Effective fields at Fe^{57} nuclei and magnetic structure of palladium-iron alloys

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The Mössbauer absorption spectra of Fe^{57} in Pd_xFe_{1-x} $(0.45 \le x \le 0.75)$ alloys with and without long-range order, as well as the magnetization curves, are investigated in fields up to 100 kOe. The spectra are computer-analyzed for an equi-atomic alloy, and the Cowley order parameters are determined. The concentration dependences of the effective fields at the Fe^{57} nuclei are interpreted in the molecular-field approximation with separation of the contributions introduced by the atoms own magnetic moment and by the moments of the neighboring iron and palladium atoms. This has yielded the projections of the magnetic moments on the magnetization axis. These projections depend on the number of nearest neighbors of a definite sort and point to a ferrimagnetic order in ordered alloys with a tetragonal lattice $(0.45 \le x < 0.62)$ and to a ferromagnetic order in alloys without long-range order and in ordered alloys with cubic lattice $(0.62 < x \le 0.75)$. The obtained atomic magnetic moments explain the observed saturation magnetizations reached after the reversal of the moments of the palladium in ferrimagnetic alloys, and agree with available neutron-diffraction data. The nature of the anomalous concentration dependence of the resistivity is discussed.

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1. INTRODUCTION

The effective field $H_{\rm eff}$ at a resonant nucleus is determined by the magnetic state of the "central" atom and its neighbors.[1] It appears that the contributions of these states if $H_{\rm eff}$ is experimentally determined in a crystal with a controllable number of magnetically active neighbors. This is obtained, for example, in ordered alloys with different order parameters or with different compositions. One can hope that the separation of the contributions made to $H_{\rm eff}$ by the "central" atom and its neighbors makes it possible, for similar objects, to determine the local magnetic moments and their dependences on the nearest surrounding, the signs of the projections on the ferromagnetism or ferrimagnetism axis, and also the coefficients that connect the magnetic moments of the central atom and of the nearest neighbors with their contributions to $H_{\rm eff}$. The criterion of the adequacy of such a description of the effective fields can be a weak dependence of the coefficients that connect $H_{\rm eff}$ with the magnetic moments on the alloy composition, as well as the agreement between the saturation magnetizations calculated from the obtained magnetic moments and determined in experiment.

Convenient objects for the solution of such a problem are ordered Pd_xFe_{1-x} $(0.5 \le x \le 0.75)$ alloys, on the magnetic structure of which contradictory opinions have been expressed. Thus, the conclusion deduced from neutron-diffraction investigations[2] that the alloys Pd_xFe_{1-x} with tetragonal lattice $(0.5 \le x < 0.62)$ are ferrimagnetic, is contested because the magnetization curves of these alloys have no characteristic singularities in strong fields.[3]

The purpose of the present study was to investigate experimentally the effective fields at Fe^{57} nuclei with different local environments in palladium alloys with iron, using Mössbauer spectroscopy and an analysis of the obtained data within the framework of a model that takes the magnetic structure of the crystal into account. Information on the employed samples and on the procedure used to computer-analyze the spectrum (and to determine the Cowley order parameters) are described in Sec. 2. Section 3 is devoted to the procedure of separating $H_{\rm eff}$ and to determining the atomic magnetic moments, their dependence on the nearest environment, and the signs of the z-projections. In Sec. 4 we present information of the saturation magnetization of the investigated alloys and interpret this information on the basis of the obtained magnetic-moment data. In the conclusion we discuss the nature of the anomalies observed on the concentration dependence of the resistivity.

2. SAMPLES AND METHOD OF ANALYZING THE MÖSSBAUER SPECTRA

2.1. The Mössbauer investigations were performed on two batches of samples. The alloys for the first batch were made of V3 grade iron and 99.99% pure palladium in an MVP-3M hermetically sealed furnace in a helium atmosphere and were subsequently rolled into foils (10–20 μm). The palladium content ranged from 45 to 75 at.% (Pd_xFe_{1-x}, $x = 0.45; 0.49; 0.50; 0.52; 0.55; 0.62; 0.67; 0.72; 0.75$). The foils were sealed in quartz ampoules and were quenched from 1200 K in water. The subsequent annealing was stepwise with soaking at 920, 770, and 720 K for three days. The equi-atomic alloy was subjected to supplementary annealing at 820 K for 1200 hours.

