Anisotropy in the attenuation of nuclear spin echoes in yttrium-iron garnet films

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The attenuation of two-pulse nuclear spin echo signals in yttrium-iron garnet single-crystal films is studied in an external magnetic field. A model is proposed which describes the experimentally observed anisotropy in the rate of relaxation of the echo signals for nuclei of octahedral iron ions. © *1995 American Institute of Physics.*

1. INTRODUCTION

The basic properties of nuclear magnetic resonance (NMR) in magnetically ordered materials result from the strong hyperfine interactions, which cause the NMR parameters to depend strongly on the state of the sample electron spin system.[1,2] One problem requiring further work is the study of the processes of nuclear spin relaxation in the presence of hyperfine interaction with the exchange-coupled electron spin system of the sample.

As an object of study we chose yttrium-iron garnet (YIG) $Y_3Fe_5O_{12}$, whose magnetic properties have been studied quite thoroughly.[1–3] The YIG crystal is an insulating ferrimagnetic with a cubic primitive cell.[1] The magnetic ions are Fe^{3+}, found in S states and occupying crystallographic positions with both tetrahedral and octahedral anion environments. The ferrimagnetism of YIG results from the negative exchange interaction between the octahedral and tetrahedral magnetic sublattices.

In order to study the nuclear relaxation processes Petrov and Paugurt[4] investigated polycrystalline specimens of YIG enriched with the magnetic isotope ^{57}Fe (spin $I=1/2$). It was found experimentally that at a temperature $T=77$ K the rate of transverse relaxation in the samples enriched with the ^{57}Fe isotope was higher than in the YIG samples with a natural concentration of this isotope. Berzhanskii and Polulyak[5] observed similar behavior in the rate of attenuation of nuclear spin echo signals in single-crystal polydomain YIG films at $T=77$ K. The noted that the longitudinal and transverse relaxation rates were correlated and that the attenuation of the echo signals was nonexponential.

Analysis of the experimental results in Refs. 4 and 5 implies that the transverse relaxation in samples of both types is due to the indirect interaction of the nuclear spins through virtual magnons of the electron magnetization (the Suhl–Nakamura interaction). It should be noted that the experimentally observed dependence of the relaxation rate on the frequency location of the spectral line was not investigated in Refs. 4 and 5 and remains obscure.

In order to study the effect of the location of the spectral line in frequency on the transverse nuclear relaxation rate in more detail, in the present work we have investigated the attenuation of two-pulse echo signals from the nuclei of ^{57}Fe in YIG films in an external saturating magnetic field.

2. EXPERIMENT

As a sample we used the YIG film with the highest concentration (≈96%) of the magnetic isotope ^{57}Fe from the series of specimens used in Ref. 5. The choice of the sample resulted from the need to obtain signal-to-noise ratios sufficient to perform the experiments in the external magnetic field. The $Y_3Fe_5O_{12}$ film was grown by liquid-phase epitaxy on a substrate of dimensions $10\times10\times0.2$. mm^3 from gadolinium–gallium garnet oriented in the (111) plane. The thickness of the film, determined interferometrically, was equal to 8 μm.

The experiments were performed in an incoherent pulsed NMR spectrometer. Mutually orthogonal stationary and radio-frequency (rf) magnetic fields were oriented in the plane of the film. The lengths of the first and second exciting rf pulses were equal respectively to 2 and 4 μs. The NMR spectra were measured by recording the dependence of the two-pulse echo signal amplitude on the occupation frequency of the exciting pulses. The attenuation curves of the echo signals were measured from the dependence of the amplitude of the two-pulse echo signal on the time interval τ between the exciting pulses for a fixed fill frequency of the exciting pulses, equal to the frequency of the spectral line being studied.

In the YIG structure the ^{57}Fe ions occupy both tetrahedral and octahedral positions. The local symmetry of the tetrahedral positions is cubic. Accordingly, for nuclei of the tetrahedral ^{57}Fe iron ions in saturating external magnetic fields only a change in the resonant frequency of a single spectral line was observed, corresponding to the hydromagnetic ratio γ. The rate at which the echo signals attenuate did not depend either on the magnitude or the orientation of the magnetic field to within the accuracy of the experiments.

