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Structural transformation in mechanosynthesized bcc Fe–Al–Si(Ge) solid solutions during heating

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Abstract

X-ray diffractometry and Mössbauer spectroscopy study of $Fe_{50}Al_{25}Si_{25}$ and $Fe_{50}Al_{25}Ge_{25}$ alloys obtained by mechanical alloying (MA) of elementary powders was carried out. Phase transformation during heating of synthesized products was studied using differential scanning calorimetry (DSC). After 2.5 h of MA monophase alloys containing bcc Fe(Al, Ge) solid solutions Fe(Al, Si) are formed. Fe(Al, Si) is partially ordered B2 type and Fe(Al, Ge) is completely disordered. DSC curves of synthesized alloys displayed the presence of exothermal peaks caused by phase transformation. The metastable Fe(Al, Si) solid solution transformed into $FeAl_{1-x}Si_x$ (B2) and $FeSi_{1-x}Al_x$ (B20) equilibrium phases. The Fe(Al, Ge) solid solution transformed into equilibrium phases through intermediate stage of $Fe_6Ge_3Al_2$ metastable phase formation. The $Fe_6Ge_3Al_2$ phase dissociated into three equilibrium phases: $FeAl_{1-x}Ge_x$ (B2), χ-Fe_6Ge_5 and η-$Fe_{13}(Ge, Al)_8$ ($B8_2$). The structure of $Fe_6Ge_3Al_2$ was calculated by Rietveld method, the distribution of Al and Ge in the elementary cell and its parameters were calculated. Mössbauer study showed that Fe(Al, Si) and Fe(Al, Ge) solid solutions are paramagnetic. In the equilibrium state the alloy containing Si is also paramagnetic while the alloy with Ge showed ferromagnetic properties.

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1. Introduction

Intermetallic compounds in Fe–Al and Fe–Si systems consist of materials with high temperature strength and corrosion resistance. Improvement of the properties of such alloys can be expected with the formation of nanostructured intermetallic phases. In this connection the study of the structural particularities of this material has both fundamental and practical importance. Phase composition and the structure of alloys obtained by mechanical alloying (MA) of three-component mixtures are determined mainly by thermodynamic parameters and kinetics of solid-state chemical reaction. The direction and rate of solid-state reaction during mechanochemical synthesis of $Fe_{50}Al_{25}Si_{25}$ and $Fe_{50}Al_{25}Ge_{25}$ alloys are connected with the competition of chemical bond formation between Fe–Al and Fe–Si (Fe–Ge) in the respective systems. The interaction between Al–Si and Al–Ge are insignificant, as in equilibrium conditions Al does not make chemical compounds with Si and Ge.

In the different experimental works, the Fe(Al) disordered solid solutions with bcc lattice (A2) were obtained by MA of equiatomic mixture $Fe_{50}Al_{50}$ [1–3] as well as the partially ordered solid solution of B2 type [4,5]. The FeSi B20 phase is formed by MA of $Fe_{100-x}Si_x$ ($x \leq 50$ at.%) [6]. The ordered phase FeGe (B20) was also obtained in ball milling of $Fe_{50}Ge_{50}$ mixture [7,8].

The $Fe_{50}Al_{25}Si_{25}$ and $Fe_{50}Al_{25}Ge_{25}$ alloys are disposed on FeAl–FeSi and FeAl–FeGe quasibinary section of equilibrium ternary diagrams of Fe–Al–Si and Fe–Al–Ge. In accordance with Fe–Al–Si diagram [9] the $Fe_{50}Al_{25}Si_{25}$ alloy in equilibrium state must contain two phases: B2 and B20. It is impossible for the authors to predict the equilibrium phase composition of $Fe_{50}Al_{25}Ge_{25}$ alloy because the Fe–Al–Ge equilibrium diagram is not available.

The aim of the present research was the determination of structures of $Fe_{50}Al_{25}Si_{25}$ and $Fe_{50}Al_{25}Ge_{25}$ formed during MA, the study of their temperature stability and the phase transformations during heating.

