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Peculiarities of magnetic properties of Nd^{3+} ions in the $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ crystal in the optically excited states $^4(F_{7/2}+S_{3/2})$ and $(^4G_{9/2}+{}^2K_{13/2}+{}^4G_{7/2})$

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ABSTRACT

Polarized absorption spectra of *f-f* absorption bands $^4I_{9/2} \rightarrow {}^4(F_{7/2}+S_{3/2})$ and $(^4G_{9/2}+{}^2K_{13/2}+{}^4G_{7/2})$ in the Nd^{3+} ion in the $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ single crystal were studied as a function of temperature in the range of 2–40 K and as a function of magnetic field in the range of 0–65 kOe at 2 K. It was found out that the selection rules for *f-f* electron transitions substantially changed in the magnetically ordered state of the crystal, and they strongly depended on the orientation of the Fe and Nd ions magnetic moments relative to the light polarization. The splitting of the excited states of the Nd^{3+} ion in the exchange field of the Fe sublattice were determined. It was revealed that the value of the exchange splitting (the exchange interaction) did not correlate with the theoretical Landé factor. The Landé factors of the excited states were experimentally found. The local reorientation field induced metamagnetic transitions were observed in the excited states. In some excited states the energetically favorable orientation of the Nd^{3+} ion magnetic moment is opposite to that in the ground state.

1. Introduction

All properties of crystals are totally defined by the electronic structure of ions in the chemical formula of the crystal. The electronically excited ion is similar to the admixture, and, consequently, it changes the local properties of the crystal. A number of phenomena connected with the optical excitation of atoms were observed, e. g., in some rare earth (RE) containing crystals of huntite structure [1–4].

The present work is mainly devoted to study of two phenomena: 1) the influence of the magnetic ordering and magnetic field on the *f-f* electron transitions properties (selection rules, in particular), 2) transformation of the local magnetic and symmetry properties in the excited 4*f* states. Actual problem of the quantum information processing (see e. g., Refs. [5–8]) made the investigations of the local properties of crystals in the optically excited states to be very important. RE containing crystals are widely used in these efforts. So, a change of the local properties near the optically excited atom was used for reading out the information in the quantum memory [6].

Ferroborates of the $RFe_3(BO_3)_4$ type, where R is the RE element, are of the growing interest due to the discovering of the multiferroic properties (i.e. correlation between magnetic, electric and elastic ordering) in many of them [9–13]. The multiferroic effects open the possibility of these materials usage in the new multifunctional devices with the mutual control of magnetic, electric and elastic characteristics. From the viewpoint of the fundamental magnetism, RE ferroborates are of interest due to a wide variety of magnetic properties and phase transitions, which result from the presence of two interacting magnetic subsystems: iron and RE ones [14].

The RE ferroborates has the trigonal huntite-like structure with the space group $R32$ (D_3^7) at high temperatures [15–17]. 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 are in the C_3 positions inside the octahedrons of oxygen ions. These octahedrons form helicoidal chains along the C_3 axis. With the lowering temperature, some ferroborates undergo a structural phase transition to the $P3_121$ (D_3^4) symmetry phase [17]. It results in the reducing of the RE ion position symmetry to the C_2 one and in appearance of two nonequivalent positions of Fe^{3+} ions

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(C_2 and C_1).

All RE ferroborates possess antiferromagnetic (AFM) ordering with the Neel temperature in the range of 30–40 K. The AFM ordering is conditioned by the exchange interaction within the iron subsystem [14]. The magnetic ordering of the RE subsystem is induced by the *f-d* exchange interaction with the Fe subsystem. The RE ions, in turn, due to their magnetic anisotropy, usually determine the direction of the Fe^{3+} magnetic moments in the magnetically ordered state. The RE ferroborates can be easy-axis or easy-plane antiferromagnets. In some of them the reorientation phase transitions occur with the temperature change [18,19].

The $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ crystal, similar to the pure Nd and Gd ferroborates, is multiferroic [20]. Magnetic properties of the crystal $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ were investigated in Ref. [21]. Below the $T_N = 32$ K the crystal has an easy-plane AFM structure and the spin-reorientation does not occur down to 2 K. At room temperature, the crystal has $R32$ symmetry and the lattice constants: $a = 9.557$ (7) Å and $c = 7.62$ (1) Å [21]. Any structural phase transitions were not found down to 2 K [21]. In the external magnetic field applied in the basal plane of the crystal a hysteresis in magnetization was found at 1–3.5 kOe. The hysteresis was observed at temperatures $T < 11$ K. Additionally the temperature dependence of the magnetic susceptibility had a singularity at $T = 11$ K (when $H < 1$ kOe). These features were ascribed to the appearance of the static magnetic domains at $T < 11$ K. Spectroscopic studies in the external magnetic field $H \perp C_3$ at 2 K [22] also revealed some features indicating the presence of the domains. The Judd-Ofelt spectroscopic parameters of the $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ single crystal were determined in Ref. [23]. Some optical and magneto-optical properties of the crystal were earlier studied in Refs. [22,24].

