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Features of the intensity behavior of Kramers doublet components in $\text{NdFe}_3(\text{BO}_3)_4$ in the transverse Zeeman geometry

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Nontrivial magnetic field dependence of the polarization of the Kramers doublet absorption lines ($15\,971\text{--}15\,978\text{ cm}^{-1}$) was observed in the range of the ${}^4I_{9/2} \rightarrow {}^2H_{11/2}$ optical transition of Nd^{3+} ion in an easy-plane antiferromagnet $\text{NdFe}_3(\text{BO}_3)_4$ in the transversal Zeeman effect geometry. Values of the transversal g factor and the effective exchange field with Fe^{3+} magnetic subsystem were determined for the excited state of Nd^{3+} from the field dependence of the doublet splitting. A semi-empirical equation was proposed for the description of the field dependence of the intensities of the polarized components of the absorption lines corresponding to the Kramers doublet $15\,971\text{--}15\,978\text{ cm}^{-1}$. Besides the scaling factors, the equation contains only the independently determined magnitudes of exchange fields for the ground and excited states as parameters.

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1. Introduction

Research on rare-earth ferrobates with the general formula $\text{RFe}_3(\text{BO}_3)_4$ (R is a rare-earth element) is of special interest due to the great variety of magnetic properties of these crystals, originating from the presence of two types of magnetic ions.¹ All members of this family have the crystal structure of huntite and are antiferromagnets with ordering temperatures of 30–40 K. Their magnetic ordering is caused by the exchange interaction in the subsystem of iron ions. As a result of its $f\text{--}d$ interaction with the latter, the rare-earth subsystem also acquires a nonzero magnetic moment. The ${}^6S_{5/2}$ ground state of Fe^{3+} ions suggests, in the first approximation, the absence of single-ion anisotropy. In the iron subsystem, the magnetic anisotropy is mainly formed due to the dipole-dipole interactions and for the rhombohedral structure of ferrobates has an easy-plane character. The exchange interaction with rare-earth ions, which, as a rule, possess appreciable crystallographic anisotropy, can substantially change the situation. Among ferrobates there are both easy-axis and easy-plane antiferromagnets. Furthermore, there are also some members of the ferrobate family the magnetic anisotropy of which changes its type with decreasing temperature. Low symmetry of the crystals (in particular, the absence of a center of symmetry) allows the Dzyaloshinsky-Moriya interaction, the consequence of which, apparently, is the observation of incommensurate spiral magnetic structures in some easy-plane ferrobates. A number of ferrobates exhibit a structural phase transition with decreasing symmetry from the high-temperature $R32$ phase to the low-temperature $P3_121$ phase.² The growing interest in studies of rare-earth ferrobates is also associated with the discovery of interplay between magnetic and electrical ordering³ in these materials, which suggests that these crystals belong to the class of multiferroics.

For single crystal $\text{NdFe}_3(\text{BO}_3)_4$, the presence of multiferroelectric properties, in particular, large electrical polarization controlled by a magnetic field, has been established.⁴ The structure of neodymium ferrobate is described by the space symmetry group $R32$,⁵ which is retained, at least, down to a temperature of 2 K.^{6,7} The rare-earth ion occupies a position with a local symmetry D_3 . Below the temperature T_N , which, according to various data,^{8–11} is in the range 30–33 K, $\text{NdFe}_3(\text{BO}_3)_4$ is antiferromagnetically ordered with the magnetic moments of Fe^{3+} and Nd^{3+} oriented in the basal plane of the crystal.^{8,9} Thus, there are three types of equivalent magnetic domains. Below the temperature $T_{IC} = 13.5$ K, the commensurate magnetic structure is transformed into a long-period antiferromagnetic spiral propagating along the C_3 axis.^{12,13} In a magnetic field applied in the basal plane of the crystal, the spiral structure is destroyed, and the crystal undergoes a transition into the spin-flop phase with the antiferromagnetism vector directed in the basal plane perpendicular to the external field.¹³ This spin-reorientation transition proceeds as a first-order phase transition.^{10,14,15}