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2. Experimental procedures

The mechanochemical synthesis of alloys was conducted by milling of elemental powder mixtures of $Fe_{50}Al_{25}Si_{25}$ and $Fe_{50}Al_{25}Ge_{25}$ compositions in a water-cooled high energy mill MAPF-2 with a drum and balls made from hardened steel. The milling was carried out in protective argon atmosphere.

Investigation methods were X-ray diffractometry (Cu Kα-radiation), Mössbauer spectroscopy (^{57}Co(Cr)-source), differential scanning calorimetry (Perkin-Elmer DSC-7). The chemical composition was determined by the method of local X-ray spectral analysis (Camebax Micro beam).

3. Results

X-ray diffraction analysis and Mössbauer spectroscopy indicated that after 2.5 h of MA of $Fe_{50}Al_{25}Si_{25}$ and $Fe_{50}Al_{25}Ge_{25}$ elemental mixtures, the initial components were already absent. The chemical composition of alloys had changed in comparison with the nominal composition of mixture components: the amount of Fe had increased, that of Al had decreased (Table 1).

The increase of Fe amount is related to the abrasive grinding of the steel balls and drum during milling. The Al losses occur probably at the removal of powder samples from a mill after a short period of milling because at this stage Al particles are glued to the vial and balls.

Fig. 1 shows XRD patterns of MA $Fe_{50}Al_{25}Si_{25}$ and $Fe_{50}Al_{25}Ge_{25}$ alloys. The $Fe_{50}Al_{25}Si_{25}$ alloy presents a partially ordered solid solution of Al and Si in α-Fe. The slight reflections of (1 0 0), (1 1 1) and (2 1 0) indicate the presence of long B2 order in the solid solution. The lattice parameter of the solid solution is $a = 0.2846 \pm 0.0002$ nm, the degree of long order is $S = 0.52$. Disordered bcc solid solution Fe(Al, Ge) with the lattice parameter of $a = 0.2872 \pm 0.0002$ nm was formed in MA of $Fe_{50}Al_{25}Ge_{25}$ (Fig. 1b). The substructure of both alloys is comparable and is characterized by nanosize domains $D = 10$ nm and lattice microdeformation $<\varepsilon^2>^{1/2} = 0.8–1.0\%$.

The Mössbauer spectrum of $Fe_{50}Al_{25}Si_{25}$ alloy (Fig. 2a) can be divided into subspectra: a singlet with isomer shift $\delta_1 = 0.24$ mm/s, a doublet with $\delta_2 = 0.24$ mm/s, quadruple splitting $\Delta E_0 = 0.55$ mm/s, width $W = 0.98$ mm/s and sextets with hyperfine magnetic fields $H_1 = 313$ kOe and $H_2 = 270$ kOe. A singlet is related to paramagnetic domains with symmetrical surrounding of Fe by non-magnetic atoms of Al and Si, that is

Table 1
Elemental content of initially $Fe_{50}Al_{25}Si_{25}$ and $Fe_{50}Al_{25}Ge_{25}$ powders

Alloy (at.%)	Composition before MA (mass%)	Composition after MA (mass%)
$Fe_{50}Al_{25}Si_{25}$		
Fe	66.98	69.14 ± 0.52
Al	16.18	13.48 ± 0.47
Si	16.84	17.38 ± 0.17
$Fe_{50}Al_{25}Ge_{25}$		
Fe	52.87	55.61 ± 0.46
Al	12.77	8.60 ± 0.32
Ge	34.36	35.79 ± 0.63

