Characteristics of low-temperature magnetic ordering of Mn impurity atoms in dilute PtFe and Pd(Co, Fe) alloys

G. M. Gurevich,[1)] A. L. Erzinkyan,[2)] V. N. Pavlov, V. P. Parfenova,[2)] B. Sedlák,[3)] S. V. Topalov,[1)] and M. Trhlik[3)]

Joint Institute of Nuclear Research, Dubna

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A study was made of the low-temperature nuclear orientation of ^{54}Mn in PtFe alloys containing 0.05, 0.1, or 1 at.% Fe, and also in Pd + 1 at.%Fe and Pd + 1 at.% ($Co_{0.8}Fe_{0.2}$) alloys. The effective magnetic field at the ^{54}Mn nuclei as a function of the sample temperature and the external magnetic field are interpreted as a manifestation of noncollinearity of the magnetic moments of Mn with respect to the direction of the macroscopic magnetization. This noncollinearity increases as a function of the Fe concentration in the alloys and can be attributed to the presence of competing ferromagnetic and antiferromagnetic interactions.

1. INTRODUCTION

The addition of Fe and Co to palladium and platinum, which are paramagnets characterized by a strong exchange enhancement, gives rise to a long-range positive spin polarization of the 4*d* and 5*d* electrons and creates ferromagnetic order even at very low concentrations of the 3*d* impurity. Such polarization gives rise to "giant" magnetic moments associated with the 3*d* atoms. The difference between the exchange enhancement factors of Pd and Pt makes the giant moments in Pt smaller than in Pd and the critical concentration for the appearance of ferromagnetism correspondingly higher. For example, in the case of **Pd**Fe this concentration is ~0.1 at.% (Ref. 1), whereas in the case of **Pt**Fe it is 0.76 at.% Fe (Ref. 2). The Mn impurity in Pd also creates a giant moment and at concentrations from 0.15 to 3 at.% it produces the ferromagnetic order. The elements Mn and Pt do not induce giant moments or ferromagnetism.[3] At Mn concentrations from 0.05 to 3.8 at.% the **Pt**Mn system behaves as a spin glass.[3,4] In this respect the **Pt**Mn alloys differ qualitatively from the **Pd**Mn system.

The macroscopic methods (such as the measurement of the magnetic susceptibility and magnetization, specific heat, electrical resistivity, etc.) used widely in studies of the magnetic behavior of dilute alloys are not always suitable in the case of low impurity concentrations. Nuclear methods (Mössbauer effect, perturbed angular correlations, nuclear orientation) make it possible to carry out investigations in a range of impurity concentrations inaccessible to macroscopic methods. In particular, the method of oriented nuclei, because of the sensitivity with which radioactive radiation can be detected, is convenient for the study of systems with extremely low impurity concentrations. Moreover, this method is very effective in investigations of the local magnetization of the impurity atoms.[5]

The observed quantity in experiments on oriented nuclei is the anisotropy of the angular distribution of nuclear radiation (usually γ radiation). In the case of a nuclear ensemble with an axial symmetry the anisotropy measured at an angle of θ relative to the nuclear orientation axis is

$$W(\theta, T) = \sum_{\text{even}} A_k U_k Q_k B_k(T) P_k(\cos\theta), \qquad (1)$$

where the coefficients A_k and U_k are governed by nuclear decay, Q_k is a geometric factor, $B_k(T)$ are the orientation functions of the parent nucleus described completely by the nuclear sublevel populations, and $P_k(\cos\theta)$ are the Legendre polynomials. The populations of the nuclear sublevels in the case of the purely magnetic interaction are governed by the ratio of the ground state splitting energy of the nucleus, $\mu B/I$, to the thermal energy kT (μ and I represent the magnetic moment and the nuclear spin, B is the magnetic field at a nucleus, and T is the absolute temperature). If all the nuclear parameters, including temperature, are known, the measurements of the angular anisotropy can be used to find the magnetic field at a nucleus.

