Violation of axial symmetry of optical properties in the trigonal crystal Nd:GdFe$_{2.1}$Ga$_{0.9}$(BO$_3$)$_4$

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ABSTRACT

Strong dependence of birefringence and absorption spectra of d–d, f–f and charge transfer transitions on the direction of light beam in the plane perpendicular to the threefold crystallographic axis has been found out in trigonal crystal Nd:GdFe$_{2.1}$Ga$_{0.9}$(BO$_3$)$_4$. X-ray measurements have shown that the crystal consists of inversion twins, whose formation is stimulated by the partial substitution of Fe by Ga. Observed violation of axial symmetry of the trigonal crystal optical properties is accounted for on the basis of assumption about stripe domain structure of the inversion twins.

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Crystals with the general formula RM$_3$(BO$_3$)$_4$ (R — Y or rare earth metal, M — Al, Ga, Cr, Fe, Sc) have huntite structure with the trigonal space group $R32$ (D_3^7) [1]. Crystals, containing Fe^{3+} ions, refer to multiferroics, which possess magnetic and electric order simultaneously (see, e.g., Refs. [2,3]). Due to this property they are widely studied in the recent years. Structure of NdFe$_3$(BO$_3$)$_4$ crystal has been studied in Refs. [4,5], and that of GdFe$_3$(BO$_3$)$_4$ in Ref. [6]. At room temperature, all Fe ions occupy C_2-symmetry positions and rare earth ions are in D_3-symmetry positions [6]. Such positions are the character of unperturbed huntite structure. However, the local symmetry of R and M atoms has a tendency to change under the influence of different effects. So, the local symmetry of Nd^{3+} ion in NdAl$_3$(BO$_3$)$_4$ crystal changes from D_3 to C_2 depending on the technology of the crystal growing [7]. The GdFe$_3$(BO$_3$)$_4$ crystal exhibits a structural phase transition at 156 K [8]. Nd:GdFe$_{2.1}$Ga$_{0.9}$(BO$_3$)$_4$ crystal [9], studied here, has revealed a peculiar structure transformation, which has resulted in observation of strong violation of axial symmetry of a trigonal crystal optical properties.

Crystals of Nd:GdFe$_{2.1}$Ga$_{0.9}$(BO$_3$)$_4$ (Nd$_2$O$_3$/Gd$_2$O$_3$ = 0.9 mass % in the melt), were grown by a group method [10], using a Bi$_2$Mo$_3$O$_{12}$-based flux, as described in Ref. [11]. We have under-

taken the X-ray study of the crystal with the KM-4 single crystal diffractometer (MoK$_\alpha$-radiation) at room temperature. Intensities of 1027 X-ray reflections were measured from the spherical sample of 0.4 mm in diameter (589 reflections were unique). A structure model was solved and refined in anisotropic approximation using SHELX-97 program [12]. It has been shown, that the structure of Nd:GdFe$_{2.1}$Ga$_{0.9}$(BO$_3$)$_4$ is identical to that of GdFe$_3$(BO$_3$)$_4$. So, the crystal belongs to space group $R32$ and has the sell parameters $a = 9.499(1)$, $c = 7.521(1)$ Å, a little smaller than those of GdFe$_3$(BO$_3$)$_4$. It was found out, that the crystal consists of inversion twins in proportion of 59/41.

