

A Study of Thermodynamic Properties of Dilute Fe–Au Alloys by the ^{57}Fe Mössbauer Spectroscopy

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The room temperature Mössbauer spectra of ^{57}Fe were measured for $\text{Fe}_{1-x}\text{Au}_x$ with the gold concentration ranging from 1 at.% till 4.8 at.%. They were analysed in terms of hyperfine parameters of their components related to unlike surroundings of the iron probes, determined by different numbers of gold atoms existing in the neighbourhood of iron atoms. Basing on the intensities of the spectrum components we determined binding energy E_b between two gold atoms in the studied materials. The latter was done for properly annealed samples using the extended Hryniewicz–Królas idea. It was found that the binding energy is positive or Au atoms interact repulsively. The extrapolated value of E_b for $x = 0$ was used for computation of an enthalpy of solution of Au in Fe. Finally the obtained value of the enthalpy was used to predict the mixing enthalpy for the Fe–Au solid solutions. The results were compared with both the corresponding values resulting from the cellular atomic model of alloys by Miedema and those derived from experimental calorimetric data given in the literature.

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1. Introduction

The iron alloys obtained by metallurgical or electrochemical procedures, are important due to their many possible industrial and technological applications. The characteristics of metallic systems such as ductility, tensile strength, magnetic property, corrosion resistance, and thermodynamic property, are markedly influenced by alloying and are quite different from those of their pure components. The magnetic and associated thermodynamic properties of Fe–Au alloys in which a nonmagnetic component is diluted with a magnetic one, or in which the components have competing ferromagnetic and paramagnetic behaviour, has been the subject of intense research by variety of methods [1–4]. By now the experimental picture of thermodynamic properties of binary iron alloys especially iron–gold system [5, 6] at high temperature liquid state is well known but despite its simplicity (no intermetallic compounds) many issues seem still unsatisfactorily understood [7]. Moreover, to the best of our knowledge, there has been no report on these properties for the more applicable Fe–Au solid alloys prepared for example in the disordered state by fast quenching from the melt and then thermally annealed in order to obtain homogeneous systems at room temperature.

Taking this into account in the present work we applied the ^{57}Fe Mössbauer spectroscopy to the $\text{Fe}_{1-x}\text{Au}_x$ solid solutions with low concentration of gold in order to extend knowledge about properties of the system being in solid state, especially the thermodynamic ones. As it is known the ^{57}Fe Mössbauer spectroscopy is able to deliver, among others, the information on interactions of

impurity atoms in diluted binary iron alloys [7–12] and the interactions determine the enthalpy of solution of impurity elements in iron [13]. This technique is especially powerful when the impurity neighbours 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 attributed to different configurations of the probe neighbours. Nevertheless, our recent studies [14, 15] show that the technique can be also successfully applied to binary iron systems for which one observes unresolved Mössbauer spectra. As far as the enthalpy of solution mentioned above is concerned it is widely used in developing and testing different models of binary alloys and methods for calculating the alloy parameters [16–20]. Moreover, the Mössbauer spectroscopy findings on the enthalpy in some cases can be unique i.e. impossible to obtain with other methods, in particular the calorimetric ones. It can happen because the Mössbauer studies provide information about enthalpy of solution at relatively low temperature, below the Curie temperature whereas the calorimetric investigations are performed for samples at relatively high temperatures, above the Curie temperature, at which influence of magnetic interactions on thermodynamic properties of studied alloys cannot be observed. Additionally, the Mössbauer studies concern iron alloys in low-temperature $\alpha(\text{bcc})$ phase in contrast to high-temperature calorimetry where most of iron systems under investigation are in $\gamma(\text{fcc})$ phase [5–14]. Finally, worth noting is the fact that the Mössbauer enthalpy of solution data, can be used for prediction of an enthalpy of mixing of the system under consideration. It is possible thanks to the proper relationship given by Sluiter and Kawazoe [21]. As far as we know till now the Mössbauer spectroscopy has not been used for such prediction in the case of the Fe–Au system.