The states of the Nd^{3+} ion in the crystal field of D_3 symmetry are Kramers doublets, which subsequently (upon magnetic ordering) split as a result of the exchange interaction with the subsystem of iron ions. From the optical absorption spectra, the exchange splitting of the ground doublet Nd^{3+} has been determined to be 8.8 cm^{-1} at 4.2 K.^{11,16} The optical absorption spectra of Nd^{3+} in $\text{NdFe}_3(\text{BO}_3)_4$ have been thoroughly studied in a broad spectral range ($1500\text{--}25\,000\text{ cm}^{-1}$) at temperatures from 4.2 to 300 K,¹⁶ and the crystal field parameters and the values of g factors for the Nd^{3+} states have been calculated. Note that studies of the optical absorption spectra of neodymium ferrobate in magnetic fields have not been carried out to date.

Earlier, when studying the spectra of $\text{Nd}_{0.5}\text{Gd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$ ferrobate,^{17,18} we have found that in the magnetically ordered state, the direction of the magnetic moment of the rare-earth ion has a large effect on the intensities of the optical f - f transitions between the components of the exchange-split Kramers doublets. This is manifested most clearly in sharp changes in the intensities of some absorption lines during the spin-reorientation phase transition in a magnetic field $\mathbf{H} \perp C_3$.

In this paper we report an unusual, in our opinion, field dependence of the polarization of the $\text{NdFe}_3(\text{BO}_3)_4$ absorption lines associated with transitions to the exchange-split components of the Kramers doublet. The effect was observed in the so-called transverse Zeeman geometry.

Studies of the transverse Zeeman effect in non-centrosymmetric uniaxial crystals have only been reported in a small number of experimental and theoretical studies.^{19–24} In particular, we refer to the experimental geometry, in which the absorption spectra are recorded for the light propagating along the optical axis of the crystal, and the external magnetic field is applied perpendicular to it. Two polarizations of light are considered: parallel and perpendicular to the direction of the field. When the crystal rotates around the optical axis, in some cases, an appreciable modulation of the intensities of the Zeeman components of the absorption lines can be observed. The symmetry justification for these effects has mainly been developed in Refs. 22–24. The effect depends on a number of components that affect the symmetry of the electronic wave functions of the ground and excited states of the ion, the optical transitions between which are observed in the experiment. In our case (trigonal D_3 symmetry of the crystal field in the position of the Kramers Nd^{3+} ion), such an angular dependence is absent. More precisely, even if it appears, it remains very weak.²² Note that the phenomena observed in the present paper do not depend on the orientation of the external field in the basal plane of the $\text{NdFe}_3(\text{BO}_3)_4$ crystal under study within the experimental error.

2. Experimental procedure

Single crystals of $\text{NdFe}_3(\text{BO}_3)_4$ were grown from the melt solution according to the method described in Ref. 25. Samples shaped as plates with parallel faces, 0.2–0.7 mm thick, oriented perpendicularly or parallel to the third-order crystallographic axis were used for measuring the absorption spectra.

To study the absorption spectra, a spectrograph DFS-13 was used. The registration of light was carried out using a linear array of photodiodes, which was a part of the multi-channel optical analyzer. The spectral resolution in the investigated region was about 0.5 cm^{-1} . Absorption spectra were recorded for the light propagating perpendicular to the C_3 axis and the direction of the E vector of the light wave parallel (π -spectra) or perpendicular to the C_3 axis (σ -spectra), as well as for the light propagating along the C_3 axis (α -spectra).

The magnetic field was created by superconducting Helmholtz coils, which, together with the sample, was immersed in a pumped helium cryostat. Measurements in a magnetic field were carried out at a temperature of 2 K.

