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Current Perspectives

Magneto-optical spectra and electron structure of $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$ single crystalA.V. Malakhovskii^{a,*}, S.L. Gnatchenko^b, I.S. Kachur^b, V.G. Piryatinskaya^b, A.L. Sukhachev^a, V.L. Temerov^a^a L. V. Kirensky Institute of Physics, Siberian Branch of Russian Academy of Sciences, 660036 Krasnoyarsk, Russian Federation^b B. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine, 61103 Kharkov, Ukraine

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ABSTRACT

Polarized absorption spectra and magnetic circular dichroism (MCD) spectra of $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$ single crystal were measured in the range of 10000–21000 cm^{-1} and at temperatures 2–300 K. On the basis of these data, in the paramagnetic state of the crystal, the *4f* states of the Nd^{3+} ion were identified in terms of the irreducible representations and in terms of $|J, \pm M_J\rangle$ wave functions of the free atom. The changes of the Landé factor during *f*-*f* transitions were found theoretically in the $|J, \pm M_J\rangle$ wave functions approximation and were determined experimentally with the help of the measured MCD spectra. In the majority of cases the experimentally found values are close to the theoretically predicted ones.

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1. Introduction

The family of the rare-earth (RE) borates with the common formula $\text{RM}_3(\text{BO}_3)_4$, where $M=\text{Al, Ga, Fe, Cr, Sc}$ and R – RE element, attracts considerable interest both in the fundamental aspect and in view of their manifold potential applications. In particular, the alumborates possess the very good luminescent and nonlinear optical properties and can be used in the mini-lasers and in the lasers with the self-doubling frequency [1–3]. The growing interest to the RE ferrobates $\text{RFe}_3(\text{BO}_3)_4$ during the last years is stimulated by discovering of the multiferroic properties (i.e. correlation between magnetic, elastic and electric ordering) in many of them [4–8]. The multiferroic effects open the possibility of these materials usage in new multifunctional devices with the mutual control of magnetic, electric and elastic characteristics.

At high temperatures the RE ferrobates crystallize in the trigonal huntite-like structure with the space group $R\bar{3}2 (D_3^d)$ [9–11]. The unit cell contains three formula units. The RE ions are located at the centers of the trigonal prisms RO_6 (the D_3 symmetry positions). The Fe^{3+} ions occupy the C_3 positions in the octahedral environment of oxygen ions; these octahedrons form helicoidal

chains along the C_3 axis. With the lowering temperature, some ferrobates with small ionic radius of RE ions undergo a structural phase transition to the $P3_121 (D_3^d)$ symmetry phase [11]. It results in reducing of the RE ion position symmetry to the C_2 one and in appearance of two nonequivalent positions of Fe^{3+} ions (C_2 and C_1).

Magnetic phase transitions in the mixed borates $\text{Nd}_x\text{Gd}_{1-x}\text{Fe}_3(\text{BO}_3)_4$ were studied by the optical spectroscopy method in Ref. [12]. It was found out that both the Neel temperature and the spin-reorientation transition temperature increase with the growth of the Nd concentration. The $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$ crystal, the same as the pure Nd and Gd ferrobates, reveals multiferroic properties [13]. Magnetic properties of the crystal $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$ were studied in Ref. [14]. It was shown that below the $T_N=32$ K it has an easy-plane AFM structure and the spin-reorientation does not occur down to 2 K. Any structural phase transitions were also not found down to 2 K.

Optical spectra of the Nd^{3+} ion in the $\text{NdFe}_3(\text{BO}_3)_4$ crystal in a wide spectral range (1500–25000 cm^{-1}) were studied in Ref. [15] and the crystal-field parameters and *g*-factors of the Nd^{3+} states were calculated. The first measurements of the optical absorption spectra of the $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$ single crystal at temperatures 90–300 K as well as their analysis with the help of the Judd-Ofelt theory were performed in Ref. [16]. Some results of study of the

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optical and magneto-optical properties of the $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$ crystal were presented in Refs. [17,18]. A number of peculiarities of the selection rules for electron transitions in the magnetically ordered state of the crystal as well as the specific features of the local environment of the excited Nd^{3+} ions were found.

In the present work, the magnetic circular dichroism (MCD) and absorption spectra of f - f transitions from 11000 cm^{-1} till the edge of the strong absorption at $\sim 22000\text{ cm}^{-1}$ are investigated. The crystal field split components of the $4f$ states are identified on the basis of the absorption and MCD spectra. The MCD spectra allow finding not only the symmetry of the states but also their origin from the states of $|J, \pm M_J\rangle$ type of the free ion, and allow finding the change of the Landé factor during f - f transitions.

2. Experimental details

$\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$ single crystals were grown from the melt solution on the base of $\text{K}_2\text{Mo}_3\text{O}_{10}$ as described in Ref. [19]. At room temperature, the crystal has lattice constants: $a = 9.557(7)\text{ \AA}$ and $c = 7.62(1)\text{ \AA}$ [14]. The absorption spectra were measured with the light propagating normal to the C_3 axis of the crystal for the light electric vector \vec{E} parallel (the π spectrum) and perpendicular (the σ spectrum) to the C_3 axis and the light propagating along the C_3 axis (the α spectrum). The spectral resolution at the low temperature measurements was approximately equal to 1.5 cm^{-1} . The absorption spectra measured in the σ and α polarizations coincide with each other within the limit of the experimental error. This implies that the absorption mainly occurs through the electric dipole mechanism.

At $T = 2\text{ K}$ the sample was placed in the liquid helium. For the measurements of absorption spectra at $T > 4.2\text{ K}$ a liquid-helium cooled cryostat was used. It had an internal volume filled by the gaseous helium where the sample was placed.