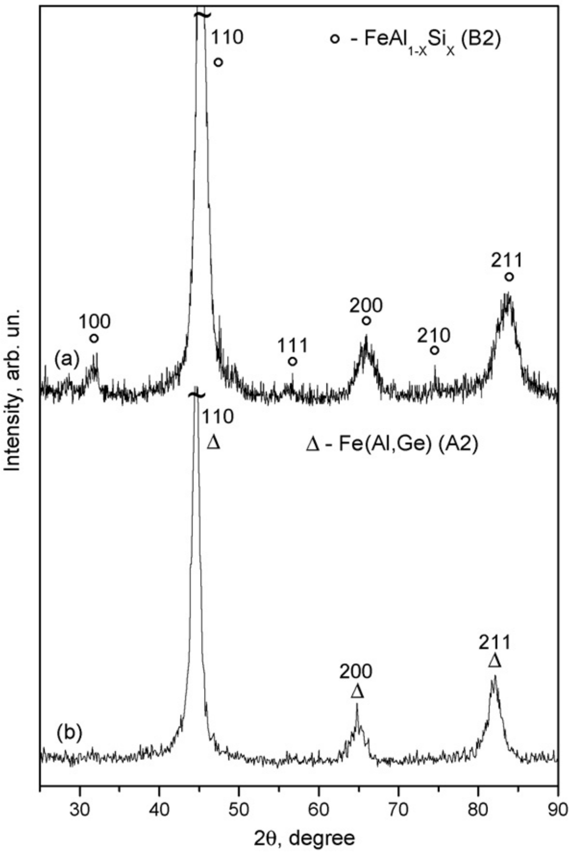


Fig. 1. X-ray patterns of $Fe_{50}Al_{25}Si_{25}$ (a) and $Fe_{50}Al_{25}Ge_{25}$ (b) after 2.5 h of MA.

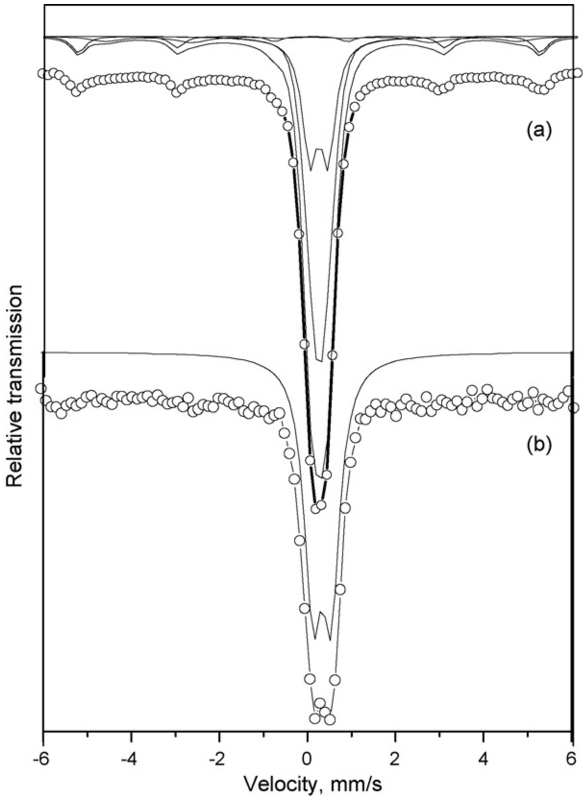


Fig. 2. Mössbauer spectra of $Fe_{50}Al_{25}Si_{25}$ (a) and $Fe_{50}Al_{25}Ge_{25}$ (b) after 2.5 h of MA.