3. Results and discussion

3.1. Temperature dependence and structure of absorption spectra

The main multiplet $^4I_{9/2}$ of the Nd^{3+} ion is split in the trigonal field into 5 Kramers doublets, which transform in the two-valued irreducible representations $3\Gamma_4 + 2\Gamma_{5,6}$ of the local symmetry group D_3 . The sublevel Γ_4 is the ground one. According to Ref. 16, the lowest excited sublevel of $\Gamma_{5,6}$ symmetry has an energy of $\sim 65 \text{ cm}^{-1}$, which at sufficiently low temperatures $T \leq T_N$ excludes the possibility of observing transitions from this level. The region of the optical absorption spectrum that is discussed in this paper refers to electronic transitions from the ground state to $^4\Gamma_4 + ^2\Gamma_{5,6}$ sublevels of $^2H_{11/2}$ multiplet. The energies of these sublevels lie in the range $15\,800$ – $16\,000 \text{ cm}^{-1}$.¹⁶ All transitions have an electric dipole character (which is confirmed by the coincidence of the α and σ spectra) and should be observed for $\Gamma_4 \rightarrow \Gamma_4$ transitions for both σ - and π -polarizations, and for $\Gamma_4 \rightarrow \Gamma_{5,6}$ transitions only in σ polarization. The absorption bands for the transitions in this group are rather weak, which indicates a high degree of their forbiddenness. The region of the spectrum shown in Fig. 1, contains absorption lines corresponding to the transitions from the main to the three highest frequency doublets of $^2H_{11/2}$ multiplet under consideration (full information on the field and temperature features of the spectra of this multiplet will be given in the subsequent publication). In Fig. 1 they are numbered in order of increasing energy. According to the classification of Ref. 16 and in full accordance with it, the polarization rules for observation of the transitions are satisfied. The symmetry of the sublevel “1” corresponds to the representation $\Gamma_{5,6}$, and the sublevels “2” and “3” correspond to Γ_4 (Fig. 1).

When the crystal undergoes a transition to the magnetically ordered state ($T_N \approx 30 \text{ K}$) some of the doublets undergo splitting (removal of the Kramers degeneracy) due to the exchange interaction with the magnetic subsystem of Fe^{3+} ions (see the diagram in the inset of Fig. 1). In the case of lines 1 and 3, there is no appreciable splitting of the excited state, and therefore only transitions from the upper component of the ground doublet appear below T_N , and their intensity decreases with decreasing temperature. At the magnetic ordering temperature, line 2 splits into three components. In accordance with Ref. 16 and our data, the exchange splitting of the ground state is 8.8 cm^{-1} , and for the state “2” it is 7.5 cm^{-1} . Since these values are similar, the transitions $2b'$ and $2a$ have close frequencies, and therefore cannot be resolved in the absorption spectrum (see the scheme).

For π -polarization below T_N , transitions $2a'$ and $2b$ are not observed. This is due to the particularity of the splitting in the exchange field of the ground and excited doublets. In the easy-plane antiferromagnetic state of $\text{NdFe}_3(\text{BO}_3)_4$, the effective exchange field is oriented parallel to the basal plane. We choose this direction as the quantization axis. The polarization rules common for the Zeeman effect are: a transition with no change in the spin projection is polarized along the direction of the magnetic field, and that with a change is polarized perpendicular to it. Accordingly, a single line corresponding to component $2a$ (and frequency $2b'$ which coincides with it) can be observed in π -polarization only in the case when the exchange interaction with the iron

