

Thermodynamic properties of Au-Fe alloys studied with ^{57}Fe Mössbauer spectroscopy

Rafał Idczak,
Robert Konieczny,
Jan Chojcan

Abstract. The room temperature Mössbauer spectra of ^{57}Fe were measured for $\text{Au}_{1-x}\text{Fe}_x$ alloys with x in the range $0.01 \leq x \leq 0.03$. The obtained data were analysed in terms of short range order parameter (SRO) and the binding energy E_b between two iron atoms in the studied materials using the extended Hryniewicz-Królas idea. The estimated negative SRO parameters and the positive binding energy suggest ordering tendencies in Au-Fe alloys at low iron concentration. The extrapolated value of E_b for $x = 0$ was used for the computation of enthalpy of the solution of Fe in Au. The results were compared with the corresponding data derived from calorimetric measurements, previous Mössbauer experiments and resulting from the cellular atomic model of alloys by Miedema.

Key words: Mössbauer spectroscopy • Au-Fe alloys • enthalpy of solution • short range order

Introduction

The magnetic and thermodynamic properties of dilute Au-Fe alloys, in which a non-magnetic gold solvent contains a magnetic iron solute, has been the subject of intense research for many years [1, 2, 6, 10–13]. Till today there are two contradictory models describing behaviour of iron impurities in the gold matrix. In particular, the calorimetric measurements [6] showed that the enthalpy of solution of iron atoms in gold matrix is positive, which indicates that the iron atoms form clusters. Further studies of atomic short range order (SRO) made by transmission electron microscopy, small-angle scattering, and X-ray diffuse scattering [2] confirms that the clustering model remains a plausible explanation of the various magnetic properties and diffuse scattering patterns observed in the Au-Fe system. On the other hand, previous Mössbauer experiments [11, 13] gave clear evidence of ordering (anticlustering) tendencies in Au-Fe alloys. Finally, in the study of magnetic short range order [1], the authors concluded on some mixture of ordering and clustering.

Taking the above into account, we decided to estimate the binding energy between two iron atoms in a gold matrix, using the extended Hryniewicz-Królas model [3, 5], the enthalpy of the solution of Fe in Au and the SRO parameters of the Au-Fe alloys at low iron concentration by ^{57}Fe Mössbauer spectroscopy.

R. Idczak[✉], R. Konieczny, J. Chojcan
University of Wrocław,
Institute of Experimental Physics,
9 M. Borna Sq., 50-204 Wrocław, Poland,
Tel.: +48 71 375 9316, Fax: +48 71 328 7365,
E-mail: ridczak@ifd.uni.wroc.pl

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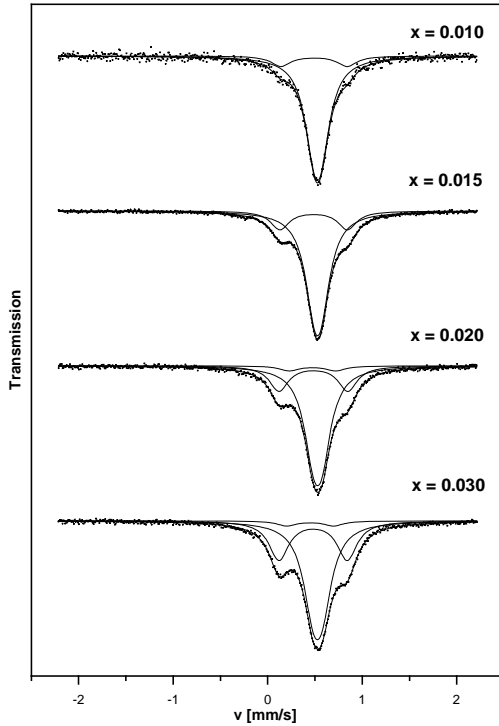


Fig. 1. The ^{57}Fe Mössbauer spectra for the $\text{Au}_{1-x}\text{Fe}_x$ alloys measured at room temperature before the annealing process at 1070 K.

