Mössbauer spectroscopy of Fe-based nanomaterials

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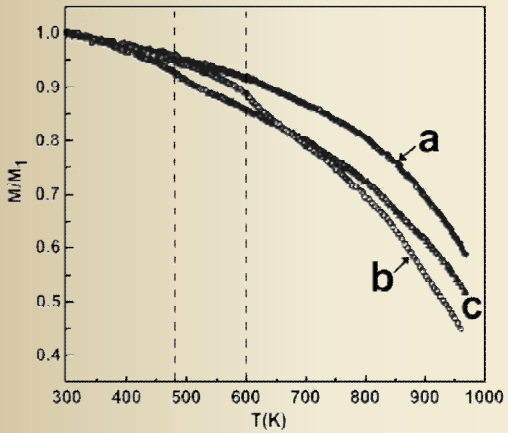
1.Introduction

There are two opinions concerning the effect of the nanosized grains on the magnetic properties and Mössbauer spectra.

1. Nanomaterials (<L> ≤ 10 nm) have a grain boundary phase (interface region) which has essential differences in the structure, fundamental magnetic properties (saturation magnetization, Curie temperature) and leads to the additional sextet in the Mössbauer spectrum.

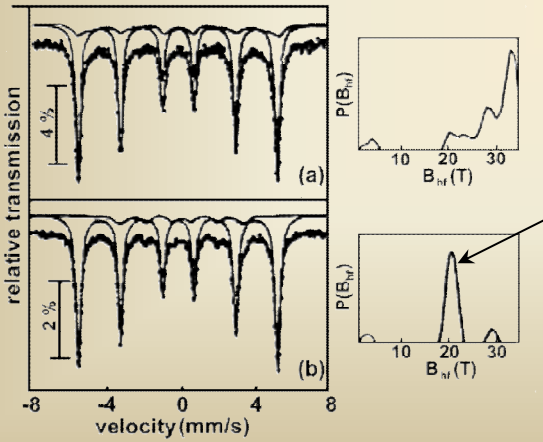
As an example, Del Bianco et al., JMMM, 179-181 (1998) 939



a – un-milled Fe powder

b – as-milled Fe powder (<L> = 8 nm) t_{mill} = 32 h

c – milled powder annealed at 695 K for 14 h



As-milled Fe powder t_{mill} = 32 h

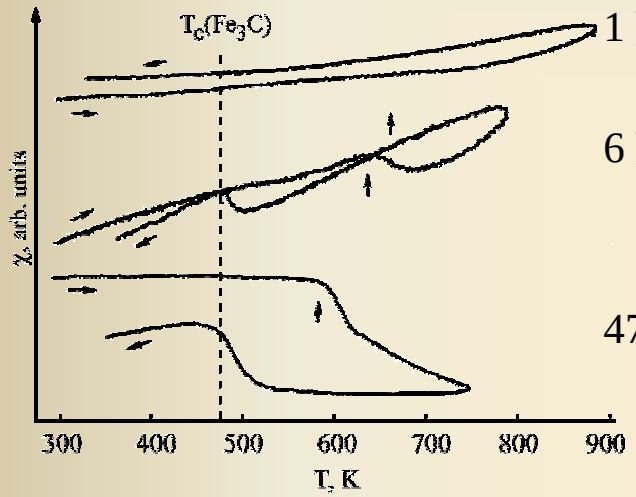
Fe_3C **?**

Milled powder annealed at 695 K for 14 h

2. In the absence of the contaminating impurities the nanocrystalline-state formation in α-Fe does not lead to essential changes in the magnetic properties and Mössbauer spectra.

As an example, Yelsukov et al., Nanostructured Mater., 12 (1999) 483.

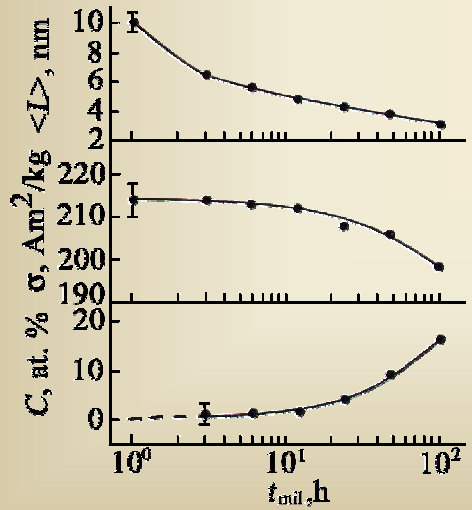
Fe milled in a liquid hydrocarbon (heptane C_7H_{16}).

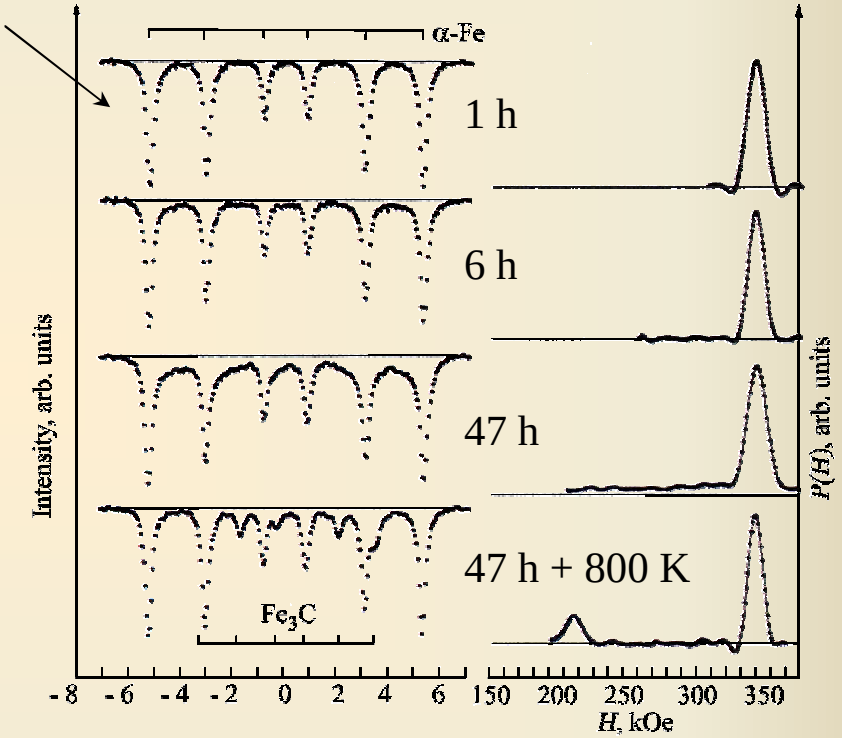


1 h ← <L> = 10 nm

6 h

47 h





Mechanical treatment

$\alpha\text{-Fe} \rightarrow n(\alpha\text{-Fe})$

$C_7H_{16} \rightarrow C$

$C_7H_{16} \rightarrow H$

$n(\alpha\text{-Fe}) + C + H \rightarrow$ amorphous (Fe-C) $\xrightarrow{800\ K} Fe_3C$

The aim of this work was to study how the nanocrystalline state affects the magnetic properties and hyperfine magnetic parameters. The solution of the problem supposes the use of special model objects in which both a nanocrystalline state and a state with the large grain size can be realized, with other conditions being equal.

