An investigation of the dilute alloy Pd(Fe,Co) by the Mössbauer effect on oriented nuclei: Relaxation and spin glass

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(Submitted 25 January 1983)
Zh. Eksp. Teor. Fiz. **85**, 627–641 (August 1983)

The hyperfine fields H_{hf} on ^{57}Fe and ^{57}Co impurities in the dilute alloy Pd(Fe,Co) with a total magnetic impurity concentration of about 0.01 at.% have been investigated by emission Mössbauer spectroscopy on oriented nuclei. The measurements were carried out at temperatures between 0.05 and 4.2 K in magnetic fields up to 50 kOe. In fields up to 1 kOe the form of the spectra is due to Fe electron spin relaxation which is determined by two contributions: by the Korringa mechanism and by spin-spin relaxation via the RKKY interaction. In this case the external field "induces" a misoriented Fe spin structure characteristic of the behavior of a spin glass in a magnetic field when its temperature is slightly above the freezing temperature. The variation of the hyperfine field on Fe corresponds approximately to the Brillouin function, but in strong fields (10–40 kOe) a linear growth of $^{Fe}H_{hf}$ is observed which is caused by the contribution of the conduction electrons to the hyperfine field. The behavior of the hyperfine field on Co deviates appreciably from the behavior of a free spin; this may be due to the destruction of the local moment of Co (Kondo compensation, spin fluctuations). The magnitude of $^{Co}H_{hf}$ is not the same as that derived from the results obtained by the angular distribution technique for 136 keV γ rays from oriented ^{57}Co nuclei. This is ascribed to misalignment of the Co spins relative to the external magnetic field. The low values of the hyperfine field observed in a magnetically ordered alloy with a high Co concentration (0.1–0.2 at.%) is interpreted by assuming that the alloy is in the spin-glass state.

PACS numbers: 76.80. + y, 75.50.Kj

1. INTRODUCTION

As is well known, Fe and Co introduced as a small impurity into Pd polarize the surrounding 4*d*-electrons of the matrix, forming a so-called giant moment. Overlap of the polarized electron clouds lead to an indirect exchange interaction between the impurities, which explains the observed ferromagnetism of dilute Pd(Fe) and Pd(Co) alloys even at $\sim$0.1 at.% concentration of the magnetic atoms.[1] The nature of the interaction between the impurities changes as their spacing increases and becomes of the alternating sign RKKY type, so that a spin glass can be formed in the alloys at lower concentrations.[2] Work[3–5] in which the iron impurity concentration was in the range 0.007 to 0.015 at.% is usually taken to indicate a possible observation of a spin glass in Pd(Fe). However, these results do not allow of a unique interpretation.

In very dilute alloys it is also possible to assess behavior and very existence of a local moment within the confines of a single impurity. It was found[4] in studies of the γ-ray anisotropy of oriented ^{60}Co nuclei in a Pd matrix that the hyperfine field $^{Co}H_{hf}$, on Co at 5 mK is appreciably less than expected from the theoretical curve calculated for the giant moment $10\,\mu_B$. The authors concluded that the Co impurity experiences a Kondo compensation of the magnetic moment. Studies[6] of Mössbauer emission spectra of a Pd(Fe,Co) alloy with concentrations of ^{57}Co$\sim$1 ppm and Fe$\sim$10 ppm showed that the iron impurity is in a paramagnetic state above 18 mK and there is no Kondo effect on iron. The same conclusion was drawn about cobalt impurity in subsequent work,[7,8] and the decreased values of H_{hf} at the ^{57}Co nucleus obtained from the ratio of the intensities of the components of the spectra in an external magnetic field are explained by the influence of relaxation on the excited levels $I = 5/2$ and $I = 3/2$ of the ^{57}Fe nucleus, which leads to a depolarization of these states.

The magnetic behavior of Fe and Co impurities in Pd cannot now, thus, be considered as understood conclusively. It is clear that it depends appreciably on the concentration of impurity atoms. In the present work a Pd(Fe,Co) alloy with a combined concentration of magnetic impurities $\sim$0.01 at.% has been studied by the Mössbauer effect method on oriented nuclei (ME/ON). The measurements were made over the temperature range 0.05 to 4.2 K in magnetic fields up to 50 kOe. Preliminary results of these experiments have been published.[9,10]

2. EXPERIMENTAL METHOD

The specimen studied, which was a radioactive ^{57}Co source in Pd, was prepared in the following way. A drop of radioactive cobalt solution was deposited on a palladium foil with resistence ratio $R_{300K}/R_{4.2K} = 500$ and having a certified iron-impurity concentration of 0.006 at.%. Cobalt was introduced by diffusion at $T = 1000$ °C over 24 h in a stream of hydrogen. After eliminating the hydrogen the specimen was remelted three times in a high-frequency furnace in an atmosphere of chemically pure argon. The specimen was fin-

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ally annealed at 1000 °C for 10 h in an argon atmosphere. The initial activity was ≈ 1 mC. Calculations with account of the impurity content in the radioactive cobalt solution (1.5×10^{-4} mg/mC Co, 2×10^{-4} mg/mC Fe, which on a calculation for 30 mg weight of the palladium foil gives respectively ≈ 0.001 at.% and ≈ 0.0013 at.%) and of the certification data for the palladium, show that the total concentration of magnetic impurities (Fe and Co) in the specimen amounts to about 0.01 at.%.

Measurements were carried out in a ^{3}He/^{4}He dilution refrigerator made in VNIIGT.[11] The specimen was soldered with Bi–Cd solder to a copper cold finger connected to the mixing chamber. The temperature was monitored by carbon and semiconductor resistance thermometers.

A magnetic field up to 50 kOe was provided by a superconducting solenoid working in the persistent current mode. The solenoid was produced by the method developed in the Kurchatov Institute, and was placed in the helium reservoir of the cryostat. The solenoid was calibrated with a semiconductor Hall probe.