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2. Experimental and results

2.1. Samples preparation and measurements

The samples of disordered $\text{Fe}_{1-x}\text{Au}_x$ alloys with $x = 0.010, 0.023, 0.034, 0.048$ were obtained at the Institute of Physics of Pedagogical University in Cracow. They were prepared by arc melting of the appropriate amounts of the gold-metal having 99.96 at.% purity and iron-metal having 99.97 at.% purity. Samples of about 1.5 g were molten three times under high purity argon atmosphere. The structure and the atomic compositions of all the specimens were determined by the X-ray diffraction (XRD) and the energy-dispersive X-ray spectroscopy (EDS), respectively. More information on this can be found in Ref. [22].

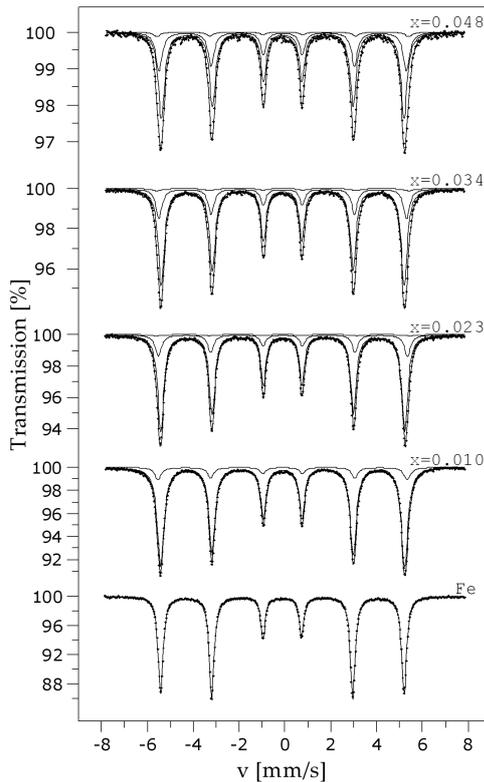


Fig. 1. The ^{57}Fe Mössbauer spectra for the $\text{Fe}_{1-x}\text{Au}_x$ alloys measured at room temperature after the annealing process at 1270 K for 2 h and slow cooling to the room temperature.

In the next step each resulting ingot was cold-rolled to the final thickness of about 0.05 mm and then the foil was cut into several similar pieces. All the obtained foils were annealed in vacuum at 1270 K for 2 h and after that they were slowly cooled to room temperature during 6 h. Under these conditions, diffusion effectively stops at about 700 K [10], so the observed distributions of atoms in the annealed specimens should be the frozen-in state corresponding to 700 K. The room temperature measurements of the ^{57}Fe Mössbauer spectra for samples of different alloys were performed twice, before and after the annealing process mentioned above.

The spectra were taken in transmission geometry by means of a constant-acceleration POLON spectrometer of standard design, using a 60 mCi ^{57}Co -in-Rh standard source with a full width at half maximum (FWHM) of 0.22 mm/s. Some of the spectra are presented in Fig. 1.

2.2. Data analysis

All the obtained spectra were analysed in terms of three six-line patterns corresponding to different hyperfine fields B at ^{57}Fe nuclei generated by different numbers of iron and gold atoms located in the first coordination shell of the probing nuclei. The number of fitted six-line spectrum components depended on concentration of Fe in the samples. The obtained fits are presented in Fig. 1. It was done under assumption that the influence of n Au atoms on B as well as the corresponding isomer shift 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:

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

where ΔB and ΔIS stand for the changes of B and IS with one gold atom in the first coordination shell of the Mössbauer probe. At the same time, we assume that the quadrupole shift QS in a cubic lattice is equal to zero because of the cubic symmetry of the investigated iron-based alloys [23]. Furthermore, it was assumed that the shape of each line is Lorentzian and the three linewidths Γ_{16} , Γ_{25} and Γ_{34} for all components of a spectrum which are related to the existence of impurity atoms in the first coordination shell of ^{57}Fe are the same and they are different from linewidths of that component, determined by the nuclear probes having in their vicinity only iron atoms. 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. Theoretically the intensities of nuclear transitions between magnetically split nuclear levels for ^{57}Fe Mössbauer spectroscopy should be like 3:2:1:1:2:3, however, the observed line intensities as presented in Fig. 1 are different from the stated ratios and especially this is well seen for pure iron spectra. The observed deviations of the line intensities are mainly caused, apart of thickness effects, by texture effects associated with the method of preparation applied for individual absorber foils.