Along with the α-Fe, we have chosen Fe-Ge and Fe-Al systems with the broad concentration region (up to 10 at. % Ge and 24 at. Al at 1073 K) of the equilibrium disordered BCC alloys. On the other hand, the BCC disordered nanocrystalline Fe-Ge and Fe-Al alloys can be easily produced by mechanical alloying.

2. Experimental

Initial powders with particle size ≤ 300 μm

The studied samples:

- α-Fe
  - **- initial** (un-milled)
  - - mechanical grinding for 16 h - **MG (16 h)**
  - - annealing of MG (16 h) sample at 773 K for 1 h - **MG (16 h) + 773 K**
- α-$Fe_{90}Ge_{10}$
  - - mechanical alloying for 16 h - **MA (16 h)**
  - - after MA (16 h) heating with the rate of 1 K/s up to 1073 K, keeping at 1073 K for 1.5 h, cooling to the room temperature with the rate of 25 K/s - **MA (16 h) + 1073 K**
- α-$Fe_{77}Al_{23}$
  - - mechanical alloying for 16 h - **MA (16 h)**
  - - after MA (16 h) heating with the rate of 1 K/s up to 1073 K, keeping at 1073 K for 1.5 h, cooling to the room temperature with the rate of 25 K/s - **MA (16 h) + 1073 K**

A planetary ball mill Fritsch P-7

- vials and balls made of hardened steel containing 1 wt. % C and 1.5 wt. % Cr
- power intensity – 2 W/g
- loading – 10 g
- atmosphere – Ar
- heating – ≤ 60°C

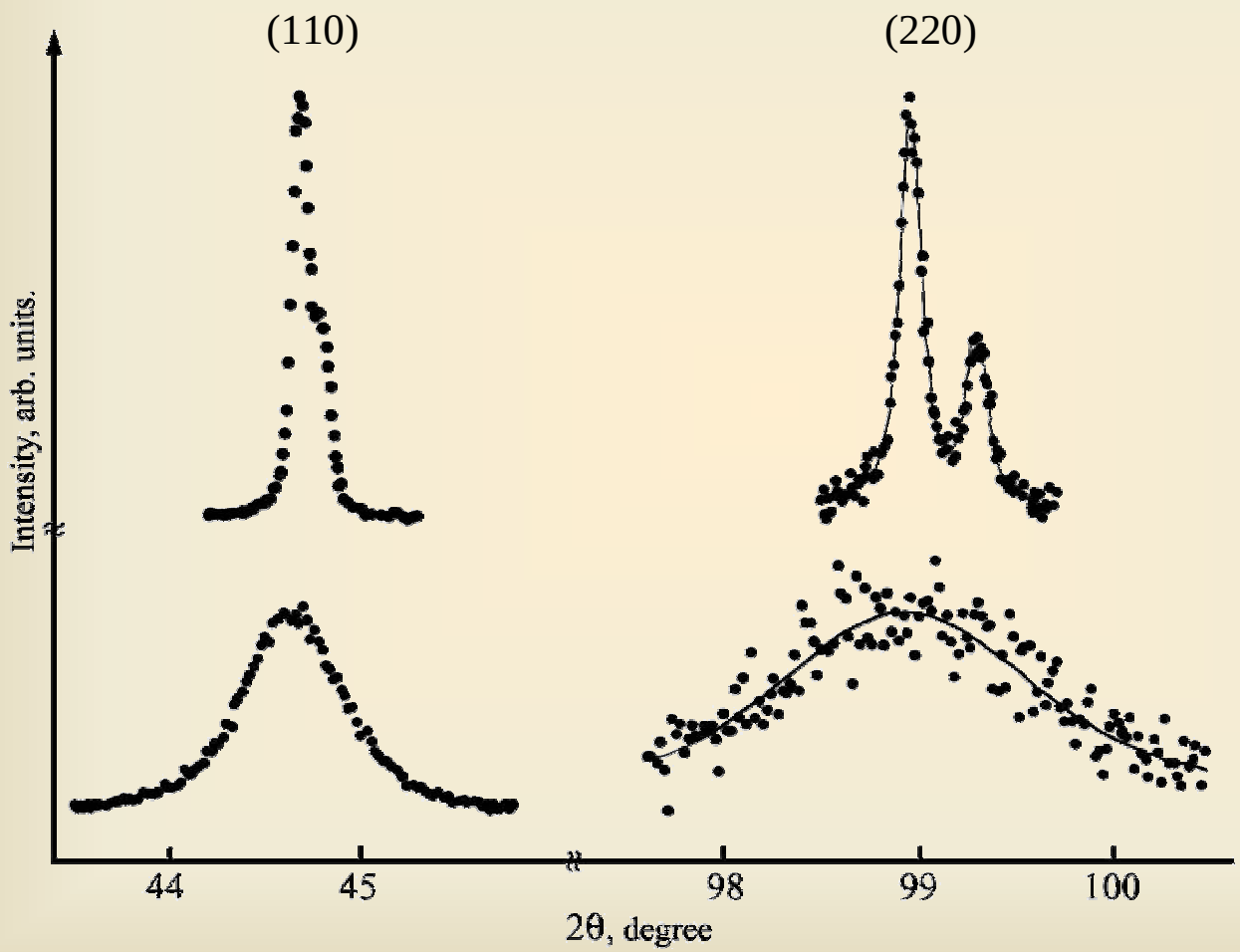
Experimental techniques

- post-milling mass increase measurements
- secondary ion mass spectroscopy (SIMS)
- Chemical analysis using Spectraflame – Modula D atomic emission spectrometer
- X-ray diffraction; Mössbauer spectroscopy; Magnetic measurements

Particles of stone-like shape with average size of 20-40 μm.

The chemical analysis data (x_{Ge} = 9.6, x_{Al} = 22.5, x_{Cr} = 0, x_C < 0.3, x_O < 0.2 at. %) as well as the lack of the samples mass change after mechanical treatment demonstrate no detectable amounts Cr, C and O impurities.

