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Simultaneous transmission and scattering Mössbauer measurements of powder samples

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Abstract. A vertical experimental set-up for simultaneous recording transmission and scattering Mössbauer spectra is described. Application of the apparatus for the study of model powder mixture of two components with different grain sizes shows differences in the relative intensity ratio of these fractions in absorption and conversion electron Mössbauer spectroscopy (CEMS) spectra. This effect, explained as a result of the size selectivity of CEMS technique, is parameterized by the grain radius ratio of components. The possible application for investigation of isolated surface nano- and microobjects is discussed.

Key words: methodology of Mössbauer spectroscopy • CEMS • micro-powders

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Introduction

Transmission Mössbauer spectroscopy applied for the study of a nano- and microobject usually deals with bulk aggregations of interacting particles. However, recently a new field of nanotechnology, related to the thin films as matrix for individual nanoparticles, such as ferromagnetic and paramagnetic precipitates in diamagnetic layers [2, 4] or hard carbides crystallites in mechanically protecting coatings [3], became especially interesting. For studying such problems, the CEMS technique seems to be more adequate or, sometimes, the only possible.

In our previous paper [1], it has been pointed out that CEMS is not only surface sensitive but also a size selective method, enhancing contribution from smaller particles. Now, we show that the comparison of transmission and CEMS spectra of powder samples containing two different fractions of different diameters may supply new information on the grain sizes. If only CEMS spectra are available, the concentration of different fractions cannot be determined from the area under the corresponding subspectra.

Apparatus

The reproducible preparation of a mixed powder sample for CEMS measurements is complicated because of segregation of fractions due to electrostatic and magnetic properties, differences in grain sizes and specific weights. These problems are especially critical for samples placed vertically when horizontally oriented drives are used. Thus, we constructed a vertical set-up

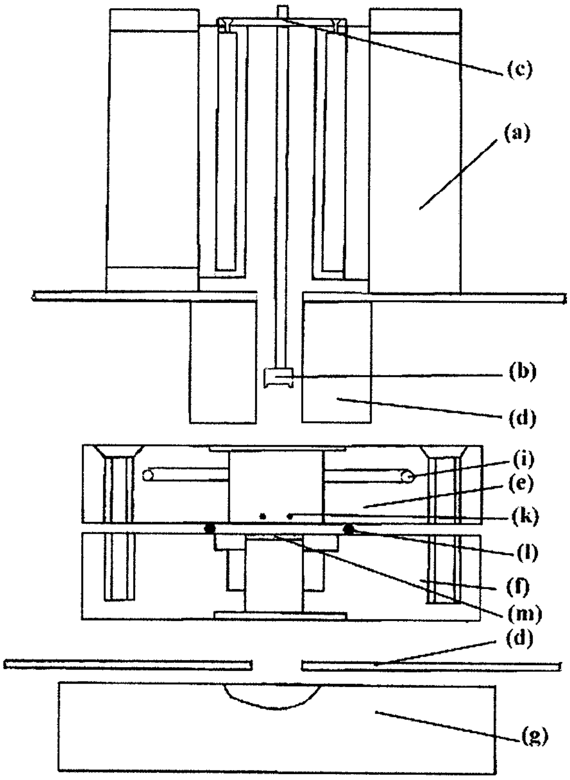

Fig. 1. A scheme of the experimental set-up. (a) – Drive in vertical position, (b) – source, (c) – source fixing point, (d) – collimator, (e) – CEMS counter module, (f) – sample holder module, (g) – proportional counter, (i) – gas-in, (k) – anode wires at zero potential, 4 mm from the sample, (l) – o-ring, (m) – sample at high voltage potential (~ –1440 V).

for simultaneous registration of CEMS and transmission spectra, see Fig. 1. Two special aspects of the system should be underlined. (a) The system has a module structure with fixed geometry. The exchange of the sample, attached to the CEMS counter, does not require demounting of the system and removing the source which is feed through a central tube of the drive. (b) The CEMS proportional, gas-flow counter is an original construction. The sample is negatively polarized (~ –1400 V) and the signal is taken from tungsten wires at a virtually zero potential directly to the operational amplifier. Such a solution reduces the electrical noises and improves the energy resolution. In consequence, the counter becomes sensitive to the low energy electrons emitted from the deeper layers of the samples [2] and may be applied for qualitative depth selective Mössbauer spectroscopy.

Experimental

The composite samples of a mixture of sifted $FeSO_4 \cdot 4H_2O$ powders (with radii R = 0.043(4), 0.034(2), 0.025(4), 0.015(4) mm; the numbers in brackets are radius distributions) and a Fe_2O_3 powder with grains of radius r = ~0.02 mm were prepared by various methods. At first, the mixed powder was simply distributed or glued to an Al foil; later, a single layer of crystallites was placed on an adhesive tape. The CEMS and transmission spectra were recorded simultaneously at room temperature.