The Hamiltonian of the interaction of a magnetic atom in an external magnetic field B_{ext} is of the form

$$\mathcal{H} = A\mathbf{I}\mathbf{S} + g\mu_B \mathbf{B}_{\text{ext}}\mathbf{S} + g_n\mu_n \mathbf{B}_{\text{ext}}\mathbf{I}. \qquad (2)$$

where S is the electron spin; g and g_n are the electron and nuclear g factors, μ_B is the Bohr magneton, μ_n is the nuclear magneton, and A is the hyperfine interaction constant.

When the electron moments are aligned completely along the external magnetic field the local quantization axes of each nucleus coincide with the macroscopic magnetization axis $\mathbf{Z}_0$, governed by the direction of the external magnetic field. The magnetic field at a nucleus is then the sum of the hyperfine and external fields:

$$B = B_{\text{hf}} \pm B_{\text{ext}}. \qquad (3)$$

According to Eq. (2) the magnetic hyperfine field is $B_{\text{hf}} = AS/g_n\mu_n$.

If the local orientation axes $\mathbf{Z}_i$ of the nuclei do not coincide with the macroscopic axis $\mathbf{Z}_0$, then measurements along $\mathbf{Z}_0$ will give the value of W which corresponds to an effective magnetic field different from Eq. (3). The effective field B_{eff} calculated from Eq. (1) ignoring the deviation of $\mathbf{Z}_i$ from $\mathbf{Z}_0$ is temperature-dependent because the angular distributions of Eq. (1) vary with temperature.[6,7] This is the reason for the high sensitivity of the nuclear orientation experiments to the effects of a local breakdown of the macroscopic symmetry. As pointed out in Ref. 6, the nuclear orientation method is much more sensitive to the noncollinearity of ($\mathbf{Z}_i$, $\mathbf{Z}_0$) than the magnetization experiments.

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We used the low-temperature nuclear orientation method to study the magnetic behavior at low concentrations of the ^{54}Mn impurity in Pt + 0.05 at.% Fe, Pt + 0.1 at.% Fe, Pt + 1 at.% Fe, and also in Pd + 1 at.% Fe and Pd + 1 at.% $Co_{0.8}Fe_{0.2}$.

2. EXPERIMENTAL METHOD

The concentrations of Fe and Co in the samples of the investigated alloys were determined using a scanning x-ray microscope. An analysis demonstrated a fairly uniform distribution of Fe and Co in the alloys. The ^{54}Mn impurity was introduced by placing a drop of a solution of $^{54}MnCl_2$ on a substrate made of a given alloy. When the substrate was dried, it was remelted in vacuum together with the deposited radioactive impurity and was subsequently rolled. The finished samples were in the form of a foil of thickness 3–5 μm. The Mn concentration in the samples was less than 10^{-5} (including the content of the stable Mn in the radioactive material). The samples containing Pd were subjected to brief vacuum annealing at 800°C immediately before measurements; this was done in order to remove the sorbed hydrogen which could affect the results.[8]

The nuclear orientation experiments were carried out using the SPIN apparatus described in Ref. 9. Samples were soft-soldered to a large-area heat exchanger together with ^{60}CoFe acting as a nuclear thermometer and were placed in the solution chamber of a ^{3}He–^{4}He refrigerator. The γ radiation from ^{54}Mn (835 keV) and ^{60}Co (1173 and 1332 keV) was recorded using two Ge(Li) detectors oriented at angles of $\theta = 0$ and 90° relative to the direction of the external magnetic field, which was created by a pair of superconducting coils.

The value of $W(\theta)$ was determined experimentally at angles $\theta = 0$ and 90° as the ratio N_T/N_∞, where N_T and N_∞ are, respectively, the counting rates at a low temperature T and at a "high" temperature (0.6–1 K) when the orientation of the nuclei was missing (and the radiation was isotropic). The measured counting rates were automatically corrected electronically for the background and the drift of the spectrometric channel. The measurements were carried out in the temperature interval 11–50 mK in an external magnetic field up to 1.2 T.

