Proceedings of the All-Polish Seminar on Mössbauer Spectroscopy, Goniądz, Poland, June 17–20, 2018

Thermodynamic Properties of Dilute Fe–Ge Alloys Studied by the ^{57}Fe Mössbauer Spectroscopy

R. Konieczny* and J. Chojcan

Institute of Experimental Physics, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław, Poland

The room temperature Mössbauer spectra of ^{57}Fe were measured for Fe–Ge containing approximately from 1 at.% till 5 at.% germanium. The spectra were analysed in terms of hyperfine parameters of their components related to unlike surroundings of the nuclear probes ^{57}Fe, determined by different numbers of germanium atoms existing in the neighbourhood of iron atoms. The intensity of the spectrum of components allowed to determine the short-range order, the binding energy E_b between two germanium atoms in the studied systems using the extended Hrynkiewicz–Królas idea and the enthalpy of solution $H_{\mathrm{Fe-Ge}}$ of germanium in iron. It was found that the germanium atoms dissolved in iron matrix interact repulsively and the estimated value of $H_{\mathrm{Fe-Ge}} = -0.88(19)$ eV/atom. Moreover, the negative values of short-range order parameters α indicate ordering tendencies in annealed samples of Fe–Ge alloys. The results were compared with corresponding values given in the literature which were obtained from calorimetric experiments and the Miedema's model of alloys.

DOI: 10.12693/APhysPolA.134.1053

PACS/topics: binary iron alloys, hyperfine parameters, binding energy, short-range order, enthalpy of solution, Mössbauer spectroscopy

1. Introduction

The melting and synthesis process of iron-based materials by metallurgical and mechanical alloying has been extensively studied during the last decades. The reasons for this intensive activity, reflected in many interesting subject concerning of the iron alloys are often presented during organized scientific and technological meetings. Furthermore, the iron alloys obtained by metallurgical methods are important due to their many possible industrial and technological applications. At the same time, this systems (e.g. Fe–Ge alloys) may be used as a model system involving several phase transformations like structural ordering [1–4] and ferromagnetic transitions [5] as well as they are regarded as a model one for experimental and theoretical studies of the thermodynamic properties [6–12].

In the present paper we applied the transmission ^{57}Fe Mössbauer spectroscopy (TMS) to the dilute binary Fe–Ge alloys in order to extend knowledge about thermodynamic properties of the system being in solid state. The TMS technique is especially powerful when the appearance of impurity atoms in the vicinity of the Mössbauer probe have a sufficiently large effect on the hyperfine field generated at the probe, to yield distinguishable components in the Mössbauer spectrum. Basing on the distributions of iron atoms in the studied materials, which is related to the intensities of the Mössbauer spectrum components one can determine for example the short-range order (SRO) parameter [13, 14], the binding energy E_b between two impurity atoms [15] and the enthalpy of solution $H_{\mathrm{Fe-D}}$ of elements — D in the ferromagnetic matrix [16]. These last one is widely used in developing and testing different models of binary alloys as well as methods for calculating the alloy parameters [8–10]. Moreover, the Mössbauer spectroscopy findings concerning the enthalpy in some cases can be useful to verify the corresponding experimental data derived from the calorimetric studies [11, 12]. However, the calorimetric investigations are performed in relatively high temperatures (1800 K) at which some of iron systems are in their high-temperature gamma phases. Such situation exists for instance in the case of the Fe–Ge system [6]. According to our knowledge in the available literature, there is no calorimetric data concerning the enthalpy of solution of germanium in the low-temperature alpha phase of iron. All the above encouraged us to use the ^{57}Fe Mössbauer spectroscopy and determine the thermodynamic parameters for dilute Fe–Ge alloys at a temperature of 700 K, where the atomic diffusion practically stops below this temperature and materials are in α-Fe phase.

