Hyperfine Interact
DOI 10.1007/s10751-013-0957-8

Mössbauer study of new functional metal/polymer nanocomposites with spatially oriented FeGa particles

S. I. Zholudev · T. Yu. Kiseleva

Abstract Mössbauer spectroscopy has been applied to study the structure and magnetostriction interdependence of metall/polymer composites with spatially oriented FeGa particles in a polymer matrix. Composites were synthesized combining modified polyurethane with nanocrystalline mechanosynthesized particles of magnetostrictive FeGa composition through polymerization to achieve a considerable magnetostrictive response. To increase magnetoelastic effects a spatial particle arrangement in the polymer matrix was generated. The magnetostrictive composition of the mechanosynthesized particles has been determined by Mössbauer spectroscopy, X-ray diffraction and TEM at different stages of ball milling. The microstructure of the composites via the particle orientation in the polymer has been researched by SEM and Conversion Mössbauer spectroscopy with the registration of resonant X-rays. The spatial particle inhomogeneity and magnetic anisotropy have been analyzed in order to reveal the factors determining the functional properties of the manufactured composites. Three-fold enhancement of the magnetostrictive response for FeGa/polyurethane composites with non-standard magnetic anisotropy has been demonstrated.

Keywords Mössbauer spectroscopy · Composites · FeGa · Mechanosynthesis · Magnetostriction

1 Introduction

Taking advantage of particular properties of constituent materials is the most important motivation for the development of metal-polymer functional hybrids. For this purpose

Proceedings of the 32nd International Conference on the Applications of the Mössbauer Effect (ICAME 2013) held in Opatija, Croatia, 1–6 September 2013

S. I. Zholudev (✉) · T. Yu. Kiseleva
Department of Physics, Moscow M.V. Lomonosov State University, Moscow Russia
e-mail: s.i.zholudev@gmail.com

Published online: 07 November 2013

particles of material with the desired functional properties determined by their phase structure can be used as filler precursors. The functional properties of these particles support a special structure performance as physical properties of the composite. Constructing functional hybrid materials by reducing the filler particle sizes introduces a rise in the surface to volume ratio and correspondingly in the strength of the particle surface interaction as the activity to polymer molecules bond [1, 2]. On the way of miniaturization of working systems, functional devices and appliances, the use of small metal particles as constituent elements of elastic composite systems allows to create miniature intellectual materials such as magnetic sensors, actuators (positioning systems) and magnetic sealing gaskets. The well-known method of producing particles with the desired phase structure is the mechanosynthesis routine [3, 4]. Through mechanical alloying of powdered metals a nanocrystalline phase structure of particles can be achieved. The desired particle structure is formed through the sequence of nonequilibrium and metastable phases as well within the particles as at the particles surfaces and interfaces. Detailed Mössbauer spectroscopy studies of the mechanochemical mechanisms have been performed to determine the conditions of intermetallics or complex oxide particle formation through mechanically activated chemical reactions [3, 5–10], formation of metal particles encapsulated by different shells [11, 12], disordered solid solutions [7, 9], amorphous phases [11, 12] and formation of alloy/oxide composite particles [13]. In all cases it was shown that the choice of the mechanosynthesis conditions, including compositions, mutual concentrations, powder sizes, ball-to-powder ratio, atmosphere and intensity (energy) of the used mill, determined the result of the mechanosynthesis: structure, sizes of particles and their distribution. The achieved imperfection, tensile stress or other manifestation of intensive deformation and shredding of materials can be a positive thing when functional properties are designed.