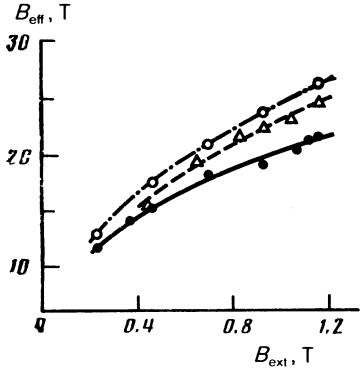

FIG. 1. Dependence of B_{eff} at the ^{54}Mn nuclei on the external magnetic field at a constant temperature of $T = 12$ mK obtained for PtFe (○—alloy with 0.05 at.% Fe; △—alloy with 0.1 at.% Fe; ●—alloy with 1 at.% Fe). The lines are drawn for clarity. The statistical errors are given in all the figures with the exception of those cases when they are smaller than the symbol used to represent the measured values.

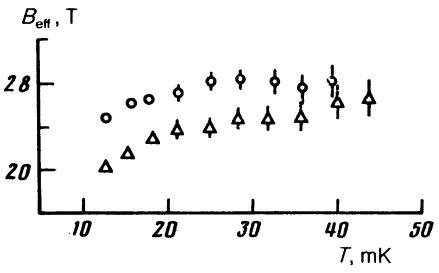

FIG. 2. Temperature dependence of B_{eff} at ^{54}Mn for Pt + 0.1% Fe in a constant external field: ○) 1.16 T; △) 0.69 T.

3. RESULTS AND DISCUSSION

1. ^{54}Mn:PtFe

The γ-ray anisotropy of W(0°) and W(90°) was determined for ^{54}Mn in PtFe alloys with Fe concentrations of 0.05, 0.1, and 1 at.% as a function of the external magnetic field and of temperature. The measured anisotropy of the angular distribution of γ rays was then converted by means of Eq. (1) to the effective magnetic field B_{eff} at a ^{54}Mn nucleus. The values of B_{eff} were plotted in Fig. 1 for several values of the external magnetic field . It is clear from this figure that for all three alloys the field B_{eff} at Mn did not reach saturation in the applied external fields. This behavior of B_{eff} could be due to the absence of complete alignment of the electron moments or formation of a spin-compensated state at the Mn sites (Kondo effect).

The observed field dependence of the γ-ray anisotropy can be understood by considering the temperature dependence of B_{eff} (the temperature dependence was determined for two or three values of the external field: $B_{ext} = 0.69, 0.93$, and 1.16 T). It is clear from Figs. 2 and 3 that B_{eff} decreased as a result of cooling. This behavior of the effective field showed unambiguously (as pointed out already) that the local quantization axes of the nuclei coinciding with the directions of the electron moments of Mn deviated from the macroscopic symmetry axis imposed by the external magnetic field.

The degree of the observed noncollinearity was estimated on the assumption that the angle of deviation was the same for all the Mn atoms. The method of least squares was

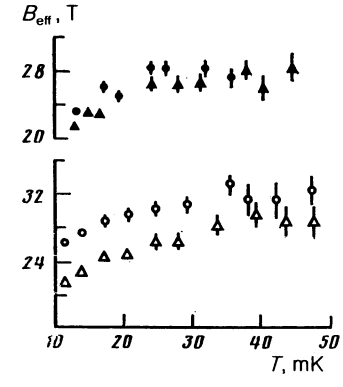

FIG. 3. Temperature dependence of B_{eff} at ^{54}Mn for PtFe alloys with 0.05 and 1 at.% Fe in constant external fields: ○) 1.16 T, △) 0.69 T (Pt + 0.05% Fe); ●) 1.16 T, ▲) 0.93 T (Pt + 1% Fe).

TABLE I. Parameters for the approximation of the temperature dependence of the angular anisotropy of γ radiation emitted by ^{54}Mn in PtFe alloys.

Fe content in alloy, at.%	B_{ext}, T	one-angle approximation		Lorentz distribution*	
		B_n, T	$\cos\varphi_0$	B_H, T	Γ
0.05	1.16	36.2(3)	0.920(2)	37.1(3)	0.099(3)
	0.69	35.0(3)	0.873(2)	36.7(4)	0.198(5)
0.1	1.16	34.0(6)	0.908(4)	35.0(6)	0.120(8)
	0.93	33.9(7)	0.891(5)	34.9(8)	0.154(11)
	0.69	33.8(6)	0.857(4)	35.8(8)	0.242(11)
1	1.16	36.8(8)	0.870(5)	38.7(10)	0.223(13)
	0.93	36.8(7)	0.855(4)	38.9(8)	0.276(13)

* In all cases it was found that $(\cos\varphi)_m = 1$.

used to approximate the temperature dependence of $W(T)$ with two parameters: $\cos\varphi_0$ (representing the magnetization $M = M_0\cos\varphi$) and B_n (the field at the nuclei B_n was equal to the vector sum of B_{ext} and B_{hf}). The parameters obtained are presented in Table I. The results of the approximation for the Pt + 1% Fe system are plotted in Fig. 4.

