Summary of Professional Accomplishments

Investigations of sigma-phase in iron-containing systems

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Introduction

My interest in a hard but brittle substance that mysteriously formed from a plastic iron-chromium alloy after annealing, was inspired by prof. Stanislaw M. Dubiel, in Mössbauer Laboratory of the Faculty of Physics and Nuclear Techniques of about 1996. This substance proved to be sigma-phase which is formed in this system at the fastest rate at 700°C. A drastic change in the Mössbauer spectrum - from magnetically split system of sextets, typical of disordered *bcc* phase alloy, to a single asymmetric line of the new phase – is related to a drastic change of magnetic properties (magnetic ordering temperature of sigma is about one order of magnitude lower than that of alpha). Our study of sigma has been focused on two aspects: technological and scientific. As a brittle phase appearing in steels during operation at high temperatures, it worsens their functional properties. It is therefore necessary to specify such systems in which the sigma can be expected to precipitate, to determine what factors affect the rate of its formation, and what measures should be undertaken to avoid it. Being involved in the Austro-Polish Bilateral Project, in collaboration with Dr. Bogdan Sepioł from Vienna University of Technology, novel *in-situ* measurements of the kinetics the sigma phase formation in the Fe-Cr alloy system were carried out, which significantly accelerated the analysis[1]. I have also actively participated in a study of the influence of Ti[2] and Al[3] impurities on the kinetics of the alpha-sigma transformation, which together with the mentioned above new method became later the basis for a doctoral dissertation by Dr. A. Błachowski. I have also launched a study of the kinetics of the reverse transformation, (dissolution of the sigma phase) by annealing at temperatures above 830°C, which, in collaboration with Dr. B. Sepioł, resulted in a determination of the activation energy for this process[4]. I also participated in a Bilateral Polish-Portuguese Project (collaboration with Dr. Benilde Costa from the University of Coimbra), within which the kinetics of the alpha-sigma phase transformation process induced by ball-milling was investigated[5].

A lot of our attention was devoted to the cognitive aspect of the sigma-phase. For several years I participated in the Bilateral Austro-Polish Project, initiated by prof. S. M. Dubiel, aimed at a systematic study of magnetic and dynamic properties of the sigma phase in Fe-Cr, Fe-V and Co-Cr systems. In collaboration with prof. W. Steiner and Dr. M. Reissner from Technical University of Vienna, systematic measurements of structural properties[6] and magnetic ones of the

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sigma in different alloys[7], were carried out. This resulted in a precise determination of the average magnetic moment and the magnetic ordering temperature for different alloy systems and compositions.

However, the complexity of the sigma phase i.e. its complex crystallographic structure combined with a chemical disorder causes that the interpretation of experimental results, hence the proper understanding of the studied phenomena, is not unique. For example, measurements of Mössbauer spectra in a strong external magnetic field, which were assumed to provide information on the magnetic properties of the individual sublattices, have not produced the expected results[8]. To overcome the stagnation in the study of this complex phase, electronic structure calculations of the sigma phase, in which the disorder on the individual sublattices was taken into account, were carried out. The possibility of conducting such calculations appeared recently, with the increase in a computing power and the development and implementation of appropriate methods. The calculations were based on the Green function method and the computer program prepared by prof. S. Kaprzyk was used. Here, a collaboration with prof. J. Toboła was especially fruitful with regard to the interpretation of some results. I have launched series of calculations of the electronic structure of the sigma phase using the original method, in which the disorder was addressed through a detailed analysis of several selected atomic configurations and the results were analyzed with regard to the distribution and number of nearest neighbors. This approach proved to be very successful and allowed the description of the properties of the sigma phase in four different iron-containing binary systems, as described in detail below.

A bit of history

The sigma phase was first described in 1927 as a non-magnetic component of an Fe-Cr-Ni alloy[9]. Its characteristic features were: high hardness and brittleness. Structural identification of the new phase took place in 1954 in the Fe-Cr system[10], and in 1983 the problem of occupation of the five sublattices in this system was solved, using neutron diffraction[11]. The quoted dates reflect a high degree of complexity of the sigma phase structure, which obviously generates difficulties in the interpretation of experimental results. Fe-Cr alloy system is still regarded as a model for the study of the sigma, the presence of which was found in approximately 50 two-component alloy systems[12] (five of which contain iron), and in a high number of ternary or more complicated alloys.