The present investigation has been undertaken to investigate the possibility of taking advantage of mechanosynthesized intermetallic FeGa particles in the functional magnetic properties of metal/polymer composite material performance. Our choice of the Fe-Ga system is explained by its considerable magnetostrictive properties studied recently [14–16]. The strong correlation of magnetostrictive functional properties with microstructure in the Fe-Ga system is a motivation for a detailed investigation of the structure evolution towards magnetostrictive particle formation by mechanosynthesis of Fe and Ga. In the Fe-Ga system equilibrium phase diagram [17] bcc ordered B2 (FeGa) and DO_3(Fe_3Ga) phases are formed on the Fe-rich side, while fcc ordered $L1_2$ (Fe_3Ga) is stable at low temperature below 580 °C in a large composition region over about 25 % Ga. Two anomalous peaks in the magnetostriction concentration dependence have been observed in $Fe_{1-x}Ga_x$ single crystalline alloys. The first of them is situated near 19 at. % of Ga and has been attributed to an increase in the magnetoelastic coupling, resulting from the formation of short-range ordered (SRO) Ga pairs along the crystallographic directions axis of the A2 structure [18]. One should note the fact that the presence of a two-phase region (A2 - DO_3) depends sensitively on the thermal history; this suggests that the enhanced magnetostriction is due to an underlying heterogeneity rather than a conventional homogeneous ferromagnetic phase. Recent neutron diffuse scattering measurements [19] confirm that the enhanced magnetostriction is directly related to the structural heterogeneity of tetragonally distorted DO_3-like nanoprecipitates.

2 Experimental

2.1 Sample preparation

The preparation technique of the composite material has the following four steps: 1) *synthesis of particles* with magnetostrictive composition by mechanical alloying of powdered Fe and Ga in relative wt% proportions 80:20. Mechanical milling of Fe powders with Ga has been realized with an AGO-2 planetary mill sealed under Ar. The vial volume was 20 cm^3. The steel balls diameters and mass were 5 mm and 200 g, respectively. The speed drum rotation was ∼1,000 rpm. 2) *preparing of the liquid polymer* substance. We apply modified polyurethane (PU); 3) *filling of the liquid polymer with mechanosynthesised particles and ultrasound intermixing*. The concentration of the filler intermetallic particles in polymers was chosen as 25 wt% which is considered as optimal for a significant magnetostrictive response [20]. The mixtures of polymer and particles were prepared by ultrasound exposure at 18 kHz (Bandelin HD2200) for 3 min for a homogeneous distribution of filler particles in the polymer matrix; 4) *particles stabilization with orientation in polymer matrix* The prepared suspensions were transferred to a teflon rectangular mold with the dimensions of 20 mm*10 mm*4 mm. Final polymerization in the mold was performed without an applied magnetic field for RO samples or under an applied magnetic field (0.5 T) for MO ones. Finally the PU composite polymerization processes were performed in an electric furnace.

2.2 Experimental methods

At different stages of Fe:Ga powder mixture mechanochemical interaction composite powders have been studied by Mössbauer spectrocopy, X-ray diffraction, transmission and scanning electron microscopy. Mössbauer spectra were obtained at room temperature using an MS1104Em spectrometer with a $^{57}Co(Rh)$ radiation source. The analysis of the spectra has been performed with Univem Software; the determination of the hyperfine fields distribution function was carried out with MsTools [21]. The powder diffraction data were collected in step scan mode at room temperature using a Panalytical Empyrean powder diffractometer equipped with a Pixel3D detector (Bragg-Brentano geometry (θ–2θscan), CuKα radiation). Transmission electron microscopy pictures of the particles and Scanning electron microscopy pictures of the composites have been obtained on a LEO 912 and a Quanta 3D FEG microscope, respectivily. The magnetostriction measurements were performed using the thermal capacitive technique in laboratory equipment with applied magnetic field up to 1 T.

3 Results and discussion

Mechanical alloying has been performed to achieve particles with magnetostrictive phase composition. Room temperature Mössbauer spectra of successive steps of this phase composition formation are shown in Fig. 1. Several steps of the mechanochemical reaction can be clearly distinguished in the spectra analysis. It was shown recently that in AGO-2 high energy planetary ball mill mechanical interaction of different powdered materials proceeds just at the early stages of milling [22]. This interaction is strongly dependent on intermixing enthalpy. The Fe-Ga system corresponds to binary systems with solid-liquid type of interactions in a mill due to the low temperature of Ga metal melting and the high local