The alloys of the second batch ($x = 0.50; 0.55; 0.62; 0.67; 0.72; 0.75$) were enriched with Fe^{57} up to 20%. Two-gram ingots of alloys of this series were homogenized at 1350 K for 10 hours and subsequently quenched in water. To obtain samples without long-range order, the thoroughly ground powders were annealed in sealed quartz ampoules at 1120 K for an hour and quenched in water. An ordered state was reached by annealing for 24 hours at a temperature 820 K $(0.50 \le x \le 0.62)$ or

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920 K ($0.67 \leq x \leq 0.75$). Control x-ray photographs (RKU-114M camera) and diffraction patterns (DRON-2 apparatus) have confirmed that the obtained compounds are single-phase and the structures belong respectively to type $L1_0$ and $L1_2$. The lattice periods were close to those reported earlier.[4]

The samples for the magnetometric measurements were prepared by a procedure similar to that described above. The state with long-range order was reached by stepwise annealing from 1300 to 700 K for 5 hours, and the samples without long-range order were obtained by quenching from 1300 K.

2.2 The Mössbauer investigations were carried out with a constant-acceleration spectrometer based on an NTA-512B multichannel analyzer. The γ-ray source was Co^{57} in a chromium matrix, with activity 20 μCi. The nonlinearity of the velocity (±1%) was determined from spectra of standard absorbers (α-Fe_2O_3 and α-Fe).

The Mössbauer spectra (MS) obtained with samples having the same composition but from different batches turned out to be identical. The MS of quanched samples have a complex picture consisting of a superposition of many simple sextet lines (Fig. 1). The equi-atomic alloy is characterized by larger values of H_{eff} than $Pd_{0.75}Fe_{0.25}$ (Fig. 2). The MS of ordered samples with compositions close to $Pd_{0.5}Fe_{0.5}$ and $Pd_{0.75}Fe_{0.25}$ are qualitatively similar to one another and on the face of it can be represented as superpositions of three or four simple subspectra, a fact reflecting a rather high degree of order. The spectra of ordered alloys with $0.55 \leq x \leq 0.60$ differ substantially from the remaining ones and are closer in general form to the MS of quenched samples; this is evidence of a much larger abundance of sets of all-possible environments of resonance atoms in these alloys.

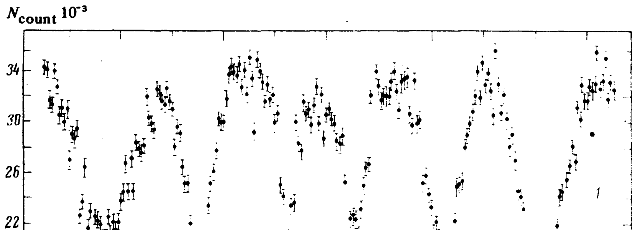

FIG. 1. Experimental (points) and theoretical (solid line) Mössbauer spectra of the alloys Pd_xFe_{1-x} (1—$x = 0.50$, without long-range order, 2—$x = 0.50$ with long-range order, 3—$x = 0.67$ with long-range order, 4—$x = 0.75$ with long-range order). N_{count}—number of counts per channel.

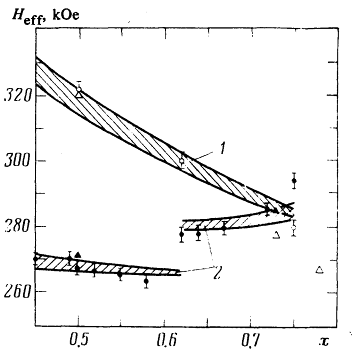

FIG. 2. Concentration dependences of H_{eff} for Pd_xFe_{1-x} alloys without (1) and with (2) long-range order (●, ○—present results, ▲, △—data of[6]). The regions of the calculated values are bounded by the parameter values $\alpha = 0$ and 0.1 in case 1 and $\alpha = 0.9$ and 0.6 in case 2.

The computer analysis of the MS of the ordered alloys of equi-atomic composition was carried out in a model that takes into account the distribution of the palladium atoms and iron atoms in the nearest environment of the resonant atoms.[5] The MS is in this case a superposition of a set of simple spectra whose parameters are interrelated and are determined both by the configuration of the environment and by the probability of the appearance of the given configuration

$$I = \sum_k P_k I_k(V); \tag{1}$$

here P_k is the probability of the appearance of a resonant atom with a definite k-th configuration of the environment, and $I_k(V)$ is the mathematical model of the simple MS for the k-th configuration. Allowance for the short-range order in the distribution of the Pd and Fe atoms for the first ($i = 1$) and second ($i = 2$) coordination spheres of the resonant atoms was carried out with the aid of the Cowley short-range order parameters (α). In this case P_k was represented as a product of the probabilities of finding $m_1 - n_1$ and $m_2 - n_2$ iron atoms in the first and second spheres, respectively:

$$P_k(n) = P(m_1 - n_1) P(m_2 - n_2), \tag{2}$$

where

$$P(m_i - n_i) = \binom{m_i}{m_i - n_i} x_{Fe}^{(m_i - n_i)} \times (1 - \alpha_i)^{(m_i - n_i)} (x_{Pd} + x_{Fe}\alpha_i)^{n_i}, \tag{3}$$

x_{Fe} is the iron concentration, x_{Pd} is the palladium concentration, m_i is the coordination number of the i-th sphere, n_i is the number of the palladium atoms in the

i-th sphere, α_i is the short-range order parameter for the i-th sphere, and $\binom{m_i}{m_i-n_i}$ are the binomial coefficients.

The mathematical model of the simple MS was chosen in the form of a sum of six Lorentzians:

$$I(V_{\text{chan}})=\sum_{l=-3}^{3}\frac{k_l' A(k_l''\Gamma)^2}{4\mathscr{V}},$$

$$\mathscr{V}=\left\{V_{\text{chan}}-\delta+\frac{l}{|l|}\left[\frac{H_{\text{eff}}}{2}-(|l|-1)\mu_B g_l' H_{\text{eff}}\right]+(-1)^{|l|}\Delta\right\}^2+\frac{(k_l''\Gamma)^2}{4}, \tag{4}$$

where δ, Δ, H_{eff}, A, and Γ are respectively the isomeric shift, the quadrupole splitting, the effective magnetic field at the nucleus, and the intensity and half-width of the absorption line; V_{chan} is the velocity of the source for a definite channel; k_l' and k_l'' are proportionality coefficients that take into account the relative changes of the intensity and the half-width for each of the l lines; g_1' is the nuclear gyromagnetic ratio for the excited state of the nucleus; μ_B is the Bohr magneton.

The dependences of $H_{\text{eff}}(n)$ and $\delta(n)$ on the number of impurity atoms in the first and second coordination sphere, which lead to a deviation from complete order, were assumed to be linear in the first approximation:

$$H_{\text{eff}\,k}(n)=H_0+\sum_{i=1}^{2}\Delta H_i n_{ik},$$
$$\delta_k(n)=\delta_0+\sum_{i=1}^{2}\Delta\delta_i n_{ik}. \tag{5}$$

The subscript k in these formulas numbers the configuration of the environment, H_0 and δ_0 are the effective field and the isomeric shift corresponding to a fully ordered state, ΔH_i and $\Delta\delta_i$ are their increments due to one of the n "illegitimate" atoms in the i-th sphere, and n_{ik} is the number of atoms in the i-th sphere for the k-th configuration. As will be shown later on, these dependences are not strictly linear in a wide interval of variation of n. The presented approximation is, nevertheless, correct enough, since the main contribution to the MS is made by configurations with only one or two "illegitimate" atoms, making it possible to neglect the nonlinearity of $H(n)$ and $\delta(n)$ in so narrow an interval of n.

The changes ΔE of the quadrupole-splitting energy following substitution of neighboring atoms is the result of a change in both the V_{zz} component of the electric field gradient tensor and of the asymmetry parameter η.[1] Using the expansion of $\Delta E(n)$ in a binomial series and confining ourselves to quadratic terms we can write down the dependence of the quadrupole splitting on the configuration of the environment in the form

$$\Delta_k(n)=(\Delta_0+c_k\beta)\left[1+\frac{f_k^2\beta^2}{6(\Delta_0+c_k\beta)^2}\right], \tag{6}$$

where Δ_0 is the quadrupole splitting for a fully ordered state, c_k and f_k are coefficients that take into account both the number and the distribution of the impurity atoms for the k-th configuration and are determined by the vector summation of the relative contributions of all the lattice ions that are taken into account, β is the increment of Δ due to the change of the V_{zz} component when one of the nearest-environment atoms is substituted in a lattice with ideal order. The first and second factors determine the change of Δ_0 due respectively to the change of the V_{zz} component and to the additional asymmetry.

When two nearest coordination spheres are taken into account, the result is the appearance of 68 possible environment configurations. Since, however, the influence of some of them were identical and some of the weight coefficients were small, it was possible to confine oneself in the computer analysis to a superposition of 10 sextet lines with 17 varied parameters (including H_0, δ_0, Δ_0, their increments, α_i, and others). The obtained principal varied parameters describing the observed spectrum for an equi-atomic alloy are listed in Table I.

TABLE I. Values of the principal parameters of the MS of the $Pd_{0.5}Fe_{0.5}$ alloy in a state with long-range order.

