Antiferromagnetic resonance in ferroborate NdFe$_3$(BO$_3$)$_4$

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The AFMR spectra of the NdFe$_3$(BO$_3$)$_4$ crystal are measured in a wide range of frequencies and temperatures. It is found that by the type of magnetic anisotropy the compound is an "easy-plane" antiferromagnet with a weak anisotropy in the basal plane. The effective magnetic parameters are determined: anisotropy fields $H_{a1}$=1.14 kOe and $H_{a2}$=60 kOe and magnetic excitation gaps $\Delta\nu_{1}$=101.9 GHz and $\Delta\nu_{2}$=23.8 GHz. It is shown that commensurate-incommensurate phase transition causes a shift in resonance field and a considerable change in absorption line width.

At temperatures below 4.2 K nonlinear regimes of AFMR excitation at low microwave power levels are observed.

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INTRODUCTION

The class of materials with coexistent magnetic and electric ordering is currently under deep investigation [1]. Among such compounds is a family of ferroborates (RFe$^{3+}$(BO$_3$)$_4$); (R being a rare-earth ion). All representatives of this family are multiferroics. The diversity of magnetic properties of ferroborates is caused by the existence of two magnetic subsystems: Fe ions and rare-earth ions. The specificity of interaction between rare-earth and iron ions dictates the orientation of Fe magnetic moments in the ordered state with respect to crystallographic axes. Of considerable importance on such systems are magnetoelastic and magnetoelectric interactions. Moreover, because of their nonlinear properties, such compounds are of great interest and show promise for laser technique. Therefore, much research is devoted to structural, magnetic, magnetoelectrical and magnetoelastic properties of the ferroborates family (e.g. see reviews [2, 3]).

At high temperatures all crystals of the RFe$^{3+}$(BO$_3$)$_4$ family have a trigonal structure of khanty mineral CaMg$_3$(CO$_3$)$_4$ that belongs to a noncentro-symmetric space group R32 ($D^3_3$) [4]. The structure fragments are shown Fig. 1. The edge-connected spiral chains of the FeO$_6$ octahedra extended along the $c$ axis are the basic elements of the structure.

The paper concerns the investigation of NdFe$_3$(BO$_3$)$_4$. The antiferromagnetic ordering of the Fe subsystem in NdFe$_3$(BO$_3$)$_4$ occurs at 30 K and it is followed by unit cell doubling along the $c$ axis. The magnetic cell of ferroborate is inconsistent with the crystallographic one [5]. The situation with Nd subsystem is not so clear. Some authors believe [4, 7] that both subsystems are ordered at the same temperature, some authors [6] claim that subsystem of Nd is just magnetizing by Fe.

The intra- and interchain interactions in the Fe subsystem are antiferromagnetic and equal to 580 and 270 kOe, respectively [5]. Detailed study of magnetization along $a$, $b$ and $c$ axes at fields up to 100 kOe and $T$=2 K are reported in Ref. [6]. At is shown that for the trigonal antiferromagnet NdFe$_3$(BO$_3$)$_4$ the anisotropy of Fe and Nd subsystems causes the magnetic moments of Fe$^{3+}$ and Nd$^{3+}$ to be oriented in parallel in the basal plane, i.e. NdFe$_3$(BO$_3$)$_4$ is a magnet with an "easy-plane" magnetization anisotropy. The existence of the triad axis gives rise to three types of domains in zero field with the axes of antiferromagnetism at an angle 120°. The antiferromagnetism vectors $\mathbf{l}$ are oriented along binary axes $C_2$. On one of the domains the antiferromagnetism vector direction coincides with the crystallographic axis $a$. At $T$=4.2
K and $H_{sf}=10 \text{kOe}$ there occurs a spin-flop transition to a state where magnetic moments are almost perpendicular to magnetic field.

The paper reports that a jump-like initiation of magnetostriction and electrical polarization is observed at magnetic fields corresponding to the spin-flop transition at is found that in this case the crystal symmetry is changed from class $\text{R32}$ to class $\text{R2}$ (monoclinic system).

The recent paper dealing with neutron scattering in NdFe$_3$(BO$_3$)$_4$ reports that at $T=13.5$ K one can observe a magnetic phase transition from commensurate ordered-magnetic phase to incommensurate long periodic helicoidal magnetic superstructure.$[2]$.