3. X-ray diffraction
α-Fe



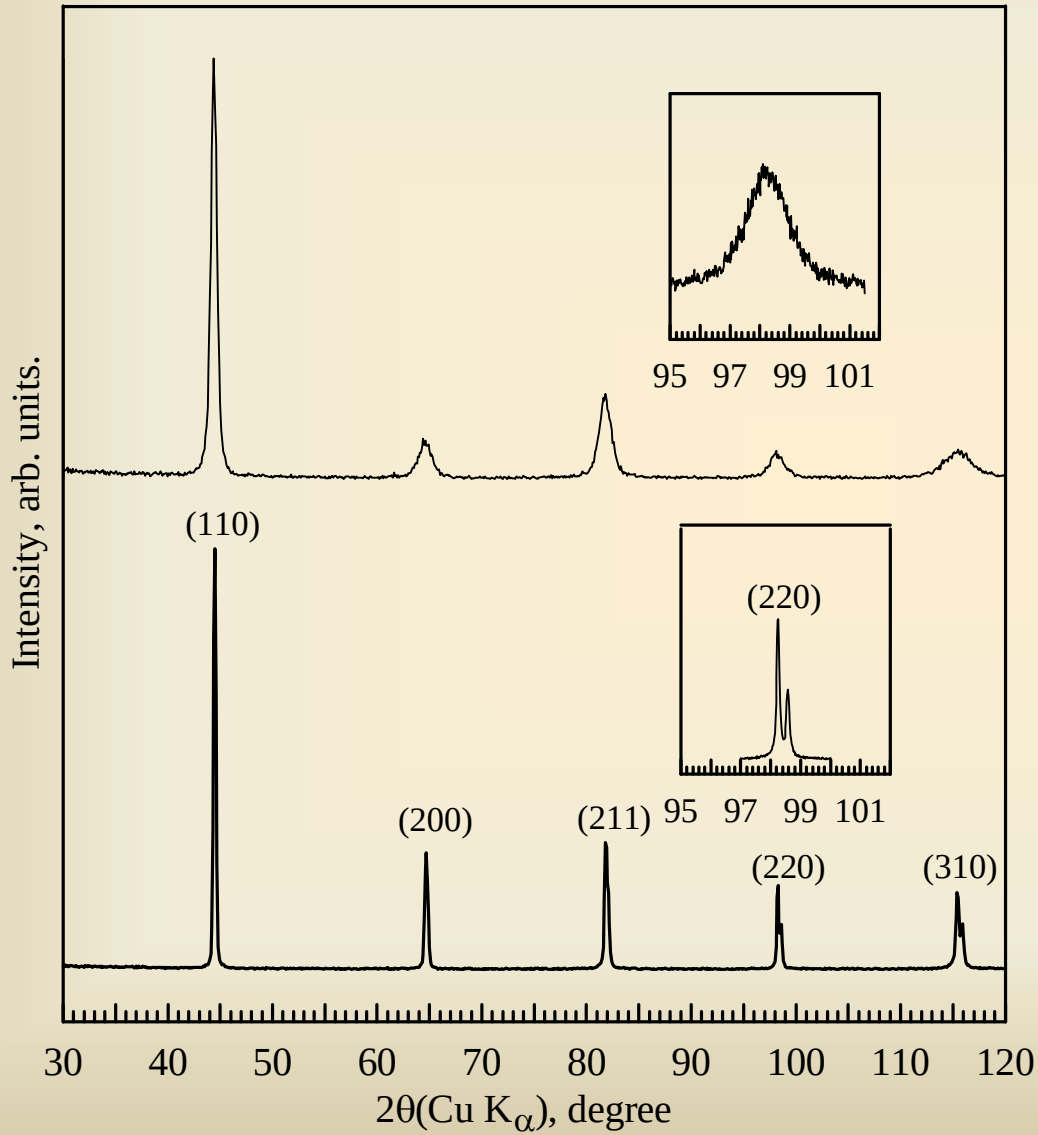
Initial

<*L*> > 100 nm

MG (16 h)

<*L*> = 9 nm

α-$Fe_{90}Ge_{10}$



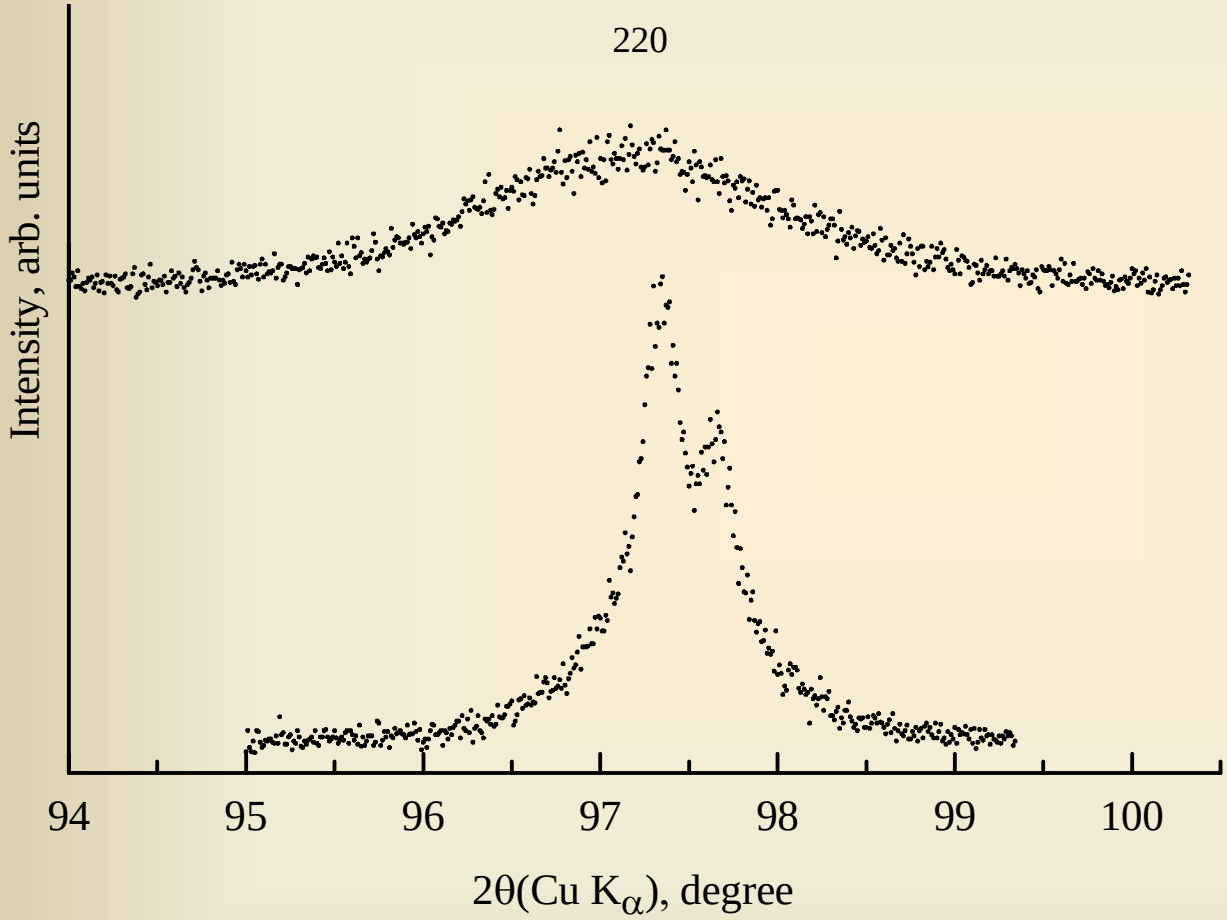
MA (16 h)

<*L*> = 8 nm

MA (16 h) + 1073 K

<*L*> > 100 nm

α-$Fe_{77}Al_{23}$



MA (16 h)