The samples prepared for optical measurements were 0.17–0.3 mm-thick plane-parallel polished plates: one sample, oriented perpendicular to the threefold crystallographic axis (C_3), and two samples, cut in mutually perpendicular planes {100} and {110}, which are parallel to C_3 axis (one of three equivalent {110} planes is perpendicular to {100} plane). Polarized absorption spectra have been studied at temperatures: 85–293 K. Three light polarizations were used: α — light wave vector $\vec{k}$ is parallel to C_3 axis of the crystal and electric vector $\vec{E}$ of light is perpendicular to C_3 axis; π — $\vec{k} \perp C_3$, $\vec{E} \parallel C_3$; σ — $\vec{k} \perp C_3$, $\vec{E} \perp C_3$. Fig. 1 presents α, π and σ-polarized absorption spectra of Nd:GdFe$_{2.1}$Ga$_{0.9}$(BO$_3$)$_4$ crystal. The broad absorption bands correspond to d–d transitions $^6A_1(^6S) \to {}^4T_1(^4G)$ and $\to {}^4T_2(^4G)$ of Fe^{3+} ion (in notations of cubic crystal field), and narrow lines belong to f–f transitions in Nd^{3+} ion.

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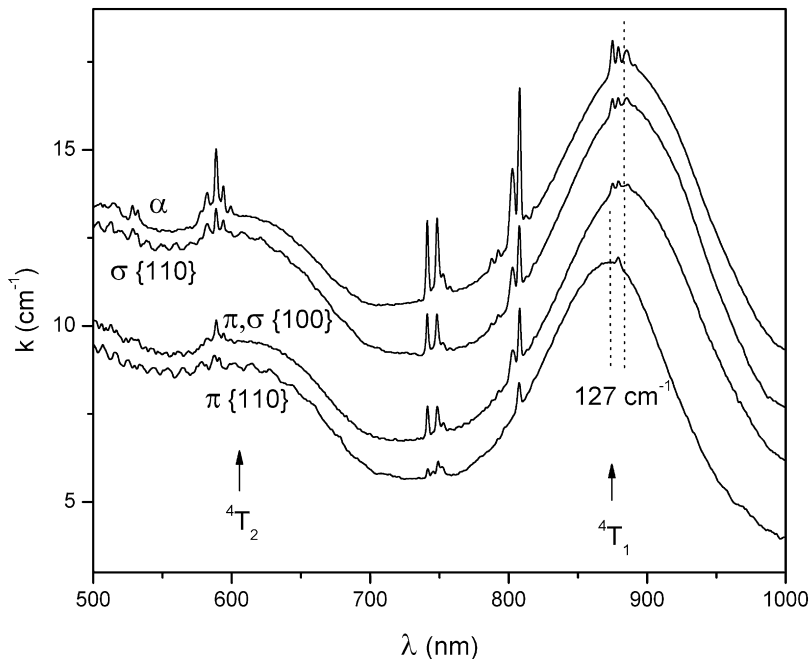*E-mail address:* malakha@iph.krasn.ru (A.V. Malakhovskii).

