

## Effect of optical $f$ - $f$ excitations on the Nd-Fe exchange interaction in Nd ferroborate with multiferroic properties

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We considered the effect of optical pumping at the  $f$ - $f$  transitions frequency on  $d$ - $f$  superexchange in the rare-earth antiferromagnetic ferroborate  $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$  between  $\text{Nd}^{3+}$  ions in the excited states of the  ${}^4G_{5/2}$ ,  ${}^2G_{7/2}$ , and  $\text{Fe}^{3+}$  in the ground state  ${}^6A_1$ . In the ferroborate,  $d$ - $f$  superexchange is directly related to the strong magnetoelectric coupling observed in the ground state of the material. We show that under optical pumping at the frequency of  $f$ - $f$  transitions  ${}^4I_{9/2} \leftrightarrow ({}^4G_{5/2} + {}^2G_{7/2})$  in the  $\text{Nd}^{3+}$  ion, the nature of the  $d$ - $f$  interaction changes to FM. The phenomena can be explained by the occupation of the excited  $\text{Nd}^{3+}$  “spin pure” states with spin 1/2, or their mixing to the optically excited states with spin 3/2 due to the spin-orbit interaction. Near optically excited ions  $\text{Nd}^{3+}$ , magnetic frustrations change from FM ordering under the  $d$ - $f$  AFM interaction to AFM ordering under the FM interaction in the basal hexagonal plane.

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### I. INTRODUCTION

Magnetic properties investigations of ferroborate single crystals with hantite structure started with  $\text{GdFe}_3(\text{BO}_3)_4$  about 20 years ago [1]. This family contains a large number of single crystals with different trivalent rare-earth ions [2]. The discovery of the multiferroic properties sharply increases the interest in these crystals [3,4]. In all rare-earth ferroborates with hantite structure the antiferromagnetic (AFM) ground state results from the AFM exchange interaction between the  $\text{Fe}^{3+}$  ions in the  ${}^6A_1$  ground states. Recently we have shown that optical excitation of a magnetic cation may change the value and the sign of its exchange interaction with a neighbor cation in the ground state [5]. This prediction has been confirmed in the paper [6] where terahertz radiation was detected from AFM iron borate  $\text{FeBO}_3$  under optical pumping at the frequency of  $d$ - $d$  transitions of the  $\text{Fe}^{3+}$  ion, and the results were explained due to the strong FM superexchange interaction of the optically excited  $\text{Fe}^{3+}$  ions with its unexcited nearest neighbors. Now, investigations of the local properties of crystals in the optically excited states become important in connection with the problem of quantum information processing (see, e.g., Refs. [7–10]).

An optically excited atom is, actually, an impurity isovalent atom, and, consequently, the local properties of the crystal, the exchange interaction, in particular, can change. Indeed the experiments [11,12] have revealed that in  $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$ : (1) values of splitting of the  $\text{Nd}^{3+}$  ion excited states in the exchange field of  $\text{Fe}^{3+}$  ions are different and differ from that in the ground state, and they do not correlate with the theoretical Landé factor  $g$  of the states; (2) in some excited states of the  $\text{Nd}^{3+}$  ion energetically favorable orientation of the  $\text{Nd}^{3+}$  ion magnetic moment was opposite to that in the ground state; (3)

the local metamagnetic transitions were observed in a number of the  $\text{Nd}^{3+}$  excited states in  $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$  [11] and of the  $\text{Ho}^{3+}$  state in  $\text{HoFe}_3(\text{BO}_3)_4$  [13]; and (4) in  $\text{HoFe}_3(\text{BO}_3)_4$  crystal in some excited states the  $\text{Ho}^{3+}$  ion was in the easy plane state, while the total crystal in the ground state was in the easy axis state [13].

In the paper we theoretically analyze experimentally observed variations [14] of the  $d$ - $f$  exchange interaction of  $\text{Nd}^{3+}$  ion in the excited  ${}^4G_{5/2}$  and  ${}^2G_{7/2}$  multiplets with the  $\text{Fe}^{3+}$  ion in the ground state  ${}^6A_1$  in the rare-earth AFM ferroborate  $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$ . The second part of the paper describes the experimental method used to analyze the orientation of the magnetic moment of  $\text{Nd}^{3+}$  ion in optically excited states. In the third part, within the multielectron approach [5], we briefly describe the exchange loop method to the  $d$ - $f$  superexchange that allows calculating particular contributions from each excited term, and where the main FM and AFM contributions are analyzed. In conclusion, the effect of spin-orbital interaction on the  $\text{Nd}^{3+}$  excited states, and some features of  $d$ - $f$  interaction are discussed.

### II. NATURE OF THE ${}^4I_{9/2}({}^4G_{5/2} + {}^2G_{7/2})$ OPTICAL ABSORPTION BAND ( $D$ BAND) IN FERROBORATE $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$ OBSERVED IN EXPERIMENTS

$\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$  crystal becomes antiferromagnetic at  $T_N = 32$  K and preserves easy plane magnetic structure down to 2 K [15]. The crystal has trigonal symmetry with the space group  $R_{32}$  and the lattice constants are  $a = 9.557(7)$  Å and  $c = 7.62(1)$  Å. The unit cell contains three formula units. Trivalent rare-earth  $\text{Re}^{3+}$  ions occupy the  $D_3$  symmetry positions. They are located at the center of trigonal prisms formed by six crystallography equivalent oxygen ions. The triangles formed by the oxygen ions in the neighboring basal planes are not superimposed on each other but are twisted through a particular angle. The  $\text{FeO}_6$  octahedrons share edges in such a

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way that they form helicoidal chains, which run parallel to the  $C_3$  axis and are mutually independent. All  $\text{Fe}^{3+}$  ions occupy the  $C_2$ -symmetry positions. Structural phase transitions were not found down to 2 K [15].