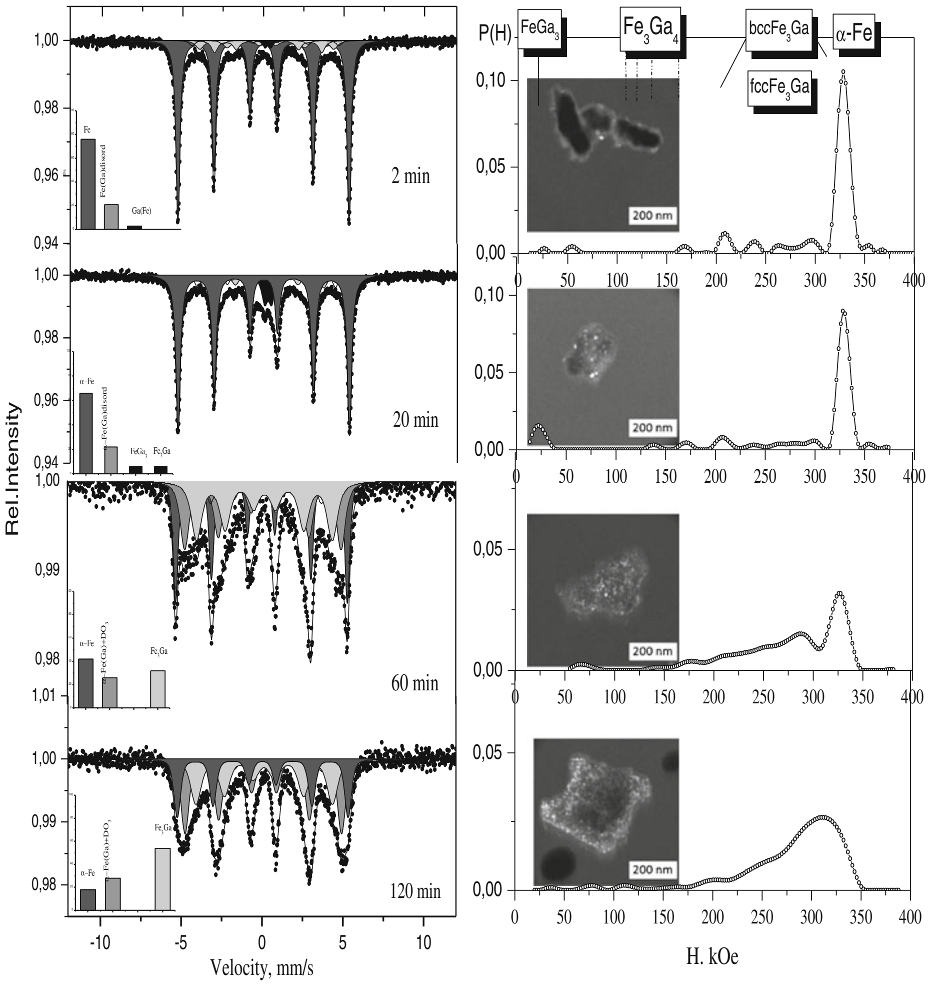

Fig. 1 Mössbauer spectra of Fe-Ga powders after consecutive steps of mechanical interaction (*left*), corresponding P(H) (*right*) and transmission electron microscopy images (in inclusion)

temperature. For this type of systems the mechanochemical interaction between the components proceeds through the formation of phases based on liquid component. As seen from the Fig. 1 the Mössbauer spectra of the milled samples represent a complex structure with superposition of several subspectra just at the early stages of interaction. This picture is getting more complicated with increasing milling time.