Fig. 1. Polarized absorption spectra of Nd:GdFe$_{2.1}$Ga$_{0.9}$(BO$_3$)$_4$ in the region of d–d transitions $^6A_1(^6S) \rightarrow {^4T_1}(^4G)$, $^4T_2(^4G)$ of Fe^{3+} ion at temperature $T = 85$ K.
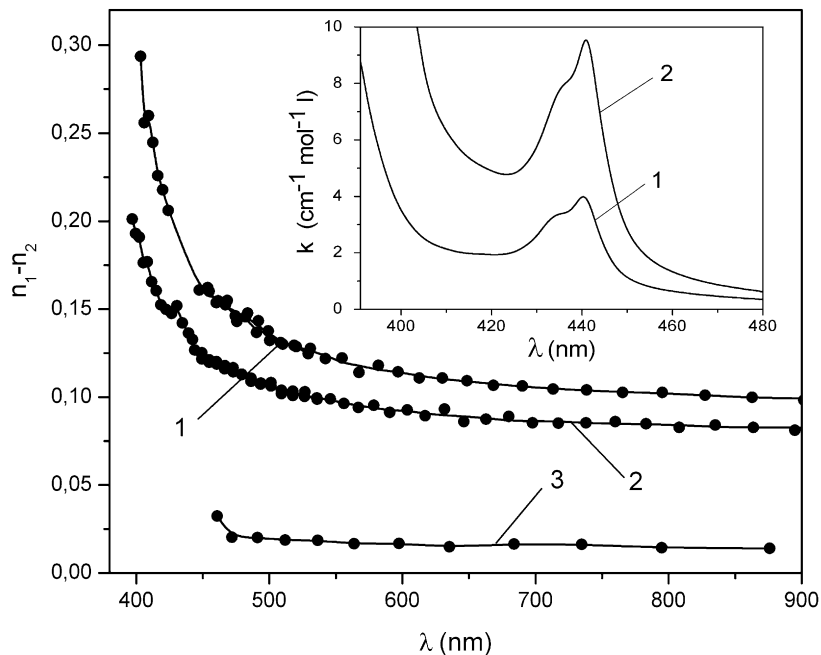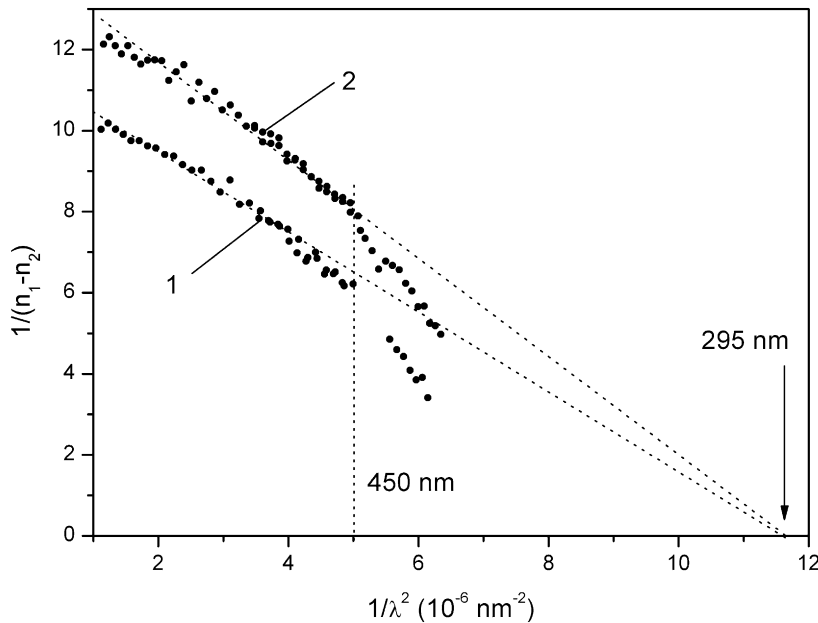

Fig. 2. Birefringence of GdFe$_3$(BO$_3$)$_4$ in planes {110} and {100} (curve 1), and birefringence of Nd:GdFe$_{2.1}$Ga$_{0.9}$(BO$_3$)$_4$ in plane {110} (curve 2) and in plane {100} (curve 3) at room temperature. Inset: α-polarized absorption spectra of Nd:GdFe$_{2.1}$Ga$_{0.9}$(BO$_3$)$_4$ (1) and GdFe$_3$(BO$_3$)$_4$ (2) in the region of d–d transition $^6A_1(^6S) \rightarrow {^4A_1}{^4E}(^4G)$ of Fe^{3+} ion at room temperature.

Trigonal crystals have one optical axis, coincided with C_3 crystal axis. This means, that linear dichroism and birefringence should not depend on the direction of light propagation in the plane perpendicular to C_3 axis, i.e., the dichroism and birefringence should exist and should be identical in samples {100} and {110}. However, we have found out that in the sample {100} π and σ spectra practically coincide, while in the sample {110} pronounced dichroism is observed (Fig. 1). Besides that, α-spectrum of f–f transitions visibly differs from their σ-spectrum (Fig. 1). At the same time, α-spectrum itself remains to be independent of polarization, i.e. optical axial symmetry in this geometry of the experiment preserves. The same situation takes place for d–d transition

$^6A_1 \rightarrow {^4A_1}{^4E}$ and for the strong absorption band edge up to room temperature.

