

Application of the self-organization methods to interpret the Mössbauer spectra of Fe–N and Fe–C austenites

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The experimental Mössbauer spectra of nitrogen and carbon austenites have been treated theoretically. A new method was used based on the self-organization principles. The experimental spectra have been expanded into the components. The parameters of hyperfine interactions in the nitrogen and carbon austenites have been calculated. To interpret the measurement results, the ab-initio FLAPW calculations of electronic structure and hyperfine interactions have been performed for the Fe_{32}A_3 ($\text{A}=\text{C},\text{N}$) ordered structure that simulates nitrogen and carbon austenite. It is shown that a low intensity doublet in the spectrum of nitrogen austenite is not caused by "dumbbells" N–Fe–N configurations, but instead can be referred to the Fe atoms including one N atom in the first coordination sphere. It has been found that a similar doublet exists in the carbon austenite spectra as well. The differences in Mössbauer spectra of the nitrogen and carbon austenites are caused only by the difference in their electric field gradient and isomer shift values.

Проведена обработка экспериментальных Мёссбауэровских спектров углеродистого и азотистого аустенитов. Использован новый метод на основе принципов самоорганизации. Проведено разложение экспериментальных спектров на компоненты. Рассчитаны параметры сверхтонких взаимодействий в углеродистом и азотистом аустенитах. Для интерпретации экспериментальных результатов, ab-initio методом FLAPW, проведена серия расчетов электронного строения и параметров сверхтонкого взаимодействия в упорядоченной структуре Fe_{32}A_3 ($\text{A} = \text{C}, \text{N}$), моделирующей углеродистый и азотистый аустениты. Показано, что малоинтенсивная дублетная линия, содержащаяся в спектре азотистого аустенита, не связана с существованием гантельных конфигураций N–Fe–N, а обусловлена атомами железа, содержащими один атом азота в первой координационной сфере. Установлено, что аналогичная дублетная линия содержится и в спектре углеродистого аустенита. Различия в Мёссбауэровских спектрах углеродистого и азотистого аустенита связаны только с различными величинами градиента электрического поля и изомерного сдвига.

1. Introduction

Nitrogen and oxygen are widely used as alloying elements when obtaining austenitic steels. In contrast to carbon steels, nitrided ones exhibit unique strength properties and corrosion resistance. Numerous studies were done for gaining knowledge what kind of changes occurring in the FCC Fe matrix due to introduction of carbon and oxygen

atoms. The main tool in those research works is the Mössbauer spectroscopy. Majority of researchers provide interpretation of the experimental spectra of nitrogen austenite being based on the model which takes into consideration three types of Fe atoms: Fe_0 atoms that do not include nitrogen atoms if the first coordination sphere, and Fe_1 - and Fe_2 atoms having in the first

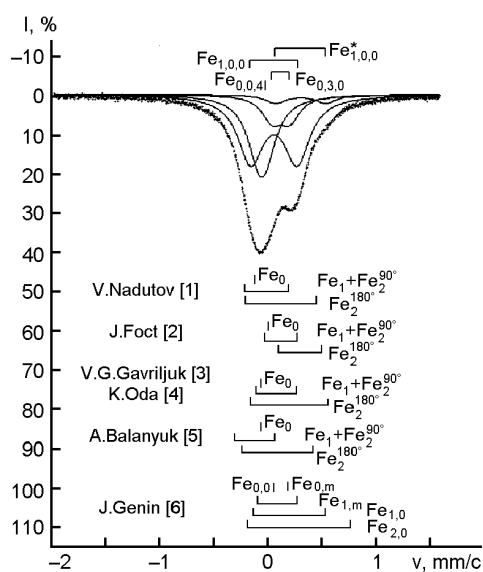


Fig. 1. Experimental Mössbauer spectrum of $Fe_{10}N$ austenite [7]. The results of spectrum expansion into components obtained in this work and by other researchers.