The octahedral positions have uniaxial symmetry, and the local symmetry axis coincides with one of the four $\langle 111\rangle$ directions. Consequently, the YIG structure has four kinds of nonequivalent octahedral positions, distinguished by the orientation of the local symmetry axis. In saturating magnetic fields the NMR spectrum of the nuclei of octahedral ^{57}Fe ions consists of four spectral lines with a width of order 0.05 MHz. The frequency location of each spectral line was described by an expression

$$\nu=(\nu_0-\gamma B)+\nu_A(3\cos^2\theta-1) \qquad (1)$$

with an anisotropy constant $\nu_A\approx-0.95$ MHz (Ref. 5). In Eq.

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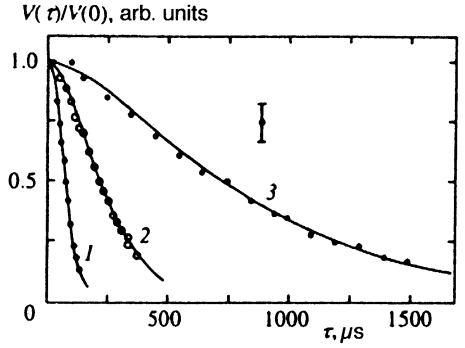

FIG. 1. Amplitude of the echo signals as a function of the time interval between exciting pulses. The experimental results correspond to $\theta=48°$ (*1*), 76° (*2*), and 90° (*3*). The solid traces are found from approximating the experimental results using Eq. (4) with $\tau_c=500$ μs and $\sigma=32$ kHz (*1*), $\sigma=5$ kHz (*2*), and $\sigma=0.78$ kHz (*3*).

(1) θ is the angle between the local third-order symmetry axis of the direction of the electron magnetization vector in the sample, determined by the orientation of the external magnetic field **B**, and ν_0 is the isotropic constant.

The frequency location of the NMR spectral line from nuclei whose local symmetry axis is normal to the plane of the film does not depend on the orientation of the field in the plane of the film. If we note that the plane (111) under discussion here has no ⟨111⟩ directions, it is convenient to choose as a reference axis the $\langle 1\bar{1}10\rangle$ direction, which lies in the plane of the film. Then, introducing the angle φ between the direction of the magnetic field and the ⟨110⟩ axis, we find

$$\cos^2\theta=\tfrac{8}{9}\cos^2(\varphi+\psi_j), \tag{2}$$

where $\psi_1=-\pi/2$, $\psi_2=-\pi/6$, $\psi_3=\pi/6$. From expressions (1) and (2) it follows that in the special case $\varphi=0$ the NMR spectrum of the octahedral nuclei consists of two spectral lines for $\theta=90°$ and $\theta\approx35.26°$. When the experiments were performed the NMR spectrum corresponding to the angle $\varphi=0$ was used to determine the orientation of the field with respect to the crystal axes.

These experiments revealed that in saturating magnetic fields the attenuation rate of the echo signals from iron nuclei in the octahedral positions was essentially independent of the magnitude but depended sensitively on the orientation of the field. The fastest attenuation was found for the echo from nuclei with $\theta\approx40$–$50°$, and the rate of attenuation fell off monotonically as $\theta\to90°$ (Fig. 1) and $\theta\to19.47°$. It follows from Eq. (2) that angles less than $\theta\approx19.47$ did not occur when the field was in the plane of the film.

In order to approximate the dependence of the amplitude V of the echo signal on the time interval τ between the exciting pulses we used the expression

$$V(\tau)=V(0)\exp(-k_n\tau^n) \tag{3}$$

with $n=1,2,3$; the coefficient k_n, which depends on the angle θ, and the initial echo amplitude $V(0)$ were found by the method of least squares. For slowly attenuating echo signals the minimum least-squares error was found with $n=1$. The similar behavior for rapidly relaxing signals was approximated best by Eq. (3) with $n=2$.

3. DISCUSSION OF THE EXPERIMENTAL RESULTS

The experimental results were analyzed using the spectral diffusion model.[6,7] In Ref. 7 it was shown that the attenuation of the echo signal can be described by Eq. (3) with $n=1$ and $n=2$ only in the case of a Lorentz–Markov process in the limiting cases of fast ($\sigma\tau_c\ll1$) and slow ($\sigma\tau_c\gg1$) spectral diffusion, respectively. Here τ_c is the correlation time of the random process and σ is the amplitude of the fluctuations. In the general case of a Lorentz–Markov process the signal of a two-pulse echo attenuates according to the law

$$V(\tau)=V(0)\exp\{-2\sigma[\tau-\tau_c\ln[2-\exp(-\tau/\tau_c)]]\}. \tag{4}$$

When Eq. (4) was used to approximate the experimental data it was assumed that the correlation time of the random process is independent of the orientation of the magnetic field with respect to the crystal axes and that the anisotropy of the rate of attenuation of the echo signals results from the anisotropy σ. Because the time for the signal amplitude to fall by a factor of e is much longer than the correlation time in the case of a fast spectral diffusion process and much less than τ_c in the case of slow spectral diffusion,[7] for the correlation time we used the estimate $\tau_c\approx500$ μs (Fig. 1).