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The current state of the art

Knowledge of the sigma phase at the beginning of the twenty-first century can be shortly characterized as follows: There are known, in most cases, concentration and temperature ranges in which the phase forms as well as factors (e.g. stress, structural defects or foreign atoms) which can effect (accelerate or retard) the rate of its growth. From the perspective of technical applications, as brittle phase, the sigma phase is highly undesirable, since it deteriorates properties of materials and accelerates corrosion. From the crystallographic point of view, the sigma phase has been classified into broad group with a high coordination number of atoms (12-16) called Frank-Kasper phases. In Fe-Cr and Fe-V systems some magnetic properties of the sigma phase were found, however, the magnetic ordering temperatures are generally low, with the exception of iron-rich sigma-Fe-V[13]. Interpretation of the results concerning structural (XRD), magnetic (VSM) or Mössbauer measurements is ambiguous, because of the complex crystallographic structure (30 atoms spread over five non-equivalent sublattices) and chemical disorder (both types of atoms are present on all sublattices).

In this situation, I started a systematic study of this phase in two-component systems containing iron, i.e. Fe-Cr, Fe-V, Fe-Mo and Fe-Re (Project KBN N202 228837). They encompassed both measurements and theoretical calculations. The latter made it possible to unambiguously interpret experimental results.

Fe-Cr system

The study was started with the model Fe-Cr system. In order to perform the calculations it was necessary to precisely describe the crystal structure and sublattice occupancies by alloying elements. Data available in the literature were very fragmentary. Commonly used X-ray diffraction technique (XRD) was, in this case, insufficient due to low distinctness between Fe and Cr atoms. Therefore, neutron diffraction (ND) measurements were performed in the ILL in Grenoble on a series of samples of Fe-Cr (and also Fe-V) alloys, at room temperature as well as at the temperature of liquid helium

The investigated samples were prepared by a standard method i.e. by annealing the master alloy of a given composition in an appropriate temperature. In order to capture the influence of the history of the sample on the arrangement of atoms in the unit cell, the samples were subjected to various processes (rolling, annealing) before the proper annealing. Also, the process of transformation of individual samples to the sigma phase was carried out at various temperatures and for different times of annealing (up to 8 months at 700°C). Based on the results of the diffraction measurements, sublattices occupancy by alloying elements as well as the influence of history of the sample on these occupations were revealed. Both alloying elements, yet with different probabilities, were found to be present on all five sublattices. The ND measurements showed a remarkable reproducibility of crystallographic parameters and sublattice occupancies being only slightly depended on samples' preparation procedure or on the alpha-sigma phase-transformation conditions. The results obtained are described in detail in [1].

Unfortunately, the knowledge of the sublattice occupancies was insufficient to properly interpret Mössbauer measurements. A Mössbauer spectrum of the sigma phase recorded in the paramagnetic phase should consist of five subspectra (quadrupole doublets) with intensities

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proportional to the amount of iron atoms present in five sublattices, and various values of isomer shift, IS, quadrupole splitting, QS and line width G. Assuming a common value of the latter parameter for all subspectra, one should use thirteen free parameters in order to fit the spectrum. Such great number of the degrees of freedom in combination with poorly resolved structure of the spectra does not allow for an unambiguous determination of these parameters.

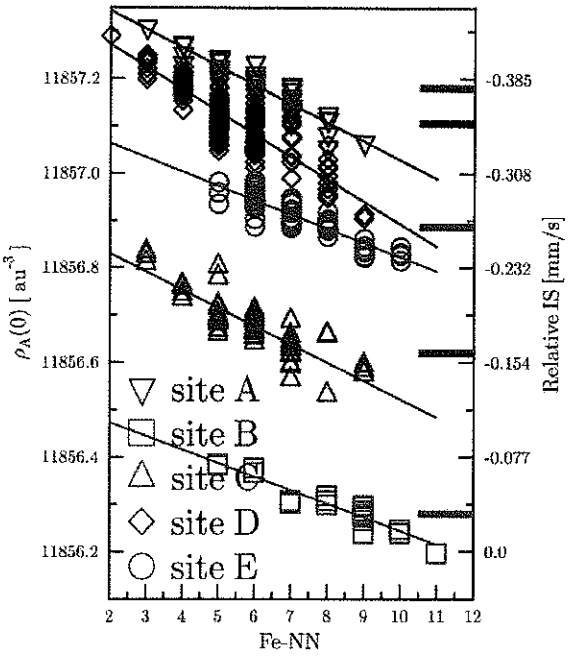

Fig. 1. *Electron densities at the nucleus of Fe calculated for each lattice site of the Fe–Cr sigma-phase (left scale) or, equivalently, isomer shifts relative to the source (right scale). Solid lines represent the best linear fits to the data. Different symbols correspond to inequivalent sites. The average values of the charge density (or isomer shifts relative to the source) are indicated on the right-hand side of the graph.*