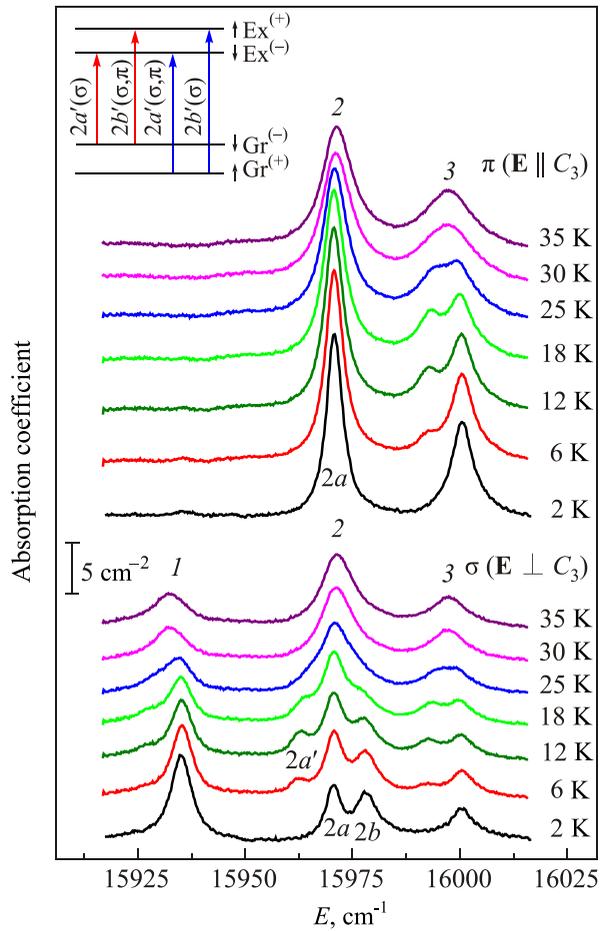


Fig. 1. Absorption spectra of $\text{NdFe}_3(\text{BO}_3)_4$ in the region of ${}^4I_{9/2} \rightarrow {}^2H_{11/2}$ optical transition of Nd^{3+} ion at various temperatures. The inset shows a scheme of transitions between the splitting components of Kramer's doublet "2."

subsystem in the ground and excited states has different signs, which is marked on the inset in Fig. 1 by the orientation of the arrows labeling the components of the doublets. This kind of "inversion" of the exchange splitting of excited doublets with respect to the ground doublet has already been observed for other Nd^{3+} multiplets in ferrobates.^{17,18} The same scheme corresponds to the field dependence of the intensities of the polarized components of the absorption lines of the Kramer's doublet $2a-2b$ in σ -polarization (see Sec. 3.4).

It should be noted that at a temperature of 2 K, at which measurements were carried out in a magnetic field, only transitions from the lower component of the ground Kramer's doublet were present in the spectrum.

3.2. Absorption spectra in an external magnetic field

The transverse Zeeman geometry (for schematics, see the insets in Fig. 2) was used to study the spectra in a magnetic field. The external field was applied perpendicular to the third-order axis of the crystal. The light propagated along the C_3 axis and was recorded in two polarizations in the basal plane: $\mathbf{E} \parallel \mathbf{H}$ and $\mathbf{E} \perp \mathbf{H}$. In the absence of a magnetic field, the spectra for the two directions of \mathbf{E} in the basal plane coincided (Fig. 2).

Figure 2 shows a series of spectra in two polarizations as a function of the magnetic field. It can be seen that the

doublets corresponding to lines 1 and 3 show no noticeable splitting in the fields up to 60 kOe. This is due to the fact that the symmetry of state "1" $\Gamma_{5,6}$ forbids the linear transverse Zeeman effect ($g_{\perp} \equiv 0$). On the other hand, for state "3," the transverse component of the g -factor is small in absolute value ($g_{\perp} = 1.083$), according to calculations.¹⁶ Experimentally, neither splitting nor even broadening of the line 3 has been observed in an external field.

Regarding doublet "2," its splitting changes with increasing the external field in a nonlinear manner (Fig. 3). According to Ref. 16, this state corresponds to a g -factor with a noticeable transverse component $g_{\perp} = 5.259$. The nonlinear nature of the $\Delta E(H)$ dependence of the doublet "2" is due to the fact that the Nd^{3+} ion experiences the superposition of two fields: the exchange field of the iron subsystem and the external magnetic field. Despite the low symmetry of the crystal and the presence of at least 6 sublattices of Fe^{3+} magnetic moments in the antiferromagnetic phase, there is no experimental observation of their mutual skew in the absence of a magnetic field. The long-period helical structure arising at temperatures below $T_{\text{IC}} = 13.5$ K (Ref. 12) should not have a noticeable effect on local interactions between the nearest exchange-coupled neighboring ions. The magnetic moments of Nd^{3+} in the ground state are oriented, according to Ref. 12, collinear with the magnetic moments of Fe^{3+} . Accordingly, it can be assumed that the exchange field \mathbf{H}_{Fe} on rare-earth ions is directed collinearly to the antiferromagnetism vector \mathbf{L}_{Fe} of the iron subsystem both in the ground state and excited state. For $H_{\text{sf}} \approx 9$ kOe, the crystal undergoes the transition to the spin-flop phase, while \mathbf{L}_{Fe} is oriented in the basal plane perpendicular to the external field;¹³ from this moment the exchange field acting on the Nd^{3+} ion, $\mathbf{H}_{\text{Fe}} \perp \mathbf{H}$. Because of the large magnitude of Fe-Fe exchange interaction ($H_E \sim 700$ kOe),^{26,27} in the first approximation, the slope of the magnetic moments of iron in the whole investigated range of fields can be neglected. The splitting of the doublet "2," thus, is described by the equation

