Spin- and charge density perturbations and short-range order in Fe-Cu and Fe-Zn BCC alloys: A Mössbauer study

A. Błachowski¹, K. Ruebenbauer*, J. Żukowski ², J. Przewoźnik ², J. Marzec ³, and A. Rakowska ⁴,⁵

¹Mössbauer Spectroscopy Division, Institute of Physics, Pedagogical University
PL-30-084 Kraków, ul. Podchorążych 2, Poland

² AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Department of Solid State Physics
Ave. A. Mickiewicza 30, PL-30-059 Krakow, Poland

³ AGH University of Science and Technology, Faculty of Energy and Fuels, Department of Hydrogen Energy
Ave. A. Mickiewicza 30, PL-30-059 Krakow, Poland

⁴ AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, Department of Surface Engineering and Characterization
Ave. A. Mickiewicza 30, PL-30-059 Krakow, Poland

⁵ Institute of Metallurgy and Materials Science, Polish Academy of Science
PL-30-059 Kraków, ul. Reymonta 25, Poland

*Corresponding author: sfrueben@cyf-kr.edu.pl

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Short title: Spin- and charge density and short-range order

Abstract

A model used to describe ⁵⁷Fe Mössbauer spectra for the binary BCC iron alloys rich in iron has been extended to account for the alloy crystallographic ordering. The ordering is accounted for by introducing single order parameter. Extension of the model is described in detail. The model has been tested applying it to the Fe-Cu alloys obtained by the arc melting and to the Fe-Zn alloys prepared by the solid state reaction. Random alloys are obtained up to ~2 at.% of Cu, and up to ~8 at.% of Zn. For higher impurity (minor alloy component) concentration it has been found that Cu atoms try to avoid Fe atoms in the iron matrix as nearest neighbors, while the opposite happens to the Zn atoms, albeit at much lesser scale, i.e., Zn-Zn interactions are much weaker than Fe-Zn interactions at the nearest neighbor distance. Perturbations to the iron magnetic hyperfine field (spin density) and electron (charge) density on the iron nucleus have been obtained for both series of alloys versus impurity concentration.
1. Introduction

Spin- and charge density perturbations around impurity located at a regular lattice site of the BCC \( \alpha \)-iron can be investigated by the 14.41-keV Mössbauer transition in \(^{57}\text{Fe}\). Usually, room temperature Mössbauer spectra are sensitive to the individual impurities located up to the second or sometimes to the third co-ordination shell of the resonant atom [1-3]. The best results are obtained for the random alloys with the impurity (minor component) concentration ranging from about 1 at.% till about 15 at.% Randomness of the alloys is achieved by the rapid quench from very high temperatures – usually, from the molten state. However, some impurities like copper have very limited solubility and attempt to quench over-saturated solution leads to some ordering of the system [4]. On the other hand, for some otherwise soluble impurities like zinc [4] one cannot apply above-mentioned procedure due to the high vapor pressure of the minor component. The problem of the high vapor pressure could be circumvented by using the solid state reaction but at the cost of possible ordering of the alloy – due to necessary prolonged annealing at much lower temperatures than the melting temperature. Many technologically important metallurgical procedures like heat treatment lead to the partial ordering of alloys. Hence, in some cases it might be interesting to investigate spin- and charge density perturbations described above for alloy with some order.

We have chosen Fe-Cu and Fe-Zn alloys to investigate the problem of the influence of the alloy ordering on the Mössbauer spectra. The copper solubility in \( \alpha \)-iron is very limited, i.e., about 2 at.% at 1130 K [4]. One can obtain metastable solution up to about 6.5 at.% by extremely fast quench from the melt, e.g. by the splat-cooling [5]. The zinc solubility is high and amounts to 42 at.% at 1055 K [4]. However, the vapor pressure equals 192.2 Pa at the melting point of 692.7 K, i.e., much below the melting point of iron – 1808 K [5]. Hence, the evaporation rate of zinc is much larger than the reaction rate with iron at temperature high enough to assure randomness of the alloy.

The paper is organized as follows. Section 2 describes extension of the standard model [6, 7] used to fit Mössbauer spectra in order to account for the alloy order. Section 3 is devoted to the experimental details, while results for the Fe-Cu and Fe-Zn alloys are discussed in Section 4. Section 5 summarizes conclusions.