Another step in the analysis of the sigma phase in the Fe-Cr system was to perform electronic structure calculations using the KKR method. Crystallographic structure, unit cell parameters and sublattice occupancies are well known, but for the calculations a chemical disorder of atoms should be also taken into account. Application of the coherent potential approximation (CPA) is not appropriate here for practical reasons (too long computation time) as well as physical ones: the Mössbauer spectroscopy is mainly sensitive to local phenomena, the state of the probe-atom is determined mostly by its nearest neighbors. However, the results which would be expected from the calculations assuming the CPA will provide only average values, what is not enough to properly interpret the spectrum. The calculations were carried out assuming the unit cell had a simple tetragonal symmetry where each of 30 sites was at the position resulting from the experimentally determined structure, and its occupation (Fe or Cr atom) resulted from the experimentally determined probabilities. In practice, independent calculations were done for 26 unit cells (as in ordered systems) representing selected representative configurations of atoms. Next, the results were averaged according to the defined probability distributions of particular configuration. As mentioned, these calculations must be carried out for the whole 30 atoms in the unit cell which is subject to the translational symmetry but without the chemical symmetry (occupations). This approach allowed determination of the charge density dependence in the nucleus (and thus - the relative isomer shift) as a function of the number of the nearest neighbors being the iron atoms for each sublattice (Fig. 1). The knowledge of the charge density distribution in the unit cell allowed to calculate the electric field gradient, and, consequently, QS values for each position. Based on thus obtained results we successfully fitted the Mössbauer spectra of the sigma in a paramagnetic state with only five free parameters. Four of them depend on conditions of the measurements and, as such, they cannot be determined theoretically by using the method. The results obtained are described in detail in [2].

The above-mentioned calculations were also carried out taking into account a spin polarization. Unfortunately, values of the average magnetic moment determined in that way are almost twice higher than those determined experimentally. On the other hand, an analysis of the unit cell symmetry permits an antiferromagnetic ordering at least for two of the five sublattices. It

is obvious that it is difficult to discuss antiferromagnetism in the context of disordered structures, but the calculations were carried out again with the initiation of antiparallel orientation of magnetic moments on the selected sublattices provided by the theory. Based on the results of such calculations it was found that the main source of the magnetization of the sample are iron atoms moments, but also chromium atoms have magnetic moments (induced) that are substantially smaller and oppositely oriented than those of iron atoms (Fig. 2). The average magnetic moment per atom in the unit cell calculated on the basis of this procedure agrees very well with the value obtained experimentally. The results obtained are described in detail in [3].

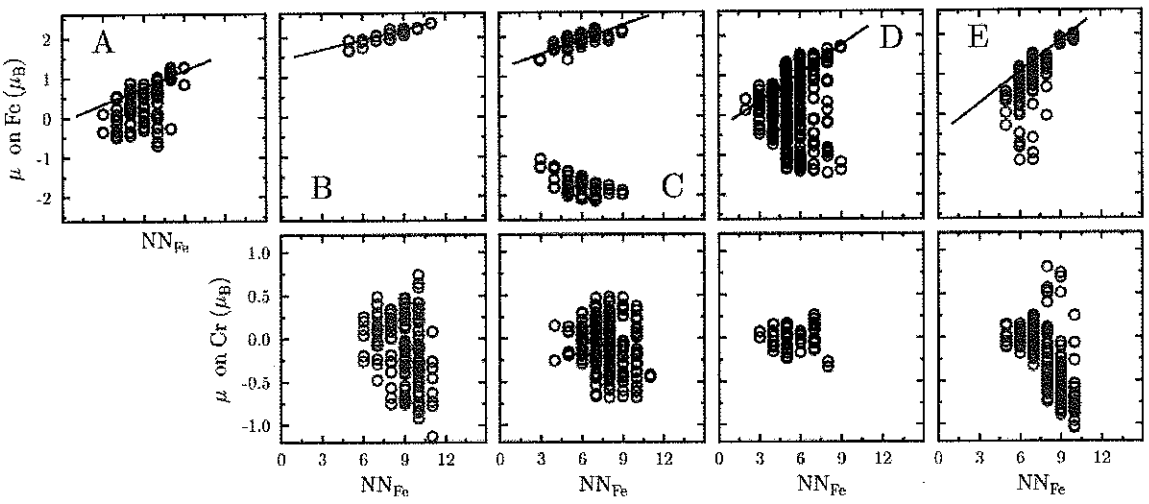

Fig. 2. *Magnetic moments of Fe and Cr atoms for five crystallographic sites versus the number of Fe atoms in the fits coordination shell, as obtained with the APM model of the magnetic ordering. Solid lines stand for the best fits to the magnetic moments in the FM ordering shown for the sake of comparison.*