Magnetic structure of the  $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$  crystal was not studied in detail. However, its magnetic properties are close to those of the related crystal  $\text{NdFe}_3(\text{BO}_3)_4$  [2,16–18]. Therefore, it is possible to suppose that magnetic structure of these crystals is also similar. With decreasing temperature in zero magnetic field, a collinear magnetic order sets in first at  $T_N \sim 30$  K, consisting of ferromagnetic hexagonal  $ab$  planes, which are stacked antiferromagnetically along the perpendicular  $c$  direction [19]. Due to the frustrated AFM exchange interaction of the  $\text{Nd}^{3+}$  ion with three  $\text{Fe}^{3+}$  ions (one of the ions is in the same basal plane, and the rest are in the neighboring ones) below temperature 13.5–16 K the magnetic structure turns into an antiferromagnetic helix propagating along the  $c$  axis [20,21]. The spin helix is rapidly suppressed by increasing the magnetic field  $\sim 2$  T applied parallel to the hexagonal basal plane. These field dependent measurements reveal that the maximum of magnetic field induced ferroelectric polarization coexists with collinear spin order [21]. Thus,  $\text{NdFe}_3(\text{BO}_3)_4$  hence belongs to a class of materials where the magnetoelectric properties are driven by the magnetic frustration of two interacting  $d$  and  $f$  subsystems. This frustration can be relieved either by forming a spin helix or by creating a ferroelectric polarization.

Indeed an element selective resonant magnetic x-ray scattering study [21] has confirmed that the magnetic order of the  $\text{Nd}^{3+}$  sublattice is induced by the  $\text{Fe}^{3+}$  spin ordering. The AFM interaction between  $\text{Fe}^{3+}$  ions in neighboring planes is quite obvious, and prevails due to structural features. However, the superexchange interaction between  $\text{Fe}^{3+}$  and  $\text{Nd}^{3+}$  ions observed both between the basal planes and in the plane itself has a frustrated character, but its AFM character is not obvious.

Polarized absorption spectra of the  $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$  single crystal obtained in the region of the transition  ${}^4I_{9/2} \rightarrow ({}^4G_{5/2} + {}^2G_{7/2})$  at  $T = 6$  K are shown in Fig. 1 [14]. The ground multiplet  ${}^4I_{9/2}$  is split in the  $D_3$  local symmetry in the following way:  $3E_{1/2} + 2E_{3/2}$ .

Symmetries and positions of the levels of the ground multiplet and excited ones (Table II) were found in Ref. [22]. The excited  $D$  manifold ( ${}^4G_{5/2} + {}^2G_{7/2}$ ) is split in the crystal field of  $D_3$  symmetry in the following way:  ${}^4G_{5/2}$ :  $2E_{1/2} + E_{3/2}$  and  ${}^2G_{7/2}$ :  $3E_{1/2} + E_{3/2}$ . Symmetries of the excited states (Table II) were found from the spectra of Fig. 1 with a help of the selection rules. It should be noted that all states  $E_{1/2}$  and  $E_{3/2}$  are not distinguishable, while they have different magnetic properties. A classification of electron states with the help of the irreducible representations does not characterize their interaction with a magnetic field. For this purpose, the total moment presentation  $|I, \pm M_I\rangle$ , where  $I$  is a total moment with its projection  $M_I$  of the state, is more suitable. This presentation is approximately valid for the crystals with axial symmetry. In this case, the crystal quantum number  $\mu$  also appears [23]. It is an analog of the magnetic quantum number  $M_I$  of a free atom. Our classification of the states does not contradict the exact results given in the work by Popova *et al.* [18]. Indeed, the crystal  $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$

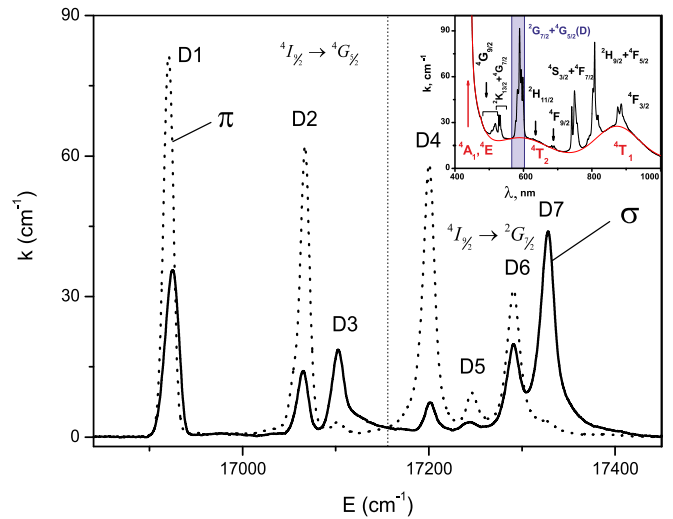


FIG. 1.  $\pi$  and  $\sigma$  polarized absorption spectra of  ${}^4I_{9/2} \leftrightarrow ({}^4G_{5/2} + {}^2G_{7/2})$  transition ( $D$  band) at 6 K. The solid line was used to indicate  $\sigma$  polarization, and spectral data taken from Ref. [14]. In the inset with the optical spectrum of  $d-d$  transitions ( $T = 300$  K,  $\sigma$  polarization, red), the  $D$  band under study is highlighted (blue).

has the axial symmetry and  $\text{Nd}^{3+}$  is in the  $D_3$  position. At room temperature, the crystal has trigonal symmetry with the space group  $R_{32}$  and remain this symmetry till 2 K [15].