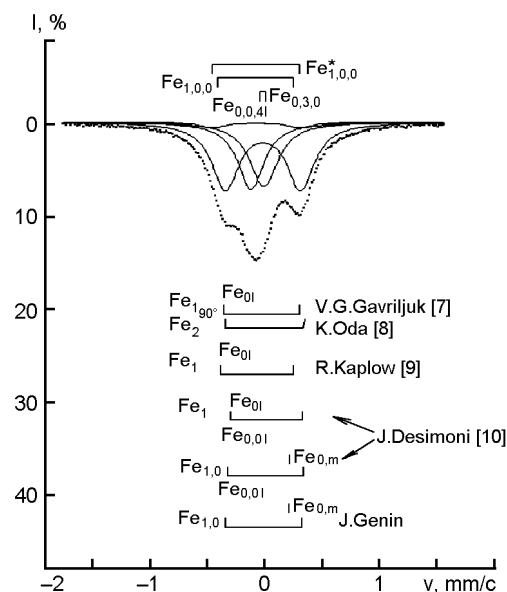


Fig. 2. Experimental Mössbauer spectrum of $Fe_{10}C$ austenite [7]. The results of spectrum expansion into components obtained in this work and by other researchers.

coordination sphere one and two nitrogen atoms, respectively. In Fig. 1, shown are expansions of those spectra into elements made by different researchers. In the carbon austenite, there are only two components related to Fe_0 and Fe_1 atoms. Same results are reported in most of publications (Fig. 2). There are numerous studies aimed at investigations of a short range order and parameters of hyperfine interactions in Fe-C and Fe-N austenites [1–11]. At the same time, different opinions exist on how to interpret the available experimental data.

In this work, we have solved two main tasks:

- the experimental Mössbauer spectra of $Fe_{10}C$ and $Fe_{10}N$ austenite have been processed to gather maximum reliable information on the hyperfine interactions parameters;
- the hyperfine interaction parameters in the ordered structures simulating $Fe_{10}C$ and $Fe_{10}N$ austenite have been calculated using high-accuracy ab-initio method. Experimental and theoretical results are analyzed in detail.

2. Results and discussions

To attain the first task, we have used a new method of experimental spectra processing [12] based on three main principles of self-organisation [13]:

- (i) synthesis of different variants of mathematical models of experimental spectrum. This principle was used to define the

model including an optimal number of resonance lines. It is assumed that the spectrum envelope curve can be presented as a superposition of separate components represented by Lorentz function. A deliberately large number of components is chosen. While searching the models containing decreasing numbers of components, the selection criteria tends to decrease, then reaches its minimum and then starts growing. At such searching, the minimum criterion value indicates the model of optimal complexity, which describes experimental spectra in most reliable way. Thus, we propose the method of mathematical modeling where the model structure is defined automatically in the course of calculation;

- (ii) a uniform estimation of the average risk value is used as the selection criterion in the method [14]:

$$\Delta = \frac{1}{n} \sum_{i=1}^n \frac{(y_i - \hat{y}_i)^2}{1 - \left(\frac{r(\ln n - \ln r + 1) - \ln \eta}{n} \right)^{1/2}}, \quad (1)$$

where y_i is the theoretical spectrum; \hat{y}_i , experimental spectrum; m , the number of Lorentz lines; n , the number of experimental points; $r = 3m + 1$, the number of degrees of freedom; η , parameter of statistical significance which regulates the number of competitive models. While processing the

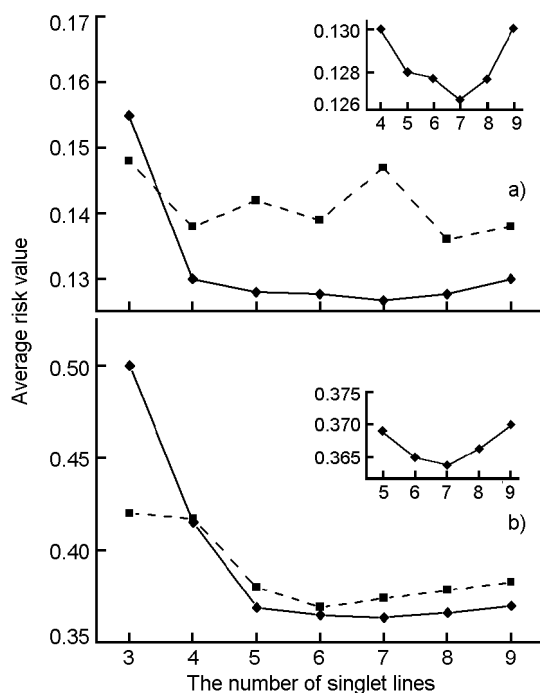


Fig. 3. Dependence of the average risk criterion on the number of singlet lines for the experimental Mössbauer spectra of Fe₁₀C and Fe₁₀N [7] alloys.

experimental spectra, it was found that such parameter does not influence significantly the value of an average risk criterion. In this work, $\eta = 0.05$ value was used;

(iii) the principle of nonterminal decision. After the calculations are performed, the several models are proposed to researcher for the spectrum expansion into elements which best describe experimental spectrum. So, certain room for decision making is offered to the researcher.