The gamma quanta were recorded along the magnetic field direction with a miniature resonance counter based on Fe–Al,[12] mounted directly on the Mössbauer vibrator. The vibrator moved with constant acceleration at a frequency 20 Hz, the motion being monitored by a laser velocity calibrator.[13]

3. RESULTS AND DISCUSSION

1. Measurements in zero magnetic field

Measurements were made in zero magnetic field in the temperature range 0.05 to 4.2 K. Some of the spectra obtained are shown in Fig. 1. At 4.2 K the spectrum consists of a single line with an apparatus width ≈ 0.5 mm·s^{-1}. The line width increases monotonically with decreasing temperature in the range 4.2 to 0.1 K; a more complicated magnetic structure occurs in the spectrum below 0.1 K. The observed shape of the spectrum can be interpreted in two ways: as some sort of magnetic ordering arising in the alloy or as some delayed paramagnetic relaxation. The very wide temperature interval over which a monotonic change in shape (broadening of a single line) occurs indicates a relaxation behavior of the iron in nearly the whole temperature range, but the appearance of satellites at $T = 0.05$ K could in principle also be connected with a freezing of part of the impurity spins. The following remark is appropriate here. The characteristic measurement time of the Mössbauer effect on a ^{57}Fe nucleus is less than 10^{-7} s (the lifetime of ^{57}Fe in the 14.4 keV level), so that spins which relax with a much larger time are practically frozen out within the present method. Conversely, spectral lines actually corresponding to frozen spins can be described by relaxations with small rate. These facts forced us to settle on a relaxation approach to describe all the observed spectra.

For this purpose we chose the Dattagupta-Blume stochastic model,[14] developed for calculating the shape of Mössbauer spectra under conditions of isotropic relaxation of the ion spin. The choice of a stochastic relaxation model was determined by the wider (in frequency range) region of applicability of theories of this class compared with relaxation perturbation theories, which are only applicable under conditions of "fast" relaxation when only a broadening of the spectral line is observed. We should note that similar spectra obtained[8] on a Pd(Fe) alloy with iron concentration ~ 10 ppm were described with the help of an anisotropic model with two different relaxation rates for rotations of the electron spin by 180° and 90° relative to the cubic lattice axis. However, the application of this model to our spectra did not give a satisfactory result. The Dattagupta-Blume model[14]

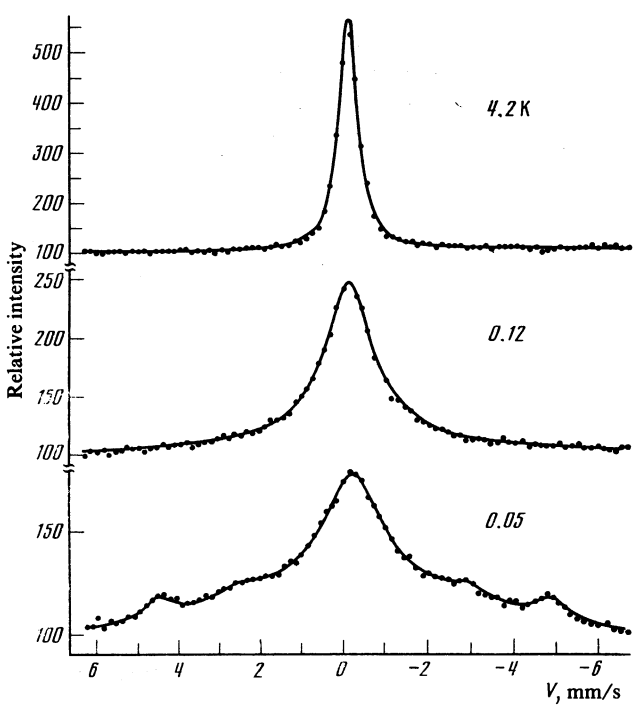

FIG. 1. Mössbauer spectra of a Pd(Fe,Co) alloy (0.01 at.% magnetic impurity) for various temperatures in the absence of an external magnetic field. Solid lines are the result of a computer analysis of the spectra.

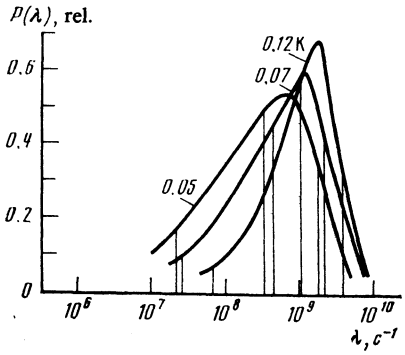

FIG. 2. Distribution of Fe spin relaxation frequencies for various temperatures. The position and length of the vertical segments correspond to the magnitudes and partial contributions of the frequencies, obtained from analyzing the spectra.

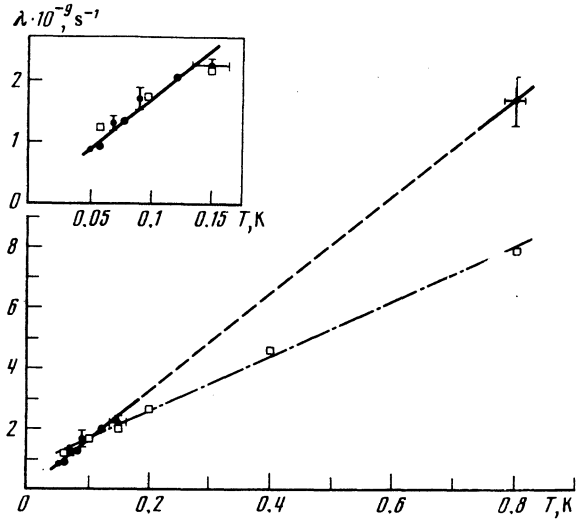

FIG. 3. Temperature dependence of Fe spin relaxation frequency: ●) mean frequency $\bar{\lambda}$ obtained in the present work: □) frequency recalculated from Ref. 6 [Pd(Fe, Co) alloy, ~0.001 at.% magnetic impurity].

also gave a poor description of the computer-reduced spectra for temperatures below 0.1 K if only one relaxation frequency λ was responsible for each spectrum. Good agreement was achieved only on using some set of frequencies λ. An approximate form constructed from this set of distributions of relaxation frequencies is shown in Fig. 2. Such a result agrees with the theoretical ideas of Kinzel and Fischer,[15] who have shown that the distribution of relaxation frequencies characteristic for spin glasses above the freezing temperature T_f is a consequence of the distribution of exchange interactions in disordered systems. The parameter T_f, however, does not necessarily coincide with the temperature determined by one or other experimental method for transition into spin glass. For example, in studies of a "classical" spin glass CuMn by neutron scattering[16] there was also a broad distribution of relaxation times at the temperature of the magnetic susceptibility peak, meaning that freezing of the Mn spins does not take place at this point. Unfortunately, there are no comprehensive data in the literature on susceptibility for the Pd(Fe) system with the required iron concentration (earlier measurements[3] were not carried out to sufficiently low temperatures), so that we cannot carry out the corresponding comparison. However, we can say, on the basis of our results, that in the study[5] of a PdFe (0.015 at.%) alloy by the muon precession method, the authors also observed at 0.11 K a slowing down of the relaxation of the iron moments to times large compared with the characteristic time of the muon experiment ($\sim 10^{-6}$ s) but did not achieve freezing of the phase.