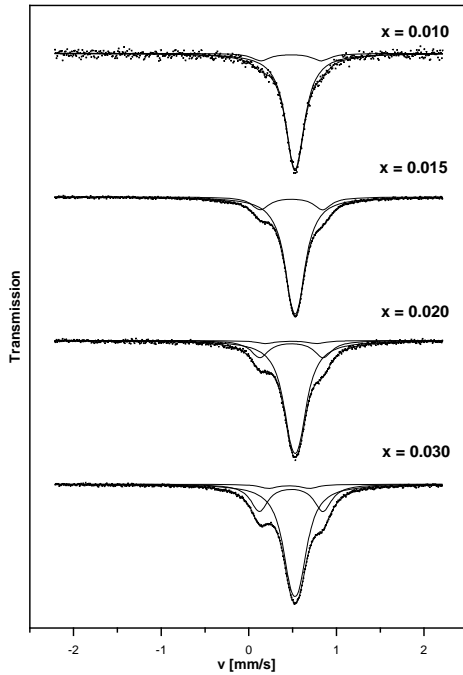


Fig. 2. The ^{57}Fe Mössbauer spectra for the $\text{Au}_{1-x}\text{Fe}_x$ alloys measured at room temperature after the annealing process at 1070 K.

Table 1. Some of the best-fit parameters of the assumed model of the ^{57}Fe Mössbauer spectrum measured for $\text{Au}_{1-x}\text{Fe}_x$ alloys. The standard uncertainties for the parameters result from the variance of the fit

x	QS ₁ (mm/s)	QS ₂ (mm/s)	QS ₃ (mm/s)	IS ₁ (relative to $\alpha\text{-Fe}$) (mm/s)	IS ₂ (relative to $\alpha\text{-Fe}$) (mm/s)	IS ₃ (relative to $\alpha\text{-Fe}$) (mm/s)
0.010	0.07(1)	0.70(1)	0	0.53(1)	0.49(1)	0
0.015	0.07(1)	0.71(1)	0	0.53(1)	0.49(1)	0
0.020	0.09(1)	0.73(1)	0.49(4)	0.53(1)	0.48(1)	0.47(2)
0.030	0.09(1)	0.72(1)	0.50(4)	0.53(1)	0.48(1)	0.45(1)

Experimental and results

Samples preparation

The samples of $\text{Au}_{1-x}\text{Fe}_x$ alloys with x in the range $0.01 \leq x \leq 0.03$, were prepared in an arc furnace. Appropriate amounts of the 99.9% pure ^{57}Fe isotope and 99.999% pure gold, were melted in an argon atmosphere. The weight losses during the melting process were below 1% so the compositions of the obtained ingots were close to nominal ones. Resulting ingots were cold-rolled to the final thickness of about 0.02 mm and then the foils were annealed in vacuum at 1070 K for 2 h. After that, they were slowly cooled to room temperature during 6 h. Under these conditions, diffusion effectively stops at a certain temperature T_d , so the observed distributions of atoms in the annealed specimens should be the frozen-in state, corresponding to the temperature. According to the data given in the literature, T_d for gold is close to 500(50) K [11, 13].

Measurements

The room-temperature measurements of the ^{57}Fe Mössbauer spectra were performed in transmission geometry by means of a constant-acceleration POLON spectrometer of standard design, using a 40 mCi ^{57}Co -in-Rh standard source with a full width at half maximum (FWHM) of 0.21 mm/s. The obtained spectra are presented in Figs. 1 and 2.

Spectra analysis

Each measured spectrum was fitted with a transmission integral for a sum of different doublets corresponding to the various quadrupole splitting, QS, and isomer shift, IS, at ^{57}Fe nuclei generated by unlike numbers of Au and Fe atoms located in the first coordination shell of the probing nuclei. The number of fitted doublets depended on the concentration of Fe in the samples and was two for $x = 0.010, 0.015$ and three for $x = 0.020, 0.030$. The values of the best-fit parameters obtained from the spectra analysis (displayed in Table 1) are in good agreement with the corresponding data given in the literature [13].