Another very important aspect of the study was the calculation of the electronic structure (using KKR and KKR-CPA methods) for the analysis of the formation energy and the stability of the Fe-Cr sigma phase. An original approach, that I have proposed, is based on the determining (based on calculations of the electronic structure) of the formation energy, as a five dimensional function of occupation of individual sites by the alloying elements. Analogous functions were also determined for the configuration and magnetic entropies. This approach allowed, for the first time in such a complex chemically disordered system, to carry out the analysis of the alloy formation energy in a realistic model of the structure, taking into account the occupancies of all five non- equivalent sublattices by both alloying elements simultaneously (earlier calculations of first principles models considered the structure of a full occupancy of crystallographic sublattice by Fe or Cr only). Further calculations and measurements of various types of entropy for the alpha and the sigma phases that were performed, allowed for the analysis of the free energy in the Fe-Cr system. It was found that if the sigma phase were formed at 0K, then the sublattice occupancies would have been different than those observed. This does not occur, as the energy of the alpha phase formation at low temperature is significantly lower than that of the sigma phase. With increasing temperature the entropy part becomes dominant (in particular the configuration one), what leads to a change in the sublattice occupancies by the alloying elements. The Gibbs free energy reaches a minimum for the remaining concentrations in a very good agreement with the experimental data. The results obtained are described in detail in [4].

Fe-V system

The sigma phase in the Fe-V system is formed in a wide range of concentrations, a few times greater than in the Fe-Cr system. This offers the perfect opportunity to carry out experimental and theoretical calculations for several compositions in order to capture trends in behavior as a function of the concentrations of elements (three configurations for the calculations were chosen, corresponding to the synthesized samples). Similarly as for the Fe-Cr sigma phase, also in this case the calculations of the electronic structure were carried out using the KKR method for many possible configurations of Fe and V atoms in the cell. On this basis, the hyperfine parameters (charge densities, crystalline field gradients) of Fe and V atoms on the individual sublattices were determined, making thereby the correct analysis (reconstruction) of the Mössbauer spectra measured in the paramagnetic state. The average values of IS, <IS> as a function of alloy composition obtained from the calculations are in a very good agreement with the experimental results. A paper outlining a detailed description of the results was published in Physical Review B [5].

The existence of a magnetic order in the Fe-V sigma phase system has already been experimentally verified. A systematic study allowed to determine the magnetic ordering temperature, average magnetic moments for different alloy compositions and magnetic properties of vanadium on different sublattices (using NMR techniques). The results obtained, however, do not provide a sufficient basis for inference about the details of the magnetic ordering in individual sublattices. Therefore, the electronic structure calculations (performed in the same way as those for the Fe-Cr system i.e. taking into account spin polarization) allowed the analysis of key values characterizing magnetism, such as magnetization, and the local magnetic moments as well as the hyperfine fields. One of the results of this theoretical study was that in the Fe-V system (as opposed to Fe-Cr), there exists a critical number of the Fe atoms as nearest neighbors, NN_{crit}, below which the Fe atom does not exhibit local magnetic properties, i.e. the spin polarization of electron states disappears at this atom. If the number of Fe atoms is greater than NN_{crit}, the magnetic moment of Fe (and V) atom is nearly linearly correlated with the number of Fe atoms in the immediate vicinity. Based on the results obtained for the ferromagnetic ordering model (FM) and the antiparallel one (APM), and taking into account small differences in the energies of formation for these models, we suggested a possibility of the existence of separate subregions of the sample, in which the mentioned various types of magnetic structures can be present. This interpretation, resulting from energetically close magnetic orderings, allowed to obtain a good agreement between the results of calculations with the experimental ones (measurements of magnetization and Mössbauer measurements at low temperatures) for samples with lower vanadium content. A partial lack agreement between the

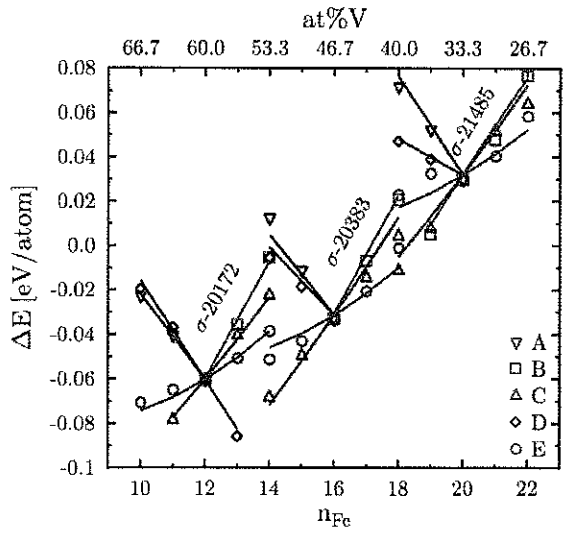

Fig. 3. *Calculated formation energy differences, ΔE, for Fe–V sigma-phase, for the chosen three basic atomic configurations and its neighborhood, versus the number of Fe atoms per unit cell (V concentration is also indicated). Solid lines stand for the best fit to the data. ΔE-values determined for occupation changes (with respect to the reference configurations) on the five lattice sites are indicated by different colors.*

