



Interactions between osmium atoms dissolved in iron observed by the ^{57}Fe Mössbauer spectroscopy

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Abstract. The room temperature ^{57}Fe Mössbauer spectra for binary iron-based solid solutions $\text{Fe}_{1-x}\text{Os}_x$, with x in the range $0.01 \leq x \leq 0.05$, were analyzed in terms of binding energy E_b between two Os atoms in the Fe-Os system. The extrapolated values of E_b for $x = 0$ were used for computation of enthalpy of solution of osmium in iron. The result was compared with that resulting from the cellular atomic model of alloys by Miedema. The comparison shows that our findings are in qualitative agreement with the Miedema's model predictions.

Key words: binding energy • enthalpy of solution • iron alloys • Mössbauer spectroscopy

Introduction

It has been proved that the ^{57}Fe Mössbauer spectroscopy is a useful tool for the study of interactions of impurity atoms dissolved in iron [1–5]. In general, an appearance of impurity atoms in the vicinity of the Mössbauer probe leads to a change of the Mössbauer spectrum hyperfine parameters such as isomer shift (IS), quadrupole shift (QS), and hyperfine magnetic field (B). The technique is especially powerful when the impurity atoms 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 neighbors. The facts are worth noticing as the impurity interactions are simply related to the enthalpy of solution of the impurity elements in iron [6] and the enthalpy is widely used in developing and testing different models of binary alloys as well as methods for calculating the alloy parameters [7–11]. As far as the experimental values of the enthalpy derived from the Mössbauer spectroscopy data are concerned, they seem to be especially handy for testing purposes because the values can correspond to a system at well determined temperature, usually being about 700 K (the diffusion of atoms in iron is not observed below 700 K [12, 13]). 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 [14, 15]. The possibility is limited because the calorimetric investigations are performed in relatively high temperatures at which most of iron systems are in their high-temperature γ (fcc) phases whereas the

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Mössbauer studies can provide credible information about enthalpy of solution in low-temperature ferromagnetic α (bcc) phase. All the above encouraged us to use the ^{57}Fe Mössbauer spectroscopy for supplying the experimental enthalpy of solution of different elements in α -Fe. In this paper we present results of the enthalpy investigations for the Fe-Os system.

Experimental and results

The samples of $\text{Fe}_{1-x}\text{Os}_x$ alloys with x in the range $0.01 \leq x \leq 0.05$, were prepared by melting appropriate amounts of the Aldrich 99.999% pure iron and 99.99% pure osmium in an arc furnace filled with argon. 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 a final thickness of about 0.05 mm. In the next step, the foils were annealed in vacuum at 1270 K for 2 h. After that they were slowly cooled to room temperature over 6 h. Under these conditions, diffusion effectively stops at about 700 K [12, 13], 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 each sample 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 0.24 mm/s. Some of the spectra are presented in Fig. 1.

Each measured spectrum was fitted with a sum of certain number of different six-line patterns corresponding to unlike hyperfine fields B at ^{57}Fe nuclei generated by different numbers of Fe and Os atoms located in the first two coordination shells of the probing nuclei. The number of fitted patterns increased with concentration of Os in the samples.

The fitting procedure was done under assumption that the influence of Os atoms on B as well as the corresponding isomer shift IS of a subspectrum, is additive and independent of the atom positions in the given coordination shell of the nuclear probe although it can be different for atoms located in various shells [16]. In other words it was accepted that for each subspectrum the quantities B and IS are linear functions of the numbers n_1 and n_2 of Os atoms located, respectively, in the first and second coordination shells of ^{57}Fe and the functions can be written as follows:

$$(1) \quad \begin{aligned} B(n_1, n_2) &= B_0 + n_1 \Delta B_1 + n_2 \Delta B_2 \\ \text{IS}(n_1, n_2) &= \text{IS}_0 + n_1 \Delta \text{IS}_1 + n_2 \Delta \text{IS}_2 \end{aligned}$$

where ΔB_1 (ΔIS_1) and ΔB_2 (ΔIS_2) stand for the changes of B (IS) with one Os atom in the first and second 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 and the three line-widths Γ_{16} , Γ_{25} , and Γ_{34} for all components of a spec-