2. Experimental and results

2.1. Measurements and samples preparation

The TMS measurements were performed at room temperature using constant-acceleration POLON spectrometer of standard design and a 50 mCi ^{57}Co-in-Rh standard source with a full width at half maximum of 0.24 mm/s. The ^{57}Fe Mössbauer spectra for each $Fe_{1-x}Ge_x$ sample were taken twice, before and after the annealing process. The obtained spectra are presented in Figs. 1, 2.

The samples of $Fe_{1-x}Ge_x$ alloys of about 1 g and concentration x ranging from 0.01 to 0.05 were prepared by arc melting of the appropriate amounts of the germanium having 99.999 at.% purity and iron having 99.98 at.% purity. Samples were molten twice in a water-cooled copper

*corresponding author; e-mail: robi@ifd.uni.wroc.pl

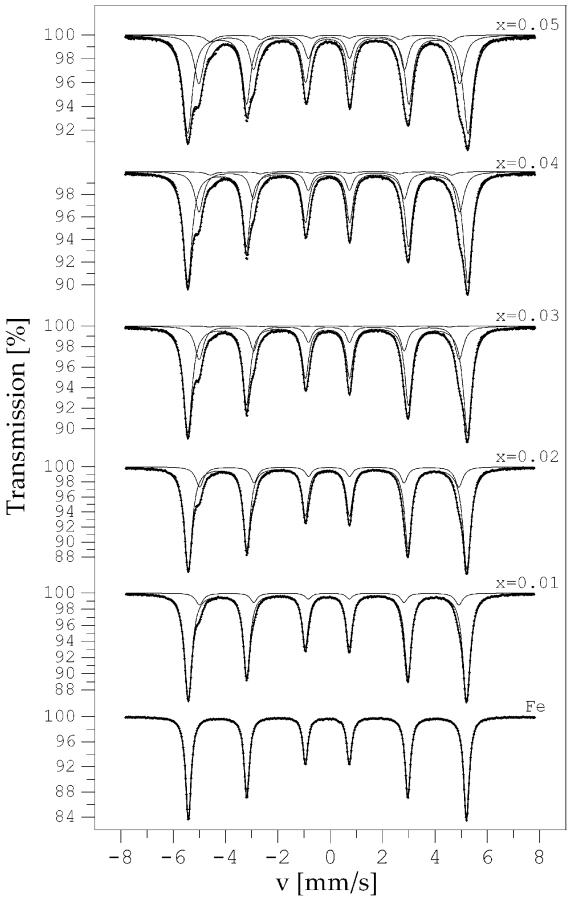

Fig. 1. The room temperature ^{57}Fe Mössbauer spectra for the $Fe_{1-x}Ge_x$ alloys measured just after the melting, fitted with a sum of various number of six-line patterns (Zeeman sextets) corresponding to different numbers of germanium atoms located in vicinity nuclear probe.