A more realistic representation of the behavior of the Mn spins was obtained by calculations assuming a Lorentzian or a Gaussian distribution of the orientations of the Mn moments relative to the external field direction. The parameters of this approximation were B_n and $(\cos\varphi)_m$ corresponding to the maximum of the distribution, as well as the half-width Γ of the distribution or the variance σ for the Lorentzian or Gaussian distributions, respectively.[4)] During the first stage of the calculations, when we used the data obtained from measurements only along the external magnetic field which yielded $W(0°, T)$, the χ^2 matching criterion did not differ greatly for the Lorentzian and Gaussian distributions. However, when the approximation was carried out simultaneously using $W(0°, T)$ and $W(90°, T)$, the matching criterion was better for the Lorentzian distribution, although the fitting parameters were practically the same. Both calculation models show that $(\cos\varphi)_m = 1$ was true of all three systems in all the external fields. The results of the calculations carried out for the Lorentzian distribution are presented in Table I.

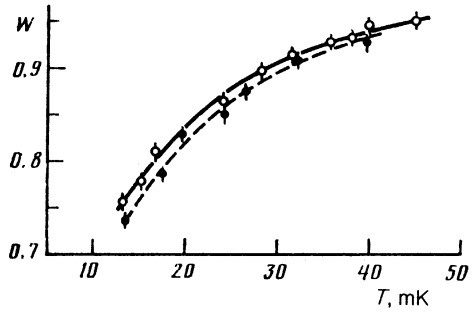

FIG. 4. Temperature dependence of the γ-ray anisotropy $W(0°, T)$ obtained for ^{54}Mn in a sample of ^{54}Mn:Pt + 1% Fe in a constant external field: ●) 1.16 T; ○) 0.93 T. The lines represent an approximation based on the assumption that the moments of all the impurity atoms experience the same deviation from the external field direction.

2. ^{54}Mn:PdFe and ^{54}Mn:Pd(Co, Fe)

Similar investigations were made of the nuclear orientation of ^{54}Mn in ferromagnetic Pd + 1% Fe and Pd + 1% ($Co_{0.8}Fe_{0.2}$) matrices. Figure 5 shows the field dependence of B_{eff} indicating that in this case the values of B_{eff} for Mn were considerably higher for both systems than in the case of PtFe matrices in the same external fields B_{ext}. As in the case of Pt alloys, the dependence $B_{eff}(B_{ext})$ was located somewhat lower for the alloy with the higher Fe content.

We also determined the temperature dependences $W(0°, T)$ in fields $B_{ext} = 0.37$, 0.56, and 1.16 T for Pd + 1% Fe and $B_{ext} = 0.32$ and 1.16 T for Pd + 1% (Co, Fe). In the field $B_{ext} = 1.16$ T the temperature dependence of B_{eff} was weak (Fig. 6) indicating that the magnetic moments of Mn were almost fully aligned. In weaker external fields there was a stronger temperature dependence of B_{eff}. The low-field temperature dependence $W(0°, T)$ was approximated using a Lorentzian distribution in accordance with the procedure described above. The same values of B_n were obtained for both alloys (Table II) and they agreed with the value of $B_{hf} = 38.0$ T reported for Mn and Pd in Ref. 10.

3. Discussion of results

We list the main results obtained for the ^{54}Mn:PtFe system.