Experimental Mössbauer spectra of Fe₁₀C and Fe₁₀N austenites [7] were

processed using the above method. At the first stage, a set of competitive models for the spectrum expansion into singlet lines was obtained. In Fig. 3, the dotted line shows how the average risk criterion value depends on the number of singlet lines in the experimental spectra models of the carbon (Fig. 3a) and nitrogen (Fig. 3b) austenites. For Fe₁₀C spectrum, the dependence of the average risk criterion value on different number of components shows lower stability as compared to Fe₁₀N spectrum. This results from the number of experimental points in the spectrum. There are 512 points for the carbon austenite while 1024 for the nitrogen austenite. For Fe₁₀C spectrum, the minimum average risk criterion corresponds to the set of eight singlet line, while for Fe₁₀N spectrum the same corresponds to six singlet lines. At the second stage of spectrum processing, we have applied an algorithm of singlet lines combination binding which resulted in sufficient decrease of an average risk criterion value. We have obtained the sets consisting of both doublet and singlet lines. Dependence of the average risk criterion on the number of singlet lines for that set is shown in Fig. 3 by solid line. In the insets in Fig. 3, it is clear that for Fe₁₀C and Fe₁₀N spectra the average risk criterion value demonstrates a pronounced minimum which corresponds to the set of seven singlet lines. This set consists of one singlet and three doublet lines. For Fe₁₀C spectrum, the combination binding became the reason for more stable behavior of the average risk criterion value and occurrence of a well-defined minimum.

Thus, the calculations have shown that experimental Fe₁₀C and Fe₁₀N Mössbauer spectra consist of the same set of compo-

Table. Results of the experimental spectra processing [7] and theoretical values of the isomeric shift δ , quadrupole splitting Δ , line width Γ in mm/s and relative fraction of iron atoms p (%) for the model structures FCC-Fe₃₂A₃ (A = C,N). Isomeric shift is shown relative to α -Fe.

		Fe _{0,4}				Fe _{1,0,0}				Fe [*] _{1,0,0}				Fe _{0,3,0}			
		δ	Δ	Γ	p	δ	Δ	Γ	p	δ	Δ	Γ	p	δ	Δ	Γ	p
Fe ₁₀ C	Expansion into components	-0.11	0.00	0.28	24	-0.07	0.66	0.28	48	-0.07	0.76	0.28	4	-0.01	0.05	0.28	24
Fe ₃₂ C ₃	Theory	-0.11	0.06	0.25	19	-0.03	0.54	0.25	38	-0.04	0.81	0.25	18	-0.01	0.05	0.28	24
Fe ₁₀ N	Expansion into components	-0.06	0.00	0.28	32	0.06	0.45	0.28	42	0.30	0.47	0.23	6	0.12	0.17	0.23	19
Fe ₃₂ N ₃	Theory	-0.06	0.10	0.25	19	0.06	0.15	0.25	38	0.06	0.36	0.25	18	0.06	0.07	0.25	25