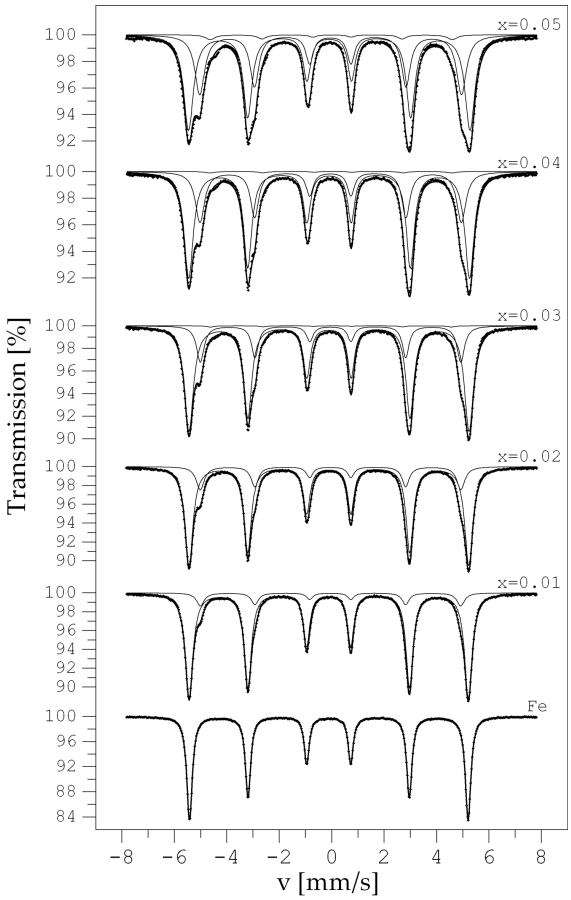

Fig. 2. The room temperature ^{57}Fe Mössbauer spectra for the $Fe_{1-x}Ge_x$ alloys measured after the annealing process at 1270 K for 2 h, fitted with a sum of various number of six-line patterns (Zeeman sextets) corresponding to different numbers of germanium atoms located in vicinity nuclear probe.

crucible under the argon atmosphere and quickly cooled to room temperature. The weight losses during the melting process were below 0.2% of the original weight, so it could be assumed that the chemical composition of the obtained ingots are close to nominal ones. In the next step each ingots were cold-rolled to the final thickness of about 40 μm. All the obtained foils were annealed in vacuum under pressure lower than 10^{-4} Pa at 1270 K for 2 h and after that they were slowly cooled to room temperature during 6 h. The slow cooling allowed to obtain homogeneous and defect free samples. Under these conditions, diffusion effectively stops at about 700(11) K [17], so the observed distributions of atoms in the annealed specimens should be the frozen-in state corresponding to this temperature.

2.2. Data analysis

The spectra were analysed in terms of sum of different six-line components. These lines correspond to the various isomer IS, quadrupole QS shifts and hyperfine fields B at ^{57}Fe nuclei generated by different chemical states of the ^{57}Fe nuclear probes. The two or three numbers of fitted six-line spectrum components depended on concentration of germanium in all $Fe_{1-x}Ge_x$ samples. The obtained fits are presented in Figs. 1, 2. The fitting procedure was done under assumption that the influence of n Ge atoms on B as well as the corresponding IS is additive and independent of the atom positions in the neighbourhood of the nuclear probe so the relationship between B, IS and n can be written as follows:

$$B(n) = B_0 + n\Delta B, \quad IS(n) = IS_0 + n\Delta IS, \tag{1}$$

where ΔB and ΔIS stand for the changes of B and IS with one germanium atom in the first coordination shell of the Mössbauer probe. Furthermore, it was assumed that the shape of each line is Lorentzian and the three linewidths Γ_{16}, Γ_{25}, Γ_{34} of subspectra were divided into two sets. The first one set concerns component of spectrum determined by the nuclear probes having in their vicinity only Fe atoms, the second one are related to the existence of Ge atoms in the first coordination shell of ^{57}Fe. The quadruple shift QS of a subspectrum were treated as a free parameters. The two line intensities ratios I_{16}/I_{34} and I_{25}/I_{34} are the same for all six-line components of the given spectrum.

The found values of the best-fit parameters for the annealed samples are displayed in Table I. They are essentially differ from corresponding data given in the literature. In Ref. [18] one can find that for the $Fe_{0.972}Ge_{0.028}$ alloy $B_0 = 33.23$ T, $\Delta B_1 = -2.38$ T, $\Delta B_2 = -0.086$ T and for $Fe_{0.80}Ge_{0.20}$ [19]: $B_0 = 34.54$ T, $\Delta B_1 = -2.36$ T, $\Delta B_2 = -1.67$ T. The example of a fit obtained under these assumptions is presented in Fig. 2 whereas the found values of the best-fit parameters are displayed in Table I.