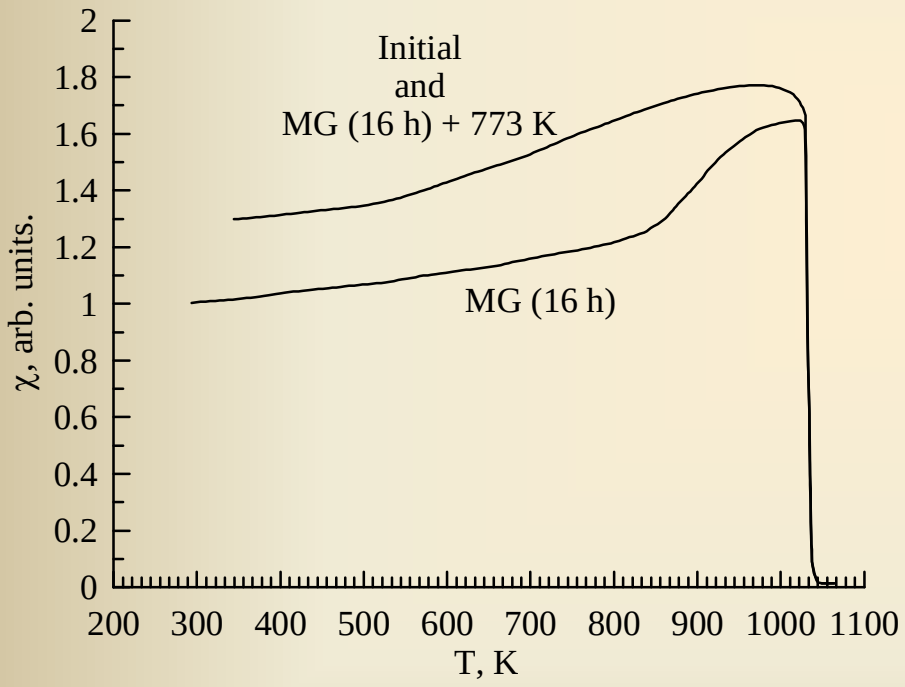
<*L*> = 8 nm

MA (16 h) + 1073 K

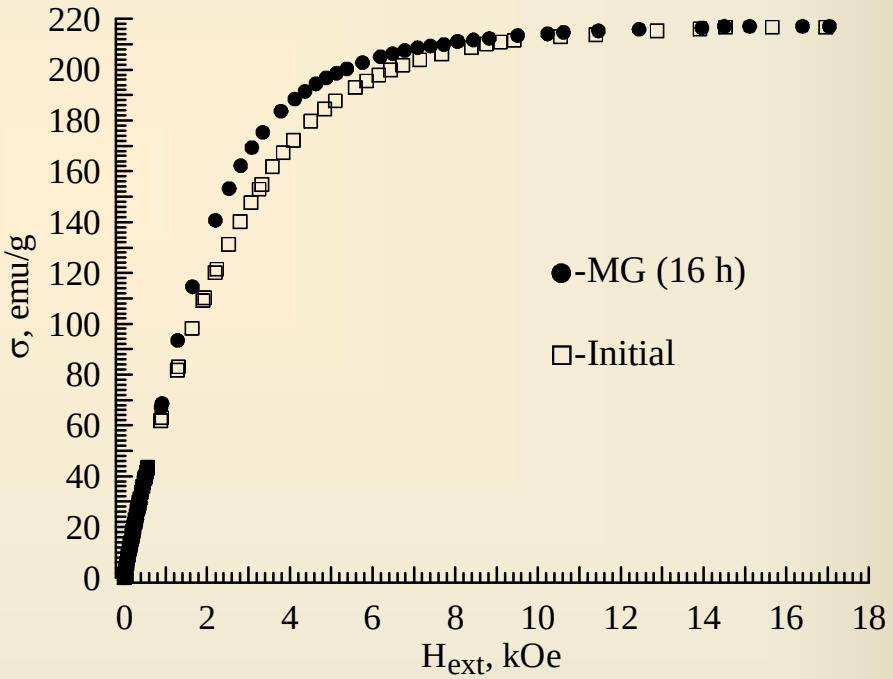
<*L*> = 30 nm

4. Magnetic measurements
α-Fe

Temperature dependences of a.c. magnetic susceptibility (heating rate of 1 K/s)

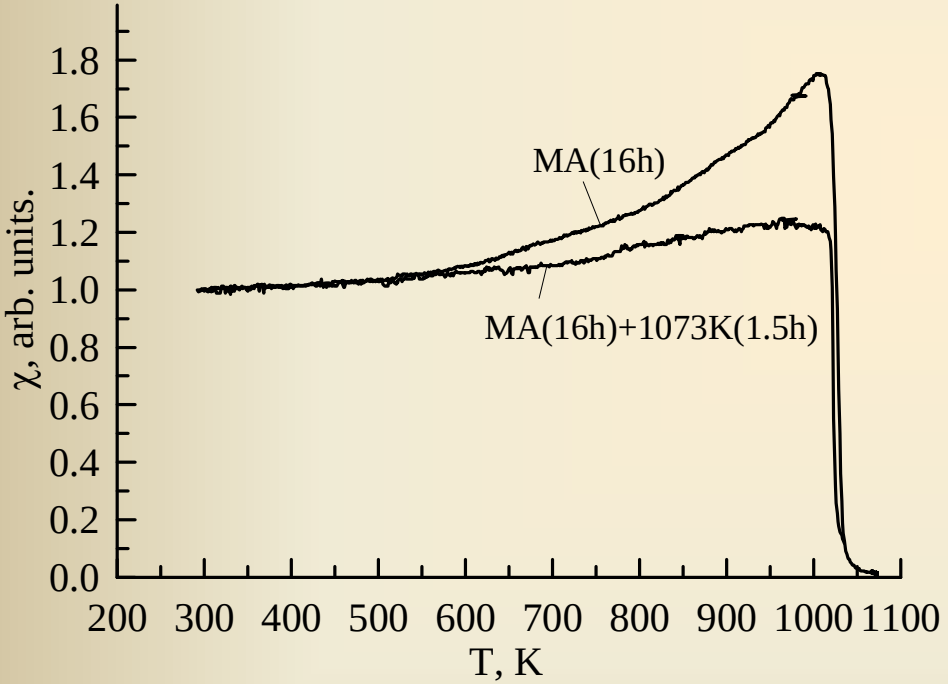


Magnetization curves (T_{meas} = 300 K)