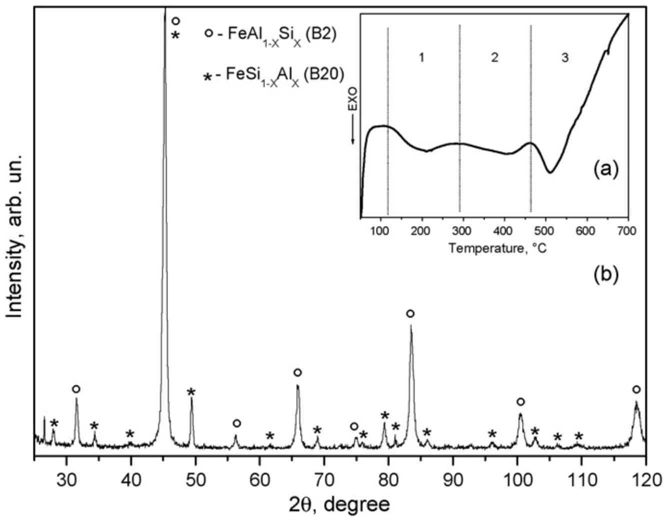


Fig. 3. DSC-curve of mechanosynthesized $Fe_{50}Al_{25}Si_{25}$ alloy during heating in calorimeter ($\nu = 40° min^{-1}$) (a) and X-ray pattern of alloy after heating up to 700 °C (b).

domains of B2 order. A doublet characterizes also paramagnetic state and corresponds to the disordered domains in bcc lattice of Fe(Si, Al) solid solution. The H_1 and H_2 values are considerably smaller than hyperfine magnetic field of α-Fe (330 kOe). Sextets with H_1 and H_2 may be related to the presence of local ferromagnetic atomic groups Fe_3(Al, Si) in the lattice of the solid solution. It is known that the Mössbauer spectrum of mechanoactivated powders of Fe_3Si is described by sextets with $H_1 = 312$ kOe and $H_2 = 280$ kOe [10] and the intermetallic compound Fe_3Al disordered by deformation has the average value of magnetic field $H = 265$ kOe [11]. It may be supposed that the presence of Al in the ferromagnetic cluster Fe_3(Al, Si) decreases the value of the magnetic field H_2 in comparison with H_2 for deformed Fe_3Si-structure.

Fig. 2b shows that the Mössbauer spectrum of $Fe_{50}Al_{25}Ge_{25}$ consists of a doublet with parameters $\delta = 0.29$ mm/s, $\Delta E_0 = 0.42$ mm/s and width $W = 0.46$ mm/s. This spectrum characterizes paramagnetic disordered bcc Fe(Al, Ge) phase.

The DSC curve of $Fe_{50}Al_{25}Si_{25}$ alloy (Fig. 3a) shows that transformations upon heating occur with release of heat. It testifies to the metastable state of mechanosynthesized solid solution Fe(Al, Si) in spite of the presence of long order. On DSC curve it is possible to distinguish exothermal effects within the temperature ranges of 130–300 and 460–650 °C. T_{max} of the biggest exothermal peak is at 513 ± 2 °C and the heat effect is $\Delta H = -52.11$ kJ/mol. The reheating of the sample showed the absence of heat effects on the DSC curves that indicates transition into stable state after 700 °C. The stable phases are $FeAl_{1-x}Si_x$ (B2) and $FeSi_{1-x}Al_x$ (B20) (Fig. 3b). The lattice parameters $a = 0.2835$ and 0.4490 nm for B2 and B20 phases, respectively. The quantitative X-ray phase analyses of the alloy annealed (750 °C, 1 h) showed that it contains 14 mass% of B20 phase. After isothermal annealing B2 phase preserves the nanocrystalline structure with size of domains no larger than 20 nm.