In most cases the above assumptions are enough to obtain reasonable results. However, gold neighbours of the Mössbauer probe have a very small effect on the hyperfine field generated at the probe (see Fig. 1), so proper decomposition of the Mössbauer spectra to several components is impossible without additional assumptions on parameters of the components. The successful analysis of the experimental data was performed by taking into account two series of the spectra, measured for samples as-obtained in an arc furnace and after a certain heat treatment at 1270 K for 2 h. The as-obtained samples were assumed to be disorder (random) alloys with the probability for the existence of n Au atoms among all $N = 8$ atoms located in the first coordination shell of an iron atom given by binomial distribution

$p_n = [N!/((N-n)!n!)]x^n(1-x)^{N-n}$. The found values of the best-fit parameters obtained under assumption mentioned above for the as-obtained samples are displayed in Table I. They are similar to corresponding data given in the literature [22] and simultaneously they are at variance with the theoretical calculations based on density functional theory (DFT) [24].

TABLE I

Parameters of the hyperfine field and isomer shift obtained for as-obtained Fe–Au 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]
0.010	33.000(4)	0.690(13)	0.0058(5)	0.0010(2)
0.023	33.000(3)	0.688(11)	0.0101(6)	0.0055(6)
0.034	32.850(5)	0.620(16)	0.0081(6)	0.0017(4)
0.048	32.810(7)	0.625(14)	0.0093(9)	0.0012(5)

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

The best-fit hyperfine parameters obtained for as-obtained specimens were used to determine other parameters for the annealed samples. The values of parameters c_1 and c_2 are presented in Table II together with calculated probabilities of finding one p_1 and two p_2 gold atoms in the first coordination shell of an iron atom in the random bcc $Fe_{1-x}Au_x$ alloy. Assuming that the Lamb–Mössbauer factor is independent of the configuration of atoms in the surroundings of the ^{57}Fe nucleus, the c_1 and c_2 parameters describe intensities of the components of a spectrum which are related to the existence of one and two Au atoms in the first coordination shell of ^{57}Fe .

TABLE II

The binding energy E_b between a pair of Au atoms in $Fe_{1-x}Au_x$ 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. The values of uncertainty for E_b were computed assuming that the uncertainty for the “freezing” temperature T_d is 11 K.

x	c_1	c_2	p_1	p_2	E_b [eV]
0.010	0.1106(10)	–	0.0746	0.0026	–
0.023	0.1797(11)	0.00829(23)	0.1563	0.0129	0.0389(29)
0.034	0.2318(13)	0.0172(10)	0.2135	0.0263	0.0352(24)
0.048	0.3022(15)	0.0347(11)	0.2721	0.0480	0.0317(19)

Using the c_1 and c_2 values we calculated the binding energy E_b for pairs of Au atoms in the studied materials. The computations were performed on the basis of the modified Hryniewicz–Królás formula [25] for a $Fe_{1-x}D_x$ system

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

where k is the Boltzmann constant, T_d denotes the “freezing” temperature for the atomic distribution in the sample ($T_d = 700(11)$ K) [10], p_n is the probability for the

existence of n D atoms among all N atoms located in the first or the first and second coordination shells of the Fe atom in a random Fe–D alloy, finally x stands for the concentration of D atoms and N , in the case of annealed samples being at the room temperature, is the total number of the lattice sites in the first or the first and second coordination shells of an atom in the bcc lattice. Based on the obtained c_1 and c_2 values we have accepted that $N = 8$ for $D = \text{Au}$. The E_b values are presented in Table II.

2.4. An enthalpy of solution of iron in cobalt

The value of $E_b(0)$, the extrapolated value of E_b for $x = 0$, was used to computation of an enthalpy $H_{\text{Fe–Au}}$ of solution of Au in Fe. The calculations were performed on the basis of the Królás model [15] for the binding energy according to which

$$H_{\text{Fe–Au}} = -zE_b(0)/2, \quad (3)$$

where z is the coordination number of the crystalline lattice ($z = 8$ for bcc lattice of iron). The determined value of $H_{\text{Fe–Au}}$ is presented in Table III together with corresponding enthalpies of solution derived from the heat H^{for} of formation of the Fe–Au systems, obtained with calorimetric experiments [5]:

$$H_{\text{Fe–Au}} = [dH^{\text{for}}/dx]_{x=0}, \quad (4)$$

and calculated using the cellular atomic model of alloys developed by Miedema [16].