As the main result of the analysis, the effective thicknesses $T_A(n)$ related to components of each spectrum were determined.

$$(1) \quad T_A(n) = \sigma_0 t_A N f c(n)$$

where n is the number of Fe atoms located in the first

shell of ^{57}Fe , σ_0 is the maximal cross-section for nuclear γ resonance absorption, t_A denotes the thickness of the absorber, N stands for the total number of resonant absorbing atoms ^{57}Fe per unit volume, $c(n)$ describes the fraction of absorbing atoms corresponding to the component under consideration and f is the Lamb-Mössbauer factor. Assuming that the Lamb-Mössbauer factor does not depend on the configuration of atoms in the surroundings of the ^{57}Fe nucleus, the fraction $c(n)$ can be easily calculated using the $T_A(n)$ values as in such case

$$(2) \quad c(n) = \frac{T_A(n)}{\sum T_A(n)}$$

The computed $c(n)$ values were used to find parameters c_0 , c_1 and c_2 being the intensities of those components of a spectrum which are related to the existence of zero, one and two iron atoms in the first coordination shell of nuclear probes ^{57}Fe , respectively: $c_0 = c(0)$, $c_1 = c(1)$ and $c_2 = c(2)$. The results are presented in Table 3.

Atomic short range order

In the $\text{Au}_{1-x}\text{Fe}_x$ alloys with the x range $0.01 \leq x \leq 0.03$, where atoms are distributed in the f.c.c. lattice, the total number of atoms located in the first coordination sphere is equal to 12. In the real alloys the distribution of impurity atoms is generally different than statistically predicted by binomial distribution. This deviation from the random state can be quantitatively described by the SRO parameter and the Mössbauer spectroscopy is a very useful tool for determination of the SRO parameter since the quadrupole splitting QS and isomer shift IS depend on the number of impurity atoms in the first coordination shell of ^{57}Fe probe. The SRO parameter α_1 for f.c.c. lattice have the following form [4]:

$$(3) \quad \alpha_1 = \frac{\langle n \rangle - x}{1 - x}$$

where:

$$(4) \quad \langle n \rangle = \frac{1}{12} \sum_{n=1}^{12} n \cdot c(n)$$

$\langle n \rangle$ is the average number of Fe atoms within the first coordination shell of ^{57}Fe probe and $c(n)$ denotes the probability of the configuration n Fe atoms which can be obtained from the analysis of the experimental Mössbauer spectra, for example. Physically, the parameter SRO measures the deviation at short range from the random state, with the negative values down to $1 - 1/x$ (ordering tendencies) and the positive values up to 1 (clustering tendencies); 0 corresponds to the random state.

Table 2. The SRO parameters α_1 in $\text{Au}_{1-x}\text{Fe}_x$ alloys deduced from the ^{57}Fe Mössbauer spectra

x	α_1 (before annealing)	α_1 (after annealing)
0.010	0.00054(60)	-0.00146(75)
0.015	0.00149(15)	-0.00241(14)
0.020	0.0083(12)	0.0012(51)
0.030	0.0046(23)	-0.0019(12)

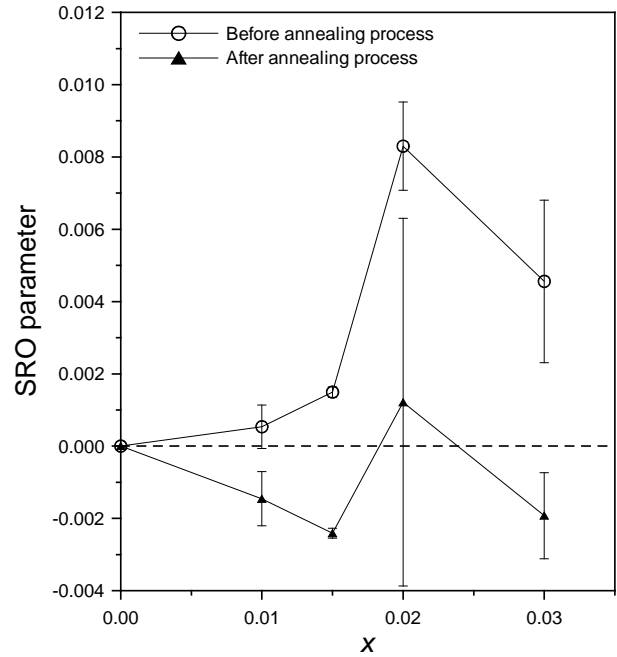


Fig. 3. The SRO parameter α_1 as a function of fraction x of Fe atoms in the $\text{Au}_{1-x}\text{Fe}_x$ alloys.