The MCD was measured in the field 5 kOe by the light-polarization modulation method using a piezoelectric modulator (details are in Ref. [20].) The spectral resolution of the MCD measurements was $\sim 10\text{ cm}^{-1}$ and sensitivity was 10^{-4} . The MCD measurements were carried out in α -polarization with the sample positioned in the gas flow cryostat.

3. Background for characterization of electronic transitions and states.

Electron states in crystals are characterized by the irreducible representations in the group of the local symmetry (D_3 in our case). These characteristics of the states are found from polarization of transitions and from selection rules of Table 1. In crystals of the axial symmetry the electron states have one more characteristic: the crystal quantum number μ . In trigonal crystals it has values [21]: $\mu = +1/2, -1/2, 3/2 (\pm 3/2)$. Additionally, in the axial crystals the electron states can be described in a first approximation by $|J, \pm M_J\rangle$ wave functions of the free atom. Between values of μ and M_J there is the following correspondence [21]:

$$M_J = \pm 1/2, \pm 3/2, \pm 5/2, \pm 7/2, \pm 9/2, \pm 11/2, \pm 13/2$$

$$\mu = \pm 1/2, (\pm 3/2), \mp 1/2, \pm 1/2, (\pm 3/2), \mp 1/2, \pm 1/2 \quad (1)$$

Table 1
Selection rules for electric dipole transitions in D_3 symmetry.

	$E_{1/2}$	$E_{3/2}$
$E_{1/2}$	$\pi, \sigma(\alpha)$	$\sigma(\alpha)$
$E_{3/2}$	$\sigma(\alpha)$	π

The states with $\mu = \pm 1/2$ correspond to the $E_{1/2}$ states and the states with $\mu = (\pm 3/2)$ correspond to the $E_{3/2}$ states in the D_3 group notations. Selection rules for the number μ in crystals are similar to those for the number M_J in free atoms [21]. For the electric dipole absorption

$\Delta\mu = \pm 1$ corresponds to

$$\mp \text{ circularly polarized and } \sigma\text{-polarized waves,}$$

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

For the linearly polarized waves, these selection rules coincide, of course, with that of Table 1.

According to the definition, the splitting of the Kramers doublets in the magnetic field directed along the C_3 axis of a crystal is:

$$\Delta E = \mu_B g_C H. \quad (3)$$

Here g_C is the effective Landé factor in the C_3 -direction. The same value in the approximation of the $|J, \pm M_J\rangle$ function is evidently defined by the equation:

$$\Delta E = 2g\mu_B M_J H, \quad (4)$$

where g is the Landé factor of the free atom. Correspondingly, the Landé factor of the Kramers doublet along the C_3 axis in the same approximation is

$$g_{CM} = 2gM_J \quad (5)$$

These values for the states of Nd^{3+} ion are given in Table 2. The states with the same μ and different M_J (see Eq. (1)) can mix in the crystal, and the resulting g_C can differ from g_{CM} . The prevailing M_J state of the free atom in the crystal field state can be found in a first approximation (Table 3) basing on the comparison of g_{CM} for the corresponding M_J (Table 2) with the theoretical g_C in the $\text{NdFe}_3(\text{BO}_3)_4$ crystal (Table 3). The MCD spectra can help to identify states in the $|J, \pm M_J\rangle$ functions approximation and to find the Zeeman splitting of lines.

The MCD conditioned by a pair of the Zeeman splitting components is evidently described by the equation:

$$\Delta k = k_{m+}\phi(\omega, \omega_0 + \Delta\omega_0) - k_{m-}\phi(\omega, \omega_0 - \Delta\omega_0) \quad (6)$$

Here k_+ and k_- are the amplitudes of (+) and (−) circularly polarized lines, ϕ are the form functions of (+) and (−) polarized lines. If the Zeeman splitting $\Delta\omega_0$ is much less than the line width, then one obtains

$$\Delta k = k_m c \phi(\omega, \omega_0) + k_m \Delta\omega_0 \partial\phi(\omega, \omega_0) / \partial\omega_0. \quad (7)$$

Here $k_m = k_{m+} + k_{m-}$ is amplitude of the line not split by the magnetic field and $c = (k_{m+} - k_{m-}) / k_m$. The first term in (7) is the paramagnetic MCD and the second one is the diamagnetic MCD.

Table 2
Landé factors of the Kramers doublets along the C_3 axis of a crystal in approximation of the $|J, \pm M_J\rangle$ functions.

	M	13/2	11/2	9/2	7/2	5/2	3/2	1/2
$^4I_{9/2}, g = 0.727$	g_{CM}			6.54	5.09	3.64	2.18	0.727
$^4F_{3/2}, g = 0.4$	g_{CM}						1.2	0.4
$^4F_{5/2}, g = 1.029$	g_{CM}					5.14	3.09	1.03
$^2H_{9/2}, g = 0.909$	g_{CM}			8.18	6.36	4.55	2.73	0.909
$^4S_{3/2}, g = 2$	g_{CM}						6	2
$^4F_{7/2}, g = 1.238$	g_{CM}				8.67	6.19	3.71	1.238
$^4G_{5/2}, g = 0.571$	g_{CM}					2.855	1.713	0.571
$^2G_{7/2}, g = 0.889$	g_{CM}				6.223	4.445	2.667	0.889
$^4G_{7/2}, g = 0.984$	g_{CM}				6.888	4.92	2.952	0.984
$^4G_{9/2}, g = 1.1717$	g_{CM}			10.54	8.202	5.86	3.515	1.1717
$^2K_{13/2}, g = 0.933$	g_{CM}	12.1	10.27	8.4	6.53	4.66	2.8	0.933

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