Parameter	Value	Parameter	Value
δ_0, mm/sec	0.392	H_0, kOe	264
$\Delta\delta_1$, mm/sec	0.002	ΔH_1, kOe	12.6
$\Delta\delta_2$, mm/sec	−0.002	ΔH_2, kOe	−12.5
Δ_0, mm/sec	0.475	α_1	−0.792
β, mm/sec	0.036	α_2	0.900

3. EFFECTIVE FIELDS AT Fe^{57} NUCLEI, ATOMIC MOMENTS AND MAGNETIC STRUCTURE

3.1. The values of H_{eff} for all the investigated alloys except the equi-atomic ones were calculated from the positions of the centers of gravity of the outermost peaks, and therefore corresponded to the most probable configurations of the environments of the resonant nuclei. The inaccuracy in the determination of the centers of gravity of the broadened lines did not exceed two or three channels, corresponding to ±2 kOe in the determined values of H_{eff}. An additional error in the determination of the field H_{eff} assigned to a definite configuration was due to identification of the centers of gravity of the absorption lines with the effective field at the nuclei having the most probable environment configurations. The values of H_{eff} obtained in this manner for alloys with and without long-range order agree well with those established earlier[6] (see Fig. 2).

3.2. We note three features of the concentration dependences of H_{eff}:

a) The effective field for the most probable atomic-environment configuration is larger in practically the entire composition region when there is no long-range order.

b) For alloys with long-range order and $0.45 \leq x \leq 0.6$ (tetragonal lattice) we have $\partial H_{\text{eff}}/\partial x < 0$, whereas at $0.62 \leq x \leq 0.75$ (cubic lattice) we have $\partial H_{\text{eff}}/\partial x > 0$.

c) In alloys with long-range order, H_{eff} changes abruptly at $x \sim 0.60$–0.62 as a result of the change in the type of crystal lattice.[4]

In the interpretation of the experimental data we start with the fact that alloys without long-range atomic order are ferromagnetic.[7] In addition, we recognize that an increase in the number of palladium atoms in the nearest environment of the iron atoms leads to an increase of the magnetic moments of the latter; the magnetic moments of the palladium atoms are smaller by one order of magnitude (~0.2 μ_B).[7] Therefore the decrease in the absolute value $|H_{eff}|$ on going from a configuration with a smaller number of iron atoms in the nearest environment must be understood as the result of a decrease in the negative contribution due to the magnetic moments of the nearest neighbors of the resonant atoms. Thus, in the case of atomic ordering or when the palladium concentration is increased (Fig. 2, curve 1), the number of the nearest Fe neighbors decreases, thereby decreasing the contribution made to H_{eff} by their magnetic moments and not offset by the increase of the magnetic moments of the iron atoms themselves. This corresponds qualitatively to item a). Items b) and c) suggest furthermore that the magnetic structures of atomically ordered alloys with tetragonal and cubic lattices are substantially different. In the simplest variant it can be assumed that at $0.5 \leqslant x \leqslant 0.6$ the iron-atom layers perpendicular to the tetragonal axis have magnetic moments that are parallel to one another, whereas the magnetic moments of the palladium atoms (whose layers are also perpendicular to the tetragonal axis and separate the iron-atom layers) are opposite to the magnetic moments of the iron atoms (i.e., ferrimagnetic ordering takes place here). The transition to atomically ordered alloys with $x > 0.62$ is accompanied by a change of the magnetic order to ferromagnetic, and this together with the increase of the magnetic moments of the iron atoms explains the jumplike increase of $|H_{eff}|$. In other words, the positive contribution made by the magnetic moments of the neighboring palladium atoms to the effective field (at $x < 0.62$) gives way to a negative contribution (at $x > 0.62$).

3.3. Let us make the described heuristic model more concrete by means of the following calculations.

It was proposed earlier[1] to calculate the effective field at the Fe^{57} nucleus by an empirical expression in which H_{eff} is represented as a result of the interaction of the spin density of the polarized s electrons of the atom with the intrinsic magnetic moment μ and with the average value $\bar{\mu}$ per atom of the alloy:

$$H_{\text{eff}} = -a\mu - b\bar{\mu}, \tag{7}$$

where a and b are proportionality coefficients.