Equation (4) was used to numerically approximate the drop in the echo signals for different values of the angle θ. For a fixed value of τ_c different values of σ were chosen successively from the interval $0.01\tau_c^{-1}\leqslant\sigma\leqslant100\tau_c^{-1}$, which made it possible to take into account both fast and slow spectral diffusion process. The mean square deviation for the curve describing the decrease in the echo was minimized for the corresponding value of the angle θ found for $\tau_c=500\pm150$ μs. The values of σ corresponding to the minimum least-square deviation for $\tau_c=500$ μs are shown in Fig. 2 as a function of the angle θ.

In order to estimate the error in determining the quantity σ the approximation described above was used for the decay curves of the echo signals obtained from the experimental dependence by varying the amplitudes of the echo signals randomly within the experimental error. By using this procedure repeatedly (on the order of 25 times for each decay curve of the echo signals) we found that this approximation is stable, and for $\tau_c=500$ μs the quantity σ was determined to better than 10%.

Furthermore, in processing the experimental dependence $V=V(\tau)$ we recovered the initial amplitudes $V(0)$ of the echo signals corresponding to zero delay for the second pulse. It was found that the initial amplitude $V(0)$ is the same for all spectral lines and does not depend on the orientation of the field in the plane of the film.

Further calculations revealed that from the smallest mean-square deviation and the best qualitative agreement between the experimental and approximate forms of $V=V(\tau)$, out of all the structural diffusion processes given in Ref. 7 the Lorentz–Markov process is the most satisfactory. It should also be mentioned that the suggested spectral diffusion process was used in Ref. 8 as well to describe the attenuation of nuclear spin echo signals in YIG samples with the naturally occurring abundance of ^{57}Fe. The results obtained using this process were probably satisfactory because

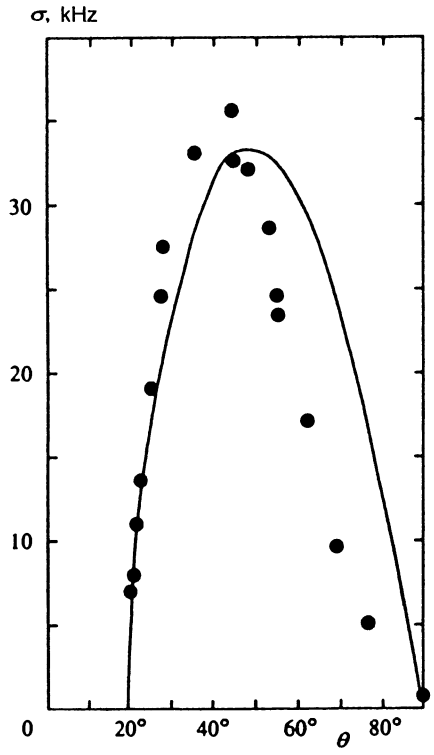

FIG. 2. Amplitude of the fluctuations as a function of the angle between the local third-order symmetry axis and the direction of the electron magnetization vector, found by approximating the experimental results using Eq. (4) with $\tau_c=500$ μs. The solid trace was obtained from Eq. (6) with $\sigma_0=25$ kHz.

the fluctuations of the local fields at the ^{57}Fe nuclei result from dynamical processes in the exchange-bound electron spin system, for which exchange narrowing and the Lorentz line shape of the magnetic resonance are typical.

In order to explain the dependence $\sigma=\sigma(\theta)$ which was found, we start from the fact that the principal mechanism for broadening of NMR spectral lines is inhomogeneous broadening due to the variation in the resonant frequencies of the nuclear spins. Based on the fact that the widths of the experimentally detected spectral lines and the inferred values of the initial echo signal amplitudes for these lines do not depend on the orientation of the magnetic field, we will treat the inhomogeneous broadening of the spectral lines of the octahedral iron nuclei as isotropic.