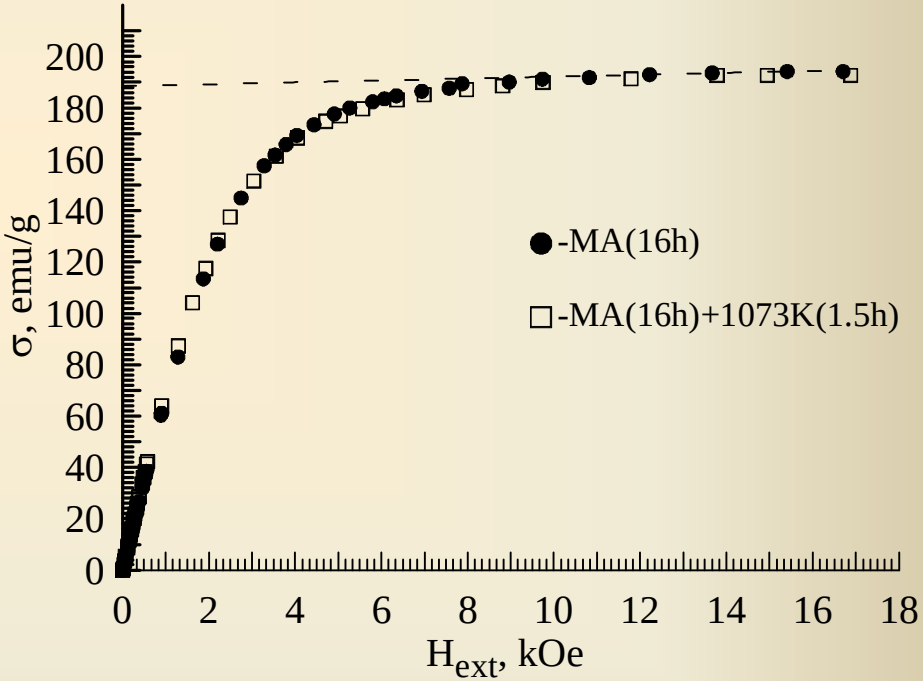


α-$Fe_{90}Ge_{10}$

Temperature dependences of a.c. magnetic susceptibility (heating rate of 1 K/s)

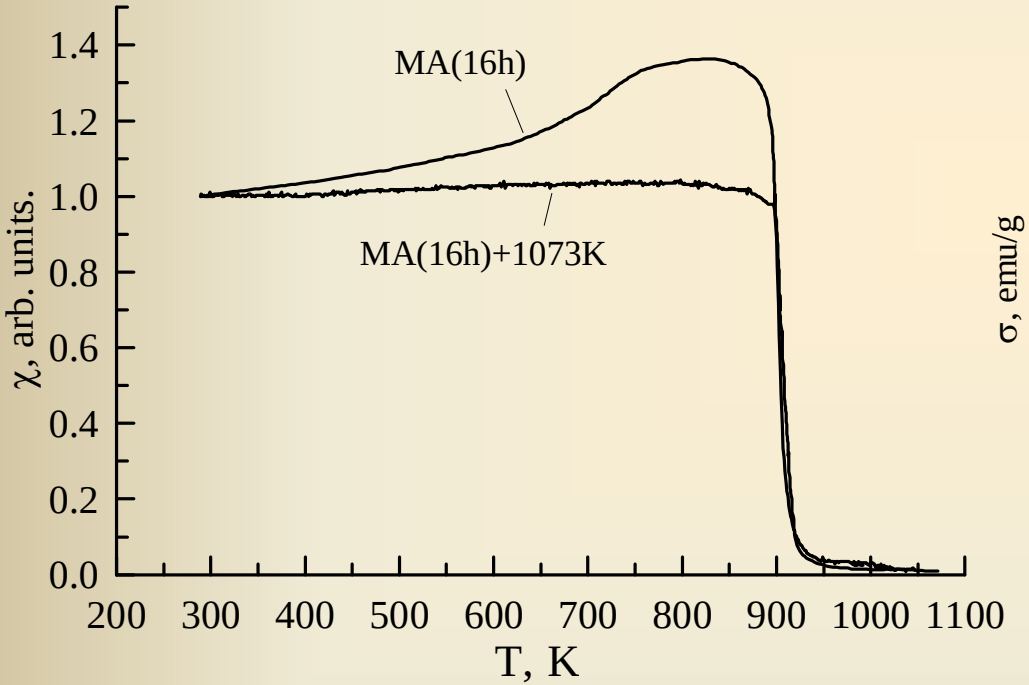


Magnetization curves (T_{meas} = 300 K)

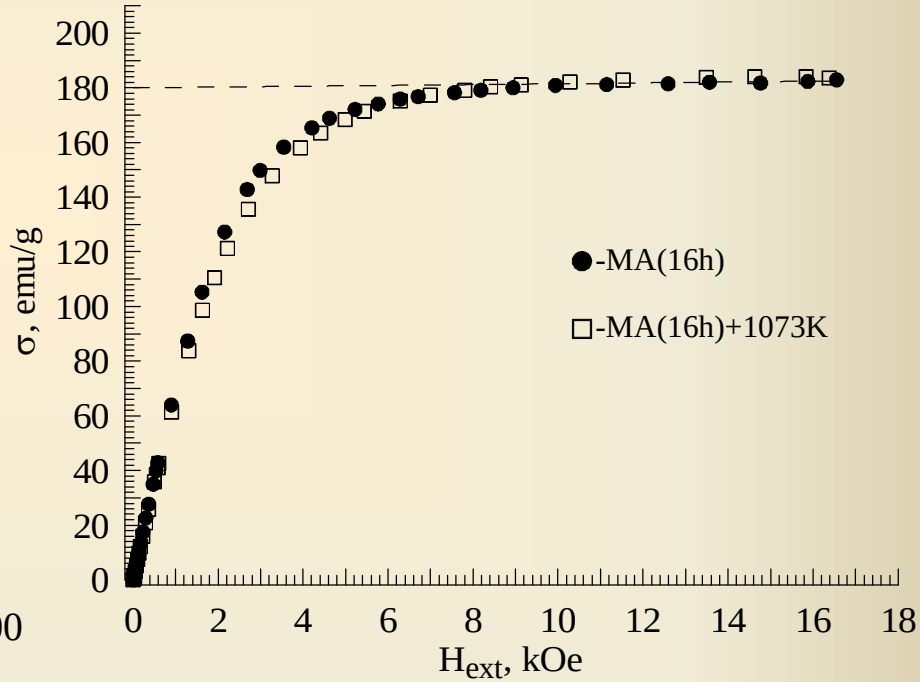


α-$Fe_{77}Al_{23}$

Temperature dependences of a.c. magnetic susceptibility (heating rate of 1 K/s)



Magnetization curves (T_{meas} = 77 K)