TABLE I

Parameters of the isomer shift and hyperfine field obtained for annealed Fe–Ge alloys. The standard uncertainties for the parameters result from the variance of the fit. Values of the isomer shift IS_0 are reported relative to the corresponding value for α-Fe at room temperature.

x	B_0 [T]	ΔB [T]	IS_0 [mm/s]	ΔIS [mm/s]
0.01	33.00(3)	−2.23(3)	0.003(1)	0.063(3)
0.02	33.05(4)	−2.23(2)	0.002(1)	0.060(2)
0.03	33.09(7)	−2.31(2)	0.007(1)	0.056(1)
0.04	33.19(9)	−2.30(2)	0.012(1)	0.053(2)
0.05	33.26(9)	−2.33(2)	0.017(1)	0.046(2)

2.3. The binding energy E_b of two germanium atoms in iron matrix

The obtained values of parameters of the best-fit model mentioned above were used to determine total intensities c_n of components of a spectrum for the annealed Fe–Ge samples. The c_0, c_1 and c_2 parameters are related to the existence of zero, one and two germanium atoms in the first coordination shell of ^{57}Fe. It was assumed that the Lamb–Mössbauer factor is independent of the configuration of atoms in the surroundings of the probe nucleus. These parameters are presented in Table II together with calculated probabilities p_n of finding Ge atoms in the first coordination shell of an Ge atom in the random *bcc* $Fe_{1-x}Ge_x$ alloy. In random alloys, the probability p_n of local configuration of impurity atoms in the first coordination shell of ^{57}Fe nucleus is described by the binomial distribution.

To the calculation of binding energy E_b for pairs of Ge atoms we used values of relative contributions c_1 and c_2 of spectrum components for annealed samples. The calculations E_b were performed on the basis of the modified Hrynkiewicz–Królas formula [20]:

$$E_b = -kT_d \ln\left(\frac{(1+2c_2/c_1)(c_2/c_1)}{(1+2p_2/p_1)(p_2/p_1)}\right), \tag{2}$$

where k is the Boltzmann constant, $T_d = 700(11)$ K is the "freezing" temperature for the atomic distribution in studied materials. Based on the obtained c_1 and c_2 values we have accepted that $N = 8$ for Ge. N is the total number of the lattice sites in the first coordination shell of an atom in the *bcc* lattice of the Fe–Ge alloys.

In the next step we determined the extrapolated value of the binding energy E_b for $x = 0$ using $E_b(0.03 \le x \le 0.05)$, which equals to 0.220(47) eV. The obtained positive values of binding energy in $Fe_{1-x}Ge_x$ alloys suggest that interaction between two germanium atoms in iron matrix is repulsive.

TABLE II

The binding energy E_b between a pair of Ge atoms in $Fe_{1-x}Ge_x$ alloys deduced from the ^{57}Fe Mössbauer spectra. The standard uncertainties for c_1 and c_2 result from the variance of the fit of the assumed model to the spectrum measured.

x	c_0	c_1	c_2	p_1	p_2	E_b [eV]
0.01	0.8892(3)	0.1108(2)	–	0.0746	0.0026	–
0.02	0.8097(5)	0.1903(2)	–	0.1389	0.0099	–
0.03	0.7469(6)	0.2488(6)	0.0043(3)	0.1939	0.0210	0.1214(53)
0.04	0.6704(5)	0.3205(4)	0.0091(3)	0.2405	0.0351	0.1105(39)
0.05	0.5960(7)	0.3739(5)	0.0301(4)	0.2793	0.0515	0.0598(24)

2.4. An enthalpy of solution of iron in germanium

An extrapolated value of $E_b(0)$ was used to computation an enthalpy $H_{\mathrm{Fe-Ge}}$ of solution of germanium atoms in α-iron matrix. The calculations were performed by using the Królas model [10] for the binding energy in the following way:

$$H_{\mathrm{Fe-Ge}} = -zE_b(0)/2, \tag{3}$$

where z is the coordination number of the crystalline lattice ($z = 8$ for α-Fe). The value of $H_{\mathrm{Fe-Ge}}$ was presented in Table III and compared with the Miedema's model predictions [8] on the enthalpy $H_{\mathrm{Fe-Ge}}$ of solution of Ge in Fe as well as the results of calorimetric experiments concerning enthalpy of formation H^{for} for the Fe–Ge alloys [6]. It is possible because the enthalpy H^{for} is related to the enthalpy $H_{\mathrm{Fe-Ge}}$ as follows:

$$H_{\mathrm{Fe-Ge}} = (\mathrm{d}H^{\mathrm{for}}/\mathrm{d}x)_{x=0}. \tag{4}$$

TABLE III

An enthalpy $H_{\mathrm{Fe-Ge}}$ [eV/atom] of solution of germanium in iron.

