Nuclear magnetic resonance of ^{57}Fe nuclei in the hexaferrite $BaFe_{12}O_{19}$

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NMR investigations have been carried out in the temperature range 77–295 K on $BaFe_{12}O_{19}$ single crystals by employing both stationary and pulse techniques. NMR signals from nuclei at the edge and center of the domain boundary were observed for the first time for all sublattices in a multisublattice ferrimagnet. The localization of the nuclei responsible for the intraboundary NMR signals has been established and the ranges of variation of the local frequencies $\delta\nu$ in the domain boundary at 77 K were determined. It is shown that for a pentahedral sublattice e and octahedral sublattice d the NMR frequencies for nuclei at the edge and center of the domain boundary are the same at temperatures of 240 and 295 K respectively. The anisotropy of the local fields δH_l for ^{57}Fe nuclei on reorientation of the magnetization vector from the c axis to the basal plane was determined by the spin-echo method. The resulting experimental values of δH_l are used to determine the anisotropy of the hyperfine fields at ^{57}Fe nuclei at 77 K.

In magnetically ordered materials NMR can be observed for nuclei situated in the domains and in the domain boundaries (DB). Turov *et al.*[1] have studied the features of NMR in DB in detail theoretically. It was shown that the existence of a range of variation of the local NMR frequencies in the DB does not mean that a line of width $\sim\delta\nu$ will be present in the spectrum observed with a stationary method. Sharp peaks can appear on a background of a broad absorption band, which correspond to local NMR frequencies of nuclei at the edge of the DB, ν_d, and nuclei in the center of a DB, ν_w. For this it is necessary that the local NMR line widths of nuclei in the center of the DB, Δ_w and at its edge, Δ_d, be appreciably less than the difference between the corresponding frequencies $|\delta\nu| = |\nu_w - \nu_d|$.

In the hexaferrite $BaFe_{12}O_{19}$ (BaM), $|\delta\nu|$ reaches a value of $\sim$2.7 MHz (Ref. 2) with a NMR line width in the domains of 60–80 kHz (Ref. 3), which differs little from the line width Δ_d for nuclei at the edge of the DB. The condition $|\delta\nu| \gg \Delta_d$ is therefore well satisfied in BaM, for at least some sublattices, and NMR lines should be observed from nuclei at the DB edge. The possibility of observing signals from nuclei in the center of the DB is not clear, since the local line widths from nuclei in the center of the DB, Δ_w, are not known.

An attempt was made[4,5] to establish the localization of nuclei responsible for the resonance lines in stationary NMR intraboundary spectra of the ferrite BaM. The authors made observations with a superregenerative type spectrometer, for different sublattices, of either a line from nuclei at the edge of the DB or from nuclei in the center of the DB.

Iron ions in the hexaferrite BaM occupy five nonequivalent crystallographic positions corresponding to five sublattices. The NMR frequencies of intraboundary signals of the sublattices from nuclei at the edge of the DB should differ a little from the frequencies of intradomain NMR signals, and it should therefore not be difficult to establish to which groups of nuclei these signals belong. For reliable identification of signals from nuclei at the DB center, it is necessary to know the values of $\delta\nu$ for the sublattices. The values of $\delta\nu$ of the sublattices at low temperatures should be close to the values of the change in NMR frequencies $\delta\nu'$ of the corresponding sublattices which results from reorientation of the magnetization vector from the c axis to the basal plane. Some differencebetween $\delta\nu$ and $\delta\nu'$ is possible on account of the change in local magnetization in the DB as the result of excitation of intraboundary magnons. Information on the magnitudes of $\delta\nu'$ of the sublattices can be obtained by studying NMR of single-domain specimens by the spin-echo technique.

An investigation of stationary NMR spectra at a low radiofrequency intensity level in the temperature range 77–295 K has been carried out in the present work. The signals from nuclei at the edge of the DB and at the DB center were recorded at 77 K for all sublattices. The results of studies of single-domain specimens by the spin-echo method were used to identify intraboundary NMR signals. The ranges of variation of local frequencies, $\delta\nu$, of the DB sublattices were determined, and the features of their temperature variations were studied. The anisotropy of local fields at ^{57}Fe nuclei on reorientation of the magnetization vector relative to the crystallographic axes was studied by the spin-echo technique at 77 K, and the anisotropy of the hyperfine field was calculated.