Despite considerable interest of experimenters to ferroborates, the resonance properties of the family remain almost unknown. There are only two reports on antiferromagnetic resonance (AFMR) in GdFe$_3$(BO$_3$)$_4$ and YFe$_3$(BO$_3$)$_4$.$[11,12]$.

The main concern of our paper is investigation of resonance properties of NdFe$_3$(BO$_3$)$_4$ in paramagnetic and magnetooordered states by using radio-frequency spectroscopic methods (EPR and AFMR).

**EXPERIMENT RESULTS AND DISCUSSION**

The measurements of magnetic resonance in paramagnetic and ordered states ($T_N=30 \text{ K}$) of the crystal for three principal lattice directions were conducted at liquid helium temperature and above with the use of the equipment described in $[11]$. The EPR spectrum were taken at frequencies of 21.7 and 76 GHz at $T=60–100$ K and external field $H$ oriented along $a$ and $c$ axes. Under such conditions one can observe a single broad EPR line of Fe$^{3+}$ ion with a $g$-factor equal to 2. The spectrum is shown Fig. 2. The EPR spectrum of ion Nd$^{3+}$, the $g$-factor of which is more than 2, is not observed for all permanent field directions because it seems likely to be very broadened due to spin-orbital coupling. The spectrum is observed only at low temperatures (20–30 K) but in this temperature range the material is already magnetically ordered. Moreover, as given in $[11,14]$, the ground doublet of multiplet $^{4}I_{9/2}$ of Nd$^{3+}$ ions is exchange splitted by 8.8 cm$^{-1}$. This suggests that the EPR spectrum of Nd is not observed in the frequency range 17–142 GHz and at $T=4.2$ K and higher.

As mentioned above in the papers cited, the ordered compound NdFe$_3$(BO$_3$)$_4$ is an "easy-plane" antiferromagnet. On the framework of two-sublattice magnet a typical frequency field dependence of the AFMR spectrum for "easy-plane" is schematically shown Fig. 3. For $H \parallel l \perp z$ the AFMR spectrum of such magnets consists of two considerably different branches one of which is a low-frequency quasi-ferromagnetic gapless branch ($\nu_1$) and the other is a high-frequency branch with energy gap $\sqrt{2H_c H_a}$ ($\nu_2$). This branch becomes zero in magnetic field $2H_c$. Besides, these branches have a point of intersection (degeneration). The magnetic field in which the two branches are crossed is arbitrarily called in literature as a field of spin-flop transition. The field value is $\sqrt{2H_c H_a}$ (the value of the field which there occurs an intersection of AFMR branches and the gap value are almost equal). When external magnetic field is directed along the principle anisotropy axis $H \parallel l \perp z$, one of the AFMR branches is a rising quadratic branch ($\nu_1$) and the other is not active.

The AFMR absorption spectra were measured in the following sequence. Since at $T=13.5$ K there occurs a magnetic phase transition to a noncommensurate phase, all frequency-field dependences of the AFMR spectrum were taken above and below this transition at two temperatures ($T=4.2$ and 14.6 K).

At $T=4.2$ K we made a search for a high-frequency branch of the AFMR spectrum. On the case of trigonal symmetry the magnetic axes $x, z$ coincide with the
magnetic structure is no longer a two-sublattice collinear
support for the statement in [7] that below 13.5 K the
gap value in both phases is equal. This provides
scribe the experimental dependence
at 4.2 K (in incommensurate phase) Eq. (1) does not de-
tence) is well described by theoretical relation (1), while
at 14.6 K (i.e. in the region of collinear structure exis-
tum at the external magnetic field oriented in the basal

crystallographic axes \( a, c \). For frequencies ranged from
17.0 to 102.0 GHz and external magnetic field perpen-
dicular to the basal plane and parallel to the principal
anisotropy axis \( C_3 (H \parallel c) \), the antiferromagnetic excitation
is not observed. The high-frequency AFMR branch
\( \nu_1(H) \) was observed at 101.9 GHz in practically zero mag-
etic field (see Fig. 4). This frequency represents an
initial splitting (or a gap of magnon excitations) for this
branch. It equals \( \Delta \nu_{high} = \sqrt{2H_a H_e} = 101.9 \) GHz. With
\( H_e = 580 \) kOe \( c \), we obtain the anisotropy value \( H_a = 1.14 \)
kOe. The AFMR high-frequency branch rises quadrati-
cally with magnetic field. Its frequency-field dependence
is shown in Fig. 4 for \( T = 4.2 \) and 14.6 K, i.e. below
and above the point of transition to an incommensurate phase. On the model of two-sublattice antiferromagnet
this dependence is given by the expression:

\[
(\nu/\gamma)^2 = 2H_e H_a + H^2, \tag{1}
\]

