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# A Dilute-Limit Heat of Solution of Aluminium in Iron Studied with $^{57}\text{Fe}$ Mössbauer Spectroscopy

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The room temperature  $^{57}\text{Fe}$  Mössbauer spectra for binary iron-based solid solutions  $\text{Fe}_{1-x}\text{Al}_x$ , with  $x$  in the range  $0.03 \leq x \leq 0.05$ , were analysed in terms of binding energy  $E_b$  between two Al atoms in the Fe–Al system. The extrapolated values of  $E_b$  for  $x = 0$  were used for computation of the dilute-limit heat of solution of aluminium in iron. The results were compared with that resulting from the Miedema's model of alloys as well as those derived from the heat of formation of the system, obtained with both calorimetric measurements and theoretical calculations. The comparison shows that our Mössbauer spectroscopy findings are in good agreement with all the other results mentioned above.

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## 1. Introduction

The  $^{57}\text{Fe}$  Mössbauer spectroscopy is a useful tool for the study of interactions of impurity atoms dissolved in iron [1–4]. The 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. According to the data given in the literature there are many binary iron systems suitable for the studies mentioned above. At the same time from the findings concerning the impurity interactions one can easily derive the dilute-limit heat of solution of the impurity elements in iron [5]. The latter considerably increases importance of the studies as the experimental values of the heat play an essential role in developing and testing different models of binary alloys as well as methods for calculating the alloy parameters [6–12]. The main source

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of such experimental data are calorimetric studies of the heat of formation of binary systems [13]. Unfortunately, sometimes there are significant discrepancies in the data obtained by different authors. This is observed e.g. for the Fe–V alloys [14, 15]. Moreover, the calorimetric investigations are performed in relatively high temperatures at which some of iron systems are in their high-temperature  $\gamma$  (fcc) phases. Such situation exists for instance in the case of the Fe–Mn system. Consequently, there is no calorimetric data concerning the heat of solution of Mn in the low-temperature  $\alpha$  (bcc) phase of Fe. All the above encouraged us to use the  $^{57}\text{Fe}$  Mössbauer spectroscopy for supplying the experimental heats of solution of different elements in  $\alpha$ -Fe. In our previous studies we collected the proper spectra for the Fe–Cr [2], Fe–V [3], Fe–Co, and Fe–Mn [4] alloys. In this work we have extended the investigations to the Fe–Al system. For the present system the shape of a spectrum is directly affected by atoms located in the first two coordination shells of the probing nuclei [16], like in the case of the Fe–Cr, Fe–V, and Fe–Co alloys, but the effect of Al atoms from the second coordination shell is relatively small, a couple of times smaller than those located in the first coordination shell of the  $^{57}\text{Fe}$  nucleus. Taking the above into account it seems that for the purpose of determination of the interactions of Al atoms in iron the Fe–Al system should be treated like Fe–Mn [17] one i.e. a system for which the shape of the Mössbauer spectrum is directly dependent only on atoms located in the first coordination shell of the probing nuclei.

## 2. Experimental and results

The samples of iron–aluminium alloys containing 3, 4, and 5 at.% of Al, were prepared by melting the Aldrich 99.999% pure iron and 99.999% pure aluminium in an arc furnace filled with argon. Resulting ingots were cold-rolled to the final thickness of about 0.05 mm and then the foils were annealed in vacuum at 1270 K for 4 h. After that they were slowly cooled to room temperature during 6 h. Under these conditions, diffusion effectively stops at about 700 K [18], so the observed distributions of atoms in the annealed samples should be the frozen-in state corresponding to 700 K.

The room temperature measurements of the  $^{57}\text{Fe}$  Mössbauer spectra were performed in transmission geometry by means of a constant-acceleration POLON spectrometer of standard design. The spectra measured are presented in Fig. 1. They were analysed, as in our previous papers [1–4], in terms of three six-line patterns corresponding to different hyperfine fields  $B$  at  $^{57}\text{Fe}$  nuclei generated by different numbers of Fe and Al atoms located in the first or in the first and second coordination shell of the probing nuclei. It was done under assumption that the effect of Al atoms on  $B$  is additive and independent of their positions in the surroundings of the probe. Moreover, it was accepted that the hyperfine field and the corresponding centre shift  $IS$  of the subspectrum are linear functions of the number  $n$  of Al neighbours of  $^{57}\text{Fe}$  with the forms:  $B = B_0 + n\Delta B$  and