1. In the case of Pt + 0.05% Fe and Pt + 1% Fe alloys the magnetic field at the nuclei B_n agreed well with the

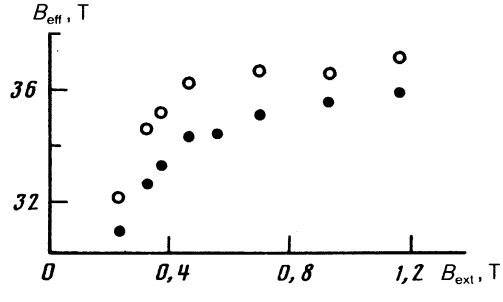

FIG. 5. Dependence of B_{eff} at ^{54}Mn on the external magnetic field at a constant temperature $T = 12$ mK obtained for alloys of Pd with Fe and Co: ○) Pd + 1 at.% (Co, Fe); ●) Pd + 1 at.% Fe.

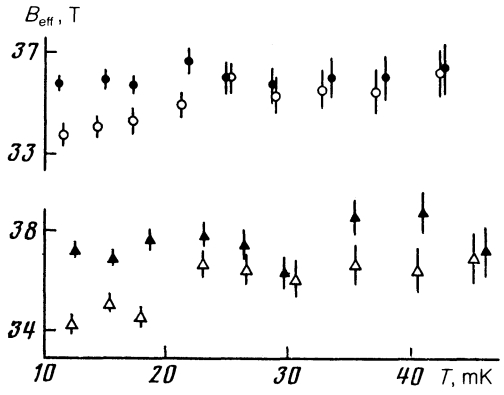

FIG. 6. Temperature dependence of B_{eff} at ^{54}Mn in a constant external field obtained for Pd + 1% Fe (●—1.16 T, ○—0.37 T) and Pd + 1% (Co, Fe) (▲—1.16 T, △—0.32 T).

known value of B_{hf} for Mn and Pt:B_{hf} = 37.5 T (Ref. 11). A somewhat lower value of B_n was obtained for Pt + 0.1% Fe.

2. The degree of noncollinearity, described by the values of cos φ_0 and Γ (or σ) in the case of the models with one angle and with a Lorentzian (or a Gaussian) distribution, increased with the Fe concentration in the alloy.

3. It was found that the values of cos φ_0 and Γ (or σ) decreased with increasing in B_{ext} (there was no correlation between B_n and B_{ext}). High-field measurements of the nuclear orientation in the same samples demonstrated that the Mn spins in Pt + 1% Fe were not completely aligned even in external magnetic fields of 8 T. In the case of Pt + 0 05% Fe and Pt + 0.1% Fe the saturation of B_{eff} began in external fields of 4 and 6 T, respectively. For comparison, it should be mentioned that the effects of the noncollinearity of the Mn spins in the alloys with $\approx 3\times 10^{-6}$ of Fe in Pt disappeared in an external field B_{ext} = 0.69 T (Ref 12).

4. Since in accordance with the matching criterion, the Lorentzian distribution model should be preferred to one with a Gaussian distribution, we concluded that a considerable fraction of the Mn spins was characterized by large angles of deviation from the macroscopic magnetization axis.

This noncollinearity of the Mn spins in PtFe alloys raises the question of the magnetic saturation of the matrix. We obtained further information on this topic by determining the nuclear orientation of the magnetic impurity ^{60}Co in the same matrices under the same conditions. These measurements showed that in the external fields used in our study the value of B_{eff} for Co reached saturation and there was no temperature dependence of B_{eff}. These results clearly indicated that the matrix was magnetically saturated. In the case of a ferromagnetic sample of ^{60}Co:Pt + 1% Fe the value of B_{eff} reached saturation faster than for the other two samples, whereas in the case of the Mn impurity the situation was exactly opposite (Fig. 1).

We therefore conclude that two types of magnetic behavior coexist in the ^{54}Mn:**Pt**Fe systems, one of which is noncollinearity ("canting") of the Mn spins and the other a magnetically ordered matrix. A considerable misorientation of the Mn spins indicated the presence of interactions hindering the alignment of Mn along the external field direction. An increase in the degree of noncollinearity of Mn as a function of the Fe content in the alloy was a clear demonstration that the source of the interactions responsible for the deviation of the Mn moments from the macroscopic magnetization direction is the presence of the Fe atoms.

