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Translated by W. F. Brown, Jr.

Investigation of the dynamic NMR frequency shift for ^{57}Fe in $FeBO_3$

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(Submitted 19 October 1977)
Zh. Eksp. Teor. Fiz. 74, 1170–1176 (March 1978)

NMR of ^{57}Fe in $FeBO_3$ is investigated by pulsed magnetic resonance techniques in the 2 to 70 K temperature range. A dynamic NMR frequency shift is observed which is due to coupling between the NMR oscillations and the low-frequency AFMR mode. The magnitude of the shift exceeds only slightly the micro-inhomogneous NMR-line broadening caused by the spread of the values of hyperfine field at the nuclei. Under these conditions the nuclear spin system possesses a number of unusual properties. Thus, the broadening of the magnetic resonance line is homogeneous, the homogeneous broadening depends on the angle between the nuclear magnetization and the equilibrium axis, and an echo signal is detected which is similar to the "solid echo" in substances with dipole broadening of the magnetic resonance line.

PACS numbers: 76.60.Jx

1. INTRODUCTION

Recently, significant progress has been achieved in the investigation of coupled nuclear-electron oscillations and the dynamics of spin motion in magnetically-ordered substances. If sufficiently large coupling exists in these substances between the electron and nuclear spin systems, their magnetic resonance spectra are restructured. The AFMR spectrum acquires a hyperfine spectral gap proportional to the nuclear magnetization, and a dynamic frequency shift (DFS, pulling) arises in the NMR spectrum. Under these conditions, the nuclear spin system possesses a number of unusual properties, such as the existence of nuclear spin waves, a dependence of the nuclear-precession frequency on the precession amplitude, deviations of the nuclei from the equilibrium axis, etc. Previously, DFS has been observed only on ^{55}Mn nuclei in weakly anisotropic antiferromagnets.[1,2,3] We have succeeded in observing DFS on the ^{57}Fe nuclei in $FeBO_3$ and investigated its properties.

Iron borate is a rhombohedral antiferromagnet with weak ferromagnetism.[4] Its magnetic properties are known quite well. NMR of ^{57}Fe in $FeBO_3$ was investigated by the spin-echo technique on polycrystal samples at helium temperatures[5] and on single-crystal samples at nitrogen temperatures.[6]

2. SAMPLES AND MEASUREMENT PROCEDURE

The measurements were made on $FeBO_3$ single-crystal plates of thickness ~0.1 mm and area ~9 mm^2 and parallel to the magnetization easy plane. The single crystals were grown in the Physics Institute, Siberian Division, USSR Academy of Sciences by a method described earlier.[7] Because gluing the $FeBO_3$ single-crystal samples leads to sharp broadening of the low-frequency AFMR line, our samples were mounted without adhesive by securing the samples between two soft foamed plastic plates. The constant magnetic field H and the RF field h were perpendicular to each other in the easy plane of the sample. The principal investigations were carried out in an external magnetic field of 20 Oe. It was shown[6] that in this field the sample can be considered as being in a one-domain state.

The NMR of the ^{57}Fe nuclei was investigated by the two-pulse spin-echo technique and from the fall-off of the free induction signal (FI) following a short RF pulse. The experiments were carried out with a Bruker SXP 4-100 pulse spectrometer in the Vichuri Physics Laboratury, Turku University (Finland).

3. INVESTIGATION OF THE FREE-INDUCTION SIGNAL

Petrov *et al.*[5] pointed out a number of nonlinear effects in the pulsed NMR of the ^{57}Fe nuclei in $FeBO_3$ at helium temperatures, which indirectly indicated the existence of DSF. To determine the dynamic characteristics of the ^{57}Fe nuclear spin systems, we carried out an investigation of the FI signal following a short RF pulse of duration $\tau_i = 1\,\mu sec$. In all experiments, the FI signal fall-off was close to exponential with a time constant T_2^*. At the same time, the following conditions were