To resolve accurately the magnetically split components we performed spectra analysis by the determination of the hyperfine field distribution function P(H). The result of the analysis is presented on Fig. 1 (right). Hyperfine field parameters for intermetallics of the Fe-Ga system found in recent publications are shown at the top of the figure. Distinct peaks in P(H) correspond to different kinds of neighbors around the ^{57}Fe atoms. It is clear that all spectra up to 60 min of milling consist of an intensive peak at 330 kOe. The contribution of this peak is related to iron atoms without Ga in the nearest surrounding. The tendency to decrease its intensity, width extension and shifting to the a smaller hyperfine field value with milling time is explained by the disordering of the iron particle structure and the formation of structures like disordered solid solutions and other types of heterogeneities at places of contacts with Ga at the iron particle surface (Fig. 1 TEM image). The interaction of Fe and Ga at the early stages of milling occurs through dissolution of a small amount of Fe in the melting component (Ga) and subsequent formation of the $FeGa_3$ phase. After prolonged intensive milling Ga diffuses into Fe, forming a diluted magnetic bcc Fe(Ga) solid solution.

Quantitative phase analysis (Fig. 1) shows that the first substantial result of the interaction is $FeGa_3$ intermetallics formation (3 % - after 2 min of activation) which is increasing its quantity up to 6 % after 12 min. Its Mössbauer spectrum presented above the experimental spectrum as a doublet is colored by dark color. This is accompanied by a reduction of bcc α-Fe quantity from 76 to 70 % with the emergence and increase of the peak intensity at smaller values of hyperfine fields on P(H).

The Mössbauer spectrum of the sample after 20 min of milling shows (Fig. 1) that with an almost invariable $FeGa_3$ content there is a redistribution of the local α-Fe surrounding: a slight reduction of the disordered component is accompanied by the allocation of an environment in the particles with a structure close to Fe_3Ga. The spectrum of this phase has hyperfine magnetic spitting with corresponding Mössbauer parameters [23, 25].

A three times increase in time of activation, till 60 min, leads to a sharp change in the phase structure. The spectrum analysis shows a total disappearance of the $FeGa_3$phase. Also the pure α-Fe environment decreases. The asymmetry of the α-Fe Mössbauer subspectrum reflects Ga appearing in the nearest environment of Fe atoms and the formation of a bcc solid solution Fe(Ga). The observed asymmetry is characteristic for the occurrence of solid solutions with different concentration and to a superposition with reflexes of disordered Fe_3Ga. Thus at this stage of mechanochemical interaction we observe the substantial growth of a component connected with a disordered solid solution of gallium in iron. The analysis of the relative intensity of the corresponding component reflects a considerable gallium concentration in solid solution. It is necessary to notice that at this stage an essential contribution to the Mössbauer spectrum is given by sextets with parameters, characteristic to intermetallic phases Fe(Ga), distorted DO_3 and Fe_3Ga.

The Mössbauer spectrum of the 120 min milled sample (Fig. 1) has a hyperfine field distribution shape with the most probable values of H_{eff} corresponding to solid solution α-Fe(Ga) and fcc-Fe_3Ga. The increase in fcc-Fe_3Ga content is accompanied by the observation of local environments with a structure like DO_3 (increases to 54 %) and a sharp decrease of the pure iron component (up to 18 %). The formed solid solution is not homogeneous yet at this time of milling. We consider that composite particles with a composition close to the magnetistrictive compound are formed mechanochemically. The composite particle fine structure consists of small monodimensional intermetallic inclusions of Fe_3Ga (3–5 nm) intermetallics in bcc Fe(Ga) (Fig. 1). According to SEM observations (not shown) the morphology of particles is typical for ball milled material containing a small amount of larger platelike particles with average dimension of 5 μm, while dominant small size powder particles have dimensions of 200–500 nm.

The obtained particles with bccFe(Ga)/Fe_3Ga composite structure have been used as fillers for hybride metal-polymer material in the form of the bulk. The X-ray diffraction (Fig. 2a) and Mössbauer spectroscopy of the resonant X-ray emission (CEMS) (Fig. 2b) show that particles did not interact with polyurethane during composite synthesis. The deterioration of the spectrum is due to the decrease of the probability of the effect connected with a smaller amount of iron in the composite system in relation to the total volume of the