In the case of the trigonal symmetry and for the half-integer total moment, between values of  $\mu$ ,  $M_I$ , and irreducible representations of states, there is the following correspondence (see Table I). The projection  $M_I$  defines the splitting of the Kramers doublets  $\pm M_I$  in the magnetic field directed along the trigonal axis. Correspondingly, the Landé factor  $g_{CM}$  of the  $\pm M_I$  doublet in the  $|I, \pm M_I\rangle$  wave functions approximation is equal to

$$g_{CM} = 2gM_I, \quad (1)$$

where  $g$  is the Landé factor of the free atom. In Ref. [18] the Landé factors  $g_C$  of the Kramers doublets in the crystal  $\text{NdFe}_3(\text{BO}_3)_4$  were calculated theoretically, based on the parameters of the crystal field. They do not coincide with  $g_{CM}$  numerically, since states with the same  $\mu$  but different  $M_I$  are mixed in crystals. However, the ratio of  $g_C$  and  $g_{CM}$  values permitted us to refer parameters  $M_I$  to the definite states (Table II). Identification of  $M_I$  for the  $D_3$  and  $D_7$  states is evident and unambiguous since in the  $D_3$  symmetry  $g_{\perp} \equiv 0$  for the states  $E_{3/2}$ , where  $g_{\perp}$  is the Landé factor in a magnetic field perpendicular to the  $C_3$  axis. Selection rules in the approximation of  $|I, M_I\rangle$  functions are governed by the number  $\mu$  and are similar to those for the number  $M_I$  in free atoms [23]. In particular, for the electric dipole absorption:

TABLE I. Relationship of values of  $\mu$ ,  $M_I$  with irreducible representations of  $\text{Nd}^{3+}$  ion states in  $\text{NdFe}_3(\text{BO}_3)_4$  ferroborate.

$M_I$	$\pm 1/2$	$\pm 3/2$	$\pm 5/2$	$\pm 7/2$	$\pm 9/2$
$\mu$	$\pm 1/2$	$\pm 3/2$	$\mp 1/2$	$\pm 1/2$	$\pm 3/2$
	$E_{1/2}$	$E_{3/2}$	$E_{1/2}$	$E_{1/2}$	$E_{3/2}$

TABLE II. Parameters of  $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$  crystal<sup>a</sup>:  $E_{12}$  is the splitting of absorption lines, shown in Fig. 2.  $\Delta E_e$  is the exchange splitting of excited states at 6 K, energies of transitions ( $E$ ) are given at 40 K.  $g_C$  and  $g_\perp$  are the theoretical Landé factors of the Kramers doublets in the crystal  $\text{NdFe}_3(\text{BO}_3)_4$ ,  $g_{CM}$  is the value of  $g_C$  in approximation of the free atom states.

Multiplet	Level	$E$ (cm <sup>-1</sup> )	Symmetry	$\mu$	$M_I$	$E_{12}$ (cm <sup>-1</sup> )	$\Delta E_e$ (cm <sup>-1</sup> )	$g_\perp$ [18]	$g_c$ [18]	$g_{CM}$	Orientation
$^4I_{9/2}$	$Gr1$	0	$E_{1/2}$	$\mp 1/2$	$\pm 5/2$		9	2.385	1.376	3.64	
$^4G_{5/2}$	$D1$	16 921	$E_{1/2}$	$\pm 1/2$	$\pm 1/2$	2	7	0.043	0.065	0.571	$\uparrow\uparrow$
	$D2$	17 062	$E_{1/2}$	$1/2$	$\pm 5/2$	13	2	1.385	1.310	2.885	$\uparrow\downarrow$
	$D3$	17 100	$E_{3/2}$	$3/2$	$\pm 3/2$	(9)	0	0	3.044	1.713	–
$^2G_{7/2}$	$D4$	17 199	$E_{1/2}$	$\pm 1/2$	$\pm 1/2$		12	2.617	0.266	0.889	$\uparrow\uparrow(?)$
	$D5$	17 240	$E_{1/2}$	$\pm 1/2$	$\pm 7/2$	17	8	0.755	3.308	6.223	$\uparrow\downarrow$
	$D6$	17 289	$E_{1/2}$	$1/2$	$\pm 5/2$		0.4	1.538	0.954	4.445	(?)
	$D7$	17 325	$E_{3/2}$	$3/2$	$\pm 3/2$	(9)	0	0	1.016	2.667	–

<sup>a</sup>Experimental results presented in Table II refer to  $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$  while the experimental results in Table I of Ref. [18] refer to  $\text{NdFe}_3(\text{BO}_3)_4$ . They indeed differ a little, but do not contradict each other. They should differ, since they refer to different crystals. According to the work [18],  $g$  factor has a nonzero perpendicular component  $g_\perp$ . Just component  $g_\perp$  is considered in our work, when the exchange interaction is discussed, since the crystal is the easy plane antiferromagnet.