$IS = IS_0 + n\Delta IS$ , where  $B_0$ ,  $\Delta B$ ,  $IS_0$  and  $\Delta IS$  are fitted parameters;  $\Delta B$  ( $\Delta IS$ ) stands for the change of  $B(IS)$  with one Al atom in the neighbourhood of the Mössbauer probe. Finally, it was assumed that the shape of each line is Lorentzian and the three line widths  $\Gamma_{16}$ ,  $\Gamma_{25}$ , and  $\Gamma_{34}$  as well as the two line area ratios  $I_{16}/I_{34}$  and  $I_{25}/I_{34}$  are the same for all six-line components of the given spectrum. It is worth noticing that the fits obtained under these assumptions are quite good — see Fig. 2. Besides that, the found values of the best-fit parameters  $\Delta B$  and  $\Delta IS$  (displayed in Table I) are in good agreement with corresponding data given in the literature; e.g. in Ref. [16] one can find that  $\Delta B$  amounts to  $-2.50$  T.

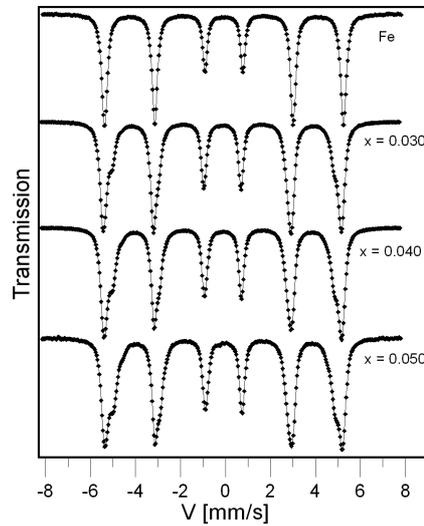


Fig. 1.  $^{57}\text{Fe}$  Mössbauer spectra for the  $\text{Fe}_{1-x}\text{Al}_x$  alloys measured at room temperature after the annealing process at 1270 K.

As the main result of the analysis the relative areas  $c_1$  and  $c_2$  of the second and third components of each spectrum were determined. The components are related to the existence of one Al atom and two Al atoms in the neighbourhood of  $^{57}\text{Fe}$ , respectively. Assuming that the Lamb–Mössbauer factor is independent of the configuration of atoms in the surroundings of the  $^{57}\text{Fe}$  nucleus, the  $c_1$  and  $c_2$  values describe intensities of the components mentioned above. The results are listed in Tables I and II.

The  $c_1$  and  $c_2$  values were used to calculate the binding energy  $E_b$  for pairs of Al atoms in the studied materials. The computations were performed, as in Refs. [1–4], on the basis of the modified Hryniewicz–Królas formula [19, 20] for a  $\text{Fe}_{1-x}\text{D}_x$  system

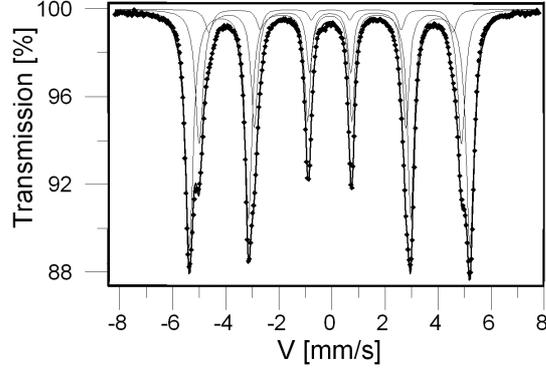


Fig. 2. The  $^{57}\text{Fe}$  Mössbauer spectrum for the  $\text{Fe}_{0.95}\text{Al}_{0.05}$  alloy measured at room temperature after the annealing process at 1270 K, fitted with three six-line subspectra.

TABLE I

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

$x$	$B_0$ [T]	$\Delta B$ [T]	$IS_0$ [mm/s]	$\Delta IS$ [mm/s]	$\Gamma_{16}$ [mm/s]
0	33.120(11)		0		0.28972(6)
0.030	32.9920(9)	-2.231(29)	0.00474(16)	-0.02384(28)	0.33600(4)
0.040	32.9220(9)	-2.176(20)	0.00834(15)	-0.02175(19)	0.33976(4)
0.050	32.902(27)	-2.169(51)	0.00407(28)	-0.02054(48)	0.3499(12)

TABLE II

The binding energy  $E_b$  between a pair of Al atoms in  $\text{Fe}_{1-x}\text{Al}_x$  alloys deduced from the  $^{57}\text{Fe}$  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 50 K.