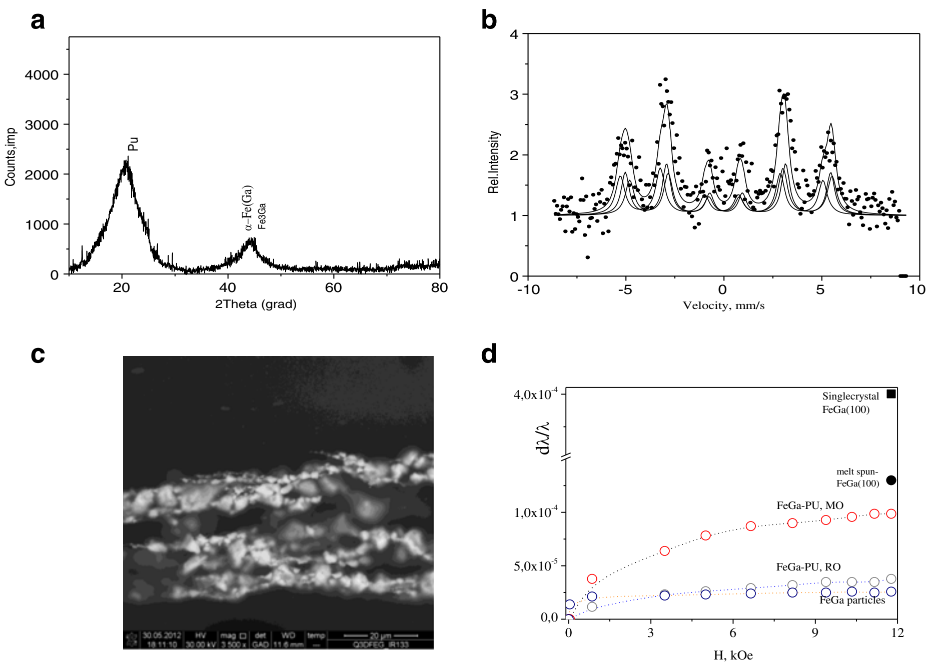

Fig. 2 X-ray diffraction (**a**), Mössbauer spectrum of resonant X-ray (**b**), SEM (**c**) of FeGa/polymer composite and field dependence of magnetostriction for magnetically oriented (MO), random oriented composites (RO), FeGa particles (**d**)

sample. In the spectrum of mechanosynthesised particles the relative intensities of the magnetic hyperfine splitting lines have changed due to the appearance of the preferred direction of the average magnetic moment in the composite sample.

Self-organization of particles in a polyurethane matrix is clearly seen on SEM images in Fig. 2c. Stabilization of the particles during the polymerization in an external magnetic field results in their spatial anisotropic orientation along the magnetic field lines: large particles are covered by chains of small particles. This non-uniform arrangement of the particles along the field lines results from the complex magnetic and gravitational forces [26] and the viscosity of the polymer. This behaviour in metal- polymer composites is typical for magnetic particles [10]. Recently it was shown [11] that intensive mechanical treatment of the iron particles (body-centered cubic structure) in a planetary ball mill leads to the formation of particles with strain induced magnetic anisotropy. It was shown that iron particles are crushed and flattened out in an elongated shape with the axis of easy magnetization along the plane of flattening. Polymerization of polyurethane filled by FeGa particles in applied magnetic field leads to their alignment along the axis of easy magnetization. According to Mössbauer line intensity analysis the FeGa particles orientation has magnetic texturing in the plane, which corresponds [27] to its easy magnetization axis.

The results of measurements of the magnetostriction ($d\lambda / \lambda$) as a function of applied field (H) (Fig. 2d) show the dependence of the particles orientation effect. It should be noted that the achievement of the saturation is greater in fields of 3–4 kOe in the case of field-oriented particles versus randomly distributed particles in the polymer matrix. The maximum value of magnetostriction reaches the value of $1*10^{-4}$. This value is considerably smaller than the values characteristic for the monocrystalline and polycrystalline [3] FeGa alloy. Directional orientation of the particles in the polymer increases the magnitude of the magnetostriction by a factor three.