The temperature dependence of frequency $\bar{\lambda}$ averaged over the set is shown in Fig. 3. This dependence is linear over the temperature range from 0.05 to 0.15 K; the point for $T = 0.8$ K, where the relaxation frequency was determined with lower accuracy, lies on the extension of the same straight line. The linear dependence of $\bar{\lambda}$ on T does not necessarily tie the relaxation only to the Korringa process, since spin-spin relaxation in a spin glass above T_f is also linear in temperature:[17]

$$\lambda \propto (T - T_f).$$

The recalculated temperature dependence of the relaxation frequency for a more dilute alloy[6] is also shown in Fig. 3, taking it into account that the quantity $1/\Delta\Gamma$ is proportional to frequency λ ($\Delta\Gamma = \Gamma - \Gamma_{app}$, where Γ and Γ_{app} are respectively the observed and apparatus widths of a single line). Both dependences give fairly close values of the relaxation rate in the temperature range from 0.05 to 0.15 K, but have different slopes, which may be due to the difference in iron concentrations in these alloys, and thus to the different values of the spin-spin contribution to the relaxation.

We note that the relaxation frequencies derived from the spectra (mean values $\bar{\lambda}$) are fairly reliable, since what is mainly important for describing the shape of a spectrum is the relation between relaxation frequency and the frequency of the hyperfine interaction, which is known.

2. Mössbauer spectra of ^{57}Fe in an external magnetic field

It follows from the Mössbauer spectra taken at 4.2 K in fields up to 50 kOe that Fe impurity shows the usual paramagnetic behavior: the dependence of hyperfine field on ^{57}Fe on external magnetic field is described by a Brillouin function with a value of the giant moment $\mu = (10.5 \pm 0.5)\mu_B$, spin $S = 4.7 \pm 0.3$, and saturation field $H_{sat} = (301.2 \pm 1.8)$ kOe (see below, curve 1 in Fig. 6). This result agrees in general with results of other authors for the same system.[1,6]

Spectra in external magnetic fields obtained at 50 mK are shown in Fig. 4. It is convenient to divide the range of magnetic fields used in the work in two as regards the form of the spectra: weak fields (up to 1 kOe), where the spectral lines are noticeably broadened as a result of the influence of relaxation, and strong fields (1–40 kOe), where there is no broadening so that the effect of relaxation can be neglected.

The Anderson relaxation stochastic model[18] was used to treat the low field spectra. In the presence of an external magnetic field $\mathbf{H}_0$, the Hamiltonian of the electron-nuclear system is written in the form:

$$\mathcal{H} = A\mathbf{I}\mathbf{S} - g\mu_B\mathbf{H}_0\mathbf{S} - g_I\mu_N\mathbf{H}_0\mathbf{I}, \quad (1)$$

where the first term is the hyperfine interaction of the electron (S) and nuclear (I) spins, the second term is the Zeeman interaction between the electron magnetic moment and the

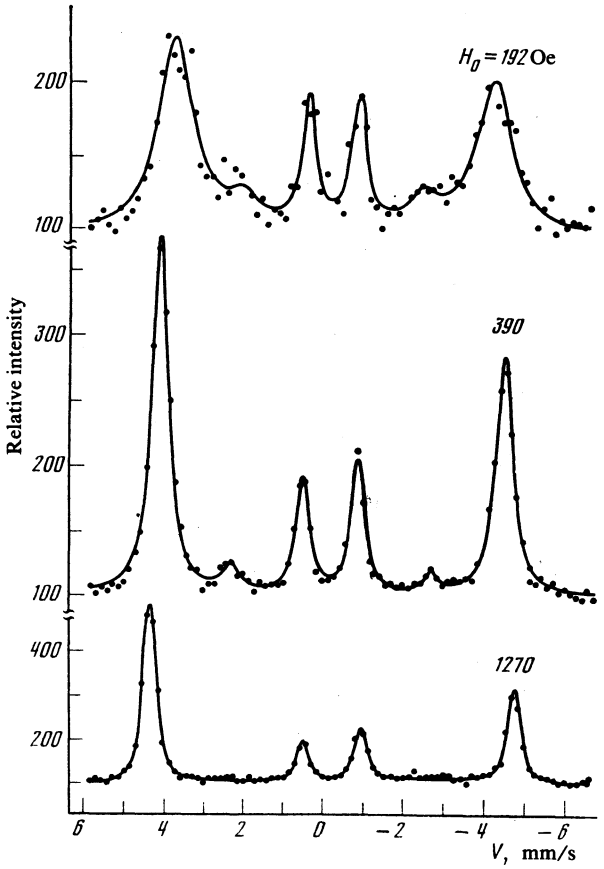

FIG. 4. Mössbauer spectra of Pd(Fe,Co) alloy (0.01 at.% magnetic impurity) in external magnetic fields at 0.05 K. Solid lines are results of computer analysis of the spectra.

field $\mathbf{H}_0$, the third term is the Zeeman interaction of the nuclear magnetic moment with the field $\mathbf{H}_0$. It is clear that for not too large $\mathbf{H}_0$ the last term is negligibly small compared with the first two. Since, furthermore, the inequality $|g\mu_B H_0| \gg A$ ($|A| \sim 1$ mK, $|g\mu_B H_0| \sim 100$ mK) is satisfied for iron, A IS can be replaced by the Hamiltonian AI_zS_z of diagonal form. This means that there corresponds to each electron level with a given magnetic quantum number m_s a nuclear Hamiltonian

$$\mathcal{H}_{\text{nucl}}^{m_s} = Am_sI_z = \hbar\omega_N^{m_s} I_z, \tag{2}$$

where $\omega_N^{m_s}$ is the corresponding Larmor precession frequency of the nuclear spin.

We can now go over to the Anderson model formalism and write the shape of the Mössbauer spectrum in the form

$$I(\omega) = \sum_{j=1}^{6} a_j \operatorname{Re}\{-\hat{W}\hat{A}_j^{-1}\hat{1}\}, \tag{3}$$

where $\hat{W}$ is the state population matrix corresponding to different m_s; the probability $\Omega_{nn'}$ of relaxation transitions between different m_s enters into the matrix $\hat{A}$; $\hat{1}$ is the unit matrix; a_j is the intensity of each of the six components of the Mössbauer spectrum.