The SRO parameters α_1 for $\text{Au}_{1-x}\text{Fe}_x$ alloys calculated using Eq. (3) are presented in Table 2 and Fig. 3. The sign inversion of α_1 in the samples on annealing process indicates that the dissolved iron atoms change behavior. In the samples just after melting in which atoms being frozen-in high temperature state, close to the melting point, the iron atoms form clusters. But after annealing process when the observed distributions of atoms should be frozen-in state corresponding to the temperature $T_d = 500(50)$ K, iron clusters disappear and alloy exhibits ordering tendencies. In terms of interactions it means that the interaction between two Fe atoms is attractive (predominance of Fe-Fe bonds) at high temperatures close to the melting point and repulsive (predominance of Fe-Au bonds) when the temperature is close to 500 K.

The binding energy E_b between two Fe atoms in Au matrix

The binding energy E_b for a pair of Fe atoms in the studied materials was calculated using the obtained c_0 and c_1 values. The calculations were performed on the basis of the modified Hryniewicz-Królas formula [3, 5], which can be written as

$$(5) \quad E_b = -kT_d \cdot \ln[(1 + 2c_1/c_0) \cdot (c_1/c_0) \cdot (1 + 2p(1)/p(0))^{-1} \cdot (p(1)/p(0))^{-1}]$$

In Eq. (5), k is the Boltzmann constant, T_d denotes the “freezing” temperature for the atomic distribution in the alloy under consideration ($T_d = 500(50)$ K), whereas $p(0)$ and $p(1)$ are the probabilities for the existence of zero and one Fe atoms among all N atoms located in the first coordination sphere of ^{57}Fe probe in the corresponding random alloy (for f.c.c. lattice $N = 12$). The values of p are computed with the binomial function $p(n) = [N!/((N-n)!n!)]x^n(1-x)^{N-n}$, where $n = 0$ or 1 and x stands for a concentration of iron

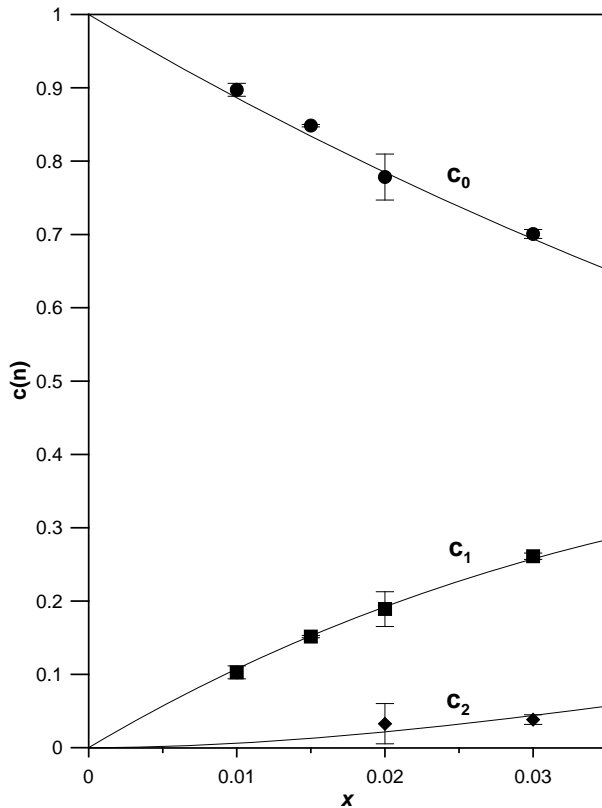


Fig. 4. A comparison between the binomial function (solid lines) and the experimentally estimated c_0 , c_1 and c_2 values in annealed $\text{Au}_{1-x}\text{Fe}_x$ alloys.

atoms in the alloy. A comparison between the binomial function and the experimentally estimated c_0 , c_1 and c_2 values is presented in Fig. 4.