As seen from Fig. 4, the experimental field dependence
at 14.6 K (i.e. in the region of collinear structure exist-
ce) is well described by theoretical relation (1), while
at 4.2 K (in incommensurate phase) Eq. (1) does not de-
scribe the experimental dependence \( \nu(H) \), even though
the gap value in both phases is equal. This provides
support for the statement in [7] that below 13.5 K the
magnetic structure is no longer a two-sublattice collinear
one.

For magnetic field orientation \( H \parallel c \perp l \) only one os-
cillation branch is observed and other AFMR excitations
are not revealed.

The frequency-field dependences of the AFMR spec-
trum at the external magnetic field oriented in the basal
plane along \( a \) axis \( (H \parallel a) \) are shown in Fig. 5. As
seen from the figure, there are two AFMR resonance
lines at this field orientation. The frequency of one of
these lines \( \nu_2 \) has an initial value in zero magnetic field,
\( \Delta \nu_2 = 101.9 \) GHz, determined by the existence of a gap
in the excitation spectrum. It is very difficult to observe
the AFMR spectrum of this branch at strict orientation
\( (H \parallel l) \) because its frequency is weakly dependent
on magnetic field and to excite oscillations at the resonance
frequency requires parallel orientation of constant and
high-frequency magnetic field \( (H \parallel h) \). But in our case it
is just observed and, as shown in Fig. 3, it corresponds
to a high-frequency \( \nu_2(H) \) branch (sometimes it is called
in literature as exchange one).

The second resonance line corresponds to a low-
frequency gapless (quasi-ferromagnetic) branch \( \nu_3(H) \)
which is of nonlinear behavior in \( \text{NdFe}_3(\text{BO}_3)_4 \).

The above behavior of the frequency-field dependences
of the AFMR spectrum at \( (H \parallel a) \) is determined by the
following conditions. As followed from Fig. 3, when the
external magnetic field is perpendicular to the principal
anisotropy axis there exists a point of intersection (or
degeneracy) of the two spectrum branches with differ-
et types of spin system oscillations. The splitting oc-
curs due to an insignificant magnetic deflection from the
basal plane. In such a case there appears an interaction
between the two types of oscillation, the degeneracy is
splitted and the magnetic field curves of resonance fre-
cquency change in their shape.

Because of the degeneracy splitting we can observe

![FIG. 3. Resonance frequency as a function of magnetic field for an antiferromagnet with easy plane magnetic anisotropy.][12]

![FIG. 4. The frequency-field dependences of the \( \text{NdFe}_3(\text{BO}_3)_4 \) AFMR spectrum for external magnetic field \( H \parallel c \perp l \) at two temperatures (4.2 and 14.6 K) below and above the transition to an incommensurate phase. The solid line presents the data calculated by Eq. (1).][14]
a high-frequency branch in polarization ($\mathbf{H} \perp \mathbf{h}$) and obtain the experimental dependences shown in Fig. 5 ($\nu_2, \nu_3$). It should be mentioned that they are little different in the collinear and incommensurate phases.

To study magnetic anisotropy, the angular dependences of the AFMR spectrum were taken in planes $ac$ and $ab$. The angular dependence of resonance field of a low-frequency mode measured at $\nu = 78.4 \text{ GHz}$ in the $ac$ plane (rotation from axis $a$ to axis $c$) is shown in Fig. 6. As is easy to see, there is a strong angular dependence of resonance magnetic field. Therefore, when the angle of permanent field deflection from axis $a$ is more than $50^\circ$, the resonance is not observed because our experimental unit can not reach the required resonance field.

The measurements of angular dependences of the spectrum in the basal plane at $\nu = 110.75 \text{ GHz}$ demonstrate a slight change in the resonance line positions along directions $a$ and $b$, suggesting the existence of magnetic anisotropy in the plane.