TABLE III

An enthalpy $H_{\text{Fe–Au}}$ [eV/atom] of solution of gold in iron.

Calorimetric data [5]	Miedema model [16]	This work
0.498	0.377	–0.186(40)

2.5. Prediction of the mixing enthalpy curve for the Fe–Au solid solutions

The determined $H_{\text{Fe–Au}}$ value is related to the concentration dependence of mixing enthalpy H_{mix} for the Fe–Au system in the following way [21]:

$$H_{\text{mix}}(x) \approx H_{\text{Au–Fe}}x^2(1-x) + H_{\text{Fe–Au}}x(1-x)^2, \quad (5)$$

where $H_{\text{Au–Fe}}$ is the enthalpy of solution of Fe in Au. On the basis of the relationship we calculated the $H_{\text{mix}}(x)$ dependence using also the $H_{\text{Au–Fe}}$ value $-38(12)$ meV/atom obtained by us in the past [26]. The mixing enthalpy H_{mix} for $Fe_{1-x}Au_x$ are presented in Fig. 2 together with the findings based on calorimetric measurements [5, 6] and resulting from the semi-empirical model of alloys by Miedema [16].

3. Conclusions

The first part of this study concerned measurements of hyperfine interactions on iron nuclei in dilute Fe–Au alloys. The values of hyperfine fields and isomer shifts determined from the ^{57}Fe Mössbauer spectra of Fe–Au alloys are at quantitative agreement with corresponding experimental data given in the literature. In case of DFT

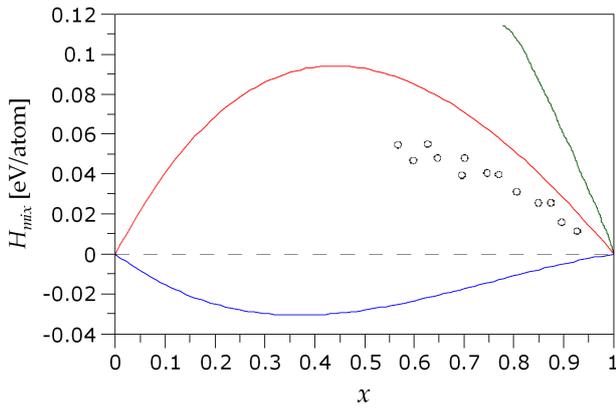


Fig. 2. Mixing enthalpy H_{mix} for $\text{Fe}_{1-x}\text{Au}_x$ alloys obtained in this work (red line), resulting from the Miedema model (green line) and derived from calorimetric measurements: Hultgren – dashed line, Topor – circles.

calculations observed differences in estimated hyperfine parameters suggest that theoretical calculations based on DFT method need some improvements.

In the second part of this work the Mössbauer data were used to determine the binding energy E_b between two gold atoms, the enthalpy of solution $H_{\text{Fe-Au}}$ of gold in α -iron as well as the enthalpy of mixing H_{mix} for the Fe–Au system. The positive values of binding energy in the annealed $\text{Fe}_{1-x}\text{Au}_x$ alloys with x in the range $0.023 \leq x \leq 0.048$ determined by the extended Hrynkiwicz–Królás model, suggest that interaction between two gold atoms is repulsive. An enthalpy of solution $H_{\text{Fe-Au}}$ of gold in iron obtained by the ^{57}Fe Mössbauer spectroscopy is of negative value equal to $-0.186(40)$ eV/atom. The value is at variance with corresponding value derived from the heat H^{for} of formation of the Fe–Au systems, obtained with calorimetric methods and resulting from the Miedema model of alloys. Additionally, the enthalpy of mixing of Fe–Au system was predicted for the first time by the Mössbauer spectroscopy, using the equation given by Sluiter and Kawazoe together with the enthalpy of solution of Au in Fe obtained in this work and the enthalpy of solution of Fe in Au measured previously.

The result is interesting because the Mössbauer spectroscopy delivers information on the dilute-limit enthalpy of solution of gold in the α (bcc) phase of Fe, being at about 700 K or in the ferromagnetic state whereas the calorimetric data concern iron systems at relatively high temperatures at which they are paramagnetic phases γ (fcc). It may be suggested that for the Fe–Au system the determined $H_{\text{Fe-Au}}$ and H_{mix} values depend on structural and magnetic properties of the system, which are influenced by temperature.

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