

## Charge and spin density perturbation on iron atom due to osmium impurity in metallic iron

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**Abstract** Samples of natural  $\alpha$ -Fe doped randomly with Os impurities up to about 9 at.% have been investigated by means of the 14.41 keV Mössbauer absorption spectroscopy of  $^{57}\text{Fe}$  vs. Os concentration and at room temperature. It has been 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. More distant impurities slightly increase iron hyperfine field. There are no discernible effects of the Os-Os interaction on the magnetic field seen by iron. On the other hand, the electron charge density on the iron nucleus is increased by the nearest neighbor Os atom as seen via changes in the isomer shift, i.e. via changes in the spectral shift. The second neighbor impurity has the opposite effect on the charge density. More distant impurities tend to decrease the charge density as well. The effect of the first and second neighbor impurities decreases with increasing overall Os concentration indicating some Os-Os interaction influencing a charge density of the conduction electrons seen on the iron nucleus.

**Key words** Mössbauer spectroscopy • charge and spin density • impurities in metal

### Introduction

The Mössbauer spectroscopy is sensitive to the charge and spin density of the electrons on the resonant nucleus. Ferromagnetically ordered alloys rich in iron and isostructural with the metallic  $\alpha$ -Fe exhibit two major contributions to the hyperfine field seen by the iron nucleus in the vicinity of the magnetic saturation region. The first one is due to the local ionic spin density, while the other one is due to the transferred spin density of the conduction band polarized by the ionic magnetic moments. On the other hand, the charge density on the resonant nucleus is perturbed by the conduction electrons of the mainly s-like character, while compared with the charge density of the isolated iron ion. One has to note that conduction electrons are strongly perturbed in the vicinity of the iron ion. One can add some non-magnetic randomly diluted substitutional impurities, and study their influence on the magnetic splitting and isomer shift [2, 3].

Impurities above mentioned perturb conduction electrons, and such perturbations depend mainly upon distance between the impurity and the point of observation, i.e. the resonant nucleus. Usually one can assume that these perturbations are additive in terms of the respective densities, i.e. charge or spin densities. Perturbation range is rather small, at least for the spin densities, and it stays in the latter case usually within three nearest neighbor shells. In many cases perturbations beyond the second shell cannot be attributed to a particular shell, and they contribute to the average field at most [8].

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**Table 1.** Chemical composition of the investigated iron-osmium alloys.

Sample	0	1	2	3	4	5
$c$ [at.%]	0	$0.64 \pm 0.12$	$2.67 \pm 0.36$	$4.74 \pm 0.26$	$6.33 \pm 0.59$	$9.11 \pm 1.32$

## Experimental

Samples of about 1 g each were prepared by arc melting of the respective amounts of natural metallic iron having 99.97+ at.% purity and osmium of 99.9 at.% purity. Samples were melted three times under argon atmosphere in order to achieve high homogeneity. Electron microprobe analysis was performed on each sample in five distinctly different areas scanning two or three rectangles in each of the above areas with the resolution  $2 \times 2 \mu\text{m}$ . Rectangles were scanned looking at about  $100 \times 100$  pixels. Samples were found to be fairly homogeneous except the highest osmium concentrations. Average osmium concentrations determined by the micro-probe method are shown in Table 1.

Mössbauer absorbers were prepared as powders obtained using a diamond file, and distributed in the epoxy resin discs. Approximately  $30 \text{ mg/cm}^2$  of Fe was used. Spectra were collected at room temperature using a commercial  $^{57}\text{Co}(\text{Rh})$  source of 25 mCi activity. A pure iron foil was used to calibrate the velocity scale. Shifts are reported relative to the shift of the pure iron kept at room temperature.