To elucidate this point, the experimental dependences $\nu_3(H)$ were taken at frequencies below the high-frequency gap and the frequency-field dependence of the quasi-ferromagnetic mode displayed a low-frequency gap (see Fig. 5, $\nu_3$). The absorption spectrum is shown in Fig. 7 (a low-field line). The experimental value of gap in zero magnetic field is $\Delta \nu_{\text{low}}/\gamma = \sqrt{2H_cH_a} = 23.8 \text{ GHz}$. Knowing the value of exchange field ($H_e = 580 \text{ kOe}$ [3]), it is easy to estimate the effective anisotropy field that is responsible for low-frequency gap in the basal plane, $H_{a1} = 60 \text{ Oe}$. It should be noted that our value of anisotropy is much higher than that ($H_{a1} = 12 \text{ Oe}$) for the Fe subsystem calculated in [3] from the measurements of magnetization.

At presence of a anisotropy in the basal plane, there should be a spin-reorientation magnetic transition of spin-flop type when the external field is $\mathbf{H} \parallel a$. The antiferromagnetism vector is turned over perpendicular to magnetic field and the frequency-field dependences strongly change. The evidence for this transition is the observation of an antiferromagnetic excitation branch $\nu_a$ (Fig. 5) in the frequency region $21-35 \text{ GHz}$ at $H > 10 \text{ kOe}$ which is suggested to be due to the excitation of AFMR "spin-flop" mode. The spectrum of the "spin-flop" mode at $T = 4.2 \text{ K}$ is shown in Fig. 7 (a high-field line). The experimental dependence for the "spin-flop" mode of a two-sublattice antiferromagnet at magnetic field above the spin-flop transition can be given by the expression:

$$ (\nu_4/\gamma)^2 = H^2 - H_{sf}^2, \quad (2) $$

As is seen from Fig. 5, the experimental field dependence at $14.6 \text{ K}$ in the collinear phase (open triangles) is well described by Eq. (2) while in the incommensurate phase ($4.2 \text{ K}$) the experimental data (dark triangles) are all out of the theoretical dependence (2). The lack of a low-frequency oscillator made it impossible for us to follow the frequency-field dependence of AFMR at frequencies lower than $20 \text{ GHz}$.

The following peculiarity of the absorption spectrum must be emphasized: the AFMR line width in the ordered commensurate phase ($\Delta H = 4.3 \text{ kOe}$ at $\mathbf{H} \parallel a$ and $\Delta H_c = 5.3 \text{ kOe}$ at $\mathbf{H} \parallel c$ for $T = 14.6 \text{ K}$) is much larger.
FIG. 7. The AFMR absorption spectrum at low frequencies (21–27 GHz), T=4.2 K. The low-field line is a "quasi-ferromagnetic" branch, the high-field one is a "spin-flop" mode. The narrow line is a DPPH signal.

FIG. 8. The temperature dependence of AFMR line width under commensurate-incommensurate phase transition at H∥a.

than that in the incommensurate system (∆H=1.9 kOe at H∥a and ∆H_c=1.54 kOe at H∥c for T=12.6 K). The spectrum is shown in Fig. 8 and Fig. 9.

The decrease in AFMR line width in the incommensurate phase is not much intelligible but it may occur to the following reasons.

For the field of about 10 kOe the spin-orientation transition is followed by a number of other effects namely, jump of magnetostriction and electrical polarization, changes in crystal symmetry. Undoubtedly, all these effects produce modifications of relaxation characteristics and absorption line narrowing.

It should be also emphasized that in the helicoidal modulated phase the vectors of AF sublattice magnetization change periodically in direction with a period of 1140˚A which is incommensurate with that of the crystal lattice. This results in that in the volume average the electrical polarization is zero unlike the homogeneous antiferromagnetic state, besides, it may produce a AFMR line narrowing.

Thus, the analysis of the frequency-field dependences of AFMR in NdFe₃(BO₃)₄ at different temperatures shows that above and below the temperature of transition to the incommensurate phase, T=13.5 K, these dependences differ considerably. An increase in temperature up to 14.5–15 K brings the experimental and theoretical data into coincidence for a two-sublattice collinear antiferromagnet at all orientations of external magnetic field (see Fig. 4 and Fig. 5).