(1)  $\Delta\mu = 1$  corresponds to  $\mp$  circularly polarized and  $\sigma$ -polarized waves,

(2)  $\Delta\mu = 0$  corresponds to  $\pi$ -polarized waves.

For the linearly polarized waves, these selection rules coincide with those for the irreducible representations. Thus, in the approximation of  $|L, M_I\rangle$  functions any state has its own set of parameters. Equations (2) and (3) and Table I permit us to estimate not only  $g_C$  factors in the  $c$  direction, but also their changes during electron transitions.

Magnetic moments of  $\text{Fe}^{3+}$  ions are FM ordered in the basal plane. Therefore, it would be possible to suppose that the splitting of the  $\text{Nd}^{3+}$  states in the exchange field of  $\text{Fe}^{3+}$  correlate with the factor  $g_\perp$ . It is not so (see Table II), since the fact that the exchange field of  $\text{Fe}^{3+}$  is formed by the  $d$ - $f$  exchange interaction with the spin of  $\text{Nd}^{3+}$  states.

Two main diagrams of transitions between components of the  $\text{Nd}^{3+}$  ion splitting in the exchange field of the iron sublattice are possible (Fig. 2). In both cases, it is supposed that  $a$  and  $b$  transitions occur without overturn of the magnetic moment. Then the favorable  $\text{Nd}^{3+}$  ion moment orientation in the excited state of the diagram of Fig. 2(b) is opposite to that in the ground state. In the case of Fig. 2(a):

$$E_{12} = E_A - E_B = \Delta E_{e1} - \Delta E_{e2}, \quad (2)$$

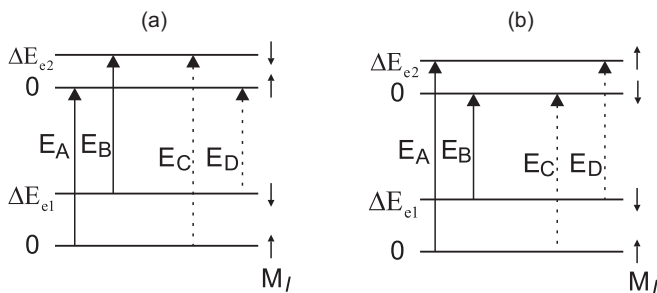


FIG. 2. The diagrams of the  $\text{Nd}^{3+}$  optical transitions in the exchange field of the iron  $\text{Fe}^{3+}$  sublattice. The transitions A and B at the  $E_A$  and  $E_B$  energy occur without overturning of the magnetic moments. (b) Diagram corresponds to a situation when the favorable moment orientation in the excited state is opposite to that in the ground state.

and in the case of Fig. 2(b):

$$E_{12} = E_A - E_B = \Delta E_{e1} + \Delta E_{e2}. \quad (3)$$

Since the exchange splitting of  $E_{3/2}$  states with  $g_\perp \equiv 0$  are zero, the splitting of transitions to such states should be equal to the exchange splitting of the ground state. The average value of such splitting which was observed gave the splitting of the ground state  $\Delta E_{e1} \sim 9 \text{ cm}^{-1}$  [24]. Comparing the experimental results presented in Table II with Eqs. (2) and (3), we find the mutual orientation of the  $\text{Nd}^{3+}$  ion moments in the ground and in the excited states. Orientation of the  $\text{Fe}^{3+}$  sublattice moments is considered to be constant. To understand the reasons for the spin orientation change on the  $\text{Nd}^{3+}$  ion, it is necessary to keep in mind that the ground multiplet is a “spin pure” state with a well-defined spin ( $LS$  approximation) [25]. Another situation exists for the optically excited multiplet states. In the  $M_I$  classification, the  $f$  states with different mutual orientations of  $L$  and  $S$  are split in energy. However, the classification does not contain information on the effect of spin-orbit mixing of states. Indeed, the optical excited  $\text{Nd}^{3+}$  states are a superposition of states with different spins but the same total moment  $I$ . For example,  $^4G'_{5/2} \approx \alpha ^4G_{5/2} + \beta ^2F_{5/2}$ , where  $\alpha^2 + \beta^2 \approx 1$ , instead of the symbolic  $^4G_{5/2}$ .

### III. EFFECT OF OPTICAL $f$ - $f$ EXCITATIONS ON THE Nd-Fe EXCHANGE INTERACTION

Let us consider the coupling of  $\text{Nd}^{3+}$  to magnetically ordered  $\text{Fe}^{3+}$  chains (see Fig. 3). Spins at the  $\text{Nd}^{3+}$  ions have FM ordering in the basal plane, due to  $d$ - $f$  superexchange AFM interaction between adjacent planes [21] with the weaker in-plane interaction.  $\text{Nd}^{3+}$  and  $\text{Fe}^{3+}$  ions are present together in the ground state of the rare-earth ferroborate, i.e., this pair of ions has lower energy than a pair of  $\text{Nd}^{2+}$ ,  $\text{Fe}^{4+}$  or  $\text{Nd}^{4+}$ ,  $\text{Fe}^{2+}$  ions (we call this configuration of electron removal from the  $\text{Fe}^{3+}$  ion and electron addition to the  $\text{Nd}^{3+}$  ion “ $d$ -hole,  $f$ -electron” and denote as  $(h_d, e_f)$ ). Similar electron removal from the  $\text{Nd}^{3+}$  ion and electron addition to the  $\text{Fe}^{3+}$  ion “ $f$ -hole,  $d$ -electron” is denoted as

