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Local magnetic properties of multiferroic $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ in the excited states of Nd^{3+} ion

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ABSTRACT

Polarized absorption spectra of single-crystal $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ were studied in the region of the transition $^4I_{9/2} \rightarrow (^4G_{5/2} + {}^2G_{7/2})$ in Nd^{3+} ion as a function of temperature (2–34 K) and magnetic field (0–65 kOe). The spectra of natural circular dichroism were measured in the range of 5–40 K. It was found out that the local magnetic properties in the vicinity of the excited ion substantially depended on its state. In particular, a weak ferromagnetic moment appears in some excited states. It was found out that the selection rules for electron transitions in the magnetically ordered state substantially deviated from those in the paramagnetic state of the crystal. They are different for different transitions and they are very sensitive to the orientation of the sublattice magnetic moment relative to the light polarization. In the spectrum of the natural circular dichroism, the transition is revealed which is not observed in the absorption spectrum.

1. Introduction

An electronically excited atom is, actually, an impurity atom, and, consequently, the local properties of a crystal in the vicinity of the excited atom can change. Spectroscopic manifestations of such local alterations connected with electronic transitions were observed in $RbMnF_3$ and MnF_2, [1] in $FeBO_3$ [2] and in some rare earth (RE) containing crystals of huntite structure [3–6]. In Ref. [7] it was shown that during the electron transition the initial state of the ion and its interaction with the environment also changed and could have an influence upon the polarization of transitions. If there are many excited atoms, not only the local properties can change. So, in Ref. [8] a phase transition under the influence of the powerful laser pulse was described.

The present work is devoted to the study of two main phenomena: 1) the influence of the magnetic ordering on the *f-f* electron transitions properties (selection rules, in particular); 2) the change of the local magnetic and symmetry properties in the excited 4*f* states. The investigation of the local properties of crystals in the optically excited states has become important in recent years in connection with the problem of the quantum information processing (see e. g., Refs. [9–12]). Crystals containing RE ions are widely used in these efforts. For example, a change of the local crystal properties near the optically excited atom was used for reading out the information in the quantum memory [10].

The family of RE ferroborates with the common chemical formula $RFe_3(BO_3)_4$ has been widely investigated during the last years. The fundamental interest to these compounds is conditioned by the coexistence and mutual influence of two magnetic subsystems: iron and RE ones which results in a large variety of magnetic properties of the crystals. All RE ferroborates are ordered antiferromagnetically at temperatures below 30–40 K. Depending on the choice of a RE ion, they can have an easy-axis or easy-plane magnetic structure. The variation of temperature and external magnetic field leads to various kinds of phase transitions, including spin-reorientation and commensurate-to-incommensurate ones. Some crystals also exhibit structural phase transitions. Additionally, it has recently been found that many of RE ferroborates demonstrate a considerable coupling between the magnetic ordering and electric polarization [13–17]. This allows one to refer these compounds to the class of multiferroics. The investigation of multiferroic materials is of great interest now, both in the fundamental aspect (clarifying the mechanism of the magnetoelectric coupling) and in view of their potential technological applications.

The $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ crystal, the same as the pure Nd and Gd-ferroborates, reveals multiferroic properties [18]. It is an easy plane antiferromagnet from $T_N = 32$ K down to at least 2 K [19]. For

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future discussion it is important that at temperatures $T<11$ K a hysteresis in the magnetization of the crystal in the easy plane was found, indicating appearance of the static magnetic domains [19]. The crystal has trigonal symmetry with the space group $R32$ and the lattice constants are: $a=9.557(7)$ Å and $c=7.62(1)$ Å [19]. Trivalent RE ions occupy D_3 symmetry positions. They are located at the center of trigonal prisms made up of six crystallography equivalent oxygen ions. All Fe ions occupy C_2-symmetry positions. Structural phase transitions were not found down to 2 K [19]. The magnetic structure of the $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ crystal was not studied in detail. However, its magnetic properties [19] are close to those of the related crystal $NdFe_3(BO_3)_4$ [20–23]. Therefore, it is possible to suppose that the magnetic structure of these crystals is also similar. In particular, neutron diffraction measurements of $NdFe_3(^{11}BO_3)_4$ testified to magnetic spiral configurations with the magnetic moments oriented parallel to the hexagonal basal plane [24]. Later [25] it was shown that in the commensurate magnetic phase below $T_N\approx 30$ K all three magnetic Fe moments and the magnetic Nd moment were aligned ferromagnetically in the basal hexagonal plane but aligned antiferromagnetically between the adjacent planes. It was also shown that in the incommensurate spiral magnetic phase (below $T\approx 13.5$ K) the magnetic structure of $NdFe_3(^{11}BO_3)_4$ was transformed into a long-period antiferromagnetic helix with single chirality. In Ref. [26] it was shown that this phase transition behaved as the first order one. Nonresonant x-ray magnetic scattering showed that the correlation length (or size) of the magnetic domains was around 100 Å [27]. An element selective resonant magnetic x-ray scattering study has confirmed that the magnetic order of the Nd sublattice is induced by the Fe spin order [28]. When the magnetic field is applied parallel to the hexagonal basal plane, the helicoidal spin order is suppressed and a collinear ordering, where the moments are forced to align in the direction perpendicular to the applied magnetic field, is stabilized [28].