2. Sensitivity of the Mössbauer spectra to the alloy ordering

We are going to consider binary alloy \( \text{A}_{1-x} \text{B}_x \) composed of atoms A and B. It is assumed that all atoms occupy regular crystal sites and each site is occupied. Some of the atoms A serve as nuclear probes distributed randomly among the bulk of the atoms A. The probes are otherwise indistinguishable from remaining atoms A. A concentration of the atoms B amounts to \( 0 < x < 1 \), while the concentration of the atoms A is equal \( 1 - x \). It is assumed that the alloy has homogeneous composition on the large scale. For a cubic BCC structure of the alloy one can define subsequent co-ordination shells around the probe atom A picked at random (average probe atom A). The shells are distinguished by a distance from the probe A and enumerated by the increasing distance using the index \( n = 1, 2, 3, ... \) with \( k_n > 0 \) denoting crystal sites available for each co-ordination shell. It is assumed that the shell order remains unperturbed by the presence of impurities B. Hence, one can define probability to find atom B on the lattice site belonging to the particular shell as \( p_n = x(1-s_n) \). The parameter \( s_n \) describes order parameter of the particular shell and it has to satisfy the condition \( (x-1)/x \leq s_n \leq 1 \) in order to satisfy the obvious condition \( 0 \leq p_n \leq 1 \). For
homogeneous alloy on the sufficiently large scale one has another condition satisfied. Namely, the following relationship holds:

$$\lim_{\sigma \to +\infty} \left[ \sum_{n=1}^{\sigma} k_n p_n \right] / \sum_{n=1}^{\sigma} k_n = x.$$  

(1)

Hence, one can conclude that the relationship $$\lim_{\sigma \to +\infty} \left[ \sum_{n=1}^{\sigma} s_n \right] = 0$$ is satisfied as well. The Mössbauer probe atom A is able to see impurity atom B to the second ($\sigma = 2$) or sometimes to the third ($\sigma = 3$) shell inclusive [1-3]. If one applies condition (1) to the $\sigma = 2$ model and BCC lattice one obtains $s_2 = -\frac{4}{3}s_1$ and the order of the alloy could be described by a single parameter $s = s_1$. For $\sigma = 3$ model and BCC lattice one can observe that the second and third shells belong to the same SC sub-lattice as the probe A, while the first shell belongs to the remaining SC sub-lattice. Hence, one can assume that $s_3 = s_2$. For such case one has again single order parameter $s = s_1$ with $s_3 = s_2 = -\frac{4}{3}s_1$. For BCC structure each site has $k_1 = 8$, $k_2 = 6$, $k_3 = 12$. There are no additional constrains on the parameter $s$ except $$(x-1)/x \leq s \leq 1$$ due to the additional conditions imposed above provided $x \leq \frac{4}{3}$ for $\sigma = 2$ model and $x \leq \frac{6}{17}$ for $\sigma = 3$ model. Above conditions are usually satisfied for alloys investigated by the Mössbauer spectroscopy, as it is impossible to see contribution due to the individual impurities B for alloys having large concentration of the component B [8]. It is important to remember that introduction of more than one order parameters leads to unreliable results while processing Mössbauer spectra even for the concentration $x$ kept as constant (sometimes determined independently). For $s > 0$ host atoms A try to avoid impurity atoms B as nearest neighbors and vice versa, while for $s < 0$ atoms A attract atoms B as nearest neighbors. One has $s = 0$ for random alloy obtained by either rapid quench from the very high temperature or due to the fact that interactions between nearest neighbors A – B (B – A) do not differ from the corresponding A – A and B – B interactions, as differences in the nearest neighbor binding energies are the main reason for ordering. Interaction energies responsible for ordering are those at temperatures high enough to assure rapid atomic jumps between lattice sites. It is worth noting that nearest neighbor interactions in the BCC lattice occur between two distinctly different SC sub-lattices composing BCC lattice. Further improvement of the model leads to completely unphysical results for the data fits as long as binary iron alloys are considered with iron being the major component and carrying the probe atoms (isotope). The concentration $x$ could be determined independently. However, one can obtain reliable values of the order parameter $s$ within both models with the concentration $x$ treated as variable provided it is not too small. The order parameter critically depends on the thermal history of the alloy (material) for measurements performed at room temperature or below [9].

A cluster of 14 atoms ($\sigma = 2$ model) or cluster of 26 atoms ($\sigma = 3$ model) seems insufficient to get reliable average – note that central atom is always the atom A of the probe due to the applied method of observation. Unfortunately, there are no local methods being able to see individual impurities located further away. However, things are not so bad as data are obtained by averaging over very large number of such clusters being separated by large
distances within the sample of the material. Different clusters contributing to the data practically do not overlap as the number of active probes \( A \) during the experiment is small compared to the number of the probe atoms present in the sample exposed to the resonant radiation. Such conditions occur even for the low concentration of the resonant isotope within atoms \( A \) – the latter atoms giving significant contribution to the body of the sample. Hence, the order parameter represents the average over the sample body exposed to the resonant radiation provided the recoilless fraction is nearly the same for all probe atoms in the direction of the resonant radiation beam.

The average magnetic hyperfine field on the nuclear probe atom \( \langle B \rangle_\sigma \) and the average shift of the Mössbauer spectrum versus established standard \( \langle S \rangle_\sigma \) (average electron density on the probe atom nucleus) could be calculated according to the expression [6, 7]:

\[
\langle B \rangle_\sigma = B^{(\sigma)}_0 + x \sum_{n=1}^{\infty} (1-s_n)k_n \Delta B_n ,
\]

\[
\langle S \rangle_\sigma = S^{(\sigma)}_0 + x \sum_{n=1}^{\infty} (1-s_n)k_n \Delta S_n .
\]

(2)

The symbol \( B^{(\sigma)}_0 \) stands for the field due to all atoms beyond the last co-ordination shell with discernible individual impurities, while symbols \( \Delta B_n \) denote perturbations of the field by individual impurities located in the shell with the index \( n \). Symbols \( S^{(\sigma)}_0 \) and \( \Delta S_n \) have the same meaning, albeit for the spectral shift.

Model outlined above converges to the standard model of the random alloy [6, 7] for \( s_n \equiv 0 \). Basically, it applies to the short-range order (SRO), but it has some limited sensitivity to either long-range order (LRO) or large-scale inhomogeneity. It seems that model outlined above gives all the reliable information available from the Mössbauer spectra obtained on the alloys described above as far as ordering of the alloy is concerned.

3. Experimental

The concentration \( x \) is expressed in at.% in this and subsequent sections. The alloys Fe-Cu were prepared by the arc melting of the appropriate amounts of iron (99.97+ at.% purity) and copper (99.95 at.% purity) under the argon atmosphere. Ingots of about 1.5 g were made. They were remelted two times to assure homogeneity. The mass loss was negligible during melting. The Fe-Zn alloys were obtained by the solid state reaction. The iron powder (99.9+ at.% purity: spherical, < 10 µm) and zinc powder (99.9 at.% purity: 100 mesh) were mixed in the appropriate amounts and pelletized under pressure of 5 tonnes/cm². The operation was performed under protective argon atmosphere (oxygen and water vapor pressure below 0.1 p.p.m.). Resulting pellets had diameter of 10 mm and they were about 4 mm thick. They were placed in the open fused silica tubes in the furnace under the flow of the argon-hydrogen mixture (0.1 % H₂ in argon). The samples were heated initially for 2 hours at 100 °C followed by the gradual temperature ramp (100 °C/hour) up to 500 °C, kept at 500 °C for 5 hours, and heated at 650 °C for 0.5 hour. Subsequently samples were cooled down with the furnace. The mass losses were from about 0.2 % for Fe₉₇Zn₃ to about 5 % for Fe₆₀Zn₄₀ (nominal compositions).
Powder X-ray diffraction patterns were obtained at room temperature by using D-5000 Siemens diffractometer with the Cu-K$\alpha_{1,2}$ radiation for Fe$_{80}$Zn$_{20}$ and Fe$_{60}$Zn$_{40}$ samples. A pyrolitic graphite monochromator was used on the detector side. Diffraction patterns were analyzed by the Rietveld method using the FULLPROF program.

The scanning electron microscopy has been applied to observe patterns of crystallites and to obtain some information about the chemical composition via the X-ray fluorescence. The high-resolution scanning electron microscope Nova 200 NanoSEM with the field emission gun was used. Samples were kept at ambient temperature.

Mössbauer absorbers were prepared in the powder form and mixed with epoxy resin for Fe-Cu and with B$_4$C for Fe-Zn. The thickness of the absorbers was about 30 mg/cm$^2$ of the alloy. Transmission Mössbauer spectra were collected for the 14.41-keV resonant transition in $^{57}$Fe applying commercial $^{57}$Co(Rh) source kept together with the absorbers at room temperature. The application Gmbernz of the Mosgraf-2009 suite [10] was used to process data within transmission integral approximation. All shifts are reported versus room temperature $\alpha$-iron.

4. Discussion of results

The X-ray diffraction pattern for Fe-Zn alloy with the highest zinc concentration is shown in Figure 1. The major phase is the BCC alloy with some traces of the second phase – probably the $\Gamma$ phase [4]. Inset of Figure 1 shows pattern for Fe$_{80}$Zn$_{20}$ alloy with barely discernible reflexes from above second phase. The lattice constant increases with addition of zinc in comparison with the lattice constant of pure iron (2.8665 Å).

![Figure 1](image)

Figure 1 Powder X-ray diffraction patterns obtained for the Fe-Zn alloys of the nominal composition Fe$_{60}$Zn$_{40}$ and Fe$_{80}$Zn$_{20}$. The Cu-K$\alpha_{1,2}$ radiation was used with the monochromator on the detector side. Some spurious reflections due to the Mo sample holder are seen as well as some reflections of the very small amplitude due probably to the $\Gamma$ phase. Lattice constants of the BCC phase are shown – note expansion of the lattice with addition of zinc.
Scanning electron microscope patterns for $\text{Fe}_{100-x}\text{Cu}_x$ (with nominal $x = 6, 10, 25$ at.%) are shown in Figure 2. For $x = 6$ copper concentration the alloy is close to the homogeneous solution. For $x = 10$ one can see BCC crystallites (magnetic domains) embedded in the almost pure copper web, as copper precipitates on the borders of the iron-copper solution. This pattern is enhanced for $x = 25$ sample. It was observed for the latter sample that some (almost pure) copper separated from the remainder of the ingot at the bottom. This part of the sample was excluded from further investigations. Dark spots occurring between BCC crystallites (together with copper decoration) are due to some spurious oxide containing iron.

![Figure 2 SEM images](image_url)

**Figure 2** SEM (scanning electron microscopy) images of the Fe-Cu alloys for three different nominal compositions. Black dots are due to some iron bearing oxide, and they are observed on the BCC crystallite borders. Copper (with very small amount of iron) is seen as light patterns decorating crystallites of the BCC phase. The alloy Fe$_{94}$Cu$_6$ is almost homogeneous, while the copper web appears for Fe$_{90}$Cu$_{10}$ alloy and gives significant contribution to the image area for Fe$_{75}$Cu$_{25}$ alloy. Oxide appears within the copper web.

Figure 3 shows Mössbauer spectra of the Fe-Cu alloys, while the essential results are summarized in Table 1. A dominant contribution to the spectrum is due to the iron atoms in the BCC alloy. Some traces of the iron bearing oxide are seen as small non-magnetic component (~3 %). A contribution to the non-magnetic part of the spectrum is enhanced for the highest copper concentration due to the overlap of small contribution caused by the iron atoms dissolved in the FCC copper matrix (~7 %) [11]. Perturbations to the spin density are seen to the second co-ordination shell with the dominant effect of the first co-ordination shell. Perturbations have opposite signs for the first and second shell. Perturbations of the electron density on the iron nucleus are very small and practically vanish beyond the first shell. Hence, one has to apply $\sigma = 2$ model to process data, as individual impurities beyond the second shell are not discernible. The maximum copper concentration $x$ as determined from the Mössbauer spectra is about 8 at.%. The order parameter $s$ is close to zero up to the solubility limit of about 2 at.%, i.e., the alloy is random up to this limit. A fast increase of the order parameter is observed for higher copper concentrations till 0.63 for 8.1 at.% of copper. It remains within allowed limits ($s \leq 1$), but it is really large. The positive values of the order parameter mean that copper and iron atoms try to avoid each other as nearest neighbors in accordance with the low mutual solubility. It means that Cu-Fe binding energy is much lower than Cu-Cu and Fe-Fe binding energies.
Figure 3 $^{57}$Fe Mössbauer spectra of the Fe$_{100-x}$Cu$_x$ alloys. Nominal Cu concentrations $x_{Nom}$ are shown on the left, while the actual concentrations $x$ found in the BCC phase on the right. Note presence of some spurious non-magnetic iron bearing oxide and very small contribution due to the iron dissolved in copper seen for the lowest spectrum. The spectrum of the pure iron is shown on top for comparison.
Table 1
Essential results for Fe$_{100-x}$Cu$_x$ alloys. The symbol x$_{Nom}$ stands for the nominal impurity (Cu) concentration, while the symbol x denotes impurity concentration within the BCC phase as determined from the Mössbauer spectra. The symbol s stands for the order parameter. The symbol $\langle B \rangle_\sigma$ denotes average hyperfine field on the iron nucleus, and the symbol $B_0^{(\sigma)}$ stands for the hyperfine field due to the atoms located beyond the last co-ordination shell with discernible individual impurities. Symbols $\Delta B_1$ and $\Delta B_2$ stand for the perturbations to the hyperfine field (spin density) due to individual impurities in the first and second shell, respectively. Here $\sigma = 2$ model applies. Symbols $\langle S \rangle_\sigma$, $S_0^{(\sigma)}$, $\Delta S_1$ and $\Delta S_2$ denote average spectral shift, contribution to the spectral shift (electron density on the iron nucleus) due to distant atoms beyond the last (second) shell with distinguishable individual impurities, and respective perturbations of the electron density due to the individual impurity in the first and second shell. The first row shows parameters of pure $\alpha$-iron.

<table>
<thead>
<tr>
<th>x$_{Nom}$ (at.%)</th>
<th>x (at.%)</th>
<th>s ±0.01</th>
<th>$\langle B \rangle_\sigma$ (T) ±0.02</th>
<th>$B_0^{(\sigma)}$ (T) ±0.02</th>
<th>$\Delta B_1$ (T) ±0.03</th>
<th>$\Delta B_2$ (T) ±0.02</th>
<th>$\langle S \rangle_\sigma$ (mm/s) ±0.002</th>
<th>$S_0^{(\sigma)}$ (mm/s) ±0.002</th>
<th>$\Delta S_1$ (mm/s) ±0.003</th>
<th>$\Delta S_2$ (mm/s) ±0.002</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>32.95</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>-0.99</td>
<td>0.33</td>
<td>0.006</td>
<td>0.002</td>
<td>0.018</td>
<td>0.006</td>
<td></td>
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<tr>
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<td>32.67</td>
<td>-1.23</td>
<td>0.37</td>
<td>0.009</td>
<td>0.005</td>
<td>0.018</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6.1(3)</td>
<td>32.35</td>
<td>32.53</td>
<td>-1.33</td>
<td>0.33</td>
<td>0.013</td>
<td>0.006</td>
<td>0.023</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
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<td>32.21</td>
<td>32.32</td>
<td>-1.63</td>
<td>0.38</td>
<td>0.015</td>
<td>0.010</td>
<td>0.029</td>
<td>-0.003</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>8.1(6)</td>
<td>32.32</td>
<td>32.45</td>
<td>-1.69</td>
<td>0.31</td>
<td>0.013</td>
<td>0.012</td>
<td>0.028</td>
<td>-0.006</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4 shows spectra of the Fe-Zn alloys with the important results gathered in Table 2. The non-magnetic contribution of ~2.5% is probably due to the spurious $\Gamma$ phase [12]. Perturbations to the spin density are quite significant till the third shell inclusive. They are all negative and larger in the absolute terms for the third shell in comparison with the second one. Hence, they exhibit some oscillations with the distance from the impurity [13, 14]. Perturbations to the electron density on the iron nucleus extend to the third shell as well. Hence, one can use $\sigma = 3$ model with confidence. Hyperfine parameters are in fair agreement with results obtained for metastable Fe-Zn alloys prepared by the R. F. cathode sputtering [15]. The maximum zinc concentration as determined from the spectra amounts to ~11 at.%. The order parameter s is virtually zero till 8.1 at.% of zinc and becomes increasingly negative with the further increase of the zinc concentration – albeit within allowed limits. Hence, the alloy is random up to about 8 at.% of zinc despite quite low temperature of synthesis. Negative values of the order parameter at higher concentrations are in agreement with the significant solubility of zinc in iron. Namely, the binding energy between iron and zinc atoms is much larger than binding energy between zinc atoms. On the other hand, Zn-Fe binding energy is not very dissimilar from the Fe-Fe binding energy giving quite large solubility of zinc in iron. The smallness of the binding energy between zinc atoms is in agreement with the exceptionally high vapor pressure of zinc at relatively mild temperatures. This fact in conjunction with the large energy barrier for the zinc atom to enter bulk iron makes it almost impossible to obtain alloy of the significant zinc concentration from the melt.
Figure 4 $^{57}\text{Fe}$ Mössbauer spectra of the Fe$_{100-x}$Zn$_x$ alloys. Nominal Zn concentrations $x_{\text{Nom}}$ are shown on the left, while the actual concentrations $x$ found in the BCC phase on the right. Note presence of some non-magnetic spurious phase – probably the Γ phase. The spectrum of the pure iron is shown on top for comparison.
Table 2

Essential results for Fe_{100-x}Zn_{x} alloys. The symbol \( x_{\text{Nom}} \) stands for the nominal impurity (Zn) concentration, while the symbol \( x \) denotes impurity concentration within the BCC phase as determined from the Mössbauer spectra. The symbol \( s \) stands for the order parameter. The symbol \( \langle B \rangle_{\sigma} \) denotes average hyperfine field on the iron nucleus, and the symbol \( B_{0}^{(\sigma)} \) stands for the hyperfine field due to the atoms located beyond the last co-ordination shell with discernible individual impurities. Symbols \( \Delta B_{1} \), \( \Delta B_{2} \) and \( \Delta B_{3} \) stand for the perturbations to the hyperfine field (spin density) due to individual impurities in the first, second and third shell, respectively. Here \( \sigma = 3 \) model applies. Symbols \( \langle S \rangle_{\sigma} \), \( S_{0}^{(\sigma)} \), \( \Delta S_{1} \), \( \Delta S_{2} \) and \( \Delta S_{3} \) denote average spectral shift, contribution to the spectral shift (electron density on the iron nucleus) due to distant atoms beyond the last (third) shell with distinguishable individual impurities, and respective perturbations of the electron density due to the individual impurity in the first, second and third shell.

<table>
<thead>
<tr>
<th>( x_{\text{Nom}} ) (at.%)</th>
<th>( x ) (at.%)</th>
<th>( s )</th>
<th>( \langle B \rangle_{\sigma} ) (T) ±0.02</th>
<th>( B_{0}^{(\sigma)} ) (T) ±0.02</th>
<th>( \Delta B_{1} ) (T) ±0.03</th>
<th>( \Delta B_{2} ) (T) ±0.02</th>
<th>( \Delta B_{3} ) (T) ±0.02</th>
<th>( \langle S \rangle_{\sigma} ) (mm/s) ±0.002</th>
<th>( S_{0}^{(\sigma)} ) (mm/s) ±0.002</th>
<th>( \Delta S_{1} ) (mm/s) ±0.002</th>
<th>( \Delta S_{2} ) (mm/s) ±0.002</th>
<th>( \Delta S_{3} ) (mm/s) ±0.002</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>3.5(1)</td>
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<td>32.96</td>
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<td>0.004</td>
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<td>0.089</td>
<td>-0.028</td>
</tr>
<tr>
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<td>0.03(3)</td>
<td>31.73</td>
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<td>-0.08</td>
<td>-1.22</td>
<td>0.049</td>
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<td>0.099</td>
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</tr>
<tr>
<td>10</td>
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<td>0.02(5)</td>
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<tr>
<td>20</td>
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<tr>
<td>30</td>
<td>10.5(3)</td>
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<td>32.71</td>
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<tr>
<td>40</td>
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<td>28.76</td>
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<td>-0.002</td>
<td>0.093</td>
<td>0.109</td>
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</table>

The average hyperfine field \( \langle B \rangle_{\sigma} \) and average spectral shift \( \langle S \rangle_{\sigma} \) are plotted versus impurity concentrations \( x \) in Figure 5 for both alloys, i.e., for \( \sigma = 2 \) and \( \sigma = 3 \) models. The linear dependence survives into ordered region for Fe-Cu alloys, where the impurity solubility is very low and the spectrum sensitivity to the impurities is low as well. Derivatives \( d \langle B \rangle_{\sigma} / dx \) and/or \( d \langle S \rangle_{\sigma} / dx \) could be used to determine impurity concentration up to 6 at.% of Cu and 8 at.% of Zn by measurement of the respective average hyperfine parameter \( \langle B \rangle_{\sigma} \) and/or \( \langle S \rangle_{\sigma} \).

Figure 5 Plot of the average magnetic hyperfine field on the iron nucleus \( \langle B \rangle_{\sigma} \) and the average spectral shift relative to the shift in \( \alpha \)-iron \( \langle S \rangle_{\sigma} \) versus impurity concentration \( x \) in the BCC phase of Fe_{100-x}Cu_{x} and Fe_{100-x}Zn_{x} alloys. First derivatives of the above quantities \( d \langle B \rangle_{\sigma} / dx \) and \( d \langle S \rangle_{\sigma} / dx \) are listed for the linear regions at low impurity concentrations.
The order parameter shown in Figure 6 increases in absolute terms with the increasing impurity concentration $x$. This is quite understandable as the ordering (clustering) becomes faster under nearly the same thermodynamic conditions while approaching the percolation limit from below. The percolation limit amounts roughly to $x = k^{-1}$ for a cubic environment and random alloy, i.e., $x = 12.5$ at.% for a percolation limit in the BCC lattice. The order parameter increases roughly in the linear fashion for the BCC Fe-Cu alloy in the range $2-8$ at.% of copper concentration.

![Figure 6](image.png)

**Figure 6** Plot of the order parameter $s$ versus impurity concentration $x$ in the BCC phase of Fe$_{100-x}$Cu$_x$ and Fe$_{100-x}$Zn$_x$ alloys. The black dot representing pure $\alpha$-iron is shown, too, with the order parameter set to zero by definition.

### 5. Conclusions

Crystallographic ordering (clustering) of the binary alloys is quite complex problem. Microscopic (local) methods could be used to obtain some valuable information, but one has to realize that their power is limited. Things are relatively easy for alloys with very diluted impurities being (some of them) simultaneously local nuclear probes. In such case one can estimate relative ratio of impurity monomers to dimers provided the hyperfine interactions are sensitive to the impurity as the nearest neighbor [16]. For alloys bearing nuclear probes within the major component (host) things are quite different. First of all the minor component cannot be too diluted in order to see any useful signal. On the other hand, unwanted (very diluted) impurities are less relevant as for the first case, where they might have concentrations comparable with the investigated species and therefore they may perturb the signal seriously – if coupled to the impurities investigated.

It has been shown that above outlined model with single order parameter (two parameters describing crystallography at most: $x$ and $s$) is numerically stable. The stability is achieved provided the minor component of the BCC alloy has sufficient influence on the hyperfine parameters (hyperfine field and/or electron density on the nucleus) to the second or third coordination shell of the nuclear probe. Actually, perturbations of the hyperfine interactions caused by individual impurities cannot be seen beyond the third shell of the probe. The model presented here accounts for all configurations of impurities within shells around the nuclear probe with discernible individual impurities. It is important feature as for ordered alloys one
cannot decide \textit{a priori} which configuration is negligible. It relies as well on the average impurity concentration within the BCC phase reducing the number of adjustable parameters.

There are many models trying to describe order of the BCC binary iron alloys with iron being the major component and simultaneously bearing the local nuclear probes, i.e., Mössbauer atoms [9, 17-19]. Some of them are very sophisticated and rely on multiple adjustable parameters. The advantages of the model outlined here seem as follows 1) it accounts for all possible atomic configurations, 2) it conserves the average impurity concentration in the particular crystal phase, 3) it uses minimal set of adjustable parameters. Hence, it is likely to produce reliable results.

References