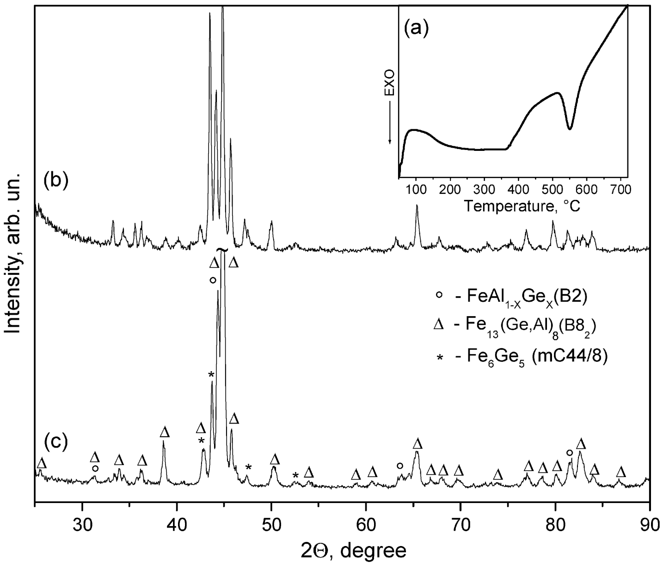


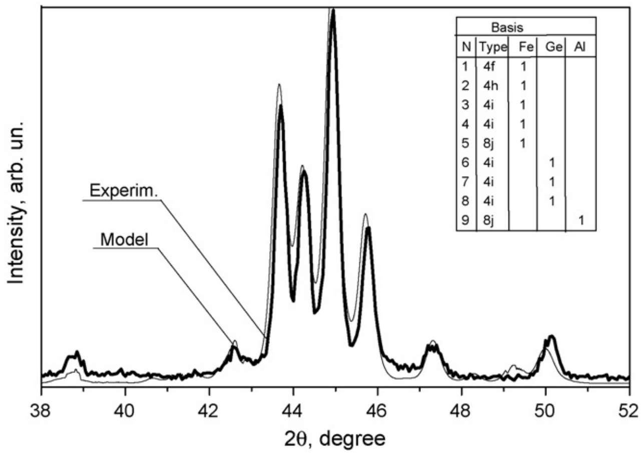
Fig. 4. DSC-curve of mechanosynthesized $Fe_{50}Al_{25}Ge_{25}$ alloy during heating in calorimeter ($\nu = 40° min^{-1}$) (a) and X-ray patterns of alloy after heating up to 700 °C (b) and after 1 h annealing at 850 °C (c).

An exothermic peak in the narrow temperature interval 520–570 °C is presented on the DSC curve of the Fe(Al, Ge) solid solution (Fig. 4a). X-ray pattern of the sample after heating to the temperature 700 °C which is shown in Fig. 4b was impossible to identify by diffraction spectra of different phases whose formation might hypothetically be expected upon dissociation of the Fe(Al, Ge) solid solution. After isothermal annealing of the sample at 750 °C for 1 h the diffraction pattern did not change. It was supposed that the bcc solid solution Fe(Al, Ge) does not dissociate as a result of heating to $T \leq 750$ °C but transforms into a phase with low symmetrical structure.

The calculation of the structure was conducted by the method of full profile analysis with Rietan program [12] using diffraction lines in the angles range $2\theta = 25$–$105°$. The calculation showed that the phase structure is described as monoclinic with space group (*mC*44/8) and elementary cell parameters $a = 0.9896$ nm, $b = 0.7931$ nm, $c = 0.7697$ nm, $\beta = 108.68°$ (RF = 3.77). We admit the cell of Fe_6Ge_5 having 44 atoms as the structure prototype of the formed ternary phase. If 24 positions of 4f, 4h, 4i and 8j type are filled by Fe atoms the distribution of Al and Ge in the remaining 20 positions will correspond to the ratio of Ge:Al = 12.1:7.9 at RF = 3.77. The calculation of the model diffractogram was made for the angles interval $2\theta = 35$–$52°$ (Cu Kα) where the most important lines of the experimental diffractogram are located.

Fig. 5 shows a superposition of experimental and model spectra for the angle interval of $2\theta = 35$–$55°$ where the most intensive lines of monoclinic phase appear. In this case the composition of the ternary phase is $Fe_{24}Ge_{12}Al_8$ or $Fe_6Ge_3Al_2$.