Within the framework of the molecular-field theory, when the paired interaction of the resonant atoms with only atoms of the nearest coordination sphere is taken into account, the influence of the environment on H_{eff} can be estimated even without using the average characteristic $(\bar{\mu})$, and by using the magnetic moments of the actual atoms:

$$H_{\text{eff}}(n) = -a\mu_{\text{Fe}}(n) - b[n\mu_{\text{Pd}}(n) + (m-n)\mu_{\text{Fe}}(n)], \tag{8}$$

where $\mu_{Fe}(n)$ and $\mu_{Pd}(n)$ are the z projections of the effective magnetic moments of the iron and palladium, and they depend on the number n of the palladium atoms in the nearest environment of the resonant atom. The relative orientation of the magnetic moments, which should influence the sign of the s-electron polarization, and therefore also the sign of the contribution to H_{eff}, can also be taken into account by reversing the sign of their z projections in (8).

Using four values of H_{eff} determined experimentally for alloys with $x = 0.50$ and $x = 0.75$, as well as the values of the effective field H_{eff} at the iron nucleus for a configuration, calculated from the data of Table I, with seven neighboring palladium atoms, we write down five equations that relate the magnetic moments and the coefficients a and b with the differences of the values of H_{eff}:

$$\begin{gathered}
H^{\text{disord}}_{x=0.50} - H^{\text{ord}}_{x=0.50} = 54, \quad H^{\text{disord}}_{x=0.50} - H^{\text{ord}}_{x=0.75} = 42, \\
H^{\text{ord}}_{x=0.75} - H^{\text{disord}}_{x=0.75} = 16, \quad H^{\text{ord}}_{x=0.75} - H^{\text{ord}}_{x=0.50} = 27, \\
\Delta H = H'_{x=0.50} - H^{\text{ord}}_{x=0.50} = 12.5,
\end{gathered} \tag{9}$$

where

$$\begin{gathered}
H^{\text{disord}}_{x=0.50} = -a\mu_{\text{Fe}}(6) - b[6\mu_{\text{Pd}}(6) + 6\mu_{\text{Fe}}(6)], \\
H^{\text{ord}}_{x=0.50} = -a\mu_{\text{Fe}}(8) - b[8\mu_{\text{Pd}}(8) + 4\mu_{\text{Fe}}(8)], \\
H^{\text{disord}}_{x=0.75} = -a\mu_{\text{Fe}}(9) - b[9\mu_{\text{Pd}}(9) + 3\mu_{\text{Fe}}(9)], \\
H^{\text{ord}}_{x=0.75} = -a\mu_{\text{Fe}}(12) - b[12\mu_{\text{Pd}}(12)], \\
H'_{x=0.50} = -a\mu_{\text{Fe}}(7) - b[7\mu_{\text{Pd}}(7) + 5\mu_{\text{Fe}}(7)];
\end{gathered}$$

$H'_{x=0.50}$ is the effective magnetic field at an Fe^{57} nucleus with one "illegitimate" iron atom in the nearest environment.

To approximate the functions $\mu_{Fe}(n)$ and $\mu_{Pd}(n)$ we tried the following expressions:

$$\left.\begin{array}{ll}
\text{variant A:} & \mu_{\text{Fe}}(n) = \mu_{\text{Fe}}(6) + (n-6)\Delta\mu_{\text{Fe}}, \\
& \mu_{\text{Pd}}(n) = \mu_{\text{Pd}}(6) - (n-6)\Delta\mu_{\text{Pd}}; \\
\text{variant B:} & \mu_{\text{Fe}}(n) = \mu_{\text{Fe}}(6) + d_{\text{Fe}}\{1 - \exp[-k_{\text{Fe}}(n-6)]\}, \\
& \mu_{\text{Pd}}(n) = \mu_{\text{Pd}}(6) - d_{\text{Pd}}\{1 - \exp[-k_{\text{Pd}}(n-6)]\}; \\
\text{variant C:} & \mu_{\text{Fe}}(n) = \mu_{\text{Fe}}(6) + d_{\text{Fe}}\exp[k_{\text{Fe}}(n-6)], \\
& \mu_{\text{Pd}}(n) = \mu_{\text{Pd}}(6) - d_{\text{Pd}}\{1 - \exp[-k_{\text{Pd}}(n-6)]\}.
\end{array}\right\} \tag{10}$$

Here $\mu_{Fe,Pd}(6)$ are the magnetic moments of the iron and palladium atoms for the main configuration (with six Pd neighbors) in the disordered equi-atomic alloy, $\Delta\mu_{Fe,Pd}$ are the increments of the moments per neighboring palladium atoms, and $d_{Fe,Pd}$ and $k_{Fe,Pd}$ are the varied parameters of the exponential functions.