It is possible to take account of only the three lowest energy levels m_s in the application of the model to our case, to simplify the computing procedure. Such an approximation is valid for fields $H_0 \gtrsim 200$ kOe because of the small population of all the higher levels, but it is too crude for weaker fields. In calculating the maximum projection $m_s = S$ corresponded to the hyperfine saturation field on ^{57}Fe and the value of S itself (or the g factor of the giant moment) entered Eq. (3) as an adjustable quantity, while the product gS remained constant, the magnitude of the giant moment, equal to $10.5\mu_B$. This implies that we are considering the relaxation of the giant moment as a whole, which is valid under conditions such that the exchange interaction of the relaxing giant moment for all the electrons in the cloud is greater than the interaction energy of this moment with electrons outside the cloud.

The chief purpose of analyzing the Mössbauer spectra with the present model is to obtain the probabilities (or frequencies) $\Omega_{nn'}$. The problem is then considerably simplified if only relaxation transitions with $\Delta m_s = 1$ are considered to be allowed.[19] The frequencies $\Omega_{nn'}$ are then related by the paired balance equations

$$W_1\Omega_{12} = W_2\Omega_{21}, \quad W_2\Omega_{23} = W_3\Omega_{32},$$

where the indices 1, 2, 3 indicate respectively the levels with $m_s = S, S-1, S-2$. In addition, Ω_{12} and Ω_{23}, according to the Wigner-Eckart theory, are proportional to the squares of the corresponding Clebsh-Gordan coefficients; out of the four frequencies $\Omega_{nn'}$ only one is thus an independent quantity. The electron relaxation time τ_{el} is related to the frequencies $\Omega_{nn'}$ by the relation[18]

$$1/\tau_{el} = \Omega_{12} + \Omega_{21}.$$

The spectra computer-calculated by the method of least squares are shown in Fig. 4 by the solid lines. The best description on the whole for all the spectra in weak fields is obtained for $g \approx 4.8$; this gives for the spin of the giant moment a value very close to 2. These values do not agree with the values of g and S found from the Brillouin function at 4.2 K. Similar discrepancies were found in other papers where various experimental methods were used; for example, the magnetic specific heat method gave a value $g \approx 6$ for a Pd(Fe) alloy with the same Fe concentration, while a measurement of magnetization and Mössbauer effect gave $g \approx 2$ (see Ref. 1). The reasons for these differences are not clear. It is possible that the results obtained from magnetization (from the Brillouin curve) reflect the static characteristics of the giant moment, while its dynamic properties appear in relaxation and specific heat. We note that varying g and S (for constant gS) has little influence on the values of the relaxation frequencies derived.

As a result of the analysis, the dependence of $1/\tau_{\text{el}}$ on external magnetic field was derived (Fig. 5). This dependence does not follow any theoretical curve for a relaxation process of any particular type; in addition, according to our results for the case of zero external field (the cross in Fig. 5) the relaxation frequency should in general increase with decreasing field for $H_0 \lesssim 100$ kOe. Such a behavior confirms the assumption made earlier about the existence of two relaxation channels in our alloy: one is the usual Korringa process and the other is related to the interactions between impurity spins. The first contribution should then grow with

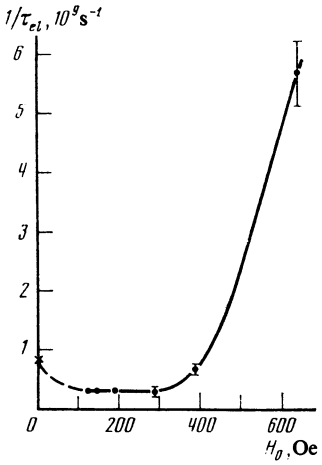

FIG. 5. Dependence of Fe spin relaxation frequency on external magnetic field at $T = 0.05$ K. The cross indicates the value of $\bar{\lambda}$ in the absence of a field.

increasing magnetic field (as the Korringa relaxation freqency increases with field), while the second falls because the field aligning the Fe spins suppresses the fluctuations of the interaction between them. An increase in spin-spin relaxation time with increasing external field ($\tau \propto H_0^{1/2}$) was observed earlier.[20]

Although the γ rays were recorded in the direction of the applied field, central components corresponding to the forbidden nuclear γ transitions $1/2 \rightarrow 1/2$, $-1/2 \rightarrow -1/2$ are present in the spectra (see Fig. 4). This may be associated with incomplete alignment of the Fe spins in fields up to 1 kOe, due to the RKKY interaction between the spins. This means that the external magnetic field which produces mean spin components $\langle S_z \rangle$ different from zero somehow "induce" randomly directed molecular fields H_{mol} in the paramagnetic system. The mean value $\overline{\Theta}$, of the angle Θ between the directions of the Fe spin and the field $\mathbf{H}_0$ is then determined by the vector sum of $\mathbf{H}_0$ and the mean field $\langle \mathbf{H}_{\text{mol}} \rangle$. The angle $\overline{\Theta}$ can easily be obtained from the intensities of the central components of the spectrum, and $\langle H_{\text{mol}} \rangle$ can also be found from this. The maximum value of $\langle H_{\text{mol}} \rangle$ is reached in practice for $H_0 \lesssim 1$ kOe, when the hyperfine field on Fe (and therefore $\langle S_z \rangle$) is close to saturations (see curve 2 in Fig. 6),

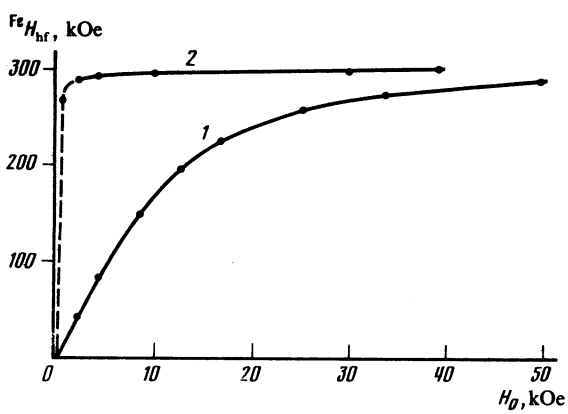

FIG. 6. Dependence of hyperfine field at a ^{57}Fe nucleus on external magnetic field: 1) $T = 4.2$ K, solid line shows the Brillouin function; 2) $T = 0.05$ K.

and is about 160 Oe. Using the relation

$$g\mu_B \langle H_{\text{mol}} \rangle \approx kT_f$$

we can obtain from this a rough estimate of the freezing temperature T_f. If we take the g factor of the giant moment to equal 2, then $T_f \approx 20$ mK. Although, therefore, we cannot have a spin glass in an alloy with the given concentration of Fe in Pd at 50 mK, the alternating-sign RKKY interaction, characteristic of this type of ordering, will show up on applying an external field which induces randomly directed molecular fields in the paramagnetic system.