According to the results of chemical analysis of the $Fe_{50}Al_{25}Ge_{25}$ alloy after MA (Table 1) the component atomic fractions corresponds to $Fe_{55.1}Al_{17.6}Ge_{27.3}$ (at.%). The Fe:(Ge + Al) ratio is equal to 1.22 and practically corresponds



Basis				
N	Type	Fe	Ge	Al
1	4f	1		
2	4h	1		
3	4i	1		
4	4i	1		
5	8j	1		
6	4i		1	
7	4i		1	
8	4i		1	
9	8j			1

Fig. 5. Experimental and model X-ray diffraction spectra superposition for monoclinic phase of $Fe_6Ge_3Al_2$ (space group *mC*44/8).

to the ratio Fe:Ge = 1.20 in Fe_6Ge_5 phase. Thus the alloy composition formed with MA is close to the composition of the ternary $Fe_6Ge_3Al_2$ phase which agrees fairly with the filling of the elementary cell of the interpreted phase. The lattice parameters calculated by means of the Nelson–Riley method from the experimental diffractogram (Fig. 4b) are the following: $a = 0.9905$ nm, $b = 0.7956$ nm, $c = 0.7706$ nm, $\beta = 108.709°$. Isothermal annealing of the alloy annealed at $T = 850$ °C for 1 h resulted in transformation of $Fe_6Ge_3Al_2$ phase into three phases: hexagonal η-Fe_{13}(Ge, Al)$_8$ ($B8_2$), cubic $FeAl_{1-x}Ge_x$ (B2) and monoclinic χ-Fe_6Ge_5 phase (Fig. 4c).

Mössbauer measurements were made on isothermally annealed alloys of $Fe_{50}Al_{25}Si_{25}$ ($T = 750$ °C, 1 h) and $Fe_{50}Al_{25}Ge_{25}$ ($T_1 = 750$ °C, 1 h and $T_2 = 850$ °C, 1 h). $Fe_{50}Al_{25}Si_{25}$ alloy after annealing at 750 °C, as well as after being heated in the calorimeter to 700 °C contained $FeAl_{1-x}Si_x$ (B2) and $FeSi_{1-x}Al_x$ (B20). Its Mössbauer spectrum (Fig. 6a) can be separated into two components: a singlet with isomer shift $\delta = 0.23$ mm/s, width $W = 0.50$ mm/s and a doublet with $\delta_2 = 0.22$ mm/s, $\Delta E_0 = 0.45$ mm/s and $W = 0.47$ mm/s. The parameters of the singlet did not change in comparison with the ones defined in the spectrum of the alloy after MA. The doublet of the annealed alloy had reduced values of isomer shift, quadruple splitting and width. The contribution of this subspectrum to the total spectrum became considerably less. If the portion of the doublet in the spectrum of the alloy after milling was 31%, then after annealing it reduced to 14%. The annealed equilibrium alloy consisted of B2 and B20 paramagnetic phases. The B20 phase is $FeSi_{1-x}Al_x$. The parameters of magnetic interaction of atoms in the lattice of this phase are fairly comparable with the characteristics of the Mössbauer spectrum of FeSi at 720 °C ($\delta = 0.212$ mm/s, $\Delta E_0 = 0.49$ mm/s) [13].

Comparing the Mössbauer spectra of the mechanosynthesized and annealed alloys with Ge (Fig. 2b and Fig. 6b and c), it can be noted that changes are observed only after annealing at 850 °C. Despite the fact that bcc solid solution Fe(Al, Ge) after annealing at 750 °C transformed into monoclinic phase $Fe_6Ge_3Al_2$, apparently, in the lattice of this phase at $T = 20$ °C ferromagnetic interaction is not observed. The Mössbauer spectrum of the phase with monoclinic structure contains a doublet analogous to Fe(Al, Ge) bcc solid solution. The doublet parameters of $Fe_6Ge_3Al_2$ are $\delta = 0.30$ mm/s, $\Delta E_0 = 0.56$ mm/s and $W = 0.62$ mm/s. Values of quadruple splitting ΔE_0 and width W for doublet of a monoclinic phase compared to the characteristics of the Fe(Al, Ge) doublet are considerably larger. It may be supposed that the doublet of monoclinic phase is formed by several components with paramagnetic interaction for different Fe–Al(Ge) atomic groups.