The next step was to select the coefficients a and b and the parameters that describe the magnetic moments in expression (10) by the gradient method of minimizing a quadratic functional made up of the differences of the left-hand and right-hand sides of (9) (variants A, B, and C were tested in succession) in two models of the magnetic structure. In the first model, I, ferromagnetic ordering was assumed in the entire concentration region (with the z projections of the magnetic moments chosen positive: $\mu_{Fe}(n) > 0$ and $\mu_{Pd}(n) > 0$). The second model, II, took into account ferrimagnetic ordering (for atomically ordered alloys) in the region $0.45 \leqslant x \leqslant 0.62$ (with the following z-projection signs: $\mu_{Fe}(n) > 0$ and

TABLE II. Values of the varied parameters obtained by solving the system (9) using the ordering model II and variant C for the functions $\mu_{Fe}(n)$ and $\mu_{Pd}(n)$.

T, K	Parameters							
	$\mu_{Fe}(6)$, μ_B	$\mu_{Pd}(6)$, μ_B	a, kOe/μ_B	b, kOe/μ_B	k_{Fe}	k_{Pd}	d_{Fe}, μ_B	d_{Pd}, μ_B,
300	2.814	0.337	74.002	5.979	0.873	0.124	0.006	0.233
4.2	2.813	0.337	74.001	6.520	0.874	0.124	0.006	0.233

$\mu_{Pd}(n) < 0$) and ferromagnetic ordering in the region $0.62 < x \leqslant 0.75$.

The computer calculation has shown that within the framework of the ferromagnetic model it is impossible to make Eqs. (9) compatible in any of the approximation variants (10). At the same time, the ferrimagnetic model provides a solution (which is furthermore unique) for the system (9) if approximation C is used. The obtained coefficients a and b and the parameters of the functions $\mu_{Fe,Pd}(n)$, listed in Table II, leads to a difference not exceeding $\pm 1.5\%$ between the left- and right-hand sides of Eqs. (9).

Similar calculations were carried out using the values of H_{eff} at 4.2 K.[6,8] Comparison of the calculation results for 4.2 and 300 K (Table II) attests to the negligibly weak dependence of the magnetic moments and of the coefficient a on the temperature and to a noticeable decrease, with increasing temperature, of the coefficient b, which reflects the influence of the neighboring atoms on H_{eff}. This can apparently be regarded as a confirmation of the applicability of the employed model (8) to describe the H_{eff} dependence on the composition.

The established values of the parameters (Table II) were used subsequently to calculate (by means of formulas (10C)) the magnetic moments of the iron and palladium atoms at different nearest-environment configurations (Fig. 3). The agreement between the established magnetic moments and those reported in[7] is seen to be good for iron atoms but noticeably worse for the palladium atoms. The latter is due to the much smaller absolute value of μ_{Pd}. It is this apparently which made it possible to interpret the data on magnetic diffuse scattering of neutrons[7] in an approximation in which $\mu_{Pd}(x)$ remains constant in the range of x from 0.5 to 0.75. At the same time, when the palladium concentration is decreased below 40 at.%, an increase of μ_{Pd} to 0.4 μ_B is also noted in[7].

So far there have been few investigations of the nature of the observed change in the magnetic moments. It can be assumed, however, that when the number of palladium atoms surrounding the iron atoms increases and tends to fill the proper d-electron shells, a redistribution of the d-electron density from the iron atoms to the palladium atoms takes place. This leads in turn to an increase of μ_{Fe}. This increase is larger the more palladium atoms in the nearest environment. The onset of magnetic moments of the palladium atoms is probably due to polarization effects. In this case, the obtained decrease of μ_{Pd} with increasing x must be attributed to a decrease in the number of polarizing iron atoms.

We note also that the described interpretation of the plots of H_{eff} against the component concentration and the state of the alloys was carried out without taking into account the possible change of the effective field at the nuclei of the resonant atoms, due to the fact that the alloy lattice is tetragonal.[1] These corrections, which are more significant for ordered alloys in the region $0.45 \leqslant x < 0.6$ (structure $L1_0$) and less significant for $0.6 < x \leqslant 0.75$ (structure $L1_2$) do not explain the entire course of $H_{eff}(x)$ without allowance for the change in the magnetic structure (region 2 of Fig. 2). At the same time, the magnetic moments, particularly those of the iron atoms, undergo the largest change in the regions where the palladium concentration is high. This gives grounds for hoping that allowance for the additional factors that change H_{eff} will not lead to a considerable change in the values of $\mu_{Fe}(n)$ and $\mu_{Pd}(n)$.