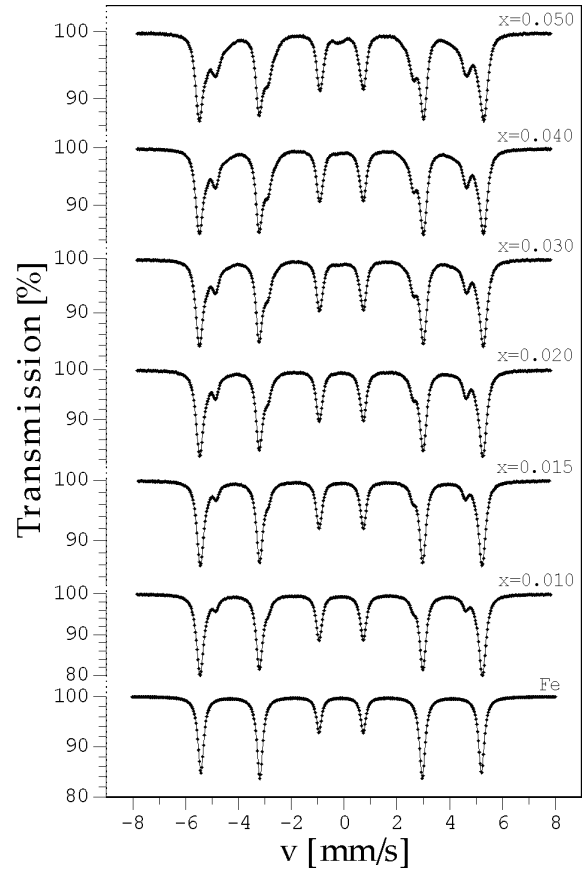


Fig. 1. ^{57}Fe Mössbauer spectra for $\text{Fe}_{1-x}\text{Os}_x$ alloys measured at room temperature after the annealing process at 1270 K.

trum which are related to the existence of impurity atoms in the two first coordination shells 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 Fe atoms. This division of subspectra into two sets with unlike linewidths takes into account the fact observed for other systems [17], that the linewidths can be influenced by an existence of large/small enough impurity atoms in the nearest neighborhood of the Mössbauer probes. It is worth noticing that the fits obtained under these assumptions are quite good – see Fig. 2a. The found values of the best-fit parameters (see Table 1) are similar to the corresponding data given in the literature [16, 18]. In Ref. [16] one can find that for the $\text{Fe}_{0.985}\text{Os}_{0.015}$ alloy $\Delta B_1 = -3.60(3)$ T, $\Delta B_2 < 0.5$ T and $\Delta \text{IS}_1 = -0.017(2)$ mm/s. In much recent work [18], it was found that the nearest neighbor single Os impurity reduces hyperfine magnetic field on the iron nucleus by 3.97 T, while the second neighbor single Os impurity decreases this field by 1.11 T. At the same time theoretical calculations based on density functional theory (DFT) give results which are different from the experimental ones; according to the calculations $\Delta B_1 = -2.70$ T, $\Delta B_2 = -0.57$ T, $\Delta B_3 = 0.38$ T, $\Delta \text{IS}_1 = -0.010$ mm/s, $\Delta \text{IS}_2 = 0.033$ mm/s and $\Delta \text{IS}_3 = 0.004$ mm/s [19].

Moreover, for spectra of annealed alloys with $x \geq 0.03$, the additional non-magnetic components were observed (Fig. 1 and Fig. 2b). These additional subspectra were accounted for by two paramagnetic singlet as such singlet components are the only ones