It is worth comparing the above results with optical properties of the similar crystal, GdFe(BO$_3$)$_4$ (also grown by us), where Fe^{3+} ions are not substituted by Ga^{3+} ions. Spectra of the same d–d transitions, measured in GdFe(BO$_3$)$_4$, appeared to have identical dichroism in {100} and {110} plains. In Fig. 2 (inset) the α-spectra of Nd:GdFe$_{2.1}$Ga$_{0.9}$(BO$_3$)$_4$ and GdFe(BO$_3$)$_4$ crystals in the region of d–d transition $^6A_1 \rightarrow {^4A_1}{^4E}$ are compared (α-spectrum of GdFe$_3$(BO$_3$)$_4$ was first obtained in Ref. [13]). The absorption is given in units of molar extinction relative to molar concentration of iron. From Fig. 2 (inset) a conclusion follows, which is of impor-

Fig. 3. Reciprocal birefringence as a function of $1/\lambda^2$ for $GdFe_3(BO_3)_4$ in planes {110} and {100} (curve 1), and for $Nd:GdFe_{2.1}Ga_{0.9}(BO_3)_4$ in plane {110} (curve 2) at room temperature.

tance for the subsequent discussion. Strong absorption band edge in $Nd:GdFe_{2.1}Ga_{0.9}(BO_3)_4$, where part of Fe atoms are substituted by Ga atoms, is substantially shifted (on 890 cm^{-1}) to higher energies as compared with $GdFe(BO_3)_4$. This means that observed strong absorption is due to charge transfer transitions between Fe^{3+} ions.

We saw above, that there is no dichroism in plane {100} of $Nd:GdFe_{2.1}Ga_{0.9}(BO_3)_4$ crystal. However, linear birefringence in the same plane exists. The birefringence of $GdFe_{2.1}Ga_{0.9}(BO_3)_4$ and $GdFe_3(BO_3)_4$ crystals both in {100} and {110} planes has been measured in the following way. We put the sample between two polarizers with the same plane of polarization so that C_3 axis of the sample was under the angle of 45° to the plane of polarization. In this case, due to interference between usual and unusual beams after analyzer, the light flow passed through the analyzer will oscillate as a function of the light wave length. It is possible to show that the birefringence can be found from the formula: $\Delta n \approx \lambda^2/[d(\lambda_2 - \lambda_1)]$, where $(\lambda_2 - \lambda_1)$ is the distance between two maxima (or minima) of the adjacent oscillations, λ is the average value of wave lengths λ_1 and λ_2, d is the sample width. Results of measurements and calculations are in Fig. 2. If the birefringence is due to difference of intensity of some strong transition in two polarizations, then, far from this transition, the birefringence as a function of wave length λ will be described by the formula:

$$\frac{1}{\Delta n} = A\left(\frac{1}{\lambda_0^2} - \frac{1}{\lambda^2}\right). \tag{1}$$

It is linear function of $1/\lambda^2$. Extrapolation of the linear part of the experimental results (Fig. 3) gives position of the effective transition (λ_0), which reflects the joint influence of all transitions upon the birefringence. Experimental function of Fig. 3 deviates from the linear one near the edge of the charge transfer transitions. This means that all charge transfer transitions are responsible for the birefringence. From Fig. 2 we see, that the birefringence of $GdFe_3(BO_3)_4$ in planes {100} and {110} are equal. The birefringence of $Nd:GdFe_{2.1}Ga_{0.9}(BO_3)_4$ in plane {110} is of the same order of magnitude as that of $GdFe_3(BO_3)_4$, but it is a little less, according to less concentration of Fe^{3+} ions. Birefringence of $Nd:GdFe_{2.1}Ga_{0.9}(BO_3)_4$ in plane {100} is of ~5 times less than it is in plane {110}.