α-$Fe_{77}Al_{23}$

ZFC and FC curves

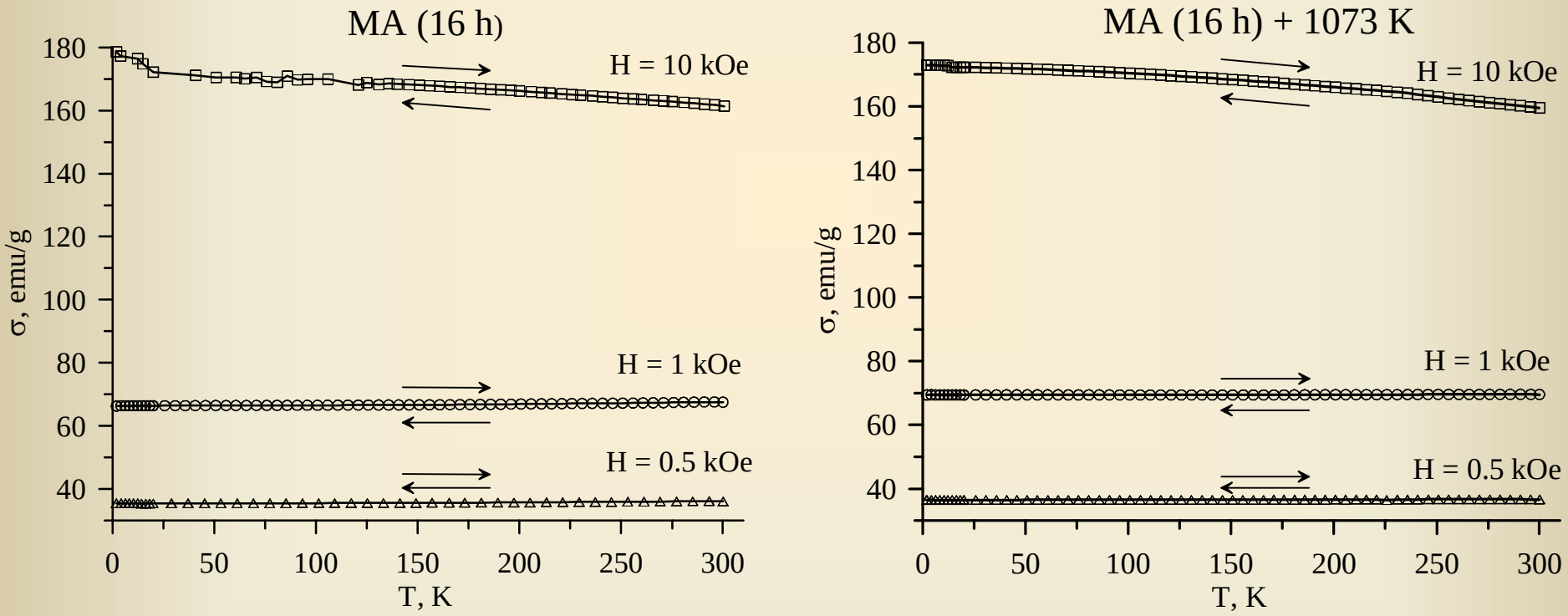


Table 1. Structural and magnetic parameters of the nanocrystalline and annealed alloys.

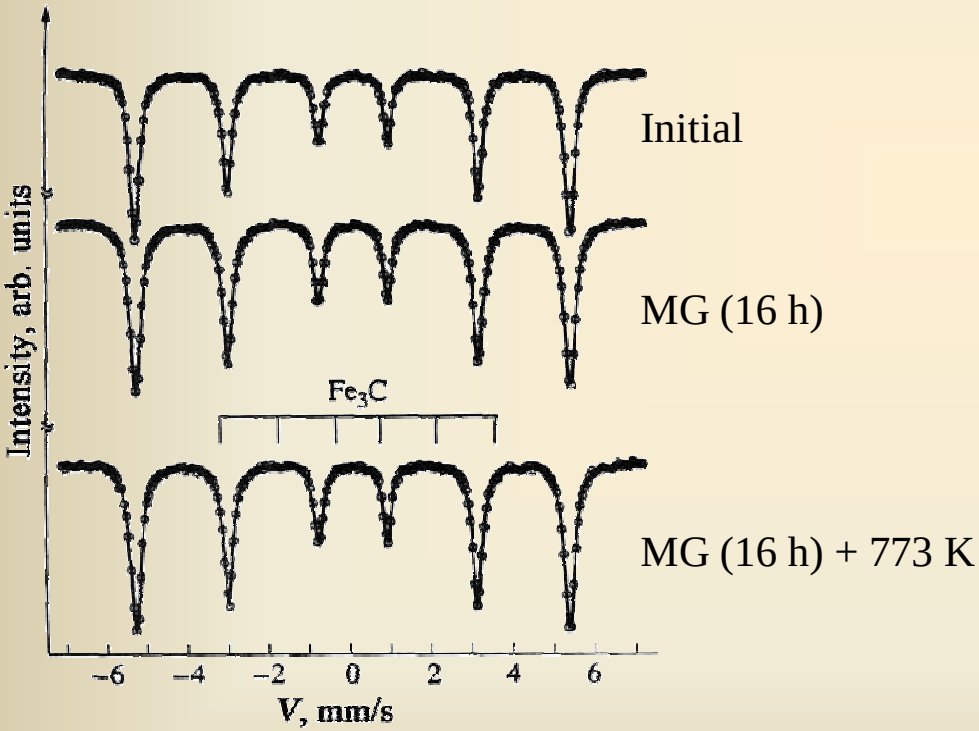
Sample		*a*, nm	<L>, nm	$<\varepsilon^2>^{1/2}$, %	σ_0, emu/g	T_c, K
α-Fe	MG (16 h)	0.2869_1*	9_1	0.22_2	217_2 (300 K)	1040_8
	Initial	0.2866_1	> 100	0.03_1	217_2 (300 K)	1043_3
α-$Fe_{90}Ge_{10}$	MA (16 h)	0.2884_1	8_1	0.26_2	188_2 (300 K)	1017_3
	MA(16 h) + 1073 K	0.2881_1	> 100	0.01_1	188_2 (300 K)	1020_3
α-$Fe_{77}Al_{23}$	MA (16 h)	0.2907_1	8_1	0.32_3	180_2 (77 K)	890_3
	MA(16 h) + 1073 K	0.2903_1	30_3	0.04_1	180_2 (77 K)	895_3

* The subscript denotes uncertainty in the last digit of the tabulated value.

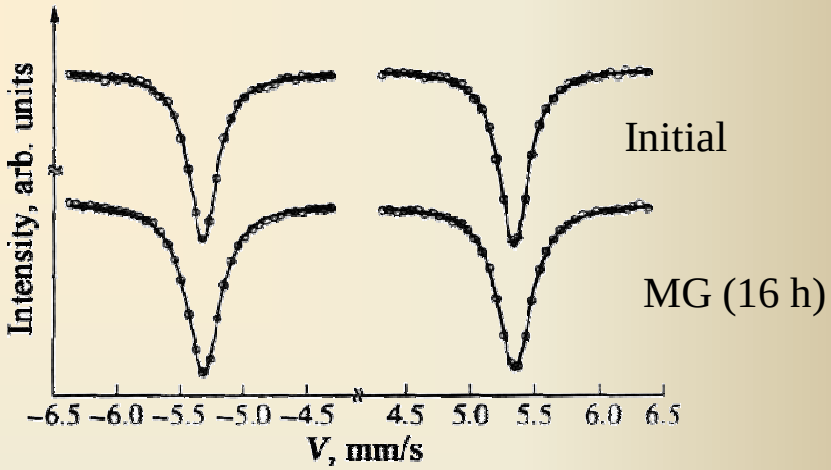
- Transition into a nanocrystalline state results in a small increase of the bcc lattice parameter and a microstrain growth;
- The σ_0 and T_c values remain unchanged;
- No features are found in the χ (T) dependences of the nanostructured samples.