So far, we have concerned linear regimes of AFMR excitation in NdFe₃(BO₃)₄. As the temperature was decreased below 4.2 K, nonlinear regimes of AFMR excitation were revealed, i.e. nonlinear-in-absorbed power effects. The experimental conditions were the same as those in the observation of the homogeneous linear AFMR, namely, the external magnetic field was oriented as H∥a, the resonance excitation frequency was 111.13 GHz and at the site of sample location in the resonator dominant was a perpendicular polarization (H⊥h). The source maximum power was 5 mw. The external mag-
FIG. 10. The resonance curves of AFMR spectrum at different levels of microwave power. $H \parallel a, \nu=111.13$ GHz, $T=2.8$ K. The narrow line is a DPPH signal. The directions of field change are shown by arrows. The spectra are shifted vertically.

FIG. 11. The angle of magnetization precession as a function of frequency for different levels of pumping by high-frequency variable field $h$.

The magnetic field was scanned in the region of absorption line, and the pump power was varied from $-2$ to $-20$ db. The resonance curves for NdFe$_3$(BO$_3$)$_4$ at $T=2$ K and different levels of variable magnetic field power are shown in Fig.10. As is seen from the figure (the two lower records), at a low microwave radiation (lower than $-15$ db) one can observe a typical linear AFMR for the "easy plane" — the first resonance line corresponds to a high-frequency oscillation mode and the second one to a low-frequency (quasi-ferromagnetic) mode. As the pumping power is increased from $-5$ db up to $-2$ db, the quasi-ferromagnetic mode line is broadened and one can observe a sharp jump of the resonance line amplitude. With up-and downward changing the direction of field there occurs a hysteresis $\Delta H_{hyst} \sim 520$ Oe, and the absorption curve displays sharp peaks.

It should be noted that many of the magnets studied and described in literature exhibit nonlinear properties only at rather high pumping power (watts) [16, 17], while in NdFe$_3$(BO$_3$)$_4$ this effect is observed at a power lower than 5 mw.

In the theory of nonlinear resonance this phenomenon is well known; it is caused by the dependence of nonlinear oscillation frequency on oscillation amplitude. The essence of the effect is that at the pump field $h$ higher than some threshold value the resonance line becomes asymmetric and ambiguous. Its top is tilted towards lower or higher magnetic fields depending on the character of magnon interaction. In real experiment, when static magnetic field is varied an instability occurs and a discontinuity or a jump of the resonance line amplitude take place [3] [18] (see Fig. 11). Nonlinear oscillations appear in magnets that feature extremely low relaxation of spin excitations. At low temperatures the nonlinear properties are observed both at ($H \parallel h$) and ($H \perp h$) polarizations when phonons are frozen out and their interaction with magnons is highly weakened.

CONCLUSIONS

1. The magnetic field dependence of resonance frequency of AFMR spectrum of NdFe$_3$(BO$_3$)$_4$ has been studied extensively in wide ranges of frequency (17–142 GHz) and temperature (4.2–17.0 K). It is found that in the spectrum of spin waves there are two branches of AFMR oscillations with considerably different values of energy gap ($\Delta \nu_{high}=101.9$ GHz, $\Delta \nu_{low}=23.8$ GHz) and their associated magnetic anisotropies ($H_{a1}=1.14$ kOe, $H_{a2}=60$ Oe).

The existence of anisotropy in the basal plane results in a "spin-flop" spin-orientation phase transition which manifests itself in the frequency-field dependence at $H \approx 10$ kOe. These experimental data suggest that according to the type of magnetic anisotropy the compound NdFe$_3$(BO$_3$)$_4$ is an "easy-plane" antiferromagnet with a weak anisotropy in the basal plane.
2. It has been shown experimentally that above 13.5 K the AFMR spectrum of NdFe$_3$(BO$_3$)$_4$ is well described in terms of the model of two-sublattice collinear antiferromagnet.

The phase transition to an incommensurate helicoidal modulated phase at 13.5 K is followed by an essential rearrangement of the AFMR spectrum which cannot be described by the above-mentioned model below 13.5 K. Changes of both resonance fields and absorption line widths are observed for all orientations of external magnetic field.

3. Our experiments have demonstrated that the compound NdFe$_3$(BO$_3$)$_4$ is a magnet with abnormally low spin-lattice relaxation at temperatures below 4 K with the resulting excitation of nonlinear AFMR.

The effects of resonance instability with increasing the power of high-frequency variable magnetic field are observed. The typical peculiarity of NdFe$_3$(BO$_3$)$_4$ is an abnormally low threshold of nonlinear regime excitation.

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