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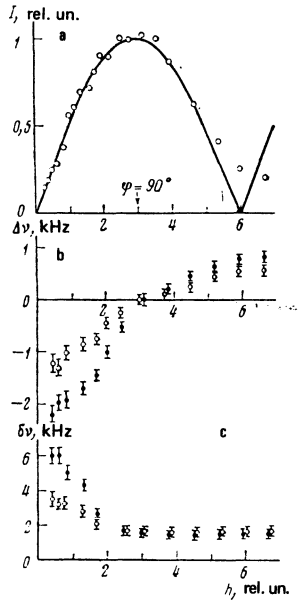

FIG. 1. Dependence of the characteristics of the free-induction signal on the RF field amplitude: (a) dependence of the free-induction signal amplitude at 4.2K; (b) dependence of the free-quency shift of the free-induction signal at $T = 4.2$ °K (○) and $T = 2$ °K (●); (c) dependence of the broadening of the NMR line at 4.2 °K (○) and 2 °K (●).

satisfied:

$$T_2^* \gg \tau_p, \quad T_2^* \gg Q/\nu_{NMR} \approx 1\ \mu\text{sec},$$
$$T_2^* \gg 1/\Delta\nu_{det} \approx 1\ \mu\text{sec},$$

where Q is the quality factor of the RF measurement circuit and $\Delta\nu_{det}$ is the detector bandwidth. It can be assumed therefore that the resonant RF pulse excites uniformly the entire nuclear-spin system, which has approximately a distribution with half-width

$$\delta\nu_{NMR} = 1/2\pi T_2^* [\text{Hz}]. \tag{1}$$

The dead time of the detector system was $t_d \approx 10\mu$sec $\ll T_2^*$. This allowed us to make a reliable extrapolation of the free-induction signal intensity to its value I_0 at the initial moment.

Figure 1 shows the dependence of I_0 on the RF field at $H_0 = 20$ Oe and $T = 4.2$ °K. This dependence can be quite well described by means of the expected relation $I_0 \sim \sin\varphi$, where $\varphi = \gamma\eta h\tau_p$ is the angle between the spins and the equilibrium axis following the RF pulse, γ is the nuclear gyromagnetic ratio, and $\eta = H_{hf}/(H + 8[\text{Oe}])$ is the RF gain due to the electron-spin system.[6] In subsequent experiments, the function $I_0(\varphi)$ was used to calibrate the spin-angle deviation following the RF signal.

We have observed that the fundamental characteristics of the FI signal—the frequency and the fall-off time—strongly depend on the amplitude of the RF pulse (on the spin angle with the equilibrium axis).

a) The free-induction frequency. Measurements of the free-induction frequency were carried out using a phase detector in which the free-induction signal frequency was compared with a reference signal. For this purpose, at the initial instant the phase difference between

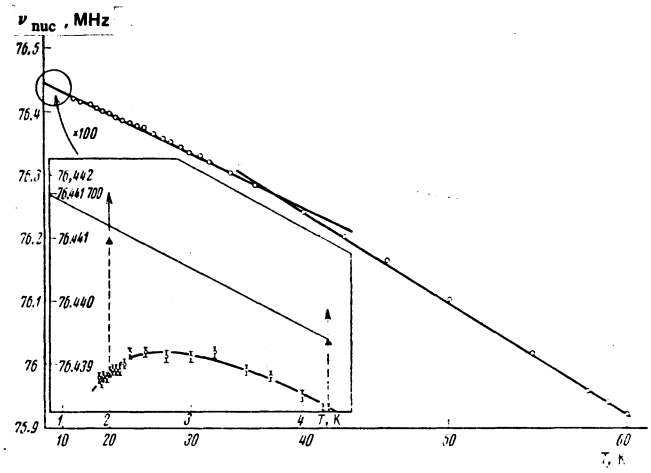

FIG. 2. Dependence of the free-induction signal frequency on the temperature at an angular deviation 20° (○) and 90° (▲) of nuclear spins from the equilibrium axis. The insert shows the enlarged encircled part of the experimental curve.

the reference signal of the detector and the RF radiation of the spin system was set at 90°. When the reference-signal frequency coincided with the center frequency of the RF radiation, their phase relationship did not change during the entire induction-signal duration, and as a result the induction signal was not observed. When the frequency of the free induction signal was different from the frequency of the reference signal, characteristic beats of FI signal amplitude were seen on the oscilloscope screen. Thus, in this experiment, the spectrometer served as a null indicator of the center of the NMR line with accuracy $\Delta\nu \approx 1/A2\pi T_2^*$, where A is the FI signal-to-noise ratio, amounting to several hundred. The FI signal frequency as a function of the RF amplitude at $H = 20$ Oe, $T = 4.2$ °K, and $T = 2$ °K is shown in Fig. 1b. The signal zero was taken to be the FI signal frequency at which the spin deviation from the equilibrium axis was equal to 90°. This behavior of the nuclear-precession natural frequency can be attributed to the presence of the DFS. Indeed, if the DFS is small compared with ν_{NMR}, the nuclear-precession frequency is described by the formula[8]

$$\nu_{NMR} = \gamma H_{hf} - \nu_{DFS}\cos\varphi, \tag{2}$$

where H_{hf} is the hyperfine field at the nuclei and ν_{DFS} is the dynamic frequency shift. This dependence is in agreement with the experimental data of Fig. 1b. The DFS is proportional to the nuclear magnetization and must therefore vary with temperature according to the Curie Law: $\nu_{DFS} \sim 1/T$.

We plotted the free-induction signal frequency as a function of the temperature at $\varphi \approx 20°$ (Fig. 2). In the temperature regions from 10° to 35 °K and from 35° to 70 °K, the variation of the NMR frequency can be satisfactorily described by the formula

$$\nu_{NMR} = \nu_0(1 - \alpha(T/T_N)^2), \tag{3}$$

and is due to the change of the hyperfine field at the nuclei. This dependence has been investigated and discussed in detail.[5] In our experiments the constant α was equal to 0.19 at $T < 35$ °K and to 0.27 at $T > 35$ °K. A

sharp departure from this dependence takes place at helium temperatures. We attribute it to the presence of the dynamic frequency shift.

The solid curve in the insert of Fig. 2, which fits well the experimental data, corresponds to the relation

$$\nu_{NMR}=76\,441\,700\left(1-0.19\left(\frac{T}{T_N}\right)^2\right)-4\,500\frac{1}{T}\ [\text{Hz}]. \quad (4)$$

Thus, the natural-oscillation spectrum of the nuclear-spin system at $\varphi=20°$ can be well described if we assume the presence of the dynamic frequency shift, which is equal to $(4800\pm500)/T$[Hz], and the hyperfine nuclear field at 0 °K is equal to $\gamma H_{hf}=76441700\pm500$ Hz.

The frequency of the free-induction signal increases when the angle of the spin deviation is increased. In Fig. 2, the free-induction signal frequency at $\varphi=90°$ is shown by the triangles. According to formula (2), under these conditions the NMR frequency should correspond to the value of the hyperfine field at the nucleus, which varies according to the expression (3) (the straight line in Fig. 2). This dependence was observed in our experiments.

b) Investigations of NMR line broadening. The time constant T_2^* of the free-induction signal fall-off is determined by the broadening of the spectrum of the excited spin system (1). In the investigated spin system, this broadening was found to be strongly dependent on the angular deviation of the spins, from the equilibrium axis. The NMR line half-width calculated from T_2^* is shown in Fig. 1b as a function of the RF-field amplitude at an external magnetic field 20 Oe and at temperatures 4.2 and 2 °K.

The more the RF pulse deflects the nuclear spin system from the equilibrium axis, the more it decreases the broadening of the spin-system spectrum. At a deviation greater than 90°, the broadening of the spin system does not depend any more on the RF-field amplitude. We call the broadening of the magnetic resonance line, which depends on the angle of spin deviation, anomalous. It was found that the magnitude of the anomalous broadening was close to the dynamic frequency shift and varied with temperature in the same manner as the dynamic frequency shift ($\delta\nu_{NMR}\sim 1/T$).

If a large RF-field pulse overheats the nuclear-spin system, the system will cool following this pulse with the characteristic time constant of the spin-lattice relaxation T_1. If later a weak RF-field pulse is applied, the free-induction signal amplitude will be $I_0\sim 1/T_{nuc}$, where T_{nuc} is the temperature of the nuclear spin system. The broadening of the NMR line obtained by measuring the free-induction-signal fall-off was $\delta\nu_{NMR}\sim 1/T_p$. Thus, the anomalous broadening of the NMR line is determined by the nuclear magnetization and depends on the projection of the nuclear magnetization on the direction of the hyperfine field.

4. SPIN ECHO SIGNAL

We used a two-pulse spin echo technique to study the nature of the NMR line broadening. It was found that the spin echo signal was not observed at small RF pulse amplitude (in the region of the anomalous broadening of the NMR line). However, when the interval τ between pulses is small, the free-induction signal has a singularity at the instant $t=2\tau$. This singularity is a function of the phase relationship between two RF pulses. Figure 3 shows the free-induction signal following a sequence of two RF pulses. The upper photo shows the signal when the phases of both RF pulses are the same. The bottom photo shows the signal when the phase difference between two RF pulses is 90°. The free-induction signal singularity arising following the second pulse is similar to the "solid echo" produced in spin systems with homogeneous dipole-dipole broadening of the magnetic resonance line.[9] Thus, we can assume that the anomalous broadening is homogeneous and is caused by an interaction similar to the dipole-dipole interaction.

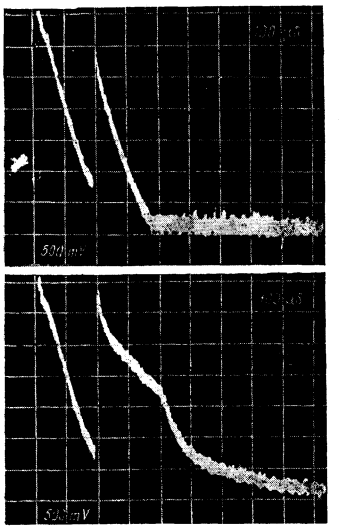

FIG. 3. Waveform of free-induction signal following the second RF pulse when both RF pulses are in phase (upper photo) and when the phase difference between two RF pulses is 90° (bottom photo).

At large RF pulse amplitudes ($\varphi>90°$), the usual spin echo signal is produced. Thus, in the inverted state, the spin system has an inhomogeneous broadening of the NMR line. Just as in[5], we have observed secondary echo signals that can be attributed to the strong nonlinearity in the spin motion under the influence of the RF field.

Using the spin echo technique, the spin-spin relaxation time constant was measured. The spin-spin relaxation had a nonmonotonic dependence on the amplitudes of both RF pulses. The spin-spin relaxation time constant was ~3 μsec at $T=2$ °K, $H_0=20$ Oe, and $\varphi>90°$. This corresponds to a homogeneous broadening of 50 Hz.

5. DISCUSSION

Note that the investigated oscillations are not pure nuclear oscillations, but a coupled nuclear-electron oscillation mode whose frequency deviation from the value γH_{hf} is called the dynamic frequency shift (DFS). The

magnitude of the dynamic frequency shift (at $\nu_{DFS} \ll \nu_{NMR}$) for an antiferromagnet is

$$\nu_{DFS} = \gamma H_{hf} \frac{\gamma_e H_E \gamma H_{hf}}{\nu_e^2} \frac{h\gamma H_{hf}}{kT} \frac{J(J+1)}{3S} c, \quad (5)$$

where γ_e is the electron gyromagnetic ratio, ν_e is the AFMR frequency, H_E is the magnitude of the exchange field, J and S are the nuclear and electron magnetic angular momenta, respectively, and c is the relative magnetic-isotope concentration (see Chap. 2 of [8]). If we use for the low-frequency branch of the AFMR the data from[7] ($\nu_e = 7.3$ GHz at $H = 20$ Oe, $T = 4$ °K), the dynamic frequency shift calculated by using Eq. (5) is equal to $5000/T$[Hz]. This is in agreement with the experimental data.

Since the electron spin system in $FeBO_3$ at helium temperatures is ordered and the nuclear spin system is paramagnetic, the kinetics of the spin motion depends strongly on the coupling between the NMR and the AFMR. Consider the oscillations of nuclear spins located at distances such that all electron spins move in phase in the case of uniform precession (the criterion of such a distance can be the value $r_{SN} = a(\gamma_e H_E/\nu_e)$, where a is the lattice constant[8]). If there is no coupling between the NMR and the AFMR, then the frequency of the nuclear-spin motion is determined by the hyperfine field at the nucleus. The inhomogeneous broadening of the NMR line is due to the spread ΔH_{hf} of the values of the hyperfine fields at the nuclei. On the contrary, with strong coupling between the NMR and the AFMR ($\nu_{DFS} \gg \gamma \Delta H_{hf}$), the nuclear spins move in phase with the electron spins, which in turn move in phase with one another at distances on the order of r_{SN}. The frequency of the coupled nuclear-electron oscillations is then $\gamma \bar{H}_{hf} - \nu_{DFS}$, where $\bar{H}_{hf}$ is the hyperfine field at the nuclei averaged over sample dimensions of the order of r_{SN} (the micro-inhomogeneous broadening averaging). In this case, the inhomogeneous broadening of the NMR line is due to the spread of ν_{DFS} and $\bar{H}_{hf}$ for the different regions of the crystal.

In the previous investigation of the dynamic frequency shift in ^{55}Mn,[1-3] this situation took place in all experiments. The situation was intermediate ($\nu_{DFS} \gtrsim \gamma \Delta H_{hf}$) in $FeBO_3$ at the helium temperatures. It can be qualitatively treated as coupled oscillations of an electron spin system with a set of nuclear spin systems with different H_{hf}. The set of natural frequencies of these coupled oscillations depends on the magnitude and the direction of the magnetic moment of each nuclear spin system. It means that the broadening of the magnetic resonance line is homogeneous, and the value of this broadening is of the order of ν_{DFS}. However, it is very difficult to obtain a quantitative estimate of the characteristics of the NMR line in this region.

The indirect interaction of nuclear-magnetic moments via the electron spin system in magnetically-ordered dielectrics is usually described within the framework of the Suhl-Nakamura interaction. The Hamiltonian of this Suhl-Nakamura interaction is of the form $A_{ij} I_i^+ I_j^-$.[8] The Suhl-Nakamura interaction, just as the dipole-dipole interaction, depends on the direction of the nuclear spins. This leads to an effect similar to the "solid echo" for the spin systems with dipole-dipole broadening of the NMR line.

CONCLUSION

We have succeeded in showing the existence of the dynamic frequency shift in ^{57}Fe nuclei with $FeBO_3$ as an example. An inverted nuclear spin system with positive NMR frequency shift has been obtained under dynamic frequency shift conditions. The kinetics of the spin motion with small dynamic frequency shift (in the order of the value of the inhomogeneous broadening of the hyperfine field at the nuclei) has a complex character, because a transition takes place from the kinetics of a paramagnetic nuclear spin system to the kinetics of coupled nuclear-electron oscillations. We assume that the large homogeneous broadening of the NMR line and the dependence of the broadening on the angle of deviation of the nuclear spins from the equilibrium axis are caused by this transition. Note that in our opinion a spin system with such properties is of interest for further theoretical and experimental investigations.

The authors are sincerely grateful to A. S. Borovik-Romanov and to V. Hovi for general guidance and a constant interest in the work, and to M. I. Kurkin, M. P. Petrov, and V. P. Chekmarev for useful discussions.

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Translated by E. Nodov