SPECIMENS AND METHOD OF MEASUREMENTS

Single crystals of BaM were used as specimens, grown by the method of solution in a molten $BaO–B_2O_3$ flux. Crystal synthesis was carried out in the temperature range 1050–1150 °C. The specimens were enriched to 100% in the isotope ^{57}Fe. The phase composition was monitored by x-ray diffraction. The crystal lattice constants of the crystals studied were $a = 5.89$ Å, $c = 23.19$ Å at room temperature. Results of measurements of the room-temperature resistivities, along the c axis ($\rho_{\parallel} = 5\times10^{10}\ \Omega\cdot\text{m}$) and in the basal plane ($\rho_{\perp} = 7.5\times10^{9}\ \Omega\cdot\text{m}$) indicate the small Fe^{2+} ion content in the ferrite composition. The crystals studied were spherical in shape.

NMR was observed by the stationary method using a device consisting of a high-frequency amplifier, at the input to which were connected the pick-up loop from the specimen

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TABLE I.

Sublattice	Frequency in the domain boundaries at 77 K, MHz			Frequency in the domains at 77 K, MHz			Frequency in the domain boundries at 295 K, MHz		
	ν_d	ν_w	$\delta\nu = \nu_w - \nu_d$	$\nu_\parallel$	$\nu_\perp$	$\delta\nu' = \nu_\perp - \nu_\parallel$	ν_d	ν_w	$\delta\nu = \nu_w - \nu_d$
e	58,53	59,25	+0,72	58,40	59,30	+0,90	54,80	54,60	−0,20
a	70,18	67,45	−2,73	70,20	67,70	−2,50	56,47	–	–
c	72,31	71,88	−0,43	72,28	71,97	−0,31	68,00	66,86	−1,14
b	74,20	75,57	+1,37	74,07	75,57	+1,50	69,78	70,38	+0,60
d	75,57	76,19	+0,62	75,40	76,15	+0,75	71,33	71,33	0

and a Kh1-42 frequency characteristic meter. The amplifier operated in a frequency band 50–80 MHz. The NMR was registered by the resonance peaks on the pick-up frequency characteristic meter. By using such a spectrometer, NMR could be observed at different voltage excitation levels from 4×10^{-4} to 0.4 V. The crystal was oriented in the pick-up loop so that the radiofrequency field should be applied along the *c* axis, in which direction the NMR signal was a maximum.

Spin-echo was observed using a spectrometer which enabled the spin-echo signal to be determined as a function of the repetition frequency of the radio frequency pulses.

RESULTS AND DISCUSSION

Nine NMR lines were recorded at a temperature of 77 K by the stationary method, with frequencies given in Table I. The external magnetic field, applied along the *c* axis led to disappearance of the NMR signal when its strength equalled to the saturation field. This fact is evidence that signals from nuclei in the DW were being observed. The NMR frequencies $\nu_\parallel$ of nuclei in the domains, at 77 K were determined by the spin-echo method in order to have a means of identifying these signals. The spin-echo spectrum is shown in Fig. 1. The spectrum consists of five lines *a*, *b*, *c*, *d*, and *e*. The lines have the form of narrow peaks with width (at half-maximum) 40–100 kHz. The identification of the lines to correspond to the five different positions of the Fe^{3+} ions in the crystal lattice has been given by Streever.[6] The frequencies of the five NMR lines determined by the stationary method at 77 K were little different from the frequencies $\nu_\parallel$ obtained by the spin-echo technique. They were interpreted as signals from nuclei at the edge of the DB (the frequencies ν_d in Table I). The values of the frequencies $\nu_\parallel$ are also given in Table I. The remaining four NMR lines were interpreted as signals from nuclei in the center of the DB (frequencies ν_w in Table I).