experimental results and the theoretical ones, observed in the case of samples with a higher content of vanadium, is likely due to a non-collinear magnetic structure or a spin-glass structure. The latter, at this stage of the study, could not be taken into account in the calculations due to the size of the unit cell and the presence of chemical disorder. A detailed description of the results can be found in a pa per published in Intermetallics [6].

Similarly as for the Fe-Cr system, but for a much wider range of concentrations, the free enthalpy of the Fe-V sigma phase was examined, based on the KKR-calculations of the total energy (Fig. 3), as well as contributions to the entropy i.e. magnetic (based on the calculated values of the local moments) and configuration (based on disordered sublattice occupancy by Fe and V atoms). The analysis of the calculated formation energy values and the mentioned types of entropy for various configurations allowed to determine the functional form of these quantities depending on the total concentration and the sublattice occupancies (5-dimensional function). Consequently, it was possible to determine a relationship of the free enthalpy and temperature, for any concentration and any sublattice occupancy. Minimizing the so-expressed free energy made it possible to determine the sublattice occupancies as a function of temperature (Fig. 4). The results obtained were critically analyzed through the use of different methods for acquiring the data (calculations in full potential or muffin-tin approximation) and their development (different models, incorporating different quantities of free parameters). It is worth noting that the above-described free energy minimization procedure based on the calculations from the first principles applied to such a complex chemically disordered system as the sigma phase, is the crowning achievement of several years of theoretical and experimental verification. The effectiveness of this approach have provided a very good agreement between the theoretically obtained results and the experimental ones (ND, Mössbauer spectroscopy). A detailed description of the results can be found in [7].

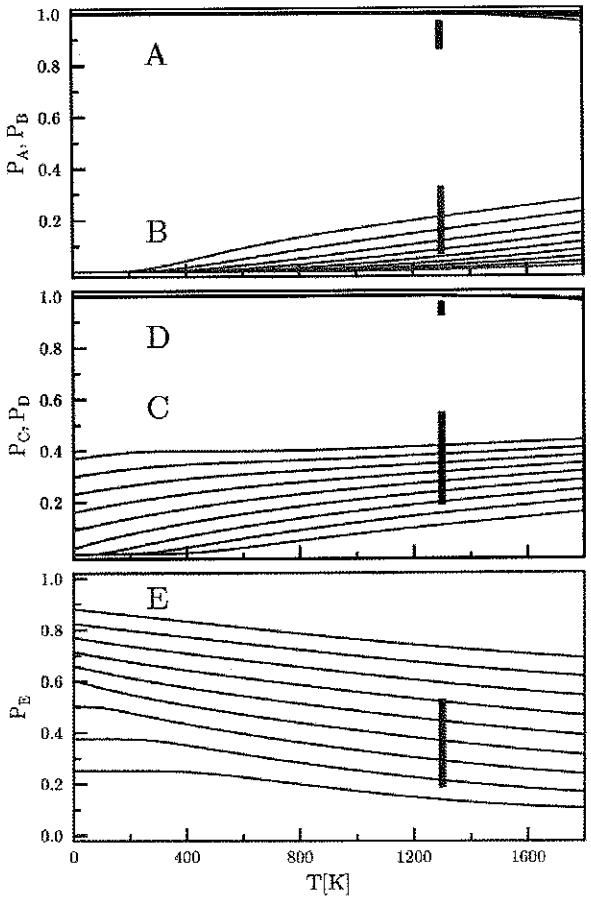

Fig. 4. *The probability of finding Fe-atoms on the five lattice sites, P_i (i=A,..,E), versus temperature. The solid lines indicate the calculated values for different compositions of the sigma-$Fe_{100-x}V_x$ with x ranging from 33 to 60 (the curves from top to bottom correspond to alloys with increasing x). The vertical bars indicate experimentally found values of P_i in the same concentration range.*