Following Ref. 5, we take the Suhl–Nakamura interactions to be the ones responsible for the attenuation of the echo signals. The main properties of the Suhl-Nakamura interactions under inhomogeneous spectral line-broadening conditions were studied by Pincus *et al.*,[9] who showed that the efficiency of these interactions decreased as a function of the inhomogeneous broadening. The reason for this is that the Suhl–Nakamura interactions arise because one nuclear spin emits a virtual electron magnetization magnon and another nuclear spin absorbs it. This process is possible only for nuclei such that the difference in the resonant frequencies is less than the interaction energy (expressed in frequency units). Consider a nucleus whose resonant frequency lies in the center of the inhomogeneously broadened spectral line. The magnitude of the effective field of the Suhl–Nakamura interactions[1,9] at this nucleus is directly proportional to the number of nuclear spins having the same resonant frequencies. As the inhomogeneous broadening increases the number of such nuclei decreases, which reduces the contribution of the Suhl–Nakamura interactions to the attenuation of the echo signal.

The direct use of the Suhl–Nakamura interactions to describe the anisotropy of the transverse relaxation of nuclear magnetization can be based on the anisotropy of these interactions. For crystallographic positions with uniaxial symmetry the anisotropic part of the effective field of the Suhl–Nakamura interactions is described by the angular factor $3\cos^2\theta-1$. The minimum value of these interactions, and hence the minimum relaxation rate, should be attained for $\theta=\theta_m\approx 54.7°$ ($\cos^2\theta_m=1/3$). The fastest attenuation should occur for an echo from nuclei with $\theta=90°$. However, this behavior is qualitatively inconsistent with that observed experimentally.

In order to get around these contradictions we assume that the electron magnetization vector at each point in the specimen deviates from the direction of the magnetic field by some small random angle, and that this variation is not static but dynamic. For anisotropic octahedral positions the orientational inhomogeneity of the electron magnetization results in a spread in the angles θ in Eq. (1), and hence in an additional spread in the nuclear resonance frequencies.

It is a characteristic of thin-film samples that the electron magnetization vector scarcely ever leaves the plane of the film. Hence the orientation inhomogeneity of the electron magnetization causes a spread in the values of the angle φ in Eq. (2). Assuming that the deviations $\delta\varphi$ are small, we find by differentiating Eq. (1) and using Eq. (2) that

$$|\delta\nu|=2|\nu_A\cos\theta\sqrt{8-9\cos^2\theta}\,\delta\varphi|. \tag{5}$$

The orientational fluctuations of the electron magnetization at each point in the sample will be assumed independent and rapid, so that if τ_{cM} is the correlation time of these fluctuations then $\tau_{cM}|\delta\nu|\ll 1$ holds and the relaxation due to spontaneous fluctuations of the resonant frequencies need not be taken into account to lowest order ("dynamic narrowing"). In the opposite limit the relaxation rate would be determined only by the fluctuations in the local magnetic fields at the iron nuclei and would not depend on the concentration of the magnetic isotope, which contradicts the experimental results of Ref. 5. On the other hand, this process can give rise to fluctuations in the effective field of the Suhl–Nakamura interaction.

Specifically, let $G(\nu)$ be the function describing inhomogeneous broadening of the spectral line in the absence of orientational inhomogeneity of the electron magnetization (the solid trace in Fig. 3). For sufficiently small values of $\delta\varphi$ the frequency spread $\delta\nu$ in Eq. (5) will be smaller than the width of the function $G(\nu)$. For orientational fluctuations of the electron magnetization (the fluctuations of $\delta\varphi$) the frequency of each of the spins whose resonant frequency for $\delta\varphi=0$ would lie in the interval $\nu_p\pm\delta\nu$ can equal the central frequency ν_p of the function $G(\nu)$. The converse is also true.

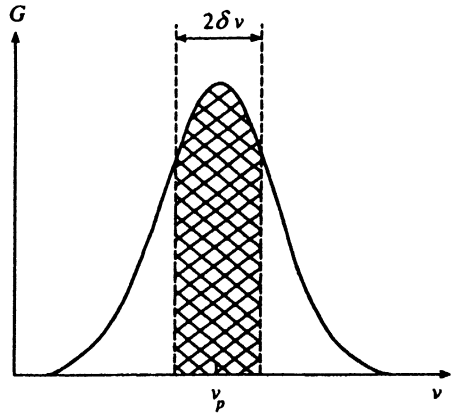

FIG. 3. The function describing inhomogeneous broadening of a spectral line (the frequency dependence of the number of resonant spins). The cross-hatched region corresponds to the range of frequency fluctuations associated with orientational inhomogeneity of the electron magnetization vector.