As already indicated, relaxation in strong fields (1 to 40 kOe) does not have a noticeable influence on the shape and position of the spectral components, so that the dependence of hyperfine field on iron, $^{Fe}H_{nf}$, on external magnetic field H_0 for the present region can be derived from the magnitude of the Mössbauer spectrum splitting. The corresponding curve is shown in Fig. 6 (curve 2). It can be seen that in fields up to 40 kOe the hyperfine field on iron still does not reach saturation. While the main rise in $^{Fe}H_{hf}$ takes place fairly rapidly (in field $H_0 < 2$ kOe), a slow monotonic increase (in absolute value) of hyperfine field is observed over the whole field range used. As an explanation we can suggest that such a hyperfine field is produced by a contribution to $^{Fe}H_{nf}$ from conduction electrons of the matrix polarized by the external field. This contribution can then be written as

$$H_{hf} = a\chi_{Pd} H_0, \tag{4}$$

where a is a coefficient equal to the hyperfine field produced at an Fe nucleus by a single polarized matrix electron (by one Bohr magneton); χ_{Pd} is the magnetic susceptibility of Pd, which at low temperatures is 7×10^{-6} cm$^3 \cdot$g^{-1} (Refs. 1,3), which in Bohr magnetons per atom and in a field 1 Oe is $\approx 1.3 \times 10^{-7} \mu_B$ (atom$\cdot$Oe)$^{-1}$. Substituting this value into Eq. (4) and also introducing there the slope $\Delta H_{hf}/\Delta H_0$ of the experimental curve 2 (see Fig. 6) observed in the field range 10 to 40 kOe, we obtain $a \approx -1600$ kOeμ_B^{-1}. Unfortunately there are only calculations of the contribution to the hyperfine field from the electrons of different s clouds for the case of an isolated iron atom,[21] so that we cannot make a proper comparison with them.

3. Hyperfine field at Co

A clearly marked asymmetry is a feature of spectra measured in an external magnetic field at 0.05 K (see Fig. 4). It is produced by polarization of the parent nucleus ^{57}Co in the effective field $^{Co}H_{eff}$. The magnitude of this field can be determined by analysis of the intensity of the components of the spectrum. In fact the intensity $I_{m_{3/2}m_{1/2}}$ of the emission line of the Mössbauer spectrum is proportional to the population $P(m_{3/2})$ of the corresponding magnetic substate of the excited state $I = 3/2$ ^{57}Fe. The level $I = 3/2$ is populated in turn as a result of the decay of ^{57}Co (the decay scheme is shown in Fig. 7). Therefore

$$I_{m_{3/2}m_{1/2}} \propto P(m_{3/2}) = \sum_{m_{7/2}} P(m_{7/2})\, Q_{m_{7/2}m_{3/2}}, \tag{5}$$

where the summation is carried out over all magnetic sub-

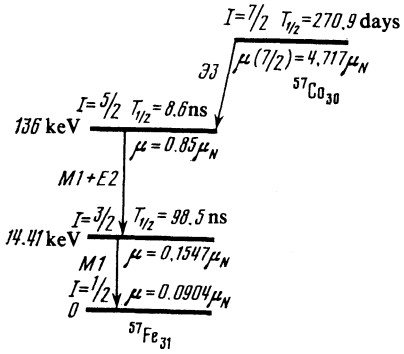

FIG. 7. Decay scheme of ^{57}Co.

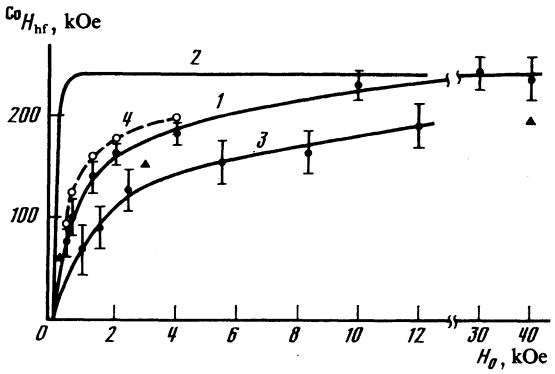

FIG. 8. Dependence of the hyperfine field at the ^{57}Co nucleus on the exeternal magnetic field: 1—ME/ON method; 2—Brillouin function ($S = 3/2$, $\mu = 9.5\,\mu_B$, $H_{sat} = 240$ kOe, $T = 0.05$ K); 3—ON method on 136-keV line[24]; 4—ME/ON with allowance for the relaxation correction; ▲—data of Ref. 4 for ^{60}Co in Pd(Fe,Co) alloys with magnetic-impurity density < 0.002 at.%.

states of ^{57}Co ($I_0 = 7/2$) and $P(m_{7/2})$ is the population of the substates determined by the Boltzmann factor. In the case of pure magnetic hyperfine interaction

$$P(m_{7/2}) = \exp\left(\frac{m_{7/2}\Delta}{kT}\right)\left[\sum_{m_{7/2}} \exp\left(\frac{m_{7/2}\Delta}{kT}\right)\right]^{-1}, \qquad (6)$$

where $\Delta = \mu_N g_{7/2}{}^{Co} H_{eff}$ is the spacing of the Co nuclear substates. In Eq. (5) $Q_{m_{7/2}m_{3/2}}$ is the matrix of the probability of transitions between substates $m_{7/2}$ and $m_{3/2}$. If the local magnetic axis for Co and Fe ions is the same, and disordering processes do not have time to take place for the excited states in the lifetime of these states, then the matrix $\hat{\mathbf{Q}}$ is expressed in terms of the Clebsh-Gordan coefficients and can be easily calculated.