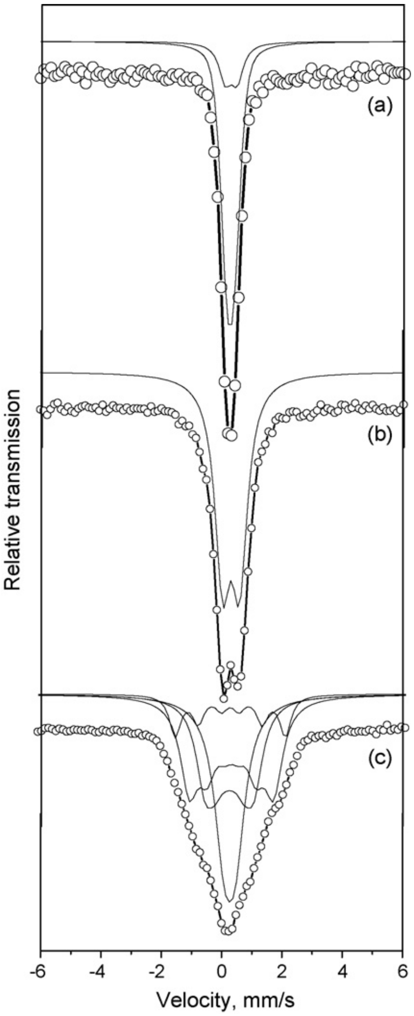


Fig. 6. Mössbauer spectra of $Fe_{50}Al_{25}Si_{25}$ annealed at 750 °C, 1 h (a), $Fe_{50}Al_{25}Ge_{25}$ annealed at 750 °C, 1 h (b) and at 850 °C, 1 h (c).

The spectrum of the alloy annealed at 850 °C contains four subspectra: a singlet with $\delta_1 = 0.21$ mm/s, a doublet with $\delta_2 = 0.26$ mm/s, $\Delta E_0 = 0.38$ mm/s and two sextets with $H_1 = 144$ kOe and $H_2 = 87$ kOe. In accordance with the phase composition of this alloy, the subspectra may be correlated with $FeAl_{1-x}Ge_x$ (B2), χ-Fe_6Ge_5 and η-Fe_{13}(Ge, Al)$_8$ ($B8_2$), respectively. The ferromagnetic phase is η-Fe_{13}(Ge, Al)$_8$. The parameters of magnetic interaction in the crystalline lattice of η-phase are comparable with the values of hyperfine magnetic fields with $H_1 = 120$ kOe and $H_2 = 92$ kOe, that were defined in previous work [14] for $Fe_{2.9}Ge_2$ which also has a hexagonal structure of $B8_2$ type.

4. Conclusions

MA of $Fe_{50}Al_{25}Si_{25}$ and $Fe_{50}Al_{25}Ge_{25}$ elementary powder mixtures resulted in the formation of bcc Fe(Al, Si) and Fe(Al, Ge) solid solutions. Fe(Al, Si) was partially B2 type ordered while Fe(Al, Ge) was completely disordered. The solid solutions are metastable and phase transformations during heating in calorimeter are accompanied by exothermic effects. After heating up to 700 °C, Fe(Al, Si) solid solution transformed into $FeAl_{1-x}Si_x$ (B2) and $FeSi_{1-x}Al_x$ (B20) equilibrium phases. Mechanically alloyed Fe(Al, Ge) solid solution transformed into another ternary phase during heating to $\leq$750 °C. The content of components in the phase corresponds to $Fe_6Ge_3Al_2$ which agrees with the verified chemical composition of the alloy after MA. The structure of this phase is monoclinic ($mC44/8$) with lattice parameters of $a = 0.9896$ nm, $b = 0.7931$ nm, $c = 0.7679$ nm, $\beta = 108.68°$ (RF = 3.77) and it transforms into three equilibrium phases: $FeAl_{1-x}Ge_x$ (B2), χ-Fe_6Ge_5 and η-$Fe_{13}(Ge, Al)_8$ ($B8_2$) in the 750–850 °C range.

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