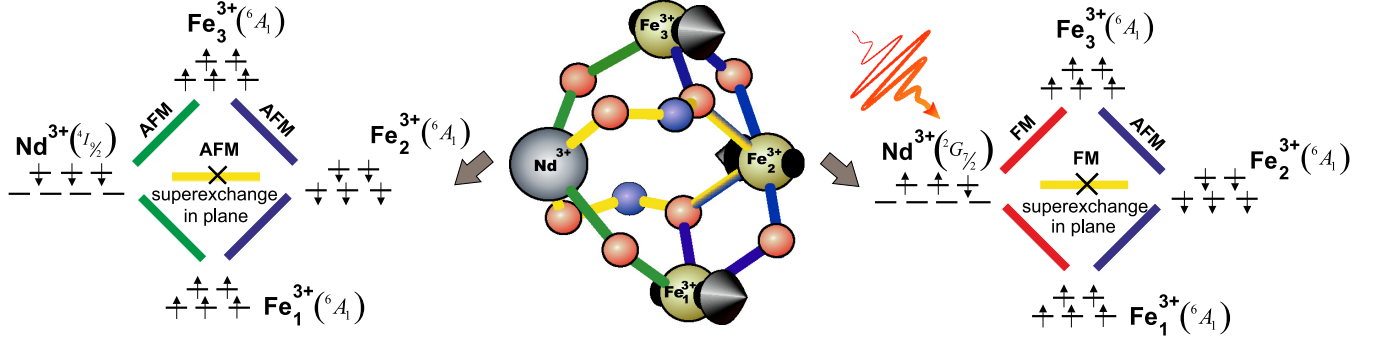


FIG. 3. Crystal structure of  $\text{NdFe}_3(\text{BO}_3)_4$  [21] with the superexchange paths between  $\text{Fe}^{3+}$ - $\text{Fe}^{3+}$  (blue AFM) and  $\text{Nd}^{3+}$ - $\text{Fe}^{3+}$  (green AFM, red FM, yellow in-plane). Only one of the three equivalent  $\text{Fe}^{3+}$  chains surrounding  $\text{Nd}^{3+}$  is shown. Magnetic frustration between  $\text{Nd}^{3+}$  and  $\text{Fe}_2^{3+}$  ions (left) persists under optical pumping at the frequency of the  $f$ - $f$  transitions (right) due to the intrachain  $\text{Fe}^{3+}$ - $\text{Fe}^{3+}$  strongest AFM coupling (blue), but it changes their nature.

$(h_f, e_d)$ :

$\Delta(h_d, e_f)$

$$= (E_f^{(e)} - E_f^{(0)}) + (E_d^{(h)} - E_d^{(0)}) = \delta\varepsilon \\ + [U_f(C_{N_0^d+1}^2 - C_{N_0^d}^2) + U_d(C_{N_0^d-1}^2 - C_{N_0^d}^2) - \delta V] > 0,$$

$\Delta(h_f, e_d)$

$$= (E_d^{(e)} - E_d^{(0)}) + (E_f^{(h)} - E_f^{(0)}) \\ = -\delta\varepsilon + [U_d(C_{N_0^d+1}^2 - C_{N_0^d}^2) + U_f(C_{N_0^d-1}^2 - C_{N_0^d}^2) + \delta V] > 0. \quad (4)$$

Here the first equation gives the energy of a hole creation in  $\text{Me}^{3+}$  ion and an electron addition to  $\text{Re}^{3+}$  ion, while the second one represents the energy of a hole in  $\text{Re}^{3+}$  and electron addition to  $\text{Me}^{3+}$  ions, where  $E_d^{(e)}$ ,  $E_f^{(h)}$ ,  $E_d^{(0)}$ ,  $E_f^{(0)}$  are the term energies of the virtual electron ( $e$ )-hole ( $h$ )  $\text{Me}^{4+}$ ,  $\text{Re}^{2+}$  and  $\text{Me}^{2+}$ ,  $\text{Re}^{4+}$  pair in Fig. 4,  $\delta\varepsilon = \varepsilon_f - \varepsilon_d$ , and  $U_f, U_d$  are intra-atomic Coulomb interactions of  $f$  and  $d$  electrons. The contribution  $\delta V = (V_{\text{Me}^{4+}} - V_{\text{Me}^{3+}}) + (V_{\text{Re}^{2+}} - V_{\text{Re}^{3+}})$  to Eq. (4) from the spherically symmetric components of the crystal field  $V(|\vec{r}_{\text{Me}^{n+}}|)$  and  $V(|\vec{r}_{\text{Re}^{n+}}|)$  is taken to be close to zero, and the monotonic displacement of all electronic  $d$  and  $f$  levels does not depend on the type of isovalent cation. In  $N_0^f$  and  $N_0^d$  coordinates of the number of  $f$  and  $d$  electrons, there is a region where the system of inequalities (4) is valid, and for each  $N_0^d(\text{Me}^{3+})$  there is a set of rare-earth ions  $\text{Re}^{3+}$  from the range  $\delta N_0^f = (1 + \lambda)/\lambda$  and  $\lambda = U_f/U_d$ . In addition to the ion  $\text{Nd}^{3+}$  in the pair of ions  $\text{Fe}^{3+}$  ( $N_0^d = 5$ ) and  $\text{Nd}^{3+}$  ( $N_0^f = 3$ ), all rare-earth ions with  $N_0^f$  in the region  $\delta N_0^f \neq 0$  can also form stable isovalent pairs. Indeed, here we observe the ferroborates not only with a pair of ions  $\text{Nd}^{3+}$  and  $\text{Fe}^{3+}$ , but also with a pair of ions  $\text{Gd}^{3+}$  and  $\text{Fe}^{3+}$ .