Calorimetric data [6]	Miedema's model [8]	This work
-0.90	-0.66	-0.88(19)

2.5. A short-range order parameter

The deviation from the random state can be quantitatively described by the short-range order parameter (SRO). This parameter for systems with bcc lattice have the following form [21]:

$$\alpha_1 = 1 - \frac{\langle n\rangle}{8x} \tag{5}$$

for the first coordination shell.

The c_n values obtained in Sect. 2.3 were used to find parameter $\langle n\rangle$ being the average number of germanium atoms in the first shell of ^{57}Fe probe:

$$\langle n\rangle = \sum_{n=1}^{8} nc_n. \tag{6}$$

The values of α_1 were determined for samples as-obtained in arc furnace as well as those annealed at 1270 K for 2 h. The results are presented in Fig. 3. As one can see for the as-obtained samples just after melting in which atoms being frozen-in high temperature state, near to the melting point, the absolute value of α_1 parameter is relatively small — close to zero. This testifies that the Ge atoms were practically randomly distributed in the iron matrix during the melting process. On the other hand, in the case of the annealed samples the situation is different because one observes negative large values of α_1 for the low concentration of impurities but with rising impurity concentration the value of SRO parameter shows a trend to increase. This finding suggests the tendency to the ordering of Ge atoms in the annealed dilute iron-based $Fe_{1-x}Ge_x$ alloys but for the larger concentration x one can observed disappearance of this trend. However, in this case the single germanium atoms occur more often near the nuclear probe than pair of the Ge atoms. It means that the germanium atoms are more likely to occur individually than form the pairs. In terms of interactions it means that the interaction between two Ge atoms is repulsive — predominance of Fe–Ge bonds.

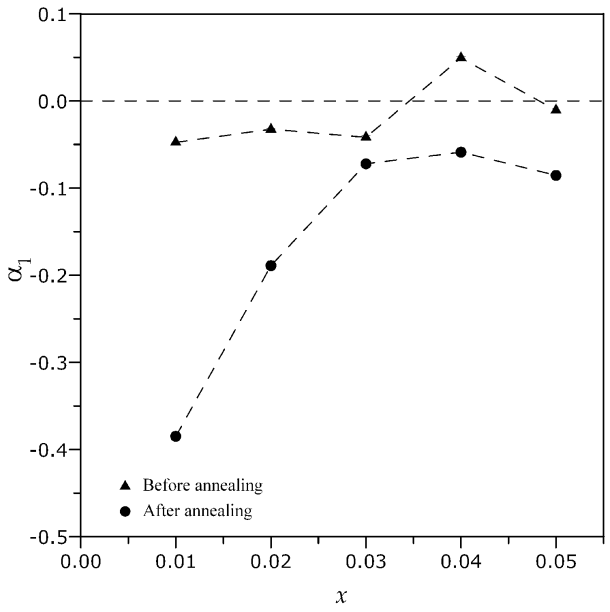

Fig. 3. The short-range order parameter α_1 as a function of fraction x of germanium atoms in the dilute iron-based $Fe_{1-x}Ge_x$ alloys.