5. Mössbauer spectroscopy
α-Fe

Mössbauer spectra of different samples of iron powder

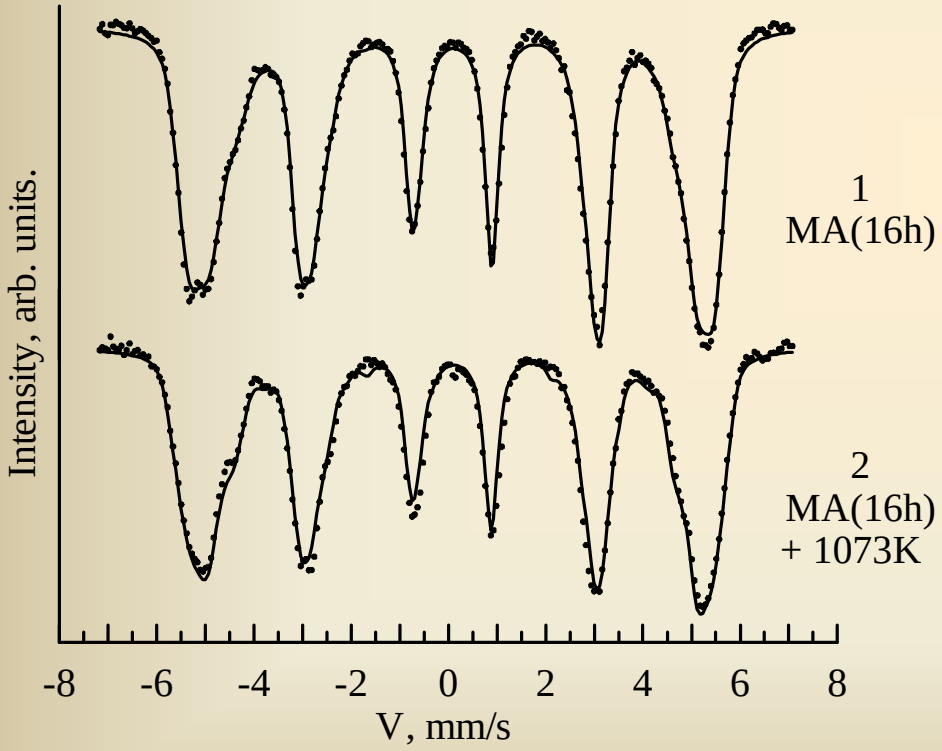


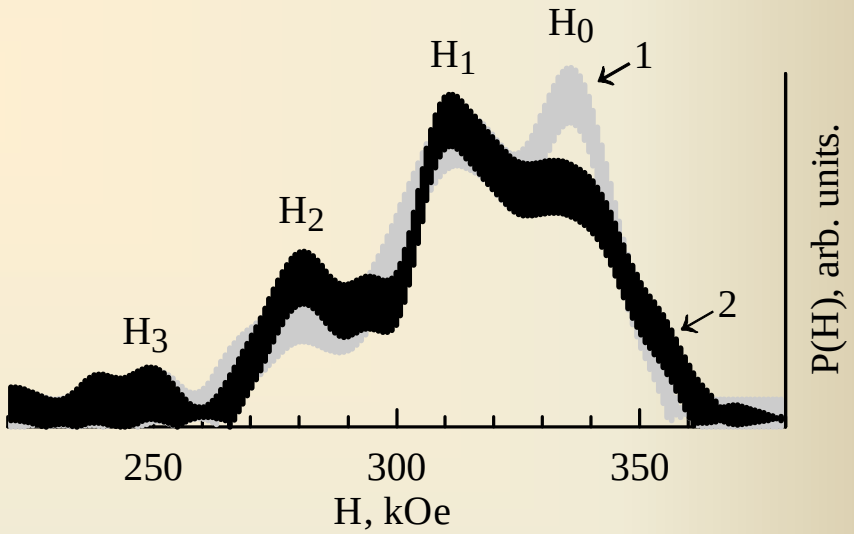
Parts of the Mössbauer spectra showing the 1st and 6th peaks



α-$Fe_{90}Ge_{10}$

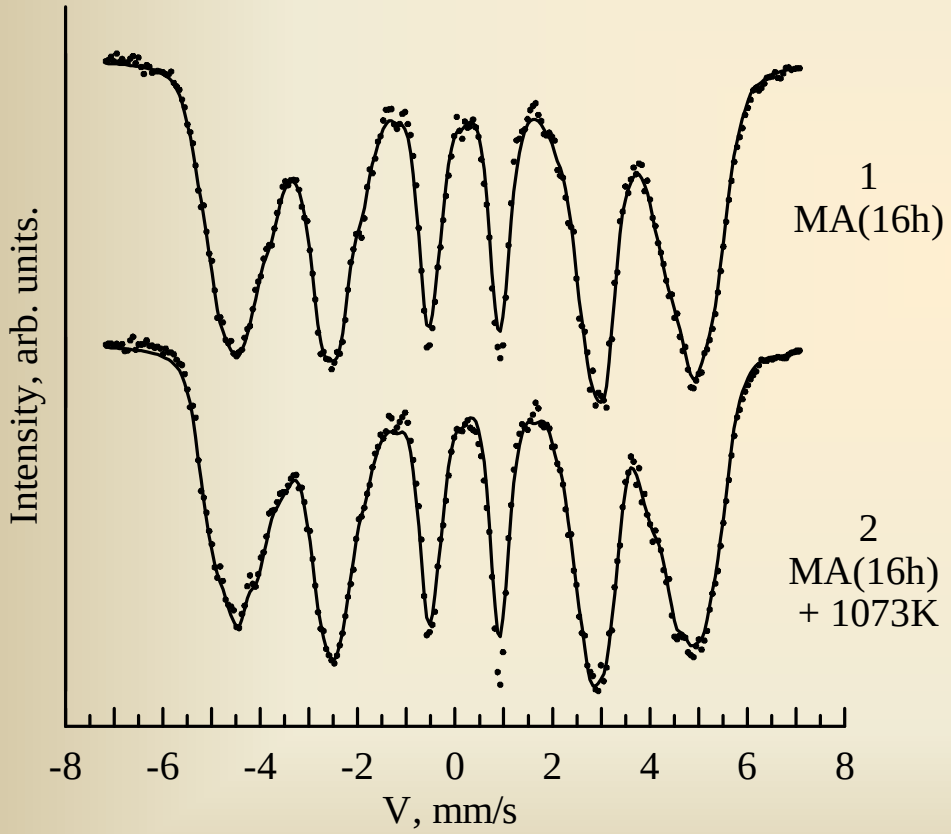
Mössbauer spectra and corresponding distributions P(H) of mechanically alloyed and annealed samples