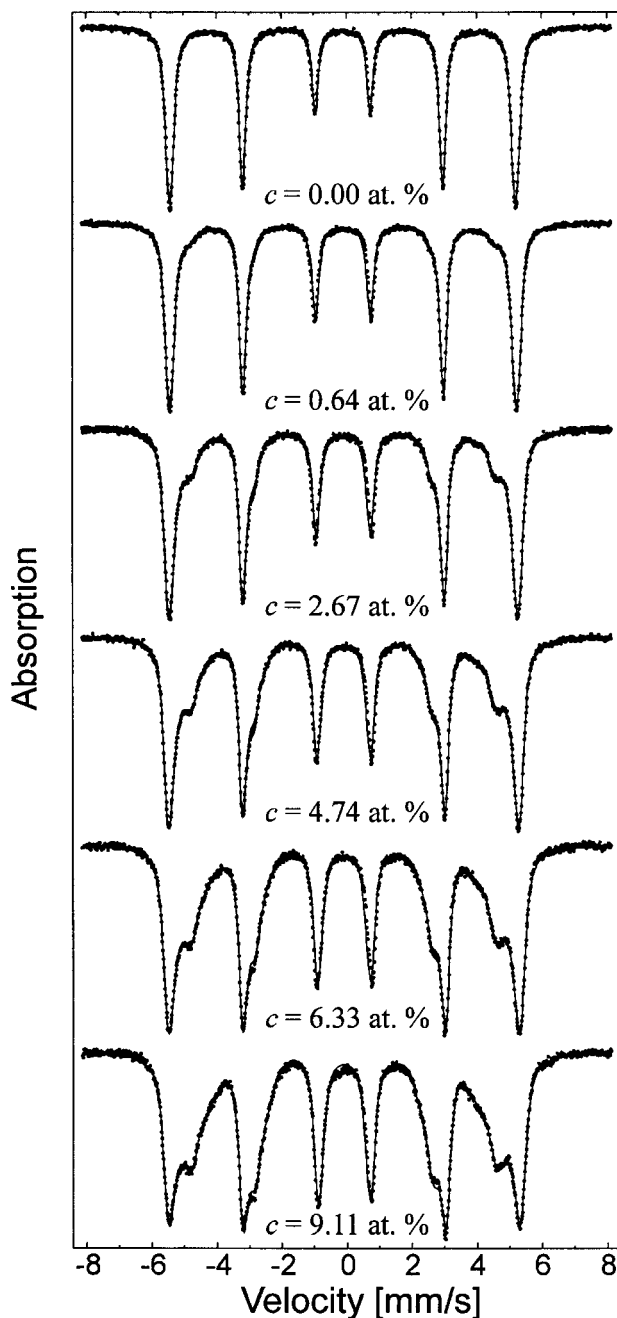
## Results and discussion

Mössbauer data were evaluated applying *Gmbern* program [1] of the MOSGRAF Mössbauer data evaluation software system [5, 6]. Data evaluation procedure was the same as discussed in Ref. [1]. Spectra fitted in the above mentioned manner are shown in Fig. 1 for  $\sigma = 2$  model [1], where  $\sigma$  stands for the number of shells to the outermost shell surrounding the resonant atom inclusively taken into account. Resulting model parameters are listed in Table 2. Parameters of this table have the same meaning as in Ref. [1], where  $c$  stands for the atomic impurity concentration, while  $\langle B \rangle_\sigma$  and  $\langle S \rangle_\sigma$  denote average field and shift, respectively. The parameters  $B_0^{(\sigma)}$  and  $S_0^{(\sigma)}$  denote field and shift due to all shells beyond the  $\sigma$  shell, respectively, provided all sites within all shells till the  $\sigma$  shell inclusive are occupied by iron. Finally, parameters  $\Delta B_s$  and  $\Delta S_s$  denote respective contributions due to a single impurity located in the shell  $s$ , where  $s = 1, 2, \dots, \sigma$ . The evolution of some of the above parameters with the varying osmium concentration is shown in Fig. 2.

In general, electron charge density on the iron nucleus decreases upon alloying osmium into  $\alpha$ -Fe as the average isomer shift increases with increasing osmium concentration. Osmium impurities located in distant shells cause a decrease of this charge density. A similar effect is observed for impurities located in the second shell. The average shift and a contribution due to distant shells scale linearly with the osmium concentration. On the other hand, effects due to a single impurity located in the first two shells tend to diminish with the increased osmium concentration indicating relevance of some Os-Os interactions within the

system as long as the charge density is considered. It has to be noted that Os as a second neighbor tends to decrease charge density, while the same Os as the first neighbor causes an increase in the electron charge density. Distant Os atoms have smaller effect on the charge density as compared with the effect of distant Pd atoms on the charge density [1].

The average hyperfine magnetic field on the iron nucleus is strongly reduced due to the very large effect of the nearest neighbor impurities causing a strong increase in the conduc-