The external magnetic field applied is the cause of the magnetostrictive properties of the sample, which is conditioned by the following factors. The body develops its own demagnetizing field, depending on the shape of the sample and the amount of magnetic material in it. This causes the elongation of the sample (positive magnetostriction). Another factor is related to the inhomogeneity of the local fields, the contribution of which depends on the short-range order in the subsystem of magnetic particles in a polymer matrix. Furthermore, for the given sample size and concentration of the filler particles in a polymer matrix the magnetostriction value should depend on the presence of interparticle spatial correlations. The determining factor according to [28] is the ratio between the number of isolated particles and particles aggregated into chained clusters. The influence of the particle chains to the overall deformation value is more significant than their length. It should be noted that in this work we used particles of a material which itself belongs to the class of high magnetostrictive materials. The presence of elastic stresses in the particles due to the mechano-chemical process used for their preparation is a reinforcing factor in increasing their magnetostrictive effect.

4 Conclusion

A new type of magnetic composites, consisting of small mechanosynthesised magnetostrictive FeGa particles dispersed in polymeric matrixes has been studied. The application of Mössbauer spectroscopy at different steps of the new metal-polymer composite formation allowed us to explain the high magnetostrictive response. The considerable magnetostrictive response in the case of chain arranged particles is explained by the formation of anisotropic arranged particle structures in polymer. Mechanochemically induced magnetic anisotropy in particles is a factor enhancing the effect of magnetostriction additionally to their arrangement in the polymer.

Acknowledgments Authors express their gratitude to the Ministry of Education and Science of the Russian Federation and Moscow State University Program of Development, Russian Foundation for Basic Research for financial support.

References

1. Kickelbick, G., (ed.): Hybrid materials. Synthesis, Characterization, and Application, p. 498. Wiley-VCH (2006)
2. Nicolais, L., Carotenuto, G., (eds.): Metal-Polymer Nanocomposites, p. 320. Wiley (2005)
3. Balaz, P.: Mechanochemistry in Nanoscience and Minerals Engineering, p. 413. Springer (2008)
4. Lyakhov, N.Z., et al. (eds.): Mechanocomposites precursor for the creation of materials with new properties, p. 432. Novosibirsk. ISBN 978-5-7692-1108-9 (2010)
5. Kiseleva, T.Yu., Novakova, A.A., et al.: Iron-based amorphous magnetic phase formation in the course of Fe and Fe_2O_3 mechanical activation. Solid State Phenom **152–153**, 25–28 (2009). doi:10.4028/3-908454-13-1.25
6. Kiseleva, T.Yu., Novakova, A.A., et al.: Mechanosynthesis of corundum ceramics / intermetallics nanocomposites. Advan. Mater. (in Russian) (6), 1–10 (2008)
7. Kiseleva, T.Yu., Grigorieva, T.F., et al.: Iron and Indium interactions during mechanical attrition. J. Alloy. Comp. **383**, 94–97 (2004). doi:10.1016/j.jallcom.2004.04.015