α-$Fe_{77}Al_{23}$

Mössbauer spectra and corresponding distributions P(H) of mechanically alloyed and annealed samples



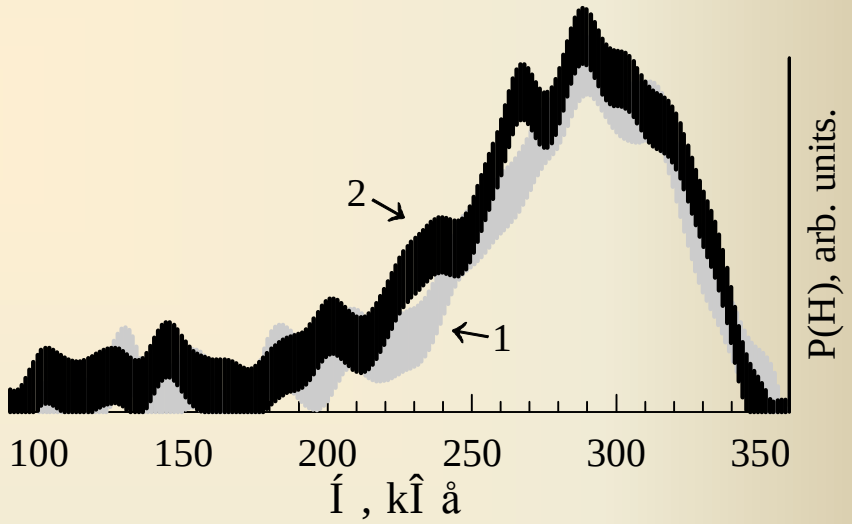


Table 2. Average hyperfine parameters of the nanocrystalline and annealed alloys.

Sample		$\Gamma_{1,6}$, mm/s	$\overline{\delta}$, mm/s	$\overline{H}$, kOe
α-Fe	MG (16 h)	0.32_1	0.01_1*	331.1_5 (300 K)
	Initial	0.27_1	0.01_1	331.0_5 (300 K)
α-$Fe_{90}Ge_{10}$	MA (16 h)	1.01_3	0.09_2	314_2 (300 K)
	MA(16 h) + 1073 K	1.14_3	0.09_2	313_3 (300 K)
α-$Fe_{77}Al_{23}$	MA (16 h)	1.47_3	0.20_3	275_3 (77 K)
	MA(16 h) + 1073 K	1.56_3	0.20_3	267_3 (77 K)

* Relative to α-Fe at room temperature.

- There is no new component in MS of the nanocrystalline α-Fe, the MS lines width increases by 20%;
- The $\overline{\delta}$ and $\overline{H}$ parameters remain unchanged for all samples;
- The lines width of the annealed $Fe_{90}Ge_{10}$ and $Fe_{77}Al_{23}$ samples is more than that of the mechanically alloyed ones.

Table 3. Fractions of area (P_k) of the Mössbauer spectrum and local atomic configurations probabilities calculated for bcc disordered alloy $Fe_{90}Ge_{10}$.

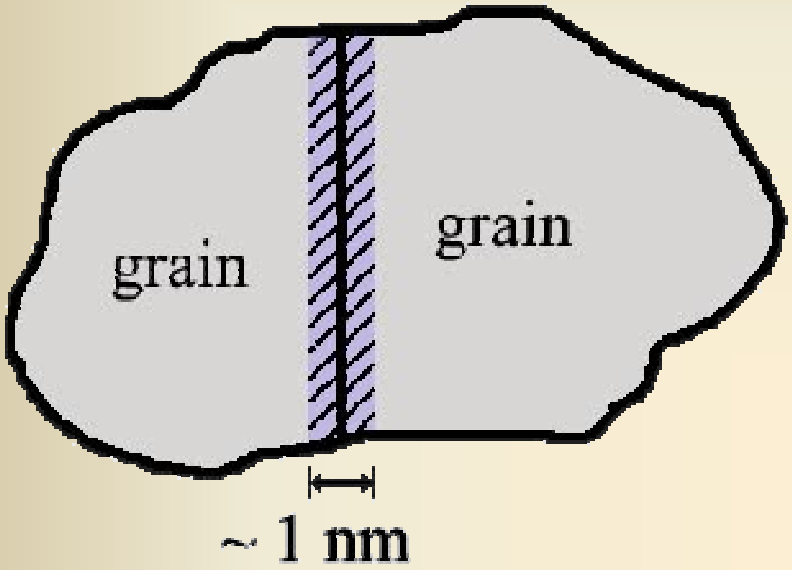
Sample	P_0, %	P_1, %	P_2, %	P_3, %	P_4, %
MA(16h)	43.3 ± 1	38.8± 1	15.7 ± 1	2.2 ± 2	—
MA(16h) + 1073K	35.2 ± 1	43.0 ± 1	19.9 ± 1	1.9 ± 2	—
Calculated using Binominal Distribution	43.05	38.26	14.88	3.31	0.05

Table 4. Local hyperfine magnetic fields and isomer shifts of mechanically alloyed – MA(16h) and with following annealing – MA(16h) + 1073K $Fe_{90}Ge_{10}$.

	MA(16h)	MA(16h) + 1073K
H_0, kOe	336 ± 2	338 ± 2
H_1, kOe	311 ± 2	314 ± 2
H_2, kOe	281 ± 3	284 ± 3
H_3, kOe	252 ± 5	244 ± 5
I_0^*, mm/s	0.05 ± 0.02	0.05 ± 0.02
I_1, mm/s	0.10 ± 0.02	0.09 ± 0.02
I_2, mm/s	0.15 ± 0.02	0.15 ± 0.02
I_3, mm/s	0.20 ± 0.04	0.25 ± 0.04

* Relative to α-Fe at room temperature.

α-Fe



Interface region

(boundary and close-to-boundary distorted zones)

Initial (<L> > 100 nm) $\rightarrow \Gamma_{1,6}$ = 0.27 mm/s
MG (16 h) (<L> = 8 nm) $\rightarrow \Gamma_{1,6}$ = 0.32 mm/s

The increase of Γ can be accounted for by a different in values and sign anysotropic contribution to HFMF for Fe atoms in interface regions.

$H = H_{is} + H_{anis}$

$H_{anis} = \frac{1}{2} h(3\cos^2\theta - 1)$

Grain: $\theta = 54°30' \rightarrow H_{anis} = 0$

Interface region: distribution of $\theta \rightarrow$
distribution of $H_{anis} \rightarrow$
$\Gamma(MG) > \Gamma(Initial)$

6. Conclusions

1. With the absence of contamination no changes have been found in the specific saturation magnetization, Curie temperature and hyperfine interaction parameters;

2. No additional sextets in the Mössbauer spectra and features in the temperature dependences of a.c. magnetic susceptibility were found either;

3. A slight broadening (~ 20%) in the Mössbauer spectrum of the nanocrystalline pure Fe is explained by random in sign and magnitude anisotropic contribution to the HFMF from the fe atoms in interface region of nanostructure.

Acknowledgements

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Thank you very much for your attention!