The direct Mn–Mn and Mn–Fe interactions were antiferromagnetic. However, because of the low Mn concentration ($\sim < 10^{-5}$) the direct Mn–Mn coupling was hardly possible in the investigated samples. We therefore have to assume that the main interaction responsible for the noncollinearity of the Mn moments relative to the external magnetic field direction is the antiferromagnetic Mn–Fe interaction which could be either direct or indirect (mediated by the Pt atoms).

The results obtained for ^{54}Mn in **Pd**(Co, Fe) indicated that the alignment of the Mn moments become more difficult as the Fe concentration increases. The fact that the noncollinearity effects in the alloys based on Pd were weaker was clearly associated with the existence of a relatively strong ferromagnetic interaction of the giant moments of Mn and Fe (or Co) in Pd. Similar noncollinearity effects of the Mn spins due to the interimpurity Mn–Fe interaction had been observed earlier at very low concentrations of Fe in Pd in weak magnetic fields.[6]

4. CONCLUSIONS

An investigation of the nuclear orientation at low temperatures has established that in ferromagnetic and paramagnetic **Pt**Fe and **Pd**Fe as well as in **Pd**(Co, Fe) alloys the Mn impurity is in a noncollinear state. The degree of noncollinearity (canting) decreases as the external field increases and the iron content decreases, but is still fairly high even when the concentration of Fe in Pt is 0.05%. The observed angular anisotropy of the emitted γ rays is described satisfactorily by a Lorentzian distribution of the orientations of the magnetic moments of the Mn atoms.

The results obtained demonstrate that the nuclear orientation method is highly sensitive to the nature of the magnetic behavior of the impurity. In particular, it is possible to

TABLE II. Parameters for the Lorentzian approximation of the temperature dependence of the angular anisotropy of γ radiation emitted by Mn in Pd-base alloys [$(\cos\varphi)_m = 1$ in all cases].

Alloy	B_{ext}, T	B_n, T	Γ
Pd+1% Fe	0.56	37.3(2)	0.012(1)
	0.37	38.3(2)	0.026(1)
Pd+1% ($Co_{0.8}Fe_{0.2}$)	0.32	38.0(3)	0.020(2)

detect the existence of spatially disordered subsystems of localized moments in ferromagnetic or paramagnetic systems.

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[1)] Institute of Nuclear Research, Academy of Sciences of the USSR.
[2)] Institute of Nuclear Physics at the Moscow State University.
[3)] Charles University, Prague.
[4)] The Lorentzian and Gaussian distributions were used in the standard forms: $L(x) = (\Gamma/2)^2/[(\Gamma/2)^2 + (x_m - x)^2]$ and $G(x) = \exp[-(x_m - x)^2/2\sigma^2]$, where $x = \cos\varphi$, and $x_m = (\cos\varphi)_m$.

[1]J. Crangle and W. R. Scott, J. Appl. Phys. **36**, 921 (1965).
[2]J. C. Ododo, J. Phys. F **9**, 1441 (1979).
[3]J. Kästner, E. F. Wassermann, K. Matho, and J. L. Tholence, J. Phys. F **8**, 103 (1978).
[4]K. Kiymac and C. B. P. Finn, J. Phys. F **12**, 333 (1982).
[5]M. Trhlik, B. Sedlák, A. L. Erzinkyan, *et al.*, J. Phys. F **18**, L237 (1988).
[6]J. Flouquet, M. Ribault, O.Taurian, *et al.*, Phys. Rev. B **18**, 54 (1978).
[7]W.D. Brewer, in *Low Temperature Nuclear Orientation* (ed. by N. J. Stone and H. Postma), North-Holland, Amsterdam (1986), p. 407.
[8]G. M. Gurevich, A. L. Erzinkyan, P. Malinskiĭ, *et al.*, Izv. Akad. Nauk SSSR Ser. Fiz. **50**, 2326 (1986).
[9]M. Finger, T. I. Kracikova, N. A. Lebedev, *et al.*, Hyperfine Interactions **22**, 461 (1985).
[10]Le Dang Khoi, P. Veillet, and I. A. Campbell, J. Phys. F **6**, L197 (1976).
[11]J. Flouquet, Ann. Phys. (N.Y.) **8**, 5 (1973/74).
[12]J. R. Thompson, J. O. Thomson, P. G. Huray, *et al.*, J. Phys. F **8** 169 (1978).

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