The obtained E_b values are displayed in Table 3. As one can see, the positive values of E_b for the samples with $x < 0.02$ suggest that the interaction between two iron atoms in a gold matrix is repulsive. For $E_b(0.02)$ and $E_b(0.03)$, the estimated uncertainties are too large to give the proper answer what is the type of interaction in these samples. In the next step we found the extrapolated value of the binding energy E_b for $x = 0$, using the E_b values derived from data for samples with the smallest content of Fe, i.e. with $x = 0.010$ and 0.015 . Such a procedure was determined by the fact that the applied Hryniewicz-Królas method of the E_b estimation was developed for very dilute alloys – with

Table 3. The binding energy E_b between the pair of Fe atoms in $\text{Au}_{1-x}\text{Fe}_x$ alloys deduced from the ^{57}Fe Mössbauer spectra. The standard uncertainties for c_0 and c_1 result from the variance of the fit of the assumed model to the spectrum measured

x	c_0	c_1	E_b (meV)
0.010	0.8973(89)	0.1027(89)	2.93(44)
0.015	0.8485(16)	0.1515(16)	1.26(61)
0.020	0.778(31)	0.189(24)	0.4(7.3)
0.030	0.7006(61)	0.2611(43)	-0.2(1.2)

Table 4. Enthalpy $H_{\text{Au-Fe}}$ (meV/atom) of the solution of iron in gold

Calorimetric data [6]	Miedema's model [9]	This work
+62	+300	-38(12)

x close to zero. The value of $E_b(0)$ obtained this way is 6.3(2.0) meV.

Enthalpy of solution of iron in gold matrix

The $E_b(0)$ value was used to compute the enthalpy $H_{\text{Au-Fe}}$ of the solution of Fe atoms in the gold matrix. The calculations were performed on the basis of the Królas model [7] for the binding energy, according to which

$$(6) \quad H_{\text{Au-Fe}} = -z \cdot E_b(0) / 2$$

where z is the coordination number of the crystalline lattice ($z = 12$ for f.c.c. lattice of Au). The obtained value of $H_{\text{Au-Fe}}$ is presented in Table 4 together with enthalpies of solution derived from a calorimetric experiment [6] and calculated using the cellular atomic model of alloys developed by Miedema [9]. The discrepancy between our and calorimetric results may be explained by the different temperatures at which the measurements were made. The calorimetric results were taken at 1123 K. As we have shown in section 'Atomic short range order', the dissolved iron atoms at high temperatures form clusters and the enthalpy of solution in these conditions should be positive. At 500 K, the studied Au-Fe alloys exhibit ordering tendencies, which indicate the negative value of enthalpy of solution.

Conclusions

The sign inversion of SRO parameters α_1 for as-obtained gold-based Au-Fe alloys on annealing indicates that the behavior of iron atoms in the materials changes with temperature. In the samples just after preparing by melting process, iron atoms form clusters which during annealing and slow cooling are being divided into individual atoms dissolved in the Au matrix. In terms of interactions it means that the interactions between Fe atoms are attractive at high temperatures of the order of 10^3 K and repulsive when the temperature is relatively low, close to 500 K.

Positive values of E_b , the binding energy between two Fe atoms in the annealed Au-Fe alloys, suggest that the interaction between iron atoms in the gold matrix being at about 500 K is repulsive when concentration of the atoms is relatively small – not exceeding about 2 at.% in our case. This conclusion coincides with that drawn above on the basis of our α_1 values.

The enthalpy $H_{\text{Au-Fe}}$ of the solution of Fe atoms in the gold matrix at about 500 K, was found to be of negative value equal to -38(12) meV/atom. This value is at variance with the corresponding positive one derived from calorimetric data [6] and calculated using the cellular atomic model of alloys developed by Miedema [9]. The observed differences in $H_{\text{Au-Fe}}$ values coming from different sources can be explained by the temperature dependence of $H_{\text{Au-Fe}}$. Such a dependence is predicted theoretically for the Fe-Mo system [8], for example.

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