To analyze the superexchange interactions in a material with optically excited  $\text{Re}^{3+}$  ions, we will use the multi-electron approach to the superexchange interaction in the Mott-Hubbard insulators [5], where the superexchange interaction results from the virtual electron-hole pair creation and

then annihilation similar to the conventional Hubbard model [26,27]. It is convenient to draw these virtual excitations as the exchange loops (Fig. 5), where one loop notes  $d$  electron addition to the initial occupied  $d^5$  configuration of  $\text{Fe}^{3+}$  ion and back ( $e_g$  red loop), and the  $4f$  (red loop) shows the  $4f$  electron removal from the ground state of  $\text{Nd}^{3+}$  ion and back in Fig. 5(a). The other  $e_g$  and  $4f$  green loops in Fig. 5(a) show one more contribution to the superexchange interaction related to  $d$  hole and  $f$  electron excitations and back. Any contribution to the exchange interaction can be represented by a virtual electron-hole pair or graphically (exchange) loop connecting electron (sector  $N_+ = N_0 + 1$  in Fig. 5) and hole (sector  $N_- = N_0 - 1$  in Fig. 5) states (see Ref. [5]). A total superexchange parameter  $J_{\text{tot}}$  is given by a sum of all possible exchange loops. When one of the cations involved in the exchange interaction is excited by optical pumping [ $\text{Nd}^{3+}$  in Fig. 5(b)], the properties of the occupied term is different, so the matrix elements for a particular exchange loop may also be different and result in the sign change in  $J_{\text{tot}}$ . For  $\text{Fe}^{3+}$

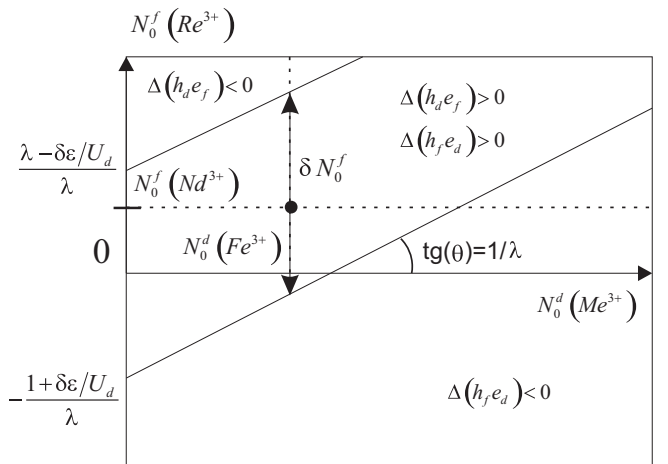


FIG. 4. Figure shows the region  $\Delta(h_d e_f) > 0$ ,  $\Delta(h_f e_d) > 0$  for the coexistence of ions  $\text{Me}^{3+}$  and  $\text{Re}^{3+}$  in coordinates  $N_0^d(\text{Me}^{3+})$  and  $N_0^f(\text{Re}^{3+})$ . The dot corresponds to the  $\text{Fe}^{3+}$  and  $\text{Nd}^{3+}$  ion pair with  $N_0^d = 5$  and  $N_0^f = 3$ .