Fe-Mo system

A systematic study of the sigma phase in the Fe-Mo system was performed for the first time. In this case a sample preparation technique was different than in the previously discussed Fe-Cr and Fe-V systems, and it involves sintering of compressed powders of pure components at temperatures of about 1400°C. After the heating process was completed, sinters were quenched in liquid nitrogen. On thus obtained samples (for different concentrations of alloying elements) XRD patterns have been measured proving the sigma phase structure of the samples. We have observed that the lattice constants *a* and *c* of the tetragonal unit cell grows linearly with the increasing content of molybdenum, but their ratio remains constant (Fig. 5). In addition, we found that Mo-atoms can preferentially occupy only three (B, C and E) of the five sublattices, whereas Fe atoms are located at all sublattices (Fig. 6). The measured Mössbauer spectra were interpreted on the basis of the calculations of the electronic structure, which was carried out similarly as for the Fe-Cr and Fe-V systems i.e. both by the KKR (for multiple configurations of Fe and Mo atoms in the cell) and the KKR-CPA methods (assumption of statistical disorder).

Interestingly, in contrast to the results obtained for the Fe-Cr and Fe-V sigma phase, in Fe-Mo-system there is no a clear dependence of the electron density of each site on the number of neighbors of given type. However, this theoretical result can properly reproduce Mössbauer spectra, measured experimentally. Observed (as experimentally and theoretically) a very weak correlation of the average IS versus Mo concentration, is the result only of changes in sublattices occupancies that cause the change in the abundance of individual subspecta. Quadrupole splitting of various sites increase linearly with increasing Mo content, with the exception of the sublattice A, where this relationship is decreasing. A detailed description of the results can be found in a paper published in Intermetallics [8].

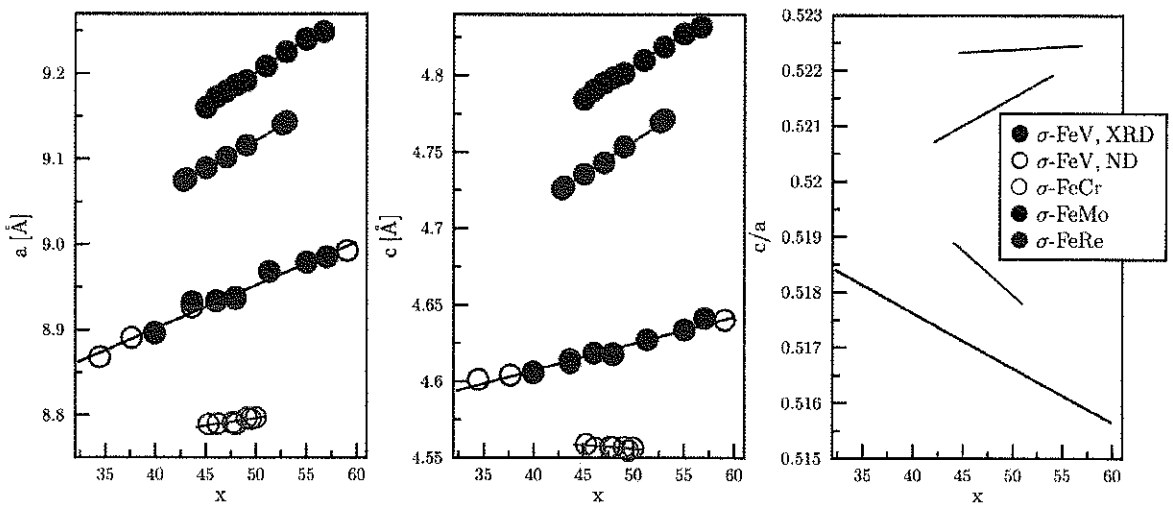

Fig. 6. *Dependence of the lattice parameters a and c as well as their ratio, c/a, of the sigma- $Fe_{100-x}M_x$ compounds (M=V,Cr,Mo,Re) versus M-concentration, as determined from the X-ray and neutron diffractograms recorded at 294 K.*

Fe-Re system

Experimental and theoretical studies of the sigma phase in Fe-Re alloys have also been undertaken for the first time. Although the Fe_3Re_2 phase was marked on the phase diagram already in 1938, but it was only in 1956 when its crystal structure was measured and interpreted as the sigma phase. By 2010 there were only five papers published in which the sigma phase in the Fe-Re system was mentioned. In four of them, the sigma-phase was always investigated "on the occasion of" studies of other phases. Unknown remained even the concentration and the temperature ranges in which this phase was present in the Fe-Re alloy system. Noteworthy, no experimental results concerning any physical properties of this phase were available in the literature so far.

The samples for investigation of the Fe-Re system were prepared by the standard technique (annealing of master alloy obtained by melting of pure components in an electric arc furnace), successively. In our study, using the X-ray diffraction and the Mossbauer effect techniques it was found that in this system, at 1530°C the sigma phase could be formed in the concentration range of 42.8-53 at% Re. Structural studies showed that the atomic positions determined in the tetragonal unit cell did not vary (within error) for samples having different concentrations, while the lattice constants *a* and *c* vary linearly with increasing Re content (Fig. 5), but their ratio increases slightly (contrary to the other systems discussed). The unit cell of the sigma Fe-Re is smaller than that observed in the Fe-Mo sigma phase, but larger than the one in the systems of Fe-Cr and of Fe-V. This observation can be related to the size of the ionic radius of the alloying atom (here Re atom). The sublattices A and D are most often occupied by Fe atoms, sublattice E to a comparable extent by Fe and Re atoms, while the occupancies of the other sublattices are dominated by Re atoms. The number of Fe atoms on the all sublattices (except A) decreases linearly with increasing

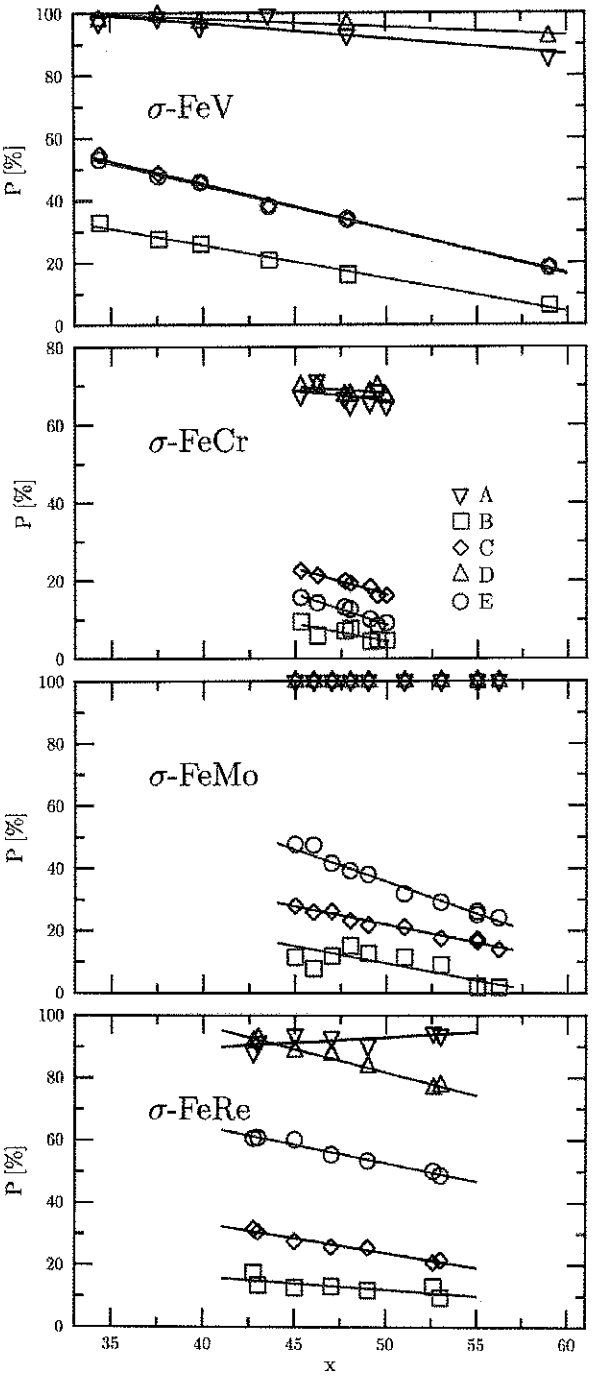

Fig. 5. Probability of finding Fe atoms at different lattice sites in the sigma- $Fe_{100-x}M_x$ compounds (M=V,Cr,Mo,Re), versus M-concentration. Error bars are smaller than the marker size. Solid lines stay for the linear fits to the data.

the content of Re. The population of Fe atoms at the sublattice A exhibits a slow growth, which is an unusual behavior i.e. not encountered in any other sigma phase alloy containing iron.

The Mössbauer spectra were measured at room temperature in a transmission geometry on powder samples (Fig. 7). A magnetic component has not been found in any of the investigated samples. A quadrupole splitting distribution analysis of the spectra, QSD, assuming a linear relationship between IS and QS, showed that increasing the content of Re practically does not change <IS>, in contrast to the Fe-V and Fe-Mo systems, where a linear dependence was observed. One should also pay attention to a very large (almost double) average quadrupole splitting, <QS>, compared with the corresponding values observed in other systems of the sigma Fe-X (X = Cr, V, Mo).

Analysis of the electronic structure of the discussed phase using the KKR method made it possible to determine the values of IS and QS for Fe atoms on each sublattice, and, consequently, enabled the correct interpretation of the Mössbauer spectra, as previously shown for the sigma Fe-Cr, Fe-V and Fe-Mo-systems. Similarly to the Fe-Mo system, in the discussed Fe-Re alloy there was no apparent correlation of the charge density with the number of the nearest neighbors of the given type, which was clearly visible in the systems of Fe-Cr and Fe-V. The KKR calculations enabled us to determine <IS>, remaining in a very good agreement with the experimentally determined values (from the quadrupole splitting distribution). The calculated QS-values are characteristic for each site and slightly increase with increasing the content of Re, except the site D, where this relationship is decreasing. As already mentioned, in comparison with the other Fe-containing sigma phases, QS-values here are significantly higher, what is consistent with the general trend of the increase of QS with increasing ionic radii of the substituent atom. The larger ionic radius obviously causes an increase of asymmetry of the charge distribution around the nucleus-probe. As shown by the calculations of the electronic structure for the Fe-Re system, electronic

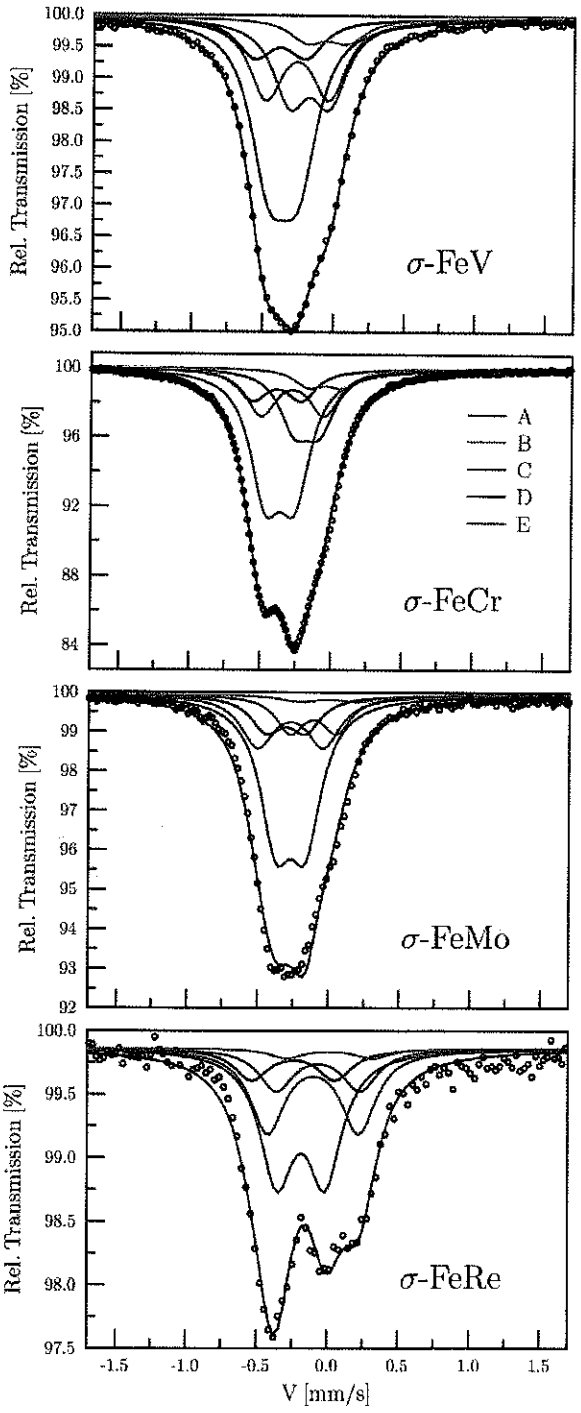

Fig. 7. ^{57}Fe Mossbauer spectra of the sigma-FeM (M=V,Cr,Mo,Re) alloys recorded at 300 K (dots) compared to the calculated ones (solid line). The subspectra related to the inequivalent sites are indicated by colored lines.

properties of the Re-atoms are primarily responsible for the high QS-values and, to a lesser extent, the expansion of the crystal lattice. A detailed description of the results can be found in [9].

At the moment the analogous comprehensive study has been extended to the selected three-component systems where the sigma phase is also present, in particular, Fe-Cr-Ni, Fe-Cr-Mo and Fe-Co-Cr (project 2012/05/B/ST3/03241 NCN). Such systems are definitely better approximation of techno-logically important alloys in which sigma phase may appear during their use. Preliminary results of both experimental and theoretical confirm the effectiveness of the proposed method for the analysis of formation energy as well as magnetic and electronic properties of the discussed phase.

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