The absorption spectra of $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ single crystal had been earlier analyzed with the help of the Judd-Ofelt theory and spectroscopic characteristics of the crystal had been obtained [29]. The optical and magneto-optical properties of the $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ crystal in the near IR spectral region were studied in Ref. [30]. Optical spectra and crystal field parameters of the related crystal $NdFe_3(BO_3)_4$ were studied in Ref. [23].

2. Experimental details

$Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ single crystals were grown from the melt solution on the basis of $K_2Mo_3O_{10}$ as described in Ref. [31]. The sample used for optical absorption measurements was a 0.2 mm-thick plane-parallel polished plate oriented parallel to the crystallographic axis C_3. Absorption spectra were measured using a diffraction monochromator MDR-23 with the diffraction grating 1200 lines/mm and linear dispersion 1.3 nm/mm. The spectral resolution was about 1.5 cm^{-1} in the studied spectral region. The light intensity was measured by a photomultiplier with further computer registration. The absorption spectra were measured with the light propagating normal to the C_3 axis of the crystal, electric vector of light being parallel (the π-spectrum) or perpendicular (the σ-spectrum) to the C_3 axis. The light was polarized by the Glan prism.

Natural circular dichroism (NCD) spectra were studied on the sample of 0.215 mm-thick cut perpendicular to the C_3 axis of the crystal and with light propagated parallel to C_3 axis (α-polarization). The NCD spectra were measured by the method of light-polarization modulation using a piezoelectric modulator (details see in Ref. [32]). Spectral resolution at NCD measurements was about 2.3 cm^{-1}.

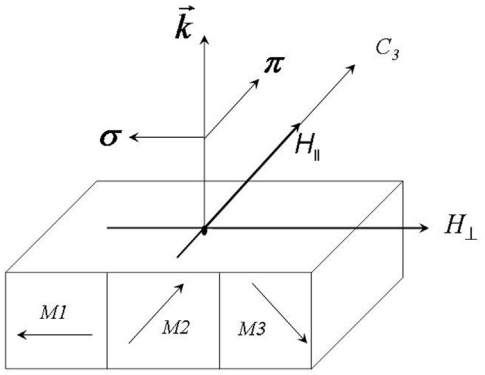

Fig. 1. Geometry of experiments.

Magnetic field was created by a superconducting solenoid with Helmholtz type coils. The magnetic field direction was parallel to the surface of the sample and perpendicular or parallel to the C_3 axis (Fig. 1). The superconducting solenoid with the sample was placed in liquid helium and all measurements in the magnetic field were fulfilled at $T=2$ K. For the temperature measurements of absorption and natural circular dichroism spectra a liquid-helium cooled cryostat was used. It had an internal volume filled by gaseous helium where the sample was placed. The temperature of the sample was regulated by a heating element.

3. Results and discussion

3.1. Identification of excited states

Polarized absorption spectra of the $Nd_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ single crystal in the region of the transition $^4I_{9/2}\rightarrow(^4G_{5/2}+^2G_{7/2})$ at $T=6$ K and at $T=33$ K (above T_N) are shown in Figs. 2a and 2b respectively. Symmetry of the ground state $Gr1$ of Nd^{3+} ion in the crystal was identified earlier [30] (see Table 1). The excited state of the 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 $^2G_{7/2}$: $3E_{1/2}+E_{3/2}$. The symmetries of the states in the D-manifold are found (Table 1) according to the linear polarizations of the absorption lines (Figs. 2a, 2b and Table 1), selection rules of Table 2 and symmetry of the ground state. The polarization of $D1(Gr2)$ and $D2(Gr2)$ transitions (Fig. 2b) from the first excited state $Gr2$ of the ground manifold gives symmetry of this state (Table 1). Shape of $D1(Gr2)$ and $D2(Gr2)$ lines is apparently due to the phonon side-bands caused by acoustic phonons.

In a trigonal crystal, for half integer total moment there are three possible values of the crystal quantum number [33]: $\mu=+1/2$, -1/2, 3/2 ($\pm 3/2$). States with $M_J=\mu\pm 3n$ (where $n=0, 1, 2, \ldots$) correspond to each μ in the trigonal symmetry [33]. As a result, the following set of states is obtained:

$$M_J=\pm 1/2, \pm 3/2, \pm 5/2, \pm 7/2, \pm 9/2;$$
$$\mu=\pm 1/2, (\pm 3/2), \mp 1/2, \pm 1/2, (\pm 3/2) \quad (1)$$

The set of the crystal field states for J-multiplets of Nd^{3+} ion is evidently found according to value of J. The states with $\mu=\pm 1/2$ correspond to the states $E_{1/2}$ and the states with $\mu=(\pm 3/2)$ correspond to the states $E_{3/2}$ in the D_3 group notations.

The electron states of a free atom in a homogeneous electric field ($C_{\infty v}$ symmetry) are split according to the absolute value of the magnetic quantum number M_J. The electron states of an atom in the trigonal crystal field are also split according to the absolute values of M_J, in the first approximation. Therefore, the atom wave functions can be described by $|J, \pm M_J\rangle$ states. In this