The frequencies of the "central" spins can also vary over the frequency interval $\nu_p \pm \delta\nu$.

In some region of the sample, the size of which is determined by the radius of the Suhl–Nakamura interactions,[1] the frequency distribution of the spins can depart from equilibrium for the fluctuations $\delta\varphi$. We consider two limiting cases: the frequencies of all the spins from the interval $\varphi_p \pm \delta\nu$ either coincide or differ from the central frequency of the function $G(\nu)$. If we take into account the fact that the magnitude of the effective field of the Suhl–Nakamura interactions is proportional to the number of resonant spins, we find that for a spin with the central frequency this field will vary from some minimum value (equal to zero to lowest order) up to a maximum, and the amplitude of the fluctuations will be proportional to the area of the cross-hatched region in Fig. 3.

Assuming that the fluctuation amplitude σ of a Lorentz–Markov process is proportional to the amplitude of the fluctuations of the effective Suhl–Nakamura interaction field, we can write

$$\sigma = \sigma_0 \cos\theta \sqrt{8 - 9\cos^2\theta}, \tag{6}$$

where the quantity σ_0 depends on the initial concentration of magnetic nuclei in the sample, the Suhl–Nakamura interaction energy, the value of $\delta\varphi$, etc. The calculated dependence $\sigma = \sigma(\theta)$ found from Eq. (6) for $\sigma_0 = 25$ kHz is shown in Fig. 2 by the solid trace.

This qualitative agreement between the calculated and experimental functions $\sigma = \sigma(\theta)$ implies that in the samples studied the anisotropy of the nuclear transverse relaxation rate is determined by the orientational inhomogeneity of the electron magnetization vector. The marked discrepancy between the theoretical curve and the experimental points in Fig. 2 may be due to the anisotropy of the inhomogeneous broadening of the NMR spectral line, a slight departure of the electron magnetization from the plane of the film, or a number of other factors not treated in the first approximation.

When experiments were carried out in an external magnetic field the longitudinal relaxation rate was evaluated from the repetition rate of the exciting pulses. It was found that the relaxation rate of the longitudinal component of the nuclear magnetization is also anisotropic and grows as the rate of transverse relaxation increases; this relationship is similar to that which was found in Ref. 5. In all probability the mechanism for longitudinal relaxation results from "modulation" of the nucleus–nucleus interactions, which is further confirmation of the need to include the dynamics of the electron spin system in analyzing nuclear relaxation in magnetically ordered materials. However, this problem requires further investigation.

4. CONCLUSION

Thus, the proposed mechanism for the anisotropy in the rate of transverse relaxation consists of modulation in the effective number of interacting nuclei as a result of orientational fluctuations of the electron magnetization. This mechanism provides a qualitative explanation for the anisotropy in the attenuation rate of signals and an interpretation for the dependence of the transverse relaxation rate on the initial concentration of nuclear spins observed experimentally in Ref. 5 in the sample for the nuclei in octahedral positions.

[1] M. I. Kurkin and E. A. Turov, *Nuclear Magnetic Resonance in Magnetically Ordered Materials and Its Applications* [in Russian], Nauka, Moscow (1990).
[2] E. A. Turov and M. P. Petrov, *Nuclear Magnetic Resonance in Ferro- and Antiferromagnetics*, Wiley, New York (1972).
[3] S. Sh. Gendelev and Yu. M. Yakovlev, *Ferrite Single Crystals in Radioelectronics* [in Russian], Radio, Moscow (1975).
[4] M. P. Petrov and A. P. Paugurt, Fiz. Tverd. Tela **12**, 2829 (1970) [Sov. Phys. Solid State **12**, 2284 (1970)].
[5] V. N. Berzhanskiĭ and S. N. Polulyak, Fiz. Tverd. Tela **31**(8), 256 (1989) [Sov. Phys. Solid State **31**, 1423 (1989)].
[6] J. R. Kluder and P. W. Anderson, Phys. Rev. **125**, 912 (1962).
[7] K. M. Salikhov, A. G. Semenov, and Yu. D. Tsvetkov, *Electron Spin Echo and Its Applications* [in Russian], Nauka, Novosibirsk (1976).
[8] S. K. Ghosh, Phys. Rev. B **5**, 174 (1972).
[9] P. Pincus, V. Jaccarino, D. Hone, and Tin Ngwe, Phys. Lett. A **27**, 54 (1968).

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