stainless steel scatterer the nuclear resonance contribution (N$_r$ - N$_∞$) to the beam of back scattered electrons was determined (Fig.1, left site) with (A) and without (B) application of the X-e⁻ coincidence technique. For that purpose the electron pulse-height spectra were recorded at zero velocity (N$_r$) and at off-resonance velocity (N$_∞$). The coincidence spectrum (A) originates only from the K-shell conversion electrons. The L-shell conversion electron and the K-LL Auger electron contributions, which were rejected from spectrum A, are clearly seen in the non-coincidence spectrum B. It is worth noticing that the intensity of the K-shell electron beam (A) decreases with the decrease in electron energy (increase in depth), which should be expected.
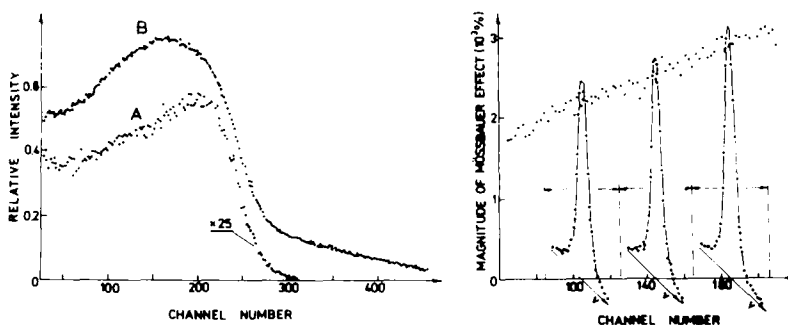
Fig.1. The nuclear resonance contribution to the beam of
back scattered electrons determined for the stainless
steel scatterer with (A) and without (B) application of
the X-e⁻ coincidence technique (left site). The coin-
cidence background corrected magnitude of depth selective
Mössbauer effect vs. electron energy recorded for the
stainless steel scatterer (right site). The coincidence
CEMS lines inserted have been recorded for the electron
energy intervals marked in the figure.

The left slope of the spectrum A reflects the depth sensitivity
of the method while the right one the energy resolution of the
conversion electron detector used.
    While penetrating through a scatterer recoil-free gamma rays
are succesively and efficiently rejected from the gamma ray beam
by the nuclear resonance absorption process. This should result
in a decrease in the magnitude of Mössbauer effect as a function of
penetration depth. The magnitude of Mössbauer effect as a function
of electron energy derived from the coincidence electron pulse-
height spectra recorded for the stainless steel scatterer at nearly
resonance (source at rest) and at off-resonance velocities is shown
in Fig.1 (right site). The magnitude gradually decreases with the
increase in depth (decrease in electron energy). The inserted
coincidence CEMS spectra recorded for selected electron energy
intervals confirm this observation. The observed depth dependence
of the magnitude of Mössbauer effect reflects the depth sensitivity
of the coincidence CEMS spectra. The data presented in Fig.1 were
carefully corrected for a detector background. It should be
noticed that the depth dependence of the magnitude of Mössbauer
effect can be used as a useful criterion for testing the energy
distribution (electron weight function) of conversion electrons.
    In order to visualize the depth sensitivity of the concidence
CEMS spectra we used the resonance scatterer composed of a duplex
layer of hematite and magnetite on the iron substrate. Three coin-
cidence CEMS spectra were simultaneously recorded (Fig.2) for the
upper (A), intermediate (B) and lower (C) equal-energy intervals
of the K-shell conversion electron spectrum. Each spectrum can be
decomposed into four Zeeman sextets. The outer sextet corresponds
to the hematite layer (top layer), the inner one to the iron
substrate (third layer) and the remaining two sextets are due to
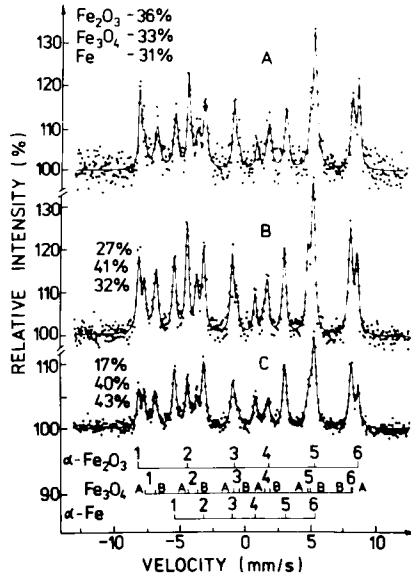the A and B sublatices of the magnetite layer (second layer).

Fig.2. The coincidence CEMS spectra simultaneously
recorded for the upper (A), intermediate (B) and
lower (C) equal-energy intervals of the K-shell
conversion electrons emerging from the duplex layer
of hematite and magnetite on the iron substrate.

The positions of the peaks arising from the various phases present
are indicated by the stick diagrams at the bottom of Fig.2. The
percentages of the total spectrum area contributed by each phase
are indicated in Fig.2. From their comparison the depth sensi-
tivity of the X-e⁻ coincidence CEMS spectra is evident. The depth
sensitivity is also visualized by the changes of line amplitude
ratios of various phases. The top hematite phase is most pro-
nounced in the A spectrum and deepest Fe phase in the C spectrum.
It should be stressed that the stream instability of the flowing
gas may spoil the depth sensitivity of the technique.
    In conclusion, the X-e⁻ coincidence technique improves the
depth sensitivity of CEMS spectra recorded with an He/CH₄ flow
proportional counter.

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