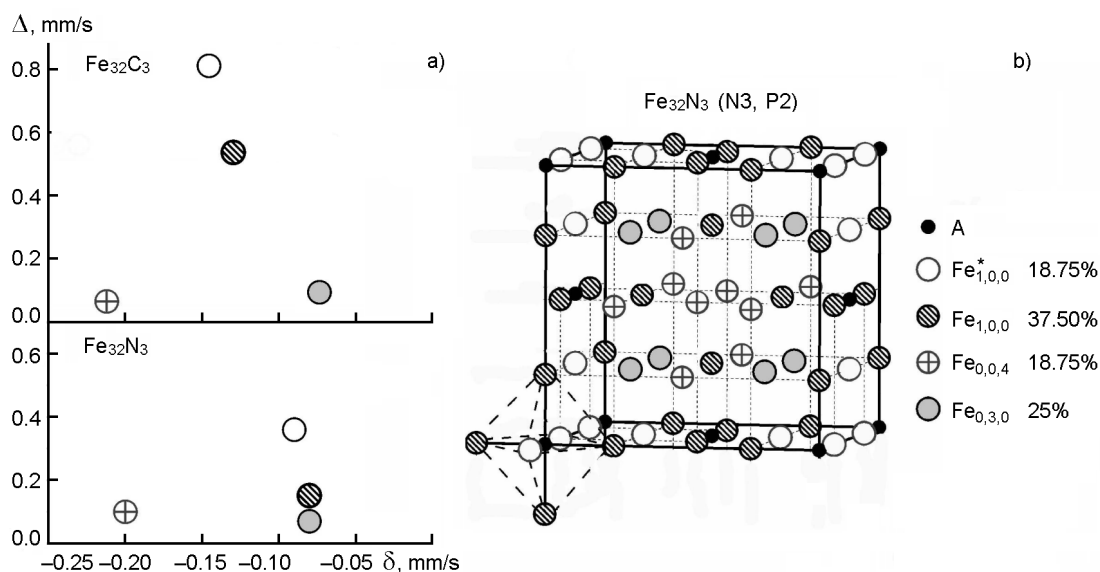


Fig. 4. (a) The values of quadrupole splittings and isomeric shifts for different types of $\text{Fe}_{m,n,r}$ atoms in Fe_{32}C_3 and Fe_{32}N_3 model structures. (b) Ordered structure Fe_{32}C_3 ($A = \text{C}, \text{N}$) simulating Fe_{10}C and Fe_{10}N austenites.

nents, namely, three doublet and one singlet lines. The results of experimental spectra processing are shown in Table and Fig. 1 and Fig. 2. The results differ essentially from those obtained by other researchers (Fig. 1 and Fig. 2).

To provide a detailed interpretation of experimental spectra, and clarify what kind of Fe atoms contribute to Mössbauer spectra as singlet and doublet lines, we have calculated theoretically the atomic and electron configurations for two ordered structures simulating carbon and nitrogen austenite. The alloying atoms are located in the model structures at most large distances from each other, which means their mutual repulsion. In [15], to model the austenite by the Fe_8A ($A = \text{C}, \text{N}$) structures, we have successfully used the FLAPW ab-initio method realized in wien2k software [16]. In this work, this ab-initio method was applied as well. We have calculated electronic structure and parameters of hyperfine interactions in the model structures of Fe_{32}A_3 ($A = \text{C}, \text{N}$) stoichiometry. Such model structure is shown in Fig. 4b. The structure is constructed to include Fe atoms described by the model of three coordination spheres. In that approach, three Fe–N coordination spheres are used, for example $\text{Fe}_{1,0,0}$ atom has one N atom in the first coordination sphere. Model structure has stoichiometry not exceeding max solubility of nitrogen in austenite, 10.3 % ($\text{Fe}_{8.7}\text{N}$) [7]. The ex-

change-correlation potential was calculated in the gradient approximation (GGA) according to Perdue-Burke-Ernzerhof model [17]. The atomic sphere radii were chosen to be touching. Radius of nitrogen atom sphere was 1.4 a.e. thus allowing us to put the Fe atom sphere radius to 2.0 a.e. As nitrogen is interstitial, a further increase of Fe atom sphere radius results in decreasing nitrogen sphere radius and lowered calculation accuracy. The accuracy of FLAPW method results depends on the following main parameters: the number of k -points in the Brillouin zone, the number of LM-components and Fourier coefficients in the expansion of electron density and potential, as well as the number of the plane waves in the intersphere region. We have used 160 plane waves per one atom in the basis set. Inside of atomic sphere, the wave function was expanded up to $l_{max} = 12$. Electron density and potential were expanded inside the spheres by the crystal harmonics basis till $l_{max} = 6$. The calculation was performed for 200 k -points in Brillouin zone. The selected parameters provided accuracy of a total energy calculation at 0.1 mRy level. 3s- and 3p-states of Fe atom were considered as semicore by introducing "local orbitals" therefor [18]. Implementation of the local orbitals made basis set more flexible, and increased calculations accuracy. As the alloy under study is paramagnetic, all calculations were performed in non spin-polarized approach.