The magnitude of the effective field at Co is obtained most simply from the relative intensity of the outer components of the Mössbauer spectrum:

$$\frac{I_{3/2,\,1/2}}{I_{-3/2,\,-1/2}} = \frac{\sum_{m_{7/2}} Q_{m_{7/2},\,3/2} \exp(m_{7/2}\Delta/kT)}{\sum_{m_{7/2}} Q_{m_{7/2},\,-3/2} \exp(m_{7/2}\Delta/kT)}. \qquad (7)$$

The formalism of the orientation factors $B_k(I)$ (Ref. 23) can also be used in calculating $^{Co}H_{eff}$. These factors are related to the population of the magnetic substates by the expression

$$B_k(I) = [(2k+1)(2I+1)]^{1/2} \sum_{m=-I}^{I} (-1)^{I+m} \begin{pmatrix} I & I & k \\ -m & m & 0 \end{pmatrix} P(m_I), \qquad (8)$$

where the brackets in the sum sign denote a $3j$ symbol and k is the order of the orientation factor.

For the $I = (3/2)$ ^{57}Fe level the factors $B_k(3/2)$ can easily be obtained from the intensities of the components of the experimental spectrum. The orientation factors of the parent nucleus ^{57}Co are obtained from $B_k(3/2)$ with the help of misorientation coefficients $U_k(7/2 \to 3/2)$ in the form

$$B_k(7/2) = B_k(3/2)/U_k(7/2 \to 3/2). \qquad (9)$$

The coefficients U_k have been tabulated.[23]

As expected, the values of the effective field at ^{57}Co for our specimen obtained both from the ratio of intensities of the outer components of the Mössbauer spectrum and from the orientation parameter B_1 agree with one another. A small disagreement is only observed in fields 30 and 40 kOe, where the mean values are taken for the hyperfine field. Since the sign of this field at Co is positive, then $^{Co}H_{hf} = H_{eff} - H_0$. The dependence of $^{Co}H_{hf}$ on external field H_0 at 50 mK is shown in Fig. 8, curve 1. Curve 2 corresponds to the Brillouin function for a spin 3/2 and magnetic moment $9.5\,\mu_B$, describing the behavior of a free giant Co moment in Pd.

The results of measurements of the angular distribution of 136 keV γ-rays of oriented ^{57}Co nuclei, carried out on our specimen,[24] are shown in the same figure (points on curve 3).

It can be seen from Fig. 8 that there is an extremely slow increase in the experimental curves 1 and 3 compared with the Brillouin curve, and also a disagreement between the values of hyperfine field obtained from measurements by different methods. Reduced values of the field at ^{57}Co were observed in ME/ON measurements.[6–8] Such behavior was explained there by relaxation destruction of the initial ^{57}Fe nuclear orientation at intermediate levels of the γ cascade (levels 5/2 and 3/2 in Fig. 7). Calculations in which the relaxation parameters determined from the broadening of the components of the Mössbauer spectrum were used, restored the variation of the hyperfine field at Co to the Brillouin curve. We carried out similar calculations. Values of the relaxation and field parameters were calculated according to Eqs. (3.6) and (3.25) of Litterst *et al.*[8] Values of the hyperfine field at ^{57}Co obtained by including relaxation processes are shown in Fig. 8 (curve 4). It is seen that for our specimen the relaxation correction is insufficient to explain the observed departures. The relaxation mechanism discussed as a reason for the observed reduction in field at Co can also not explain the results obtained on our specimen by the oriented-nuclei method (ON). It was indicated[8] that the relaxation destruction of the initial ^{57}Co orientation has about the same effect on the 3/2 and 5/2 ^{57}Fe levels. In measurements of the 136

keV γ-ray anisotropy, reorientation due to relaxation only shows up for the 5/2 level. If, therefore, this process had a noticeable influence, then the field measured by the ON method would be larger than the field obtained from the Mössbauer spectrum. In fact the opposite situation occurs.

Another explanation of the behavior of the hyperfine field at Co was given by Flouquet *et al.*,[4] who interpreted their results as the Kondo effect on the Co impurity. The Kondo temperature was determined as $T_K = 0.12 \pm 0.01$ K. The form of our experimental curve (curve 1) can be described according to the resonance level model[25] by the expression

$$^{Co}H_{hf} = \frac{2^{Co}H_{sat}}{\pi} \operatorname{arctg}\left(\frac{g\mu_B H_0}{kT_0}\right), \tag{10}$$

which is also valid for the model of spin fluctuations of the moment. We obtain a similar value for the characteristic temperature $T_0 = 0.14 \pm 0.04$ K. We consider the temperature T_0 as a parameter characterizing the process of desctruction of the impurity local moment as a result of interaction with the conduction electrons of the matrix (Kondo compensation of the moment, spin fluctuations). We cannot, however, understand the difference noted above in values of hyperfine fields, measured on one and the same specimen by the ME/ON method and by the method of γ-ray distribution from oriented nuclei, by such a mechanism without additional assumptions.

In explaining this difference we want first of all to point out that we only obtain in fact the first order orientation parameter $B_1(7/2)$ [see Eq. (8)] from Mössbauer spectra, while the orientation parameter $B_2(7/2)$ is measured by the ON method. Equations (7) and (9), on the basis of which $^{Co}H_{hf}$ is determined, are valid in the case of collinear hyperfine fields for the initial long-lived state $I_0 = 7/2$ (^{57}Co) and the intermediate excited states of ^{57}Fe; such a situation is usually met in work on ferromagnets. We now consider the case when the collinearity mentioned is absent and the field on Fe after K capture is turned through some angle θ relative to the original direction of the field on Co. Since the hyperfine field on Fe in external fields $H_0 \gtrsim 1$ kOe is oriented along H_0 (**Z** axis), this means that the Co magnetic moments are oriented axisymmetrically, forming an angle θ with the direction of the external magnetic field (local axes Z'). If the nuclear Larmor precession frequency, $\omega_N{}^I$, satisfies the condition $\omega_N{}^I \tau_I > 1$ (where τ_I is the lifetime of the corresponding excited state), which is fulfilled for the level $I = 5/2$, then it can be shown that the k-th order orientation parameters of the intermediate state I relative to the axis of quantization Z are related to the orientation parameters of the initial state I_0 relative to the axis by the relation

$$B_k(I, Z) = U_k(I_0 \to I) B_k(I_0, Z') P_k(\cos\theta), \tag{11}$$

where P_k is a Legendre polynomial.

It follows from Eq. (11) that the orientation of ^{57}Co is effectively reduced by the factor $P_k(\cos\theta)$. The "fictitious" hyperfine field determined from Eq. (9) neglecting the noncollinearity of fields, will therefore be less than the true field by an amount determined by the angle θ. It can also be seen from Eq. (11) that different moments of the orientation are weakened in different degrees, so that the values of the fictitious fields determined by different moments of orientation will differ. In particular, the hyperfine field determined by the nuclear orientation method (from the orientation factor B_2) will always, for noncollinearity of fields, be less than the field obtained from measurements of relative intensities of components of the Mössbauer spectrum (from the factor B_1). We should note that similar differences should be obtained in the case of collinear hyperfine fields rotated through an angle θ to the Z axis, which was not realized in our experiments.