Information on the plots of $\mu_{Pd}(n)$ and $\mu_{Fe}(n)$ have made it possible to estimate the average effective fields at the nuclei in alloys of various compositions. To this end, formula (8) was used for preliminary calculation of the values of $H_{eff}(n)$, which were subsequently averaged with weight factors $P_n(x)$, which show the probabilities of the appearance of configurations with 10 nearest palladium neighbors:

$$\bar{H}_{eff}(x) = \sum_n P_n(x) H_{eff}(n). \qquad (11)$$

It is assumed here that the $P_n(x)$ depend not only on the alloy composition but also on the short-range order parameters α. The values of α were chosen in the intervals from 0.9 to 0.6 for alloys with long-range order and from 0.0 to 0.1 for alloys without long-range order. The results of the calculations are shown in Fig. 2 by the hatched regions, which account with sufficient accuracy for all the regularities of the concentration dependence of the effective field for states with and without long-range order. Some deviations of the calculated values from the experimental ones (especially at $x = 0.75$) can be attributed to the degree of ordering of the alloys.

4. SATURATION MAGNETIZATION, AVERAGE MAGNETIC MOMENTS, AND RESISTIVITY

4.1. The most important criterion of the adequacy of the proposed model and reliability of the data on the

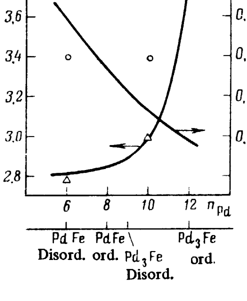

FIG. 3. Plots of $\mu_{Fe}(n)$ and $\mu_{Pd}(n)$ (variant C) for alloys of palladium with iron ($\Delta - \mu_{Fe}$, $\circ - \mu_{Pd}$—data of[7]).

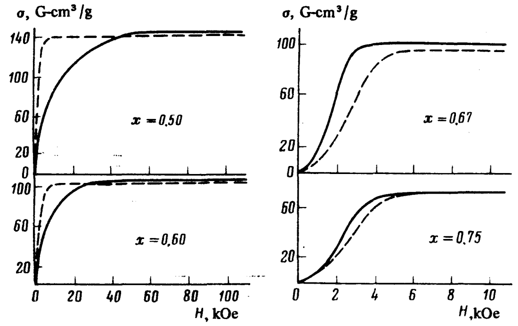

FIG. 4. Field dependences of the magnetization of Pd_xFe_{1-x} alloys in states with (solid lines) and without (dashed) long-range order.

magnetic moment determined from the MS is the relation between the mean values of these moments and those obtained from the saturation magnetization.

In view of the difficulty of attaining technical saturation of the alloys with tetragonal lattice, particularly as a result of the high value of the magnetic-anisotropy energy, the published plots of the magnetization σ of the palladium alloys with iron[3] do not contain the values of σ in strong fields for the entire calculated region of compositions. We have therefore investigated the magnetization of four samples ($x = 0.50; 0.60; 0.67; 0.75$) in states with and without long-range order in magnetic fields up to 100 kOe at a temperature 4.2 K. We used an installation that ensured information with an error not exceeding ± 5%. Figure 4 shows the obtained experimental data. For a sample with equi-atomic composition and in a state with long-range order, saturation was reached in a field ~60 kOe, in agreement with the data of[3]. In a somewhat weaker field (~40 kOe) saturation of another compound with tetragonal lattice is also reached ($x = 0.60$), whereas all the investigated alloys with cubic lattice, i.e., without long-range order, as well as alloys with order of $L1_2$ type, revealed saturation in fields that are weaker by one order of magnitude.

The data obtained on the saturation magnetizations were used to estimate the average magnetic moments (Fig. 5). If we start from the proposed ferrimagnetic model for alloys with tetragonal lattice, then the difficulty of reaching saturation must be attributed not only to the large magnetic-anisotropy constants[3] but also to the decrease of the absolute values of the z projections for the palladium sublattice with increasing magnetizing field and the resultant reversal of the magnetic moments of the palladium atoms and their becoming oriented parallel to the magnetic moments of the iron atoms.

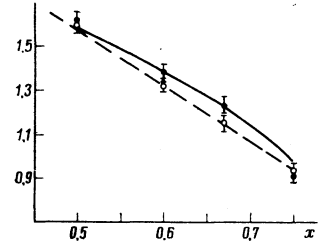

FIG. 5. Concentration dependences of the average magnetic moments, determined from the saturation magnetizations (dark circles—state with long-range order, light circles—without long-range order) and calculated from formula (4) for states with (solid) and without (dashed) long-range orders.