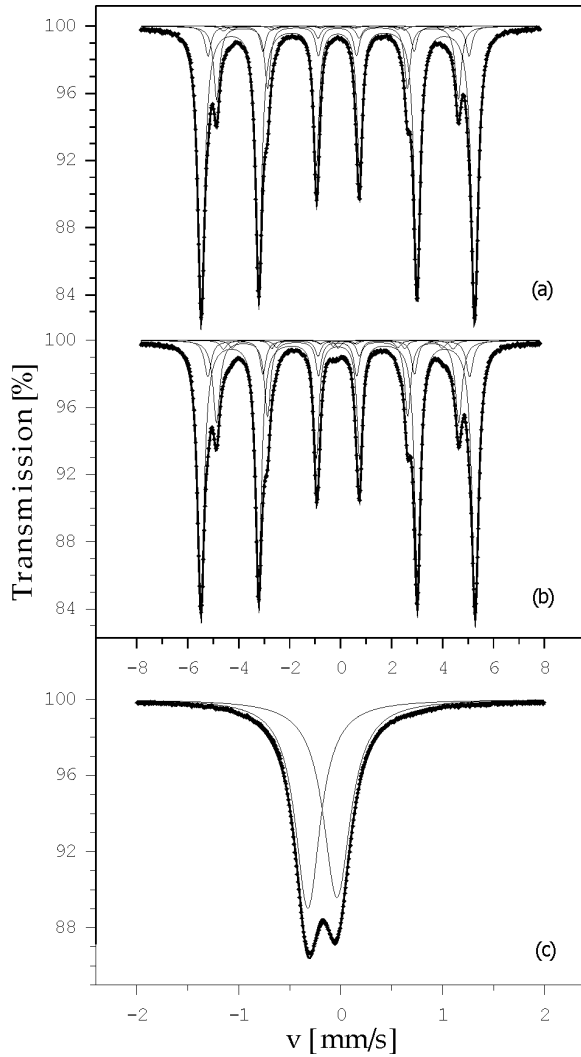


Fig. 2. The ^{57}Fe Mössbauer spectrum for the $\text{Fe}_{0.980}\text{Os}_{0.020}$ (a), $\text{Fe}_{0.970}\text{Os}_{0.030}$ (b), and $\text{Fe}_{0.800}\text{Os}_{0.200}$ (c) alloys measured at room temperature after the annealing process at 1270 K, fitted with six six-line and two single-line sub-spectra.

in the case of more concentrated systems like e.g. the $\text{Fe}_{0.80}\text{Os}_{0.20}$ alloy (see Fig. 2c) [20].

As the main result of the above analysis the values of parameters c_1 and c_2 of each spectrum were determined. Assuming that the Lamb–Mössbauer factor is independent of the configuration of atoms in the surroundings of the ^{57}Fe nucleus, the parameters are total intensities of those components of a

spectrum which are related to the existence of one and two Os atoms in the two first coordination shells of nuclear probes ^{57}Fe , respectively (see Fig. 2a).

$$(2) \quad \begin{aligned} c_1 &= c(1,0) + c(0,1) \\ c_2 &= c(2,0) + c(1,1) + c(0,2) \end{aligned}$$

where $c(n_1, n_2)$ denotes an intensity of a subspectrum determined by the Mössbauer nuclei having n_1 Os atoms in their first coordination shell and n_2 Os atoms in their second coordination shell. The results are listed in Table 2.

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

$$(3) \quad E_b = -kT_d \ln\left(\frac{(1 + 2c_2/c_1)(c_2/c_1)(1 + 2p(2)/p(1))^{-1}(p(2)/p(1))^{-1}}{p(1)}\right)$$

In Eq. (3), k is the Boltzmann constant, T_d denotes the ‘freezing’ temperature for the atomic distribution in the sample ($T_d = 700(50)$ K) whereas $p(1)$ and $p(2)$ are probabilities for the existence of one and two Os atoms among all N atoms located in the first two coordination spheres of the ^{57}Fe probe in corresponding random alloy (for bcc lattice $N = 6 + 8 = 14$). The values of p are computed with the binomial function $p(n) = [N! / ((N-n)!n!)]x^n(1-x)^{N-n}$ where $n = 1$ or 2 and x stands for a concentration of osmium atoms in the alloy. It is worth noticing that the Hryniewicz–Królás method allows to determine the value of binding energy E_b only for pairs of impurity atoms existing in a binary solid solution $\text{Fe}_{1-x}\text{D}_x$ and the E_b value can be specially credible when the solution is the only phase of the studied alloy because in such a case the concentration of impurity atoms in the solid solution can be determined quite precisely, on the basis of original weights of the alloy components. The obtained E_b values are collected in Table 2.