The observed differences in the values of the hyperfine fields measured by different methods can be explained on the basis of the above by noncollinearity of these fields on the parent (Co) and daughter (Fe) nuclei.[1)] Obviously, if such a noncollinearity exists, then besides the effective destruction of the Co local moment, it provides its own contribution to a reduction in the measured hyperfine field compared with the Brillouin function. We note that since there are no physical bases for the existence of some definite value of the angle θ, an averaging has to be carried out over the corresponding distribution of angles in Eq. (11). It is natural to suppose that this distribution becomes narrower as the external field increases, while the average angle $\bar{\theta}$ decreases. Calculations carried out according to Eq. (11) show that to explain the observed disagreement between the ME/ON ($H_{hf}^{Co} = 230$ kOe and ON results ($H_{hf}^{Co} = 190$ kOe) in a field $H_0 = 10$ kOe, the angle θ must be 25°. Taking account of the distribution gives a slightly smaller value for the average angle $\bar{\theta}$.

The model discussed assumes that the actual process of measuring the change in direction of the hyperfine field does not affect the orientation of the nuclear system; i.e., that the rotation time T_{rot} is much less than the lifetime of the intermediate states and than the inverse frequency of the hyperfine interaction for these levels. In our case this means that

$$T_{rot} < 10^{-9} \text{ s}. \tag{12}$$

The time of rotation is, in fact, the time for electron relaxation of the Fe ion (the time for readjustment of the electron cloud as a result of K capture is shorter than 10^{-12} s, so that it can be neglected). The dependence of relaxation frequency on the magnitude of the external magnetic field, given in the previous section (see Fig. 5), shows that the condition of Eq. (12) is entirely satisfied in fields $H_0 \geqslant$ kOe.

It would be natural to explain the misorientation of the Co spins relative to the external field, characterized by some distribution of the angles θ, as for the Fe spins, by the alternating-sign RKKY interaction between the spins. However, these interactions should be more than an order of magnitude stronger for Co than for Fe. Hamzic and Campbell,[26] who measured the magnetoresistance of dilute Pd(Co) alloys, associated the hindered alignment of the Co moments along the external field with two possible causes: a) the RKKY interaction mentioned and b) the interaction between the Co orbital momentum with the random local crystal fields. However, we cannot consider the question of the existence of an unquenched orbital momentum for the Co ion in a cubic Pd matrix as finally cleared up at present.[27]

Table I Hyperfine fields at Co nuclei in dilute Pd(Fe,Co) alloys

№	Concentration at.%	Method	$^{Co}H_{hf}$, kOe	T_{meas}, K	H_0 kOe	Reference
1	0.5 (Co) 1.0 (Co)	NMR	230±5 220±5	0.6	1—15	[28]
2	1.0 (Co)	ON	225±20	(2—3)·10^{-2}	8	[29]
3	0.03 (Co)	ON	130±10	(3—6)·10^{-2}	5.7	[30]
4	0.05 5·10^{-4} (Co)	ON	205±25	(1—3)·10^{-2}	0—15	[31]
5	0.1 (Co, Fe) 0.03 (Co, Fe)	EM/ON	260±20 147±20	0.15	0	[32]
6	(7—78)·10^{-4} (Fe, Co)	ON	195±6	(3—12)·10^{-3}	40	[4]
7	(7; 0.7)·10^{-4} (Co) 10^{-3} (Fe)	EM/ON	190±10	28·10^{-3}	10	[8]
8	0.1 (Co, Fe)	EM/ON	110±20	5.2·10^{-2}	0	Present work
9	0.01 (Fe, Co)	EM/ON	240±20	5·10^{-2}	40	Present work
10	0.01 (Fe, Co)	ON	190±20	(17—35)·10^{-3}	12	[24]

We suggest that the large value for the interaction of a Co spin with the surrounding spins, essential to explain the observed disorientation, is connected with the nature of the Co spin which interacts more strongly than Fe with the conduction electrons. The Kondo effect which evidently occurs for Co in Pd (see above) can be considered as evidence for this.

We also studied Pd(Fe,Co) alloys with magnetic impurity concentrations (predominantly Co) in the range 0.1 to 0.2 at.% to clarify the problem of the reasons for the reduction in hyperfine field at Co. The transition to a magnetically ordered state for this specimen was spread over a large temperature interval (from 6.0 to 1.3 K). The Mössbauer spectrum at 50 mK in the absence of an external field corresponded to a magnetically ordered state for iron with a saturation value of the magnetic moment for all atoms (the Mössbauer spectrum splitting corresponded to a saturation field for Fe in Pd equal to 295 kOe); at the same time the field on Co measured by the asymmetry of the spectrum was $^{Co}H_{hf} = 120 \pm 20$ kOe, which is appreciably less than the saturation field for ferromagnetic specimens for concentrations 0.5 to 1 at.% measured by NMR and ON (see Table I). A lowered value $^{Co}H_{hf} = 147 \pm 20$ kOe was also observed in the absence of an external magnetic field for specimens with impurity concentrations 0.03 at.%.[32] On the basis of these results it can be proposed that ordering of the Co spins of the spin glass type arises in the concentration region given. Underestimates of the field can be obtained because of noncollinearity of the hyperfine fields on Co and Fe and (or) as a result of an unstable spin glass configuration.[33] In the latter case the observed value of the field on Co will depend on the relation between the fluctuation time of the spin configuration, T_{fl}, and the nuclear spin-lattice relaxation time.

CONCLUSIONS

It has thus been shown, as a result of analyzing Mössbauer spectra of a very dilute Pd(Fe,Co) alloy, that above 0.05 K the iron ions are in the paramagnetic state. The broad distribution of relaxation frequencies for the Fe electron spins, and also the dependence of the relaxation frequency on temperature and on the magnitude of the external magnetic field indicate the existence of two contributions to the relaxation: the first is related to the Korringa mechanism, the second is caused by a spin-spin interaction of the RKKY type. The latter is revealed on application of a magnetic field (up to 1 kOe), which induces a misoriented magnetic structure in the spectrum of Fe spins, evidently characteristic for the behavior of a spin glass in a magnetic field and existing slightly above the freezing temperature.