8. Novakova, A.A., Khenkin, L.V., et al.: Formation of graphite encapsulated iron nanoparticles during mechanical activation and annealing analyzed by mössbauer spectroscopy. Hyperfine Interact. **189**(1–3), 105–110 (2009). doi:10.1007/s10751-009-9934-7
9. Novakova, A.A., Grigorieva, T.F., et al.: Fe(In) solid solution formation during mechanical attrition. J. Alloy. Comp. **434–435**, 455–458 (2007). doi:10.1016/j.jallcom.2006.08.102. (SPEC. ISS.)
10. Kiseleva, T.Yu., Novakova, A.A., et al.: Structural study of Fe-Al nanomaterial produced by mechanical activation and self-propagating high-temperature synthesis. Moscow University Phys. Bull. **63**(1), 55–60 (2008). doi:10.1007/s11972-008-1011-8
11. Kiseleva, T., Novakova, A., et al.: Amorphous shell formarion on the Iron particles during mechanosynthesis in Fe2O3/Fe/(Ga,Al) mixtures. Solid State Phenom. **170**, 139–143 (2011). doi:10.4028/www.scientific.net/SSP.170.139
12. Kiseleva, T.Yu., Novakova, A.A., et al.: Mechanochemically induced formation of amorphous phase at oxide nanocomposite interfaces. J. Phys. Conf. Ser. **217**(1) (2010). doi:10.1088/1742-6596/217/1/012106
13. Polyakov, A.O., Kiseleva, T.Y., et al.: Step-by-step powder composite mechanosynthesis for functional nanoceramics. J. Phys. Conf. Ser. **217**(1) (2010). doi:10.1088/1742-6596/217/1/012081
14. Atulasimha, J., Flatau, A.B.: Topical review: A review of magnetostrictive iron-gallium alloys. Smart Mater. Struct. **20**, 043001 (2011)
15. Rafique, S., Cullen, J.R., et al.: Magnetic anisotropy of FeGa alloys. J. Appl. Phys. **95**(11), 6939–694 (2004)
16. Hristoforou, E., Ktena, A.: Magnetostriction and magnetostrictive materials. J. Magnet. Magnet. Mater. **316**, 372–378 (2007)
17. Okamoto, H.: The fe-ga (iron-gallium) system. Bull. Alloy Phase Diag. **11**(6), 576–581 (1990). doi:10.1007/BF02841721
18. Clark, A.E., Wun-Gogle, M., et al.: Magnetostrictive properties of body-centered cubic Fe-Ga and Fe-Ga-Al alloys. IEEE Trans. Magn. **36**, 3238–3240 (2000)
19. Cao, H., Gehring, P.M., et al.: Role of nanoscale precipitates on the enhanced magnetostriction of heat-treated galfenol (Fe1_xGax) alloys. Phys. Rev. Lett. **102**, 127–201 (2009)
20. Dobrzański, L.A., Wydrzyńska, A., et al.: Magnetostrictive properties of epoxy-bonded Tb0, 3Dy 0, 7Fe1,9 composites. J. Adv. Mater. Res. **89–91**, 633–638 (2010). doi:10.4028/www.scientific.net/AMR.89-91.633
21. Rusakov, V.S.: Mössbauer Spectroscopy of Local-Inhomogeneous Systems, p. 430. Almaty Publ. (2000)
22. Grigor'eva, T.F., Kiseleva, T.Y., et al.: Study of the products of interaction between iron and gallium during mechanical activation. Phys. Metals Metallograph. **113**(6), 575–582 (2012). doi:10.1134/S0031918X12060075
23. Gaudet, J.M., Hatchard, T.D., et al.: Properties of Fe-Ga based powders prepared by mechanical alloying. J. Magnet. Magnet. Mater. **320**, 821–829 (2007)
24. Dunlap, R.A., McGraw, J.D., et al.: Mössbauer effect study of structural ordering in rapidly quenched Fe-Ga alloys. J. Magnet. Magnet. Mater. **305**, 315–320 (2006)
25. Newkirk, L.R., Tsuei, C.C.: Mössbauer study of hyperfine magnetic interactions in fe-ga solid solutions. J. Phys. Rev. B **4**(11), 4046–4053 (1971). doi:10.1103/PhysRevB.4.4046
26. Novakova, A.A., Smirnov, E.V., et al.: Magnetic anisotropy in Fe3O4—PVA nanocomposites as a result of Fe3O4-nanoparticles chains formation. J. Magnet. Magnet. Mater. **300**(1), e354–e356 (2006). doi:10.1016/j.jmmm.2005.10.119
27. Novakova, A.A., Agladze, O.V., et al: Detection of anisotropy effects in compact nanocrystalline iron. J. Surf. Invest. X-Ray Synchrot. Neutron Techniq. **16**(12), 1863–1867 (2001). ISSN: 10274510
28. Reicher, Y.L., Stolbov, O.V.: Modelling of magnetostrictive strain in soft magnetic elastomer. Comput. Contin. Mech. T **2**(2), 85–95 (2009)