$$\Delta E = \mu_B g_{\perp} \sqrt{H_{\text{Fe}}^2 + H^2}. \quad (1)$$

Figure 3 presents an approximation of the experimental data $\Delta E(H)$ by the dependence (1). Strictly speaking, it is applicable for $H=0$ and $H > H_{\text{sf}}$. For $H < H_{\text{sf}}$, it is necessary to take into account the local angles between the moments of Fe^{3+} , Nd^{3+} and the external field in the helicoid, but the smallness of H_{sf} in comparison with H_{Fe} in this range of fields does not lead to a significant deviation of the experimental $\Delta E(H)$ from Eq. (1). From the best fit of the parameters, we determined the g -factor and the magnitude of the exchange field for excited state "2." According to our measurements, $g_{\perp} = 5.65$ (which is quite close to the value of 5.259 calculated in Ref. 16) and $H_{\text{Fe}} = 28$ kOe.

3.3. Magnetic field dependences of the intensities of polarized components

As can be seen in Fig. 2, the intensities of lines 1 and 3 vary very little with increasing the external magnetic field. At the same time, the intensities of the exchange-split components of the doublet "2" exhibit significant changes. As

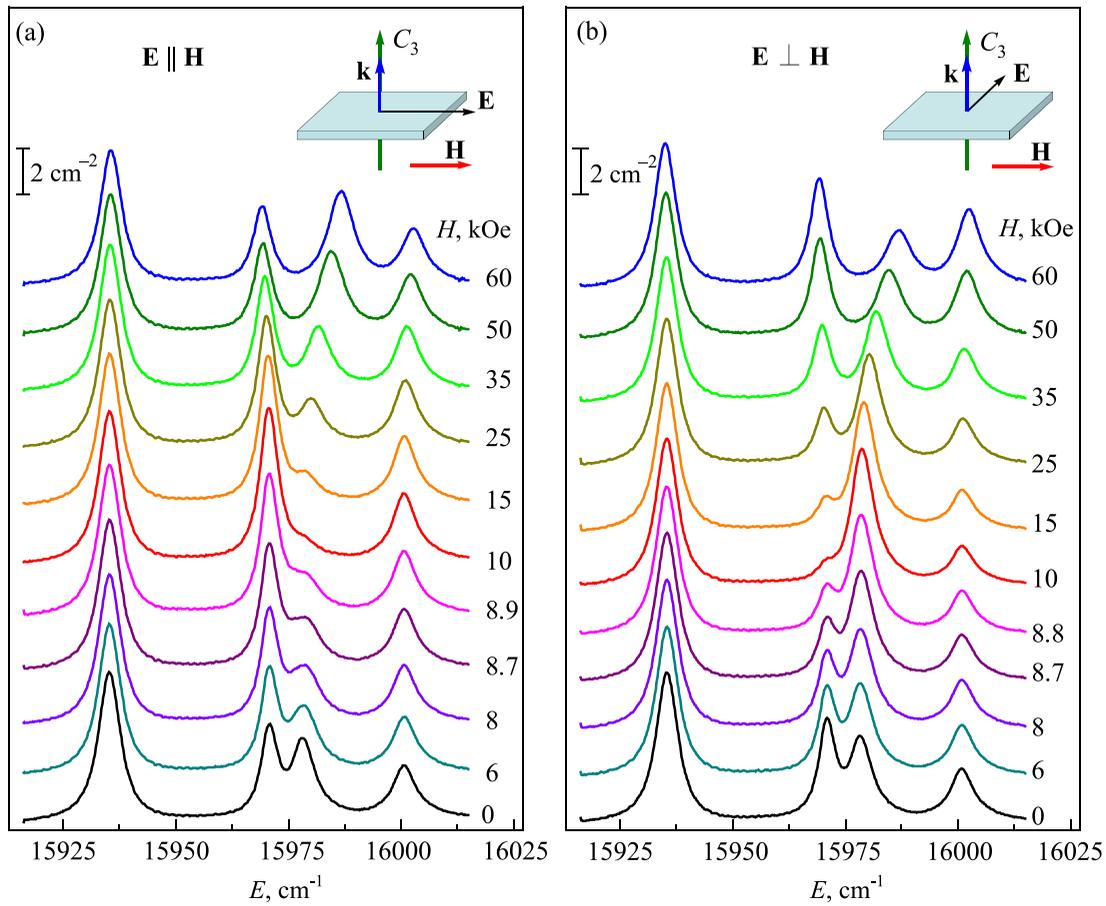


Fig. 2. Absorption spectra of $\text{NdFe}_3(\text{BO}_3)_4$ in an external magnetic field $\mathbf{H} \parallel C_3$ (a) and $\mathbf{H} \perp C_3$ (b) for two polarizations in the basal plane of the crystal. $T = 2 \text{ K}$. The insets show the geometry of the experiment.

the spin-flop transition is approached, one of the components weakens and practically disappears at H_{sf} , while the intensity of another component increases significantly. With further increasing the magnetic field (for $H > H_{\text{sf}}$), the direction of changes is reversed. In this case, the evolution of intensity observed in the polarizations $\mathbf{E} \parallel \mathbf{H}$ and $\mathbf{E} \perp \mathbf{H}$ are inverted with respect to each other. The magnetic field dependences of the integrated intensities of the polarized components of lines 2a and 2b are shown in Fig. 4.