According to Onsager principle [14]:

$$\varepsilon_{ij}(\vec{H}_0, \vec{k}, \vec{E}_0) = \varepsilon_{ji}(-\vec{H}_0, -\vec{k}, \vec{E}_0). \tag{2}$$

Here ε_{ij} is dielectric permittivity tensor, $\vec{H}_0$, $\vec{E}_0$, $\vec{k}$ are external magnetic and electric fields and light wave vector, respectively. Dependence on the light wave vector indicates an influence of the space dispersion. From (2) it follows that tensor ε_{ij} can be decomposed to symmetric and anti-symmetric parts, when space dispersion exists: $\varepsilon_{ij} = \varepsilon_{ij}^s + ig_{ij}$. Anti-symmetric part of the tensor (g_{ij}) is odd function of $\vec{k}$ (in the first approximation $\sim k$), and symmetric part of the tensor (ε_{ij}^s) is even function of $\vec{k}$ (in the first approximation $\Delta\varepsilon_{ij}^s \sim k^2$). According to Kurie principle [15], a crystal under external influence possesses only those elements of symmetry, which are common for the crystal and for the influence. In particular, vector $\vec{k}$ changes sign with the inversion of space. Therefore, in centrosymmetric crystals $g_{ij}(\vec{k}) = 0$, i.e., natural circular dichroism (NCD), connected with the tensor g_{ij}, does not exist. Discussed crystals have no center of inversion. Therefore, they can possess NCD, but of opposite sign in different inversion twins. We have measured spectra of NCD in crystals $Nd:GdFe_{2.1}Ga_{0.9}(BO_3)_4$ and $GdFe_3(BO_3)_4$ in α-polarization. Indeed, $GdFe_3(BO_3)_4$ reveals noticeable NCD ($\Delta k/k \sim 10^{-2}$), while NCD in $Nd:GdFe_{2.1}Ga_{0.9}(BO_3)_4$, consisting of inversion twins, is close to zero. In this experiment $\vec{k}$ is parallel to C_3 axis, and if z-axis is also parallel to C_3 axis, dielectric permittivity tensor has the form:

$$\hat{\varepsilon} = \begin{vmatrix} \varepsilon_{xx} & ig(k) & 0 \\ -ig(k) & \varepsilon_{yy} & 0 \\ 0 & 0 & \varepsilon_{zz} \end{vmatrix}. \tag{3}$$

Here $\varepsilon_{xx} = \varepsilon_{yy} \neq \varepsilon_{zz}$ and the difference $\varepsilon_{zz} - \varepsilon_{xx}$ will depend on k^2. However, this difference cannot be observed in principle, since for it observation the light beam should be directed perpendicular to $C_3(z)$ axis and the tensor $\hat{\varepsilon}$ will change, because its form is connected with the direction of $\vec{k}$, owing to the Curie principle. The tensor $\hat{\varepsilon}$ will lose axial symmetry relative to C_3 axis and will depend on the direction of $\vec{k}$ in the plane perpendicular to C_3 axis — the very phenomenon, observed in $Nd:GdFe_{2.1}Ga_{0.9}(BO_3)_4$. However, this explanation has two contradictions with the experiment. (1) Violation of the axial symmetry of the optical properties
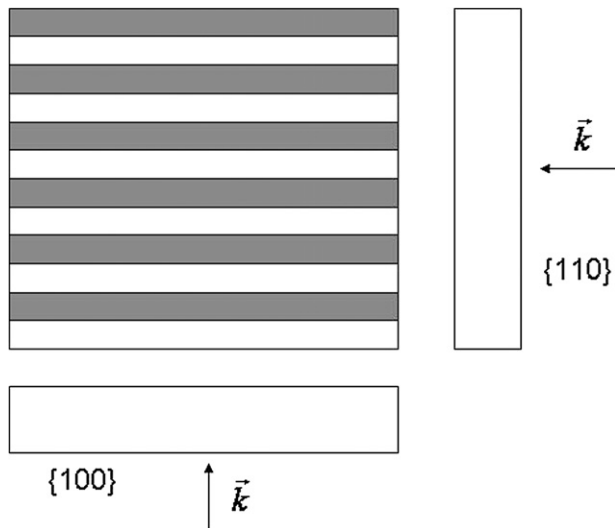
Fig. 4. Model of the inversion twins domain structure.