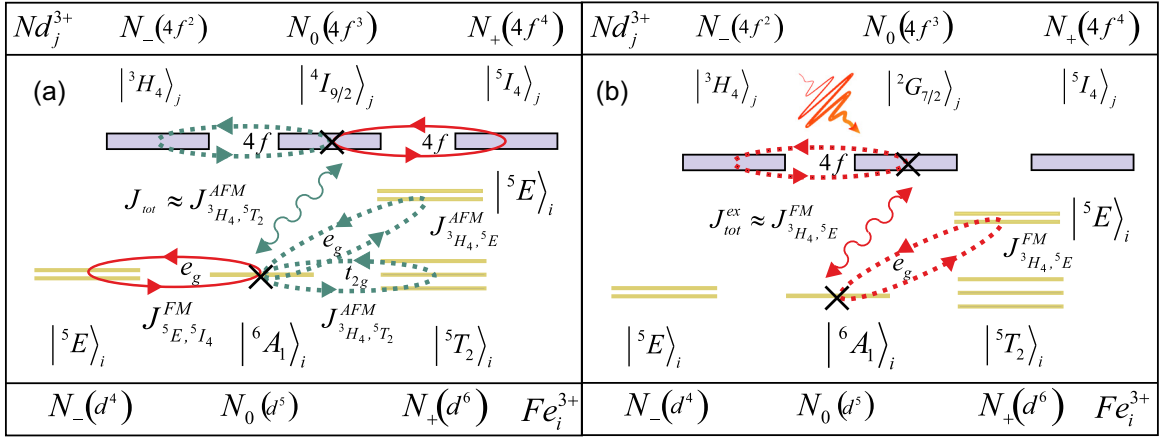


FIG. 5. Two main contributions  $J_{3H_4,5E}^{AFM}(e_g)$  (green dotted loop) and  $J_{5E,5I_4}^{FM}(e_g)$  (red solid loop) to the  $d$ - $f$  superexchange  $J_{tot} \approx J_{3H_4,5E}^{AFM}(e_g) + J_{3H_4,5T_2}^{AFM}(t_{2g}) + J_{5E,5I_4}^{FM}(e_g) \approx J_{3H_4,5T_2}^{AFM}(t_{2g})$  with the  $e_g$  participation of orbitals at the  $Fe^{3+}$  ion are shown, and contribution  $J_{3H_4,5T_2}^{AFM}(t_{2g})$  from  $t_{2g}$  electrons is also shown by the green dotted loop. (b) The only possible contribution  $J_{3H_4,5E}^{FM}(e_g)$  (red dotted loop) to the  $d$ - $f$  superexchange  $J_{tot}^{ex}$  between  $Fe^{3+}$  and  $Nd^{3+}$  ions, where the latter is in the optically excited multiplet  $^2G_{7/2}$  or  $^4G'_{5/2} \approx \alpha^4 G_{5/2} + \beta^2 F_{5/2}$  states.

ions such an example is given for  $d$ - $d$  excitation with 2 eV energy (the  $^2T_4$  absorption band in  $FeBO_3$ , see also the inset in Fig. 1) [6].

There are two AFM and FM contributions to the  $d$ - $f$  superexchange [see Fig. 5(a)] and both come with strongly overlapping  $e_g$  orbitals at the  $Fe^{3+}$  ion. Moreover, the ground state of the  $Nd^{3+}$  ion is practically a pure spin multiplet  $^4I_{9/2}$  with an experimental spin value  $2.7 \mu_B$  [21]. According to this scheme, the AFM contribution  $J_{3H_4,5E}^{AFM}(e_g) + J_{3H_4,5T_2}^{AFM}(t_{2g})$ , and FM contribution  $J_{5E,5I_4}^{FM}(e_g)$  take place in the spin Hamiltonian  $\hat{H}_{d-f} = -\sum_{ij} J_{tot}(\gamma) \hat{S}_i^d \hat{S}_j^f$ , where  $J_{tot}$  has the property of additivity in the states of a virtual  $d$ - $f$  electron-hole pair  $J_{tot} = \sum_{eh} J_{eh}^r(\gamma)$ , where  $\gamma = e_g(t_{2g})$ , depending on which electron (hole)  $e_g$  or  $t_{2g}$  at ion  $Fe^{3+}$  is involved in the interaction. For the interaction between nonequivalent ions  $i$  and  $j$  the sign of exchange interaction can be found due to a rule [5]:

$$|S_{i,\lambda} - S_{j,\lambda'}|_{\lambda \neq \lambda'} = \Delta S, \rightarrow \tau = \text{AFM},$$

$$|S_{i,\lambda} - S_{j,\lambda'}|_{\lambda \neq \lambda'} = \Delta S \pm 1, \rightarrow \tau = \text{FM}, \quad (5)$$

where  $\lambda(\lambda') = h, e$  and  $\Delta S = |S_i - S_j|$ . Since both contributions come with the participation of  $e_g$  orbitals, it is necessary to estimate the magnitudes of  $\Delta(h_d, e_f)$  and  $\Delta(h_f, e_d)$  denominators in  $J_{eh}^r \sim t_{ij}^2(\gamma)/\Delta(h, e)$  exchange contribution:

$$\Delta(^5E, ^5I_4) = \delta\varepsilon + [U_f(C_{N_{0+}^f}^2 - C_{N_0^f}^2) + U_d(C_{N_{0+}^d}^2 - C_{N_0^d}^2)] = \delta\varepsilon + 3U_f - 4U_d,$$

$$\Delta(^3H_4, ^5E) = -\delta\varepsilon + [U_d(C_{N_{0+}^d}^2 - C_{N_0^d}^2) + U_f(C_{N_{0+}^f}^2 - C_{N_0^f}^2)] = -\delta\varepsilon - 2U_f + 5U_d. \quad (6)$$

Both contributions in Eq. (6) correspond to different electron-hole pairs, due to which the denominator  $\Delta$  in  $J_{tot}$  is different. From Eq. (6) it follows that the ratio  $U_f = 0.4(4.5U_d - \delta\varepsilon)$  corresponds to  $J_{3H_4,5E}^{AFM}(e_g) = J_{5E,5I_4}^{FM}(e_g)$  with the denominator  $\Delta = 0.2(7U_d - \delta\varepsilon)$  (see Fig. 5), and therefore AFM and FM

contributions involving  $e_g$  electrons cancel each other out. The total superexchange  $J_{tot} = J_{3H_4,5E}^{AFM}(e_g) + J_{3H_4,5T_2}^{AFM}(t_{2g}) + J_{5E,5I_4}^{FM}(e_g) \approx J_{3H_4,5T_2}^{AFM}(t_{2g})$  in ground state has an AFM character with involved  $t_{2g}$  orbitals. For example, if  $U_d \sim \delta\varepsilon \sim 6$  eV, then  $\Delta(^3H_4, ^5E) = \Delta(^5E, ^5I_4) = 7.2$  eV and  $U_f = 8.4$  eV.