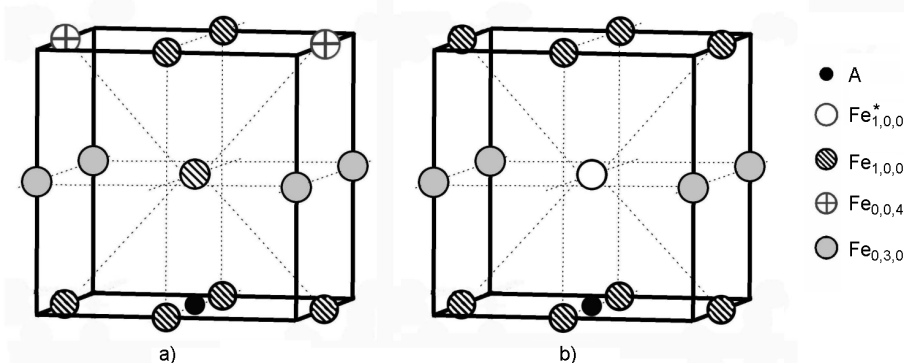


Fig. 5. Nearest neighborhood of iron atoms having interstitial atoms ($A = C, N$) in the first coordination sphere: (a) $Fe_{1,0,0}$, (b) $Fe_{1,0,0}^*$.

The unit cell of the model structure has a monoclinic symmetry (space group No.3, $P2_1$, [19]) and contains 32 Fe atoms, of which 20 are nonequivalent. For the model structure, structural optimization corresponding to its space group was done. Such optimization included the determination of equilibrium volume, equilibrium tetragonal deformation and equilibrium positions of Fe and N atoms in the unit cell.

Using the calculated equilibrium parameters of the model structure lattice and positions of the atoms in the unit cell, we have calculated the components of electric field gradients (EFG) tensor as well as the electron structure on all Fe atoms nuclei. The electric field gradients V_{ij} were recalculated to quadrupole splittings of nucleous levels of Fe atoms in accordance with the formula for paramagnetic case

$$\begin{aligned} \Delta[\text{mm/s}] &= \frac{ec}{2E_\gamma} QV_{zz} = \\ &= 1.041 \cdot Q[b]V_{zz} [10^{21} \nu/m^2], \end{aligned}$$

where c is speed of light; E_γ , the energy of γ quanta used by ^{57}Fe nuclei; Q , the ^{57}Fe nucleus quadrupole moment; $0.16b$ value was used according to [20]. Electron density ρ on nuclei was recalculated to isomeric shift of nuclear levels δ (relative to BCC Fe) according to

$$\delta = \alpha[\rho - \rho_0],$$

where ρ_0 is the density of electrons on Fe atom nucleus in BCC lattice; α , calibration constant characterizing the ^{57}Fe isotope nucleus. As known values of calibration constant hardly match with each other, we have used $-0.26a_0^3$ mm/s value obtained in

[21]. This value correlates better with the experimental data -0.36 ± 0.03 [22] than -0.22 value obtained before by Eriksson and Svan [23].

The calculations have shown that on the nuclei of $Fe_{1,0,0}$ atoms having one interstitial atom in the nearest neighborhood, the largest electric field gradient occurs. In Fig. 4, there are calculated values of quadrupole splittings and isomeric shifts on the nuclei of the four Fe atom types in the model structure $Fe_{32}A_3$ ($A = C, N$).

Let us to compare the EFG formation on $Fe_{1,0,0}$ nuclei for the $Fe_{32}N_3$ and $Fe_{32}C_3$ structures. Fig. 4a and Table show that quadrupole splitting on $Fe_{1,0,0}$ atom nucleus in $Fe_{32}C_3$ structure exceeds thrice the same in $Fe_{32}N_3$ structure. In [15], the reasons for so significant difference were defined. It is shown that the total contribution from $2s$ -, $2p$ -electronic shells of alloying element to EFG on the $Fe_{1,0,0}$ atoms nuclei remains almost constant when going from nitrogen to carbon. The main reason for higher EFG value in carbon case is sufficiently different distribution of $3d$ electron density on $Fe_{1,0,0}$, atoms containing nitrogen and carbon atoms in the nearest neighborhood.