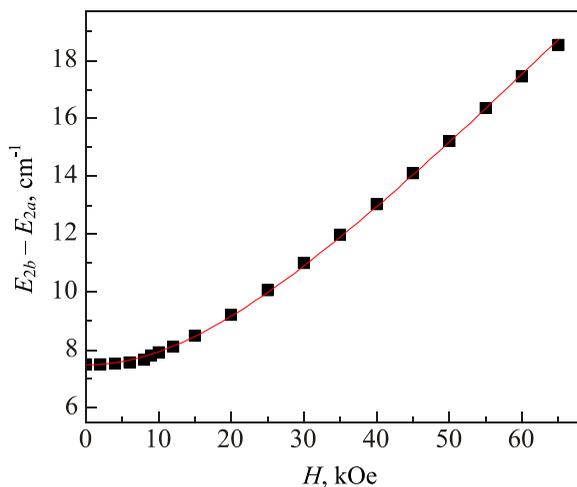


Fig. 3. Magnetic field dependence of the splitting of doublet “2.” $\mathbf{H} \perp C_3$. $T = 2 \text{ K}$. The points denote the experimental data; the solid line shows the approximation by Eq. (1).

A characteristic feature of the intensity “transfer” is that the total intensity of each of the lines $I(\mathbf{E} \parallel \mathbf{H}) + I(\mathbf{E} \perp \mathbf{H})$ is practically independent of the external field in the spin-flop phase (Fig. 5). The same result is obtained when recording the absorption spectra for $\mathbf{H} \perp C_3$ in unpolarized light.

3.4. A model description of the field dependences of polarized components for transition 2

To construct a semiempirical model describing the experimentally observed field dependence of the polarized components of the absorption lines of transition 2, we start from the one-ion approximation. Specifically, we assume that the optical properties of the crystal associated with the absorption bands under discussion are formed in a system of non-interacting rare-earth Nd^{3+} centers, which in the spin-flop phase are separated into two equivalent “antiferromagnetic” sublattices, differing by the antiparallel direction of \mathbf{H}_{Fe} . In this case, the external field \mathbf{H} for both sublattices is the same. The direction of the effective field $\mathbf{H}_{1,2}^{\text{eff}} = \pm \mathbf{H}_{\text{Fe}} + \mathbf{H}$ forms the direction of the magnetic moment for the respective state, ground or excited, in both sublattices.

The intensity of the absorption line is understood as a quantity $I = \int_0^\infty k(\omega) d\omega$, where $k(\omega)$ is the experimentally measured spectral dependence of the absorption coefficient within the band (line). In turn, I is proportional to the oscillator strength of the dipole transition related to the band. First, we determine the relation between the “local” optical parameters of each center and the optical properties of the crystal as a whole.