In the next step we found the extrapolated value of binding energy E_b for $x = 0$, using the E_b values derived from data for samples with the smallest content of Os, that is, with $x = 0.010$ and 0.015 . Such procedure was determined by the fact that the applied Hryniewicz–Królás method of the E_b estimation was developed for very dilute alloys with x close to zero. Finally, the found value of $E_b(0)$

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

x	B_0 [T]	ΔB_1 [T]	ΔB_2 [T]	IS_0 [mm/s] (relative to $\alpha\text{-Fe}$)	ΔIS_1 [mm/s]	ΔIS_2 [mm/s]
0.010	33.309(17)	-3.875(82)	-1.482(25)	0.0014(11)	-0.0164(10)	0.0209(21)
0.015	33.241(17)	-3.898(77)	-1.456(22)	0.0020(11)	-0.0182(10)	0.0230(17)
0.020	33.414(18)	-3.903(56)	-1.529(15)	0.0050(12)	-0.0177(11)	0.0243(12)
0.030	33.516(19)	-3.931(52)	-1.548(13)	0.0084(13)	-0.0164(12)	0.0271(10)
0.040	33.545(20)	-3.948(47)	-1.576(11)	0.0104(14)	-0.0170(10)	0.0258(11)
0.050	33.631(33)	-3.974(81)	-1.421(15)	0.0137(21)	-0.0183(11)	0.0216(12)
	$\text{IS}_{\text{Os-rich}}$ [mm/s] (relative to $\alpha\text{-Fe}$)			$\text{IS}_{\text{Fe-rich}}$ [mm/s] (relative to $\alpha\text{-Fe}$)		
0.200	-0.2133(30)			0.0737(31)		

Table 2. The binding energy E_b between a pair of Os atoms in $\text{Fe}_{1-x}\text{Os}_x$ 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 spectra 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]
0.010	0.1367(19)	0.00247(11)	0.1229	0.0081	0.0858(68)
0.015	0.1592(21)	0.00585(16)	0.1725	0.0171	0.0664(51)
0.020	0.2321(23)	0.0211(18)	0.2153	0.0286	0.0270(64)
0.030	0.2974(20)	0.0417(11)	0.2827	0.0568	0.0273(28)
0.040	0.3386(19)	0.0627(12)	0.3294	0.0892	0.0300(26)
0.050	0.4039(34)	0.1091(19)	0.3593	0.1229	0.0196(21)

equal to 0.125(23) eV, was used for computation of the enthalpy $H_{\text{Fe-Os}}$ of solution of osmium in iron. The calculations were performed on the basis of the Królas model [6] for the binding energy according to which

$$(4) \quad H_{\text{Fe-Os}} = -z \cdot E_b(0)/2$$

where z is the coordination number of the crystalline lattice ($z = 8$ for $\alpha\text{-Fe}$). The resulting value of enthalpy $H_{\text{Fe-Os}}$ of solution, which is $-0.500(92)$ eV/atom was compared to the value of -0.177 eV/atom, obtained from the cellular atomic model of alloys developed by Miedema [7].

Conclusions

The positive value of the binding energy E_b between two osmium atoms in single-phase, ferromagnetic solid solutions $\text{Fe}_{1-x}\text{Os}_x$ with x not exceeding about 0.02 suggests that the Os atoms interact repulsively in the materials. In case of alloys with higher Os concentration, $x \geq 0.03$, we also received positive values for the binding energy E_b , but they are not very precise due to the clustering process of Os atoms. The clustering process leads to a local increase in osmium concentration and nucleation of new phases with hcp and fcc structures. Consequently the concentration of Os in the solid solution is different from the known value of x for the whole alloy, used in the E_b computations.

The value $-0.500(92)$ eV/atom for the enthalpy $H_{\text{Fe-Os}}$ of solution of osmium in α -iron, derived from the ^{57}Fe Mössbauer spectra, is in qualitative agreement with that of -0.177 eV/atom, resulting from the semi-empirical Miedema’s model of alloys which is based on hundreds calorimetric data concerning the heat of formation for different binary systems. Both $H_{\text{Fe-Os}}$ values mentioned above are negative but absolute values of them are essentially different.

Although till now, in the available literature, one cannot find proper theoretical calculations of $H_{\text{Fe-Os}}$, we hope that our experimental findings presented in this paper will stimulate such computations in future, just as it happened for instance in the case of the Fe-Mo system.

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