The calculations have demonstrated that in the $Fe_{32}A_3$ ($A = C, N$) model structure not all $Fe_{1,0,0}$ atoms forming octahedron around the interstitial (Fig. 4b) are equivalent to each other. There are certain $Fe_{1,0,0}$ and $Fe_{1,0,0}^*$ atoms with considerably different electric field gradients appearing on their nuclei (Table). This results from the different atomic neighborhood in the first coordination sphere, which is shown in Fig. 5. $Fe_{1,0,0}$ and $Fe_{1,0,0}^*$ neighborhood differ sufficiently. As a result, a higher electric field gradient occurs on $Fe_{1,0,0}^*$ atoms nuclei. These atoms may contribute to Mössbauer

spectra as a low intensity doublet with a large quadrupole splitting as it is shown in Fig. 1 and Fig. 2. Small values of quadrupole splittings on the $\text{Fe}_{0,0,4}$ and $\text{Fe}_{0,3,0}$ atoms nuclei in Fe_{32}A_3 ($\text{A} = \text{C}, \text{N}$) structure result from symmetrical neighborhood of those atoms in the first coordination sphere.

The theoretical calculations correlate well with the above results of the experimental spectra processing. An ordered structure presented in the work seems to serve as a good model of nitrogen and carbon austenites. It follows from the studies that Mössbauer spectra of Fe_{10}C and Fe_{10}N austenites can be presented by the same set of the components. This set consists of a singlet line of iron atoms having symmetric environment, the doublet with a small quadrupole splitting and two doublets with significantly larger quadrupole splitting which occurs on the $\text{Fe}_{1,0,0}$ and $\text{Fe}_{1,0,0}^*$ atoms nuclei. It is to note that theoretical results that are based on the only model structure are insufficient to describe comprehensively the short range order and thermodynamic properties of Fe–C and Fe–N austenites. There is a need in a scrupulous study of a short range order concentration and temperature dependences based on the potential of N–N and C–C interatomic interaction in FCC Fe. Only such approach allows to study in detail the contribution made by different iron atoms into the Mössbauer spectra of austenite. Results of such studies will be presented in our further publication.

3. Conclusion

Processing of experimental Mössbauer spectra of Fe_{10}C and Fe_{10}N austenites using a new method has shown that those spectra consist on the same set of the components, namely one singlet and three doublets. In those spectra, two doublets have been found with a large quadrupole splitting (being substantially larger for Fe_{10}C austenite) and considerably different intensity. Theoretical calculations of the superfine interaction parameters the Fe_{32}A_3 ($\text{A} = \text{C}, \text{N}$) model structure correlate with the results of the experimental spectra processing. It has been shown that two doublets in the spectrum

can be related to the presence of $\text{Fe}_{1,0,0}$ and $\text{Fe}_{1,0,0}^*$ atoms. The low intensity doublets probably are not related to existence of N–Fe₂–N dumbbell configurations but rather occur due to the presence of $\text{Fe}_{1,0,0}^*$ atoms.

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Застосування методів самоорганізації для інтерпретації Месбаурівських спектрів аустенітів Fe–N та Fe–C

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Проведено обробку експериментальних Месбаурівських спектрів вуглецевого та азотистого аустенітів. Використано новий метод на основі принципів самоорганізації. Проведено розклад експериментальних спектрів на компоненти. Обчислено параметри надтонкої взаємодії у вуглецевому та азотистому аустенітах. Для інтерпретації експериментальних результатів проведено *ab-initio* методом FLAPW серію розрахунків електронної будови і параметрів надтонкої взаємодії в упорядкованій структурі $Fe_{32}A_3$ ($A = C, N$), яка моделює вуглецевий та азотистий аустеніти. Показано, що дублетна лінія з малою інтенсивністю, яка міститься у спектрі азотистого аустеніту, не пов'язана з існуванням "гантельних" конфігурацій N–Fe–N, а обумовлена атомами заліза, які містять один атом азоту у першій координаційній сфері. Встановлено, що аналогічна дублетна лінія присутня також у спектрі вуглецевого аустеніту. Відмінність Месбаурівських спектрів вуглецевого та азотистого аустенітів пов'язана тільки з різними значеннями градієнта електричного поля та ізомерного зсуву.