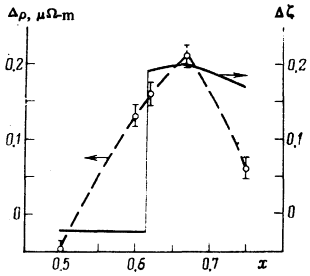

FIG. 6. Plots of $\Delta\rho(x)$ and $\Delta\zeta(x)$. Points—data of[4] on the values of $\Delta\rho$.

4.2. It is easy to estimate the values of the average magnetic moments on the basis of the data given in Sec. 3, using the expression

$$\bar{\mu}(x)=\sum_j\sum_n x_j\mu_j(n)P_n(x), \tag{12}$$

where j = Fe or Pd. The results of such calculations are shown in Fig. 5 by solid and dashed lines respectively for alloys with and without long-range order. The good agreement between these values and those obtained from the saturation magnetization is convincing evidence of the reliability with which the magnetic moments were determined from the Mössbauer-spectroscopy data.

We note that the average values of the magnetic moments are not very sensitive to changes of the order parameter α. The slightly larger value of $\bar{\mu}(x)$ for alloys with long-range order is the consequence of the increase, with increasing order, of the weighting coefficients for configurations with complete order (or configurations close to them), which leads to an increase of the contribution of the larger magnetic moment of the iron (see Fig. 3).

4.3. The obtained $\mu_j(n)$ dependences permit a semi-quantitative explanation of the causes of the previously described appreciable increase of the resistivity when the Pd_xFe_{1-x} alloys go over from a state without long-range atomic order to a state with long-range order, with a maximum jump

$$\Delta\rho=\rho(T_c-200\,\mathrm{K})-\rho(T_c+200\,\mathrm{K})>0,$$

which reaches 0.2 μΩ-m near $x = 0.67$ (Fig. 6, dashed). The sign can be qualitatively attributed to the increase of the magnetic moments of the iron atoms with increasing order, and, consequently, with increase of the magnetic contribution to the carrier scattering.

We represent next the total resistivity ρ in the form of three terms,[10]

$$\rho=\rho_0+\rho_{\text{phon}}+\rho_{\text{magn}}, \tag{13}$$

which reflect the contributions to the residual resistivity from the statistical imperfections of the crystal, and from the scattering by phonons and magnetons, respectively. Lowering the temperature and passage through the atomic-ordering point obviously decreases ρ_{phon} and ρ_0, whereas ρ_{magn} increases.

Indeed, in the molecular-field approximation[10] we have

$$\rho_{\text{magn}}(x) = A\zeta(x)\ , \tag{14}$$

where A is a proportionality coefficient that can be regarded as constant in first-order approximation[10] and

$$\zeta(x) = \sum_j \sum_n x_j P_n(x) S_j(n)\,[S_j(n)+1]. \tag{15}$$

Here $j =$ Fe, Pd; $S_j(n)$ is the spin of the j-th atoms, defined as $S_j(n) = \mu_j(n)/g_j$ (g_j is the Landé factor).

The difficulty of separating the components ρ_0 and ρ_{magn} does not make it possible to determine with sufficient accuracy the value of A and to estimate theoretically the contribution ρ_{magn} to the resistivity. However, even the definition of $\Delta\zeta(x)$

$$\Delta\zeta(x) = \zeta_{\text{ord}}(x) - \zeta_{\text{disord}}(x)\ , \tag{16}$$

leads to certain conclusions (see Fig. 6).

Firstly and most importantly, if the weighting coefficients $P_n(x)$ in (15) are so redistributed that the contribution of the larger values of the magnetic moments increases when the alloys become ordered, the required sign of $\Delta\zeta$ is obtained (positive according to the measurement of ρ). On the other hand the disparity between the theoretical ($\Delta\zeta(x)$) and experimental ($\Delta\rho(x)$) plots at $0.6 < x < 0.64$ is apparently due to the presence of ordered microscopic regions, of the CuAu and Cu_3Au type, in the samples with these concentrations investigated in[4], a fact attributed to the short time of their isothermal treatment. In addition, it must be borne in mind that $\Delta\zeta$ takes into account the change of only the magnetic part of the resistivity and not of the entire resistivity.

5. CONCLUSION

The data presented above illustrate the possibility of using Mössbauer spectroscopy to separate the contributions made to the effective field at the Fe^{57} nucleus by the intrinsic magnetic moments of the electron shell of the resonant atom and the magnetic moment of the nearest neighbors. A similar procedure of calculating H_{eff}, which can apparently be extended also to include other systems, makes it possible to determine simultaneously the magnetic moments of the alloy components and their dependence on the nearest environment, and also to draw some conclusions on the type of magnetic ordering of the atoms.

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