The growth of the hyperfine field on Fe with increasing external field in the region of large (above 10 kOe) fields is probably produced by a contribution to this field from the conduction electrons polarized by the external field.

The behavior of a Co ion in Pd is appreciably different from the behavior of a free spin. The slowing down of the growth of $^{Co}H_{hf}$ with an increase in external field can be explained by the effective destruction of the Co local moment (Kondo compensation, spin fluctuations). The difference between results for $^{Co}H_{hf}$ obtained by the ME/ON and ON methods on one and the same specimen point to disorientation of the Co spins relative to the external field and to noncollinearity of the fields on the parent (^{57}Co) and daugher (^{57}Fe) nuclei.

The lowered value of $^{Co}H_{hf}$ in an alloy with magnetic impurity concentrations (predominantly Co) in the range 0.1 to 0.2 at.% is interpreted on the assumption that at 50 mK the alloy is in the spin glass state.

The direction of the electron spins can be established by comparing the results of measurements of hyperfine fields carried out by the ME method and by the ON method of angular distributions of γ-rays, and conclusions about the existence of a spin glass can be drawn.

[1)]In principle the difference between the fields determined from different orientation factors can be related to the inapplicability of the effective field approximation, but we have so far no basis for assuming that this approximation is inapplicable in our case.

[1]G. I. Niewenhuys, Adv. Phys. **24**, 515 (1975)
[2]I. Ya. Korenblit and E. F. Shender, Usp. Fiz. Nauk **126**, 233 (1978) [Sov. Phys. Usp. **21**, 832 (1978)].
[3]G. Chouteau and R. Tournier, J. Phys. (Paris) **32**, C1-1002 (1971).
[4]J. Flouquet, O. Taurian, J. Sanchez, M. Chapellier, and J. L. Tholence, Phys. Rev. Lett. **38**, 81 (1977).
[5]K. Nagamine, N. Nishida, S. Nagamiya, O. Hashimoto, and T. Yamazaki, Phys. Rev. Lett. **38**, 99 (1977).
[6]W. Gierisch, W. Koch, F. J. Litterst, G. M. Kalvius, and P. Steiner, Magn. and Magn. Mat. **5**, 129 (1977).
[7]A. M. Afanas'ev, F. J. Litterst, and W. Gierisch, J. Phys. Lett. **39**, L183 (1978).
[8]F. J. Litterst, A. M. Afanas'ev, V. D. Gorobchenko, and G. M. Kalvius, J. Phys. C **12**, 5551 (1979).

[9]V. A. Andrianov, E. P. Kaminskaya, M. G. Kozin, A. Yu. Pentin, and V. S. Shpinel', Proc. 15th All-Union Conf. on Physics of Magnetic Phenomena, Perm', Part II, p. 170 (1981).
[10]V. A. Andrianov, M. G. Kozin, A. Yu. Pentin, V. V. Turovtsev, and V. S Shpinel', Proc. 12th All-Union Conf. on Low Temperature Physics, Kishinev, Part I, p. 75 (1982).
[11]S. T. Boldarev, M. G. Kozin, and V. S. Shpinel', Proc. 31st Conf. on Nuclear Spectroscopy and Structure of the Atomic Nucleus, Samarkand, p. 627 (1981).
[12]K. P. Mitrofanov, M. V. Plotnikova, and N. I. Rokhlov, Prib. Tekh. Eksp. No. 2, 75 (1970) [Instrum. and Exp. Techn. **13**, 390 (1970)].
[13]S. I. Reiman and K. P. Mitrofanov, Prib. Tekh. Eksp. No. 2, 66 (1980) [Instrum. and Exp. Techn. **23**, 358 (1980)].
[14]S. Dattagupta and M. Blume, Phys. Rev. B **10**, 4540 (1974).
[15]W. Kinzel and K. H. Fischer, Solid State Commun **23**, 687 (1977).
[16]A. P. Murani, Solid State Commun. **33**, 433 (1980).
[17]K. H. Fischer, Physica (Utrecht) **86–88B**, 813 (1977).
[18]F. Hartmann-Boutron, Ann. Phys. (France) **9**, 285 (1975).
[19]M. Blume and R. Orbach, Phys. Rev. **127**, 1587 (1962).
[20]B. D. Dunlap, G. R. Davidson, M. Eibschutz, H. J. Guggenheim, and R. C. Sherwood, J. Phys. (Paris) **35**, C6, 429 (1974).
[21]R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).
[22]J. G. Dash, R. D. Taylor, D. E. Nagle, P. P. Craig, and W. M. Visscher, Phys. Rev. **122**, 1116 (1961).
[23]K. S. Krane, Nucl. Data Tables **11**, 407 (1973).
[24]V. A. Andrianov, M. G. Kozin, A. Yu. Pentin, V. S. Shpinel', M. Rotter, B. Sedlak, P. Chizhek, and I. Englikh, Proc. 33 Conf. on Nuclear Spectroscopy and Structure of the Atomic Nucleus, Moscow, p. 517 (1983).
[25]K. D. Schotte and D. Schotte, Phys. Lett. A **55**, 38 (1975).
[26]A. Hamzic and I. A. Campbell, J. Phys. Lett. (France) **42**, L17 (1981).
[27]A. L. Erzinkyan, V. V. Murav'eva, V. P. Parfenova, and V. V. Turovtsev, Hyperfine Interactions, **12**, 227 (1982).
[28]M. Katayama, K. Kumagai, T. Kohara, K. Asayama, I. A. Campbell, N. Sano, S. Kobayashi, and J. Itoh, J. Phys. Soc. Jpn. **40**, 429 (1976).
[29]A. L. Erzinkyan and V. P. Parfenova, Zh. Eksp. Teor. Fiz. **67**, 1886 (1974) [Sov. Phys. JETP **40**, 937 (1974)].
[30]V. P. Parfenova, N. E. Alekseevskiĭ, A. L. Erzinkyan, and V. S. Shpinel', Zh. Eksp. Teor. Fiz. **53**, 492 (1967) [Sov. Phys. JETP **26**, 324 (1968)].
[31]M. F. Cracknell, J. C. Gallop, and G. V. H. Wilson, Phys. Lett. A **24**, 719 (1967).
[32]T. Ericsson, M. T. Hirvonen, T. E. Katila, and P. Reivari, Proc. 12th Int. Conf. Low. Temp. Phys. Kyoto 1970, Ed. E. Kondo, Academic Press of Japan (1971) p. 765.
[33]S. E. Barnes, Phys. Lett. A **87**, 121 (1981).

Translated by R. Berman