Results

The quadrupole Fe^{2+} doublet of $FeSO_4 \cdot 4H_2O$ and Zeeman sextet of Fe^{3+} in Fe_2O_3 are clearly distinguished in Mössbauer spectra, see Fig. 2. The intensity ratio of these two subspectra, determined from transmission measurement, is proportional to the amount of iron in these two compounds. It differs from the corresponding intensity ratio obtained from CEMS spectra; the difference depends on the ratio of grain radii and the composition of the specimen. For thick samples made by simple mixing, such differences were poorly reproducible, being influenced by the process of sample preparation. On the contrary, the results for the samples consisting of single layer of mixed $FeSO_4 \cdot 4H_2O$ and Fe_2O_3 on the scotch tape exhibited a clear trend. The T to C ratio, where T and C are the Fe^{2+}/Fe^{3+} intensity ratios in transmission (I_{TR}/I_{Tr}) and CEMS spectra (I_{CR}/I_{Cr}), respectively, is a linear function of the $FeSO_4 \cdot 4H_2O$ grain radius, R, see Fig. 3.

Discussion

The results obtained for thick samples were not reproducible, which reflects the fact that the process of the sample preparation was not fully controlled. Probably, in these samples big and small grains overlapped differently, being more or less exposed to CEMS. Moreover, in this case, the transmission spectra may be significantly influenced by the thickness effect; the estimated effective thickness of a single $FeSO_4 \cdot 4H_2O$ grain with R = 0.04 mm is about 1. In any case, comparison of the transmission and CEMS spectra may give same information on the morphology and grain segregation in granular composites. In case of a single layer of isolated grains, the linear T/C dependence on the R radius may be explained in simple terms.

The intensity ratio of Mössbauer lines of the two components, in the form of spherical particles with radii R and r in transmission experiment, T, and CEMS spectrum, C, are:

$$T = \frac{I_{TR}}{I_{Tr}} = \frac{\frac{4}{3}\pi R^3 \rho_R g_R f_R N_R}{\frac{4}{3}\pi r^3 \rho_r g_r f_r N_r} \tag{1}$$

$$C = \frac{I_{CR}}{I_{Cr}} = \frac{\pi R^2 \rho_R g_R \lambda_R f_R N_R}{\pi r^2 \rho_r g_r \lambda_r f_r N_r} \tag{2}$$

where N are the number of particles per cm^2, ρ, g and f are the density, mass concentration of iron and recoil free fraction, respectively, and λ is the thickness of the surface layer sensitive to CEMS technique. Subscripts r and R refer to the components with grain radius r and R, respectively. Here, the influence of thickness effect on the intensity of transmission spectra was neglected.

Consequently, for the T/C ratio one obtains:

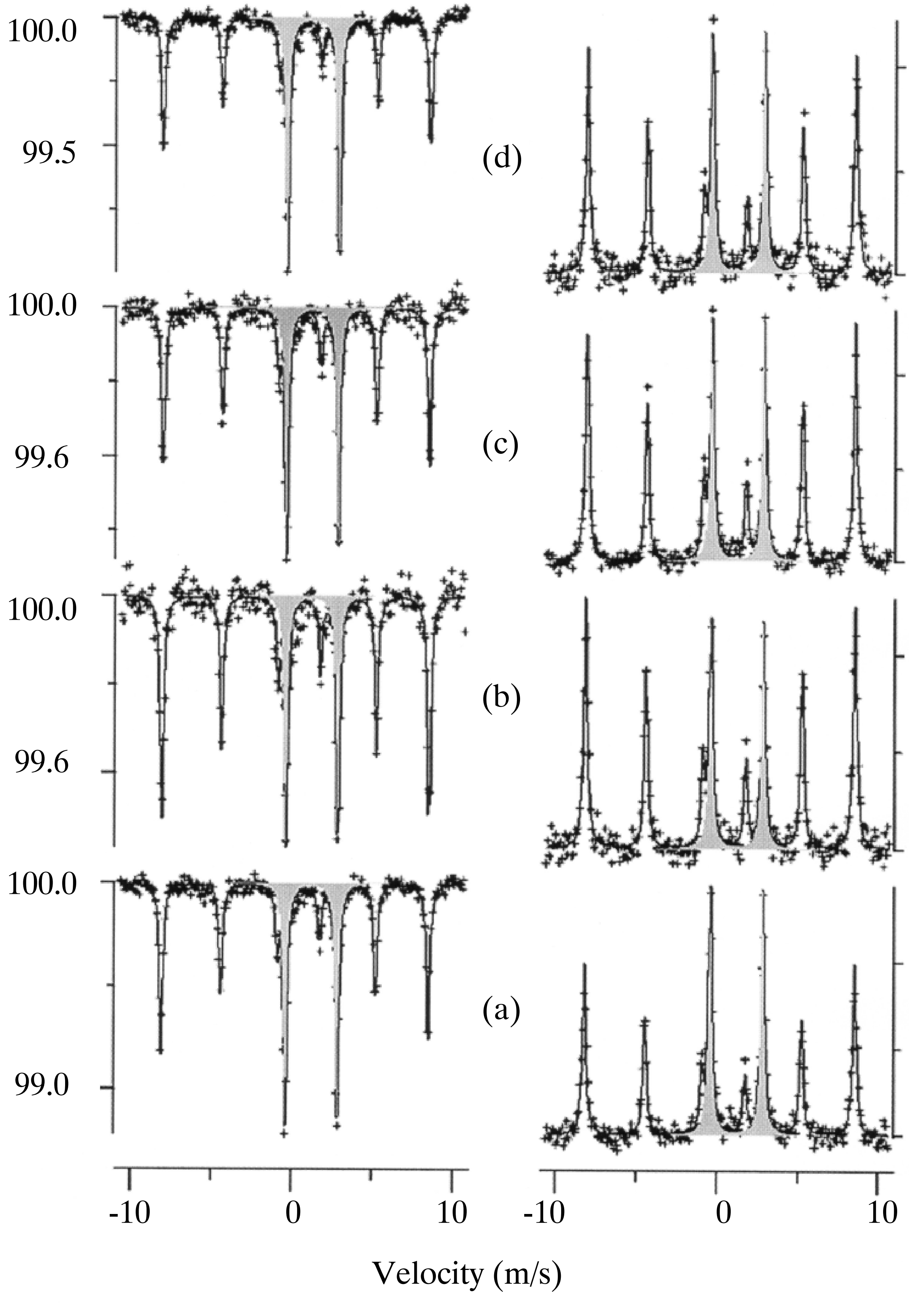

Fig. 2. Transmission (left) and CEMS (right) spectra of the $FeSO_4$ and Fe_2O_3 powder mixture. The shadowed subspectra correspond to the $FeSO_4$ fraction with different grain radius: (a) – 0.015(4) mm, (b) – 0.025(4) mm, (c) – 0.034(2) mm, (d) – 0.043(4) mm.

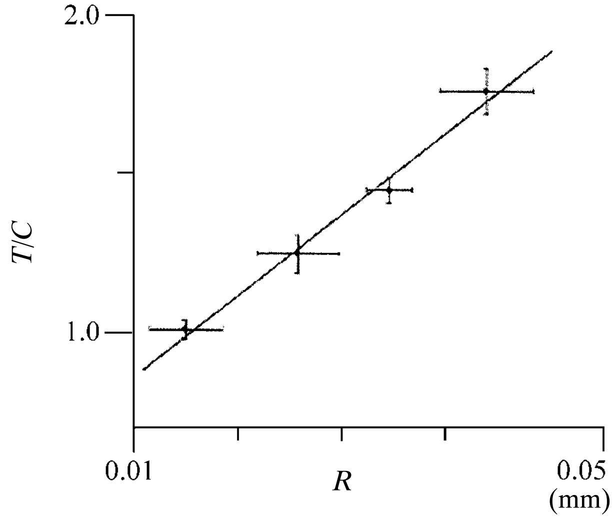

Fig. 3. Comparison of phase population determined from transmission and CEMS experiments: the ratio of the $FeSO_4$ to Fe_2O_3 fractions measured in transmission (T) and in CEMS experiment (C) vs. the radius of $FeSO_4$ grains, R.

$$T/C = (1/r)\cdot R \tag{3}$$

This result shows that the difference in the intensity ratio of any two powder components in the transmission and CEMS spectra may be explained by the difference in the grain of radii. Our data confirmed fully these calculations: the solid line in Fig. 3 is a linear fit of T/C in function of R; its slope determines the radius of Fe_2O_3 equal to 0.020(5) mm, in agreement with the observation under optical microscope.

Conclussions

The described vertical set-up makes possible the simultaneous recording of the transmission and CEMS Mössbauer spectra, which may eliminate artifacts related to the sample preparation. Such experiments may lead to the determination of the radius ratio of any two types of isolated in surface layers nano- or microobjects. It should be underlined, however, that the derived formula applies strictly only if: (a) the grains do not overlap, and (b) the radius of grains is bigger than the penetration depths (~100 nm) of 7.3 keV conversion electrons. In any case, the presented result and discussion clearly show that when determining the composition of powder composites from CEMS spectra, one should be aware of the fact that this technique is “size selective”.

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