**Fig. 1.** Mössbauer spectra of the iron-osmium alloys.

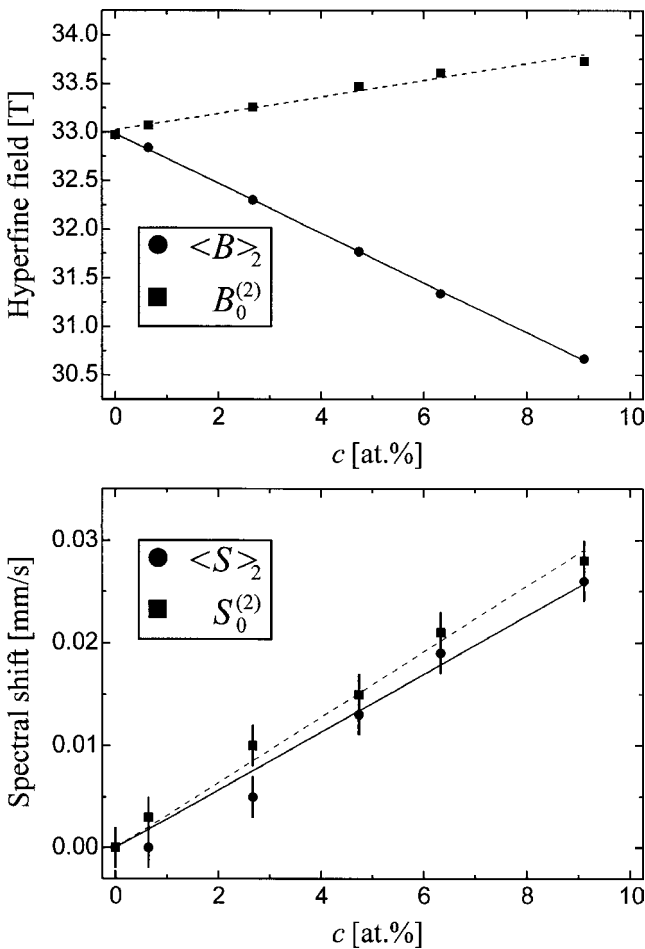
**Table 2.** Parameters of the hyperfine field and isomer shift for various Os concentrations. The last row shows respective averages, where appropriate. The value of the  $\Delta B_1$  parameter shown in *italic* was not taken into account while calculating respective average value.

$c$ [at. %]	$\langle B \rangle_2$ [T] $\pm 0.02$	$B_0^{(2)}$ [T] $\pm 0.02$	$\Delta B_1$ [T] $\pm 0.02$	$\Delta B_2$ [T] $\pm 0.02$	$\langle S \rangle_2$ [mm/s] $\pm 0.002$	$S_0^{(2)}$ [mm/s] $\pm 0.002$	$\Delta S_1$ [mm/s] $\pm 0.002$	$\Delta S_2$ [mm/s] $\pm 0.002$
0	32.97				0			
0.64	32.84	33.07	-3.99	-0.92	0	0.003	-0.077	0.018
2.67	32.30	33.26	-3.96	-1.23	0.005	0.010	-0.037	0.019
4.74	31.77	33.47	-3.98	-1.15	0.013	0.015	-0.017	0.012
6.33	31.34	33.61	-3.94	-1.14	0.019	0.021	-0.014	0.010
9.11	30.67	33.73	-3.74	-1.12	0.026	0.028	-0.012	0.009
			<b>-3.97</b>	<b>-1.11</b>				

tion electrons spin polarization on the iron nucleus. Second neighbor impurities have a similar, albeit weaker, influence. Particular contributions  $\Delta B_s$  very weakly depend upon Os concentration, and hence Os-Os interactions seem absent as long as the spin density of the conduction band is considered in contrast to the behavior of the charge density. Distant impurities have small, albeit measurable effect. They cause a decrease in the spin density of the conduction

electrons. On the other hand, distant Pd impurities have no effect on the spin density, provided they are located beyond the third shell [1].

The average fields  $\langle B \rangle$  and shifts  $\langle S \rangle$  obtained by the Hesse-Rübartsch method [4] in the same manner as in Ref. [1] are listed vs. osmium concentration in Table 3, while the resulting normalized distributions of the hyperfine field are shown in Fig. 3. The same figure shows corresponding distributions obtained by the data treatment described above. Average values obtained by the Hesse-Rübartsch method agree quite well with the values obtained by the previous method. It has to be noted that the binomial distribution method [1] does not produce simple histogram with evenly spaced points. On the other hand, hyperfine field distributions have a quite different shape for these two methods. One has to note that the Hesse-Rübartsch method [4] is a simple mathematical method having no physical background, and hence it might produce unrealistic distributions for partly resolved spectra.