The magnetic moments of atoms in the center of the DB lie in the basal plane. Identification of the lines from nuclei in the center of the DB can be carried out if the changes in frequencies of the sublattices on reorientation of the spin moments of the atoms from the *c* axis to the basal plane are known. These changes in frequency were measured by the spin-echo method on a specimen magnetized to saturation by an external field. The crystal was rotated about an axis passing through the basal plane, in such a way that the *c* axis should subtend an angle φ with the direction of the external field within the limits from 0 to 180°. The experiment was carried out in a field of 24.1 kOe. The points in Fig. 2 show the experimental dependence of the change in spin-echo signal frequency $\Delta\nu'(\varphi) = \nu(\varphi) - \nu(0)$ on the change in orientation of the magnetic field. The form of the $\Delta\nu' = f(\varphi)$ relation is not the same for the different sublattices. Such a behavior of $\Delta\nu'$ becomes understandable if it is taken into account that the magnetization vector $\mathbf{I}_s$ departs from the magnetic field $\mathbf{H}$ for field directions intermediate between the basal plane

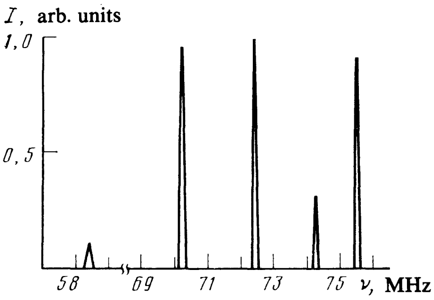

FIG. 1. Spin-echo spectrum of ^{57}Fe nuclei in the domains of the hexaferrite $BaFe_{12}O_{19}$ at 77 K.

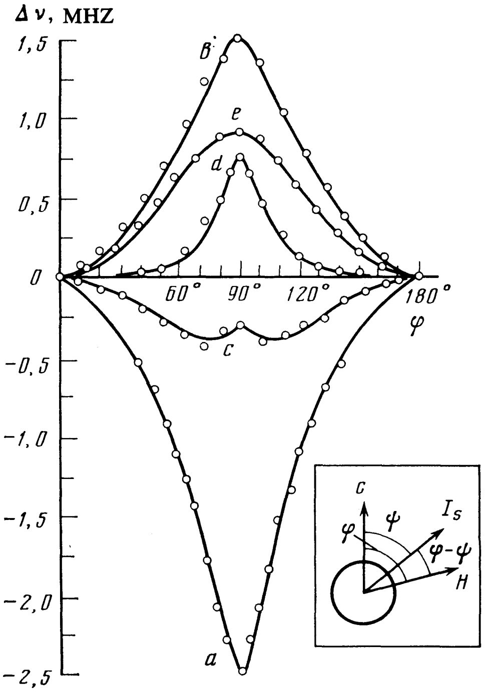

FIG. 2. The dependence of the frequency change $\delta\nu' = \nu(\varphi) - \nu(0)$ of echo signals in $BaFe_{12}O_{19}$ on changing the magnetic field orientation at a temperature of 77 K.

and the c axis. The relative orientation of the vectors $\mathbf{I}_s$ and $\mathbf{H}$ is shown in the inset to Fig. 2. One must also take into account that the projection of the magnetic field on the direction of the hyperfine field has different signs for different sublattices. The relation $\Delta\nu' = f(\varphi)$ can be written in the form

$$\Delta\nu'(\varphi) = \pm(\gamma/2\pi)H[\cos(\varphi-\psi)-1]+\delta\nu'\sin^2\psi, \tag{1}$$

where $\gamma/2\pi$ is the gyromagnetic ratio for ^{57}Fe nuclei, equal to 0.1377 kHz/Oe.

The sign in front of the first term in Eq. (1) is determined by the sign of the projection of the external field onto the direction of the hyperfine field of the corresponding sublattice, and can be determined from the shift in spin-echo signal of the sublattice on increasing the field applied in the direction of easy magnetization. It follows from our results and those of Petrov and Kunevich[3] that a plus sign must be used in Eq. (1) for sublattices a and c, and a minus sign for sublattices b, e, and d. The angle ψ can be found from the condition for a minimum of the free energy of the magnetic crystal. This condition leads to a transcendental equation of the form

$$\frac{H_a}{2H}=\frac{\sin(\varphi-\psi)}{\sin 2\psi}, \tag{2}$$

where H_a is the anisotropy field. This field for BaM is 16.2 kOe at 77 K. Solution of Eq. (2) for the given values of H_a and H for the angle $\varphi = 90°$ gives $\psi = 90°$. The values of $\delta\nu'$ for the sublattices can be determined from the experimental $\Delta\nu' = f(\varphi)$ relation, since $\Delta\nu' = \delta\nu'$ for $\varphi = \psi = 90°$. Results for $\delta\nu'$ of all the sublattices are given in Table I. The $\Delta\nu'(\varphi)$ relations were calculated from the values of $\delta\nu'$ according to Eqs. (1) and (2). They are shown in Fig. 2 by the full lines. As can be seen from the figure, the agreement between the calculated and experimental relations is completely satisfactory. Knowing the values of $\delta\nu'$, the NMR frequencies of the sublattice, $\nu_\perp$, for the case when the magnetic moments of the atoms lie in the basal plane can be determined

$$\nu_\perp=\nu_\parallel+\delta\nu'. \tag{3}$$

The lines of the stationary NMR were identified as from nuclei at the center of the DB, according to the values of $\nu_\perp$. The values of $\nu_\perp$ and ν_w are given in Table I. As can be seen from the table, $\nu_\perp$ for sublattice b differs little from $\nu_\parallel$ for sublattice d. This provides a basis for thinking that the line of frequency 75.57 MHz determined by the stationary method is a superposition of lines with frequencies ν_w for sublattices b and ν_d for sublattice d.

The values of $\delta\nu$ for sublattices a and c of BaM at 4.2 K were determined by Valez Gonzales *et al.*,[2] and are equal to -2.7 MHz and -0.55 MHz respectively. This result is in reasonable agreement with our results obtained for a temperature of 77 K.

Zalesskiĭ[4] considered the influence of an external magnetic field, perpendicular to the c axis, on the NMR frequencies ν_d and ν_w of nuclei in the DB. According to the calculation carried out there, ν_w should vary linearly with increasing field but ν_d should vary nonlinearly. Experimental dependences of ν_d and ν_w on external magnetic field are shown in Fig. 3, for sublattice e of the hexaferrite BaM at 77 K. It can be seen from the figure that the frequency ν_d changes nonlinearly, while ν_w changes linearly with increasing field as predicted by Zalesskiĭ.[4]

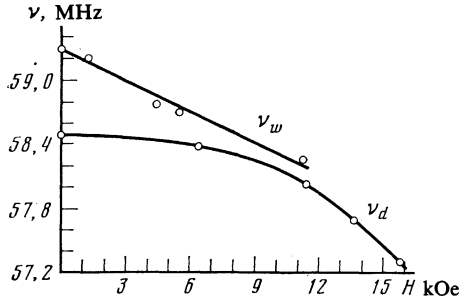

FIG. 3. The dependence of the frequencies ν_d and ν_w on the strength of a magnetic field perpendicular to the direction of easy magnetization for sublattice e at 77 K.

A dependence of the NMR signal amplitude on the magnitude of the radiofrequency voltage fed to the pick-up loop with the specimen was observed in investigating NMR by the stationary method. Parts of the frequency characteristic, drawn with the help of a graph plotter, are shown in Fig. 4 and two NMR peaks can be seen, corresponding to nuclei at the center of the DB and at the DB edge of the c sublattice. It can be seen from the figure that an increase in radiofrequency voltage fed to the pick-up coil containing the crystal under study leads to a weakening of the NMR signals, which is evidence of their saturation. At a voltage of 0.1 V the signal had weakened down to the sensitivity level of the recording apparatus. It should be noted that the disappearance of NMR signals from nuclei at the center of the DB and from nuclei at its edge occurs at approximately one and the same voltage.

The amplification coefficient for radiofrequency field is a maximum for nuclei at the center of the DB and a minimum for nuclei at the edge of the DB, while the relaxation rate is a maximum for nuclei at the center of the DB and a minimum for nuclei at the DB edge.[7] The disappearance of the NMR signals for nuclei in different parts of the DB with increase in radiofrequency voltage at the pick-up coil can, therefore, occur at one and the same value of it.

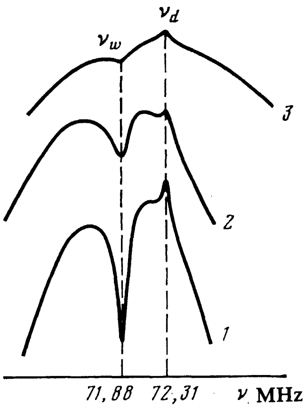

FIG. 4. NMR peaks on the frequency characteristic at 77 K for sublattice c for various voltages on the pick-up coil: 1) 2×10^{-3} V; 2) 4×10^{-2} V; 3) 2×10^{-2} V.

TABLE II

Sublattice	$H_{\parallel}$ kOe	$H_{\perp}$ kOe	δH_l kOe	δH_l kOe (Ref. 10)	δH_c kOe
e	424,1	430,6	+6,5	+10	−3,5
a	509,8	491,6	−18,2	−11	−7,2
c	524,9	522,6	−2,3	−2,2	−0,1
b	537,7	549,7	+12,0	+16	−4,0
d	547,5	553,0	+5,5	+10	−4,5

The shape of the NMR signals from nuclei of sublattice *c* for a low radiofrequency voltage level (see Fig. 4, curve 1) is noteworthy. Such a signal shape is associated with the following fact. In the presence of large amplification coefficients in the DB, the radiofrequency field at the nuclei can be so high that saturation of the imaginary part of the nuclear susceptibility takes place. In this case an NMR signal arises as a result of modulation of the loss in the electron subsystem due to the dispersive part of the nuclear susceptibility. The NMR signal recorder therefore corresponds to the dispersion curve of the nuclear susceptibility. Calculation of the dispersion signal for the case of the absence of local broadening in the DB ($\Delta_d \approx \Delta_w$) and for satisfaction of the condition $\delta\nu \gg \Delta_d$ was carried out by Nagai *et al.*[8] The shape of the NMR signal shown in Fig. 4 agrees fairly well with this calculated dependence. This is evidence that the condition $\Delta_d \approx \Delta_w$ holds for sublattice *c* at 77 K.

The stationary method of observing NMR employed, enabled the change in the frequencies ν_w and ν_d in the DB to be followed on raising the specimen temperature from 77 to 295 K. The NMR lines were then observed on the screen of the Kh 1-42 cathode ray display and there was no need to identify them on changing the temperature. The values of the frequencies ν_w and ν_d at 295 K are shown in Table I. Due to its small intensity it was not possible to record the NMR signal of nuclei in the center of the DB for sublattice *a* at this temperature. For sublattice *d* at room temperature, a superposition of the NMR lines of nuclei at the center and edge of the DB was observed, which led to an appreciable growth in the signal. The frequencies ν_d and ν_w for sublattice *c* coincided at the temperature of 240 K; the signal frequency in this case was equal to 56.6 MHz. The value of the frequency ν_w then became less than ν_d by 0.20 MHz at a temperature of 295 K.

As a result of intraboundary magnons, the frequency ν_w in the DB should fall more sharply with increase in temperture compared with the frequency ν_d.[7] This should lead to an approach of the resonance frequencies for $\nu_w > \nu_d$, and on the other hand, to their separation for $\nu_w < \nu_d$. This is, evidently, the reason for $|\delta\nu|$ decreasing with increasing temperature for sublattices *e*, *b*, and *d*, for which at low temperatures $\nu_w > \nu_d$, and increasing for sublattice *c*, for which under the same conditions $\nu_w < \nu_d$.

Knowing the values of $\nu_{\parallel}$ and $\delta\nu'$, the local fields at the nuclei H_l and the anisotropy of these fields H_l on reorientation of the magnetization vector from the *c* axis to the basal plane can be calculated. The values of $H_{\parallel}$ and δH_l of the sublattices at 77 K are given in Table II. For different sublattices the H_l have different signs and differ appreciably in absolute magnitude. The anisotropy of the dipolefield δH_d and the anisotropy of the hyperfine field H_{hyp} may be the source of the anisotropy in the local field. The contributions of H_d and H_{hyp} cannot be separated from results obtained by the NMR method. The anisotropy of the dipole fields in BaM has been calculated.[9] The values of δH_d from that work and the values of $\delta H_{\text{hyp}} = \delta H_l - \delta H_d$, calculated by using the experimental values of δH_l obtained in the present work are shown in Table II for a temperature of 77 K. We regard two facts which can be deduced from Table II as significant. The magnitude of $|\delta H_{\text{hyp}}|$ for the tetrahedral *c* sublattice is much less than for the octahedral *a*, *b*, and *d* and the pentahedral *e* sublattice. In spite of the different signs for δH_d, the values of δH_{hyp} of the sublattices are of one sign, which provides a basis for suggesting the existence of a general mechanism responsible for the value of δH_{hyp} of the sublattices.

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