is not observed in $GdFe_3(BO_3)_4$ in spite of existence of the space dispersion effect manifested in NCD. (2) Linear dichroism and birefringence, connected with the space dispersion, are small effects of the second order of magnitude as compared with NCD, but we observe very large effects, especially as concerns the linear birefringence.

The charge transfer transitions, responsible for the linear birefringence, are connected not only with the change of state of an electron, but also with its space motion. Therefore, according to impulse conservation law, the electron transfer must occur mainly in the direction of light propagation ($\vec{k}$-direction). The only substantial difference between $Nd:GdFe_{2.1}Ga_{0.9}(BO_3)_4$ and $GdFe_3(BO_3)_4$ crystals is, that the former consists of the inversion twins. Therefore charge transfer can occur or inside one twin or between different twins. These situations are not equivalent. Probability of the charge transfer transitions between Fe^{3+} ions is proportional to square of the overlap integral of Fe^{3+} wave functions, modified by hybridization with wave functions of the environment. In non-centrosymmetric complex these wave functions are asymmetric and the asymmetry is opposite in the inversion twins. Therefore, the overlap integral for Fe^{3+} ions, which belong to one twin and to different twins, will be different. In this case domain structure in the plane perpendicular to C_3 axis becomes to be important. Observed phenomenon can be accounted for by the stripe domain structure, shown in Fig. 4. The sample {100} is cut along the stripes, and the sample {110} is cut across the stripes. Then in the sample {110} the charge transfer takes place inside the stripe domain of one type, while in {100} sample part of such transitions happen between inversion twins. Relative amount of such transitions depends on the width of the domains. Taking into account strong difference of the birefringence in two light wave directions, we can suppose, that the width of the domains is of the order of the crystal elementary sell size.

The question remains: why f–f and d–d transitions reveal pronounced dependence on the light beam direction, although these transitions take place certainly in one domain? Electron transitions occur under the influence of not only the external electric field, but also under the influence of the internal field, created by polarization of surrounding atoms. It is possible to show [16], that in isotropic case the absorption coefficient for weak transitions (such as f–f and d–d ones) is described by the formula:

$k = 2\pi L(\varepsilon')\varepsilon''/(\lambda n' \ln 10)$. Here: ε'' is imaginary part of the dielectric permittivity, responsible for f–f or d–d absorption; ε' and n' are real parts of the dielectric permittivity and refractive index, which are mainly due to strong transitions outside the region of f–f or d–d absorption; $L(\varepsilon')$ is the Lorentz correction. When ε' and n' are strongly anisotropic, the absorption coefficient (k) becomes anisotropic even with the isotropic ε''.

It is impossible to assume something about domain structure in C_3 direction. However, any domain structure will not destroy axial symmetry of optical properties, when light propagates in C_3 direction. Indeed, we saw above, that tensor $\hat{\varepsilon}$ remains to be axially symmetric in this case, and the same was confirmed experimentally (α-spectrum does not depend on polarization). At the same time, a domain structure can influence the intensity of charge transfer transitions and, as a consequence, can influence the intensity of f–f and d–d transitions as well. In particular, α-spectrum differs both from σ- and π-spectra (see Fig. 1).

Thus, partial substitution of Fe by Ga stimulates formation of inversion twins, but every twin and the crystal as a whole remain to be trigonal. Observed unusual optical properties from phenomenological viewpoint are the consequence of space dispersion, but the large value of the effects is due to domain structure of the inversion twins. Additional optical anisotropy, being connected with the light wave vector direction, is induced by the light itself and, consequently, it gives potential possibility of light to light influence.

Acknowledgements

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