2. Experimental details

$Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ single crystals were grown from the melt solution on the base of $K_2Mo_3O_{10}$ according to Ref. [25]. 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 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.

Magnetic field was created by a superconducting solenoid with the Helmholtz type coils. The superconducting solenoid with the sample was placed in the liquid helium and all measurements in the magnetic field were fulfilled at $T = 2$ K. For the temperature measurements of absorption spectra a liquid-helium cooled cryostat was used. It had an internal volume filled by the gaseous helium where the sample was placed.

3. Results and discussion

Absorption spectra of the *f-f* transitions were studied in the temperature range of 2–40 K and in the magnetic field 0–65 kOe at the temperature 2 K. Absorption spectra of the studied *f-f* transitions are given in Fig. 1.

The irreducible representations of states (Table 1) were found from polarizations of the transitions and from the selection rules of Table 2. In crystals there is one more characteristic of states: the crystal quantum number μ. Additionally, in crystals with the axial symmetry, wave functions of states can be described by $|J, \pm M_J\rangle$ states of the free atom in a first approximation. In a trigonal crystal, for the states with the half integer total moment there are three possible values of the crystal quantum number [26]: $\mu = +1/2, -1/2, 3/2\ (\pm 3/2)$, and between values of μ and M_J there is the correspondence:

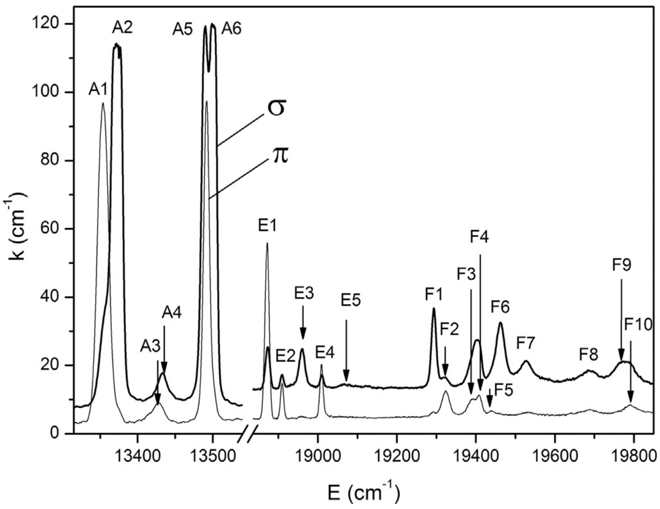

Fig. 1. Polarized absorption spectra of the $^4I_{9/2} \rightarrow {}^4S_{3/2} + {}^4F_{7/2}$ transitions (A band) and of the $^4I_{9/2} \rightarrow {}^4G_{9/2} + {}^4G_{7/2} + {}^2K_{13/2}$ transitions (E + F bands) at $T = 2$ K.

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

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

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. The values of M_J of the studied states were determined in Ref. [27]. In the $|J, \pm M_J\rangle$ functions approximation, the effective Landé factor of the Kramers doublet along the C_3 axis is [28]:

$$g_{CM} = 2gM_J. \qquad (2)$$

Here g is the Landé factor of the free atom. Values of g_{CM} of the studied states are presented in Table 1. In the same Table the theoretical values of g_C in the $NdFe_3(BO_3)_4$ crystal [29] are given. States with the same μ and different M_J (see Eq. (1)) can mix in crystal, and the resulting g_C can be both smaller and larger than g_{CM}.

In the exchange field of the iron sublattice, both the ground and the excited states of the Nd^{3+} ion can be split. So, between components of these splitting four transitions are possible. The main possible diagrams of the splitting and transitions are presented in Fig. 2. In Fig. 2A the splitting between a and b lines, $\Delta E_{12} = (E_a - E_b)$, is equal to the difference between the exchange splitting of the ground and excited states $\Delta E1$ and $\Delta E2$, respectively, while in Fig. 2B it is equal to their sum. In both cases, *a* and *b* transitions are supposed to occur without overturn of the magnetic moment. However, then the favorable moment orientation in the excited state of Fig. 2B diagram will be opposite to that in the ground state. The *c* and *d* transitions in both diagrams occur with the overturn of the magnetic moment, but this does not mean that they are always forbidden (see below).

When $\Delta E2 = 0$, the diagrams of Fig. 2A and B are equivalent and transitions *c* and *d* coincide with the transitions *a* and *b*, respectively, and they have no sense separately (Table 3). This takes place for the states of the $E_{3/2}$ symmetry with $g_\perp = 0$ (Table 1). Then at the lowest temperature the splitting ΔE_{12} will give the exchange splitting of the ground state. However, not all transitions demonstrate the temperature dependent splitting ΔE_{12} connected with the exchange splitting of the ground state. This means that the