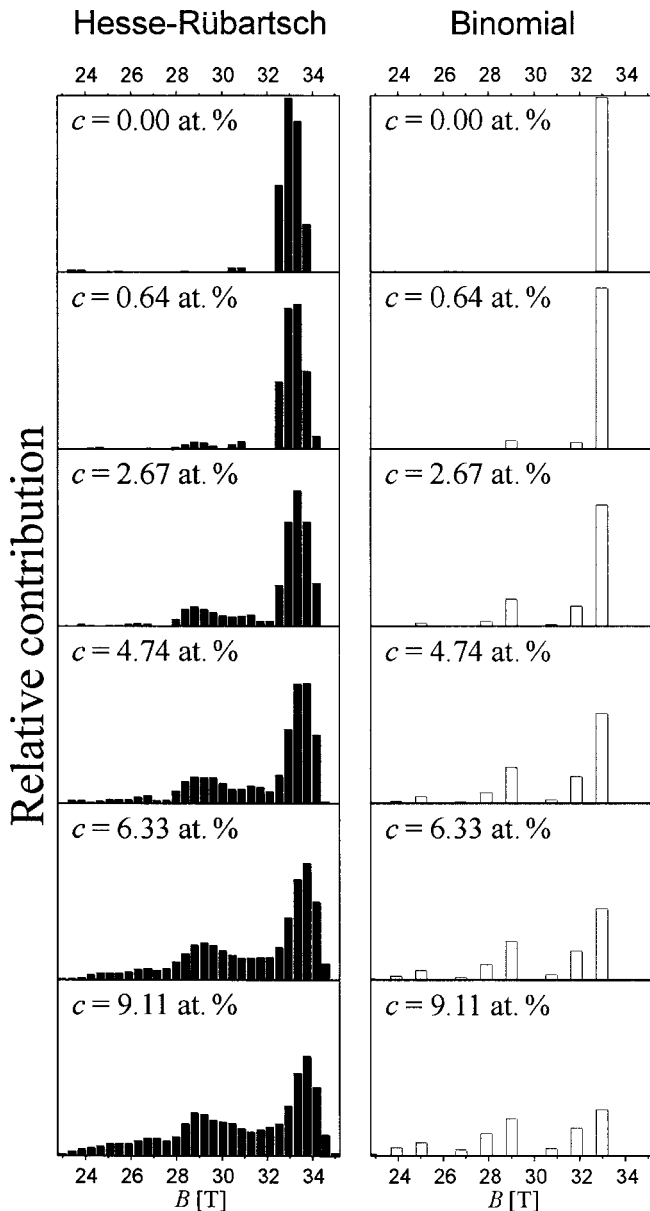
**Fig. 2.** Average hyperfine field  $\langle B \rangle_2$  and isomer shift  $\langle S \rangle_2$  plotted vs. osmium concentration together with the contribution to the field  $B_0^{(2)}$  and shift  $S_0^{(2)}$  due to the osmium impurities located beyond the  $\sigma = 2$  shell.

## Conclusions

It has been found that the perturbation of the spin density on the iron nucleus due to the Os impurity is of short range and oscillatory character. Individual impurities are able to perturb the above spin density to approximately second neighbor distance, but more distant impurities tend to change slightly the average spin density on iron. Similar perturbation of the charge density is oscillatory as well. It seems to be of somewhat longer distance than the perturba-

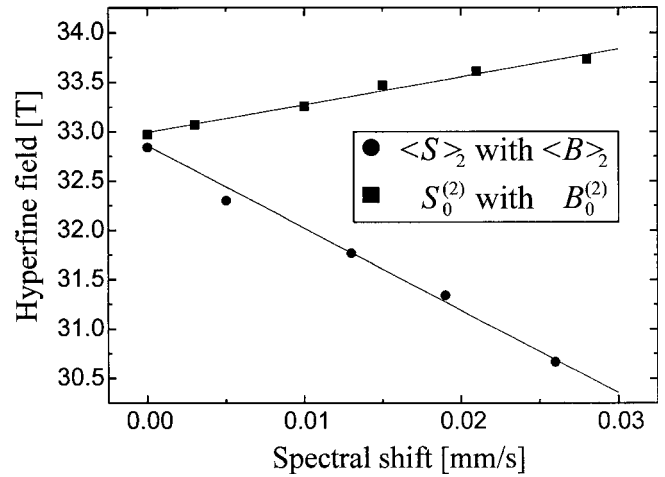
**Table 3.** Average field  $\langle B \rangle$  and average shift  $\langle S \rangle$  vs. Os concentration obtained by the Hesse-Rübartsch method.

$c$ [at. %]	$\langle B \rangle$ [T] $\pm 0.02$	$\langle S \rangle$ [mm/s] $\pm 0.002$
0	33.04	0
0.64	32.84	0.003
2.67	32.30	0.008
4.74	31.74	0.014
6.33	31.24	0.020
9.11	30.70	0.026



**Fig. 3.** Distributions of the hyperfine field obtained by the Hesse-Rübartsch method for various osmium concentrations. Distributions obtained by the binomial method are shown for comparison.

tion of the spin density, as the individual perturbation of the charge density due to a single impurity located as the first or second neighbor tends to diminish with increasing Os concentration. Figure 4 shows the correlation between the average isomer shift and the average magnetic field. The same figure shows the correlation between the shift due to distant impurities and respective contribution to the field. The average field decreases with increasing isomer shift, i.e. with decreasing charge density. On the



**Fig. 4.** Correlation between isomer shift and hyperfine field parameters.

other hand, a contribution to the field due to distant impurities increases with decreasing charge density.

Vincze and Campbell [7] investigated previously iron-osmium alloy having a nominal osmium concentration of 1.5 at.%. They found that the nearest neighbor Os atom reduces iron field by 3.6 T. The above result agrees reasonably with our results, considering that they did not performed measurements for various Os concentrations.

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