$x$	$c_1$	$c_2$	$p(1)$	$p(2)$	$E_b$ [eV]
0.030	0.23486(56)	0.00138(46)	0.194	0.021	0.187(24)
0.040	0.29998(50)	0.02961(41)	0.240	0.035	0.0281(22)
0.050	0.3403(14)	0.0562(12)	0.279	0.051	0.0083(17)

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

where  $k$  is the Boltzmann constant,  $T_d$  denotes the “freezing” temperature for the atomic distribution in the sample ( $T_d = 700$  K),  $p(n) = [N!/((N-n)!n!)]x^n \times (1-x)^{N-n}$  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 practically 8 or  $8 + 6 = 14$  — 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 = Al. The  $E_b$  values are presented in Table II.

In the next step we found the extrapolated value of  $E_b$  for  $x = 0$  using  $E_b(0.03)$  and  $E_b(0.04)$ . Finally, the  $E_b(0)$  value was used for computation of the dilute-limit heat  $H_{\text{FeAl}}$  of solution of Al in iron. The calculations were performed on the basis of the Królas model [5] for the binding energy according to which

$$H_{\text{FeAl}} = -zE_b(0)/2, \quad (2)$$

where  $z$  is the coordination number of the crystalline lattice ( $z = 8$  for  $\alpha$ -Fe). The result is displayed in Table III together with the findings based on calorimetric measurements and theoretical calculations of the heat of formation  $H$  of the Fe–Al alloys as well as the values resulting from Miedema’s model of alloys. The heat of formation is related to the heat of solution in the following way:

$$H_{\text{FeAl}} = [dH/dx]_{x=0}, \quad (3)$$

and according to the Miedema’s model

$$H_{\text{FeAl}} = \left[ 2V_{\text{Al}}^{2/3} / (n_{\text{Fe}}^{-1/3} + n_{\text{Al}}^{-1/3}) \right] \left[ -P(\Delta\phi)^2 + Q(\Delta n^{1/3})^2 - R \right], \quad (4)$$

where  $V_{\text{Al}}$  is the atomic volume of Al,  $\phi$  is the electronegativity,  $n^{1/3}$  is the cubic root of the electron density at the boundary of bulk Wigner–Seitz cells and  $\Delta$  denotes the differences in a given parameter for Fe and Al. The coefficients  $P$ ,  $Q$ , and  $R$  are empirical constants;  $PN_{\text{A}} = 14.1 \text{ kJ V}^{-2} (\text{d.u.})^{-1/3} \text{ cm}^{-2}$ ,  $Q/P = 9.4 \text{ V}^2/(\text{d.u.})^{2/3}$  and  $R/P = 2 \text{ V}^2$  for alloys of a transition metal with a non-transition one;  $N_{\text{A}}$  is the Avogadro number, d.u. is about  $4.6 \times 10^{22}$  electrons per  $\text{cm}^3$ ;  $\phi_{\text{Al}} = 4.20 \text{ V}$ ,  $\phi_{\text{Fe}} = 4.93 \text{ V}$ ,  $n_{\text{Al}} = 2.70 \text{ d.u.}$ ,  $n_{\text{Fe}} = 5.55 \text{ d.u.}$ ,  $V_{\text{Al}} = 10.0 \text{ cm}^3/\text{mol}$ ,  $V_{\text{Fe}} = 7.1 \text{ cm}^3/\text{mol}$ .

TABLE III

The dilute-limit heat  $H_{\text{FeAl}}$  [eV/atom] of solution of aluminium in iron.

Calorimetric data [13]	Miedema’s model [6]	<i>Ab initio</i> calculations [12]	This work
−0.616(87)	−1.258	−1.068	−2.65(39)

### 3. Conclusions

The value of the dilute-limit heat  $H_{\text{FeAl}}$  of solution of aluminium in  $\alpha$ -iron, determined from the  $^{57}\text{Fe}$  Mössbauer spectra is in good agreement with corresponding value resulting from the Miedema’s model of alloys as well as those derived

from the heat  $H$  of formation of the system, obtained with both calorimetric measurements and theoretical calculations. All the  $H_{\text{FeAl}}$  values mentioned above are negative and of the order of 1 eV. This suggests that the interactions between Al atoms in iron are strongly repulsive.

Our “Mössbauer” heat  $H_{\text{FeAl}}$  amounts to  $-2.65(39)$  and its absolute value is a couple of times greater than corresponding “calorimetric” and “*ab initio*” values as one could expect. That is due to the way of computing the  $H_{\text{FeAl}}$  values on the basis of the available heats of formation  $H$  which gives underestimated values of  $H_{\text{FeAl}}$ . We also observed the same regularity concerning the Mössbauer and calorimetric data for previously studied systems of Fe with V, Cr, and Co [4].

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