3. Conclusions

The Mössbauer study of the binding energy in the annealed $Fe_{1-x}Ge_x$ alloys with $x \leq 0.05$, reveals that values of E_b are positive and that means the two Ge atoms dissolved in Fe matrix interact repulsively. Moreover, it was observed ordering-type correlations — a predominance of Fe–Ge bonds manifested as a negative value of the short-range order parameters. This fact confirms our findings on the positive binding energy which was obtained using modified Hrynkiewicz–Królas method. An enthalpy of solution H_{Fe-Ge} of germanium in iron obtained by the ^{57}Fe Mössbauer spectroscopy is of negative value equal to $-0.88(19)$ eV/atom. The value is at good agreement with corresponding value derived from the heat H^{for} of formation of the Fe–Ge systems, obtained with calorimetric methods and resulting from the Miedema's model of alloys. The discrepancy in the values could be explained by the fact that calorimetric methods as well as Miedema's model were based on measurements performed at high temperatures at which Fe–Ge alloy is in paramagnetic state.

In the author's opinion, the thermodynamic parameters were estimated experimentally for the first time for Fe–Ge system in α-Fe phase with atomic distributions corresponding to the temperature about 700 K. Moreover, these unique experimental Mössbauer data could play an important role in developing and testing different models of the binary Fe–Ge alloys as well as methods for calculating the system parameters.

Acknowledgments

This work was supported by the University of Wrocław under project 0420/2707/18.

References

[1] I.S. Golovin, T.V. Ivleva, S. Jäger, P. Jencus, Hartmut Neuhäuser, S.A.T. Redfern, C. Siemers, *Solid State Phenom.* **137**, 59 (2008).

[2] I.S. Golovin, H. Neuhäuser, S.A.T. Redfern, H.-R. Sinninge, *Mater. Sci. Eng. A* **521-522**, 55 (2009).

[3] E. Jartych, D. Oleszak, L. Kubalova, O.Ya. Vasilyeva, J.K. Zurawicz, T. Pikula, S.A. Fedotov, *J. Alloys Comp.* **430**, 116 (2007).

[4] A.F. Cabrera, F.H. Sanchez, *Phys. Rev. B* **65**, 094202 (2002).

[5] Q.Z. Chen, A.H.W. Ngan, B.J. Duggan, *J. Mater. Sci.* **33**, 5404 (1998).

[6] D.S. Kanibolotsky, O.A. Bieloborodova, N.V. Kotova, V.V. Lisnyak, *J. Therm. Anal. Calorim.* **71**, 583 (2003).

[7] M. Huang, T.A. Lograsso,*Appl. Phys. Lett.* **95**, 171907 (2009).

[8] A.R. Miedema,*Physica B* **182**, 1 (1992).

[9] G. Bonny, R.C. Pasianot, L. Malerba, A. Caro, P. Olsson, M.Y. Lavrentiev, *J. Nucl. Mater.* **385**, 268 (2009).

[10] K. Królas, *Phys. Lett. A* **85**, 107 (1981).

[11] R. Boom, F.R. De Boer, A.K. Niessen, A.R. Miedema, *Physica* **115B**, 285 (1983).

[12] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, *Selected Values of Thermodynamic Properties of Binary Alloys*, American Society for Metals Metals Park, Ohio 1973.

[13] R. Idczak, R. Konieczny, J. Chojcan, *Solid State Commun.* **159**, 22 (2013).

[14] R. Konieczny, R. Idczak, *Nukleonika* **60**, 69 (2015).
[15] R. Konieczny, R. Idczak, J. Chojcan, *Nukleonika* **60**, 75 (2015).
[16] R. Konieczny, R. Idczak, *Nukleonika* **62**, 109 (2017).
[17] R. Idczak, R. Konieczny, J. Chojcan, *Physica B* **407**, 2078 (2012).
[18] S. Dubiel, W. Zinn, *Phys. Rev. B* **28**, 67 (1983).
[19] A.F. Cabrera, F.H. Sanchez, *Phys. Rev. B* **65**, 94202 (2002).
[20] J. Chojcan, *J. Alloys Comp.* **264**, 50 (1998).
[21] J.M. Cowley, *Phys. Rev.* **120**, 1648 (1960).