To consider the superexchange interaction between  $Fe^{3+}$  and the optically excited  $Nd^{3+}$  ions, it is necessary to take into account that the latter is not spin pure. Spin-orbit interaction leads to the mixing of states with different spins. Here, mixing of states with only spins 3/2 and 1/2 is possible. Let us estimate the changes in the  $d$ - $f$  superexchange involving  $Nd^{3+}$  excited states with spin 1/2, for example,  $^2G_{7/2}$  or  $^4G'_{5/2}$ , instead of the multiplet  $^4G_{5/2}$ . In this case, only FM contribution  $J_{tot}^{ex} \approx \alpha^2 J_{3H_4,5E}^{FM}(e_g) + \beta^2 J_{3H_4,5T_2}^{AFM}(t_{2g}) \approx \beta^2 J_{3H_4,5E}^{FM}(e_g)$  with involved  $e_g$  orbitals of the  $Fe^{3+}$  ion is possible [see Fig. 5(b)]. We observe that the contribution to the  $d$ - $f$  superexchange from optically excited spin 1/2 states with  $\Delta(^3H_4, ^5E) = \Delta(^3H_4, ^5E) - hv_{f-f}$ , where  $hv_{f-f} = E_{2G_{7/2}} - E_{4I_{9/2}}$  (or  $E_{4G'_{5/2}} - E_{4I_{9/2}}$ ), has FM character, but its magnitude depends on the spin-orbit mixing. This is probably due to the FM  $d$ - $f$  interaction  $J_{tot}^{ex}$  with  $Nd^{3+}$  ions in the multiplet state  $^4G'_{5/2}$ . Thus, our analysis results in a conclusion of the FM interaction for the excited  $Nd^{3+}$  term. To obtain the more accurate magnitude of  $J_{tot}$  one has to do more complicated computations. Nevertheless, for a qualitative explanation of the experimental data discussed above in Sec. II, our analysis is sufficient.

#### IV. CONCLUSIONS

The ions  $Nd^{3+}$  at the ground state have a well-defined spin, and the AFM and FM contributions to the  $d$ - $f$  exchange, with the participation of electrons of the  $Fe^{3+}$  ion, practically cancel each other out  $J_{3H_4,5E}^{AFM}(e_g) \approx J_{5E,5I_4}^{FM}(e_g)$ . However, there is an additional AFM contribution  $J_{3H_4,5T_2}^{AFM}(t_{2g})$  with the participation of  $t_{2g}$  electrons, and the total superexchange is probably of the same magnitude  $J_{tot} \approx J_{3H_4,5T_2}^{AFM}(t_{2g})$ . The optically excited multiplet states of the  $Nd^{3+}$  ions do not have

a definite spin. As a consequence, the contribution to the  $d$ - $f$  superexchange from only one virtual electron-hole pair corresponds not to one, but several terms of both FM and AFM types. In ferroborate the states with spin 3/2 and 1/2 can be mixed. Moreover,  $\text{Nd}^{3+}$  ions in an optically excited state with spin 3/2 participate in the AFM interaction, but  $\text{Nd}^{3+}$  ions in a state with spin 1/2 have the FM superexchange. The general picture is complicated by spin-orbit mixing. However, calculations show that the  $d$ - $f$  superexchange for the multiplets with spin 1/2 predominates  $J_{3H_4,5E}^{\text{FM}}(e_g) \gg J_{3H_4,5T_2}^{\text{AFM}}(t_{2g})$  and  $J_{\text{tot}}^{\text{ex}} \approx \beta^2 J_{3H_4,5E}^{\text{FM}}(e_g)$ . A small admixture of them in the optically excited  $\text{Nd}^{3+}$  state  ${}^4G'_{5/2} = \alpha {}^4G_{5/2} + \beta {}^2F_{5/2}$  can lead to the FM  $d$ - $f$  interaction between the two basal planes. Note also the magnetic frustrations between  $\text{Nd}^{3+}$  and  $\text{Fe}^{3+}_2$  ions in a single basal plane (on the left in Fig. 3) change their nature under optical pumping at the frequency of the absorption lines  $D2$  and  $D5$  (on the right in Fig. 3), and can be accompanied by changes in the helicoidal ordering at the temperature  $< 16$  K and in the electric dipole moment. Moreover, the frustrations could just be destroyed by the  $d$ - $d$  optical pumping, due to the AFM superexchange between ions  $\text{Fe}^{3+}$  ions is changed to FM. However, the nature of the  $d$ - $f$  superexchange between  $\text{Nd}^{3+}$  and  $\text{Fe}^{3+}$  ions, where the latter only is in excited state  ${}^4T_2$  (see the inset in Fig. 1) [6], is still unknown.

We also add that, in contrast to the exchange interaction in a material with  $3d$  ions, where

$$\begin{aligned} \Delta(he) &= (E_d^{(e)} - E_d^{(0)}) + (E_d^{(h)} - E_d^{(0)}) \\ &\approx [U_d(C_{N_d^+}^2 - C_{N_d^0}^2) + U_d(C_{N_d^-}^2 - C_{N_d^0}^2)] \\ &\equiv U_d, \end{aligned} \quad (7)$$

regardless of the  $\text{Me}^{n+}$  ion, there is no any formal prohibition in Eq. (6) on pairs of  $\text{Me}^{n+}$  and  $\text{Re}^{m+}$  ions with small  $\Delta(he)$  and the  $d$ - $f$  superexchange  $J_{\text{tot}} \sim t_{ij}^2(\gamma)/\Delta(he)$  can be relatively large [28]. However, a volume of the magnetic ordered phase will depend on a temperature, provided that  $\Delta(he) \sim kT$  and  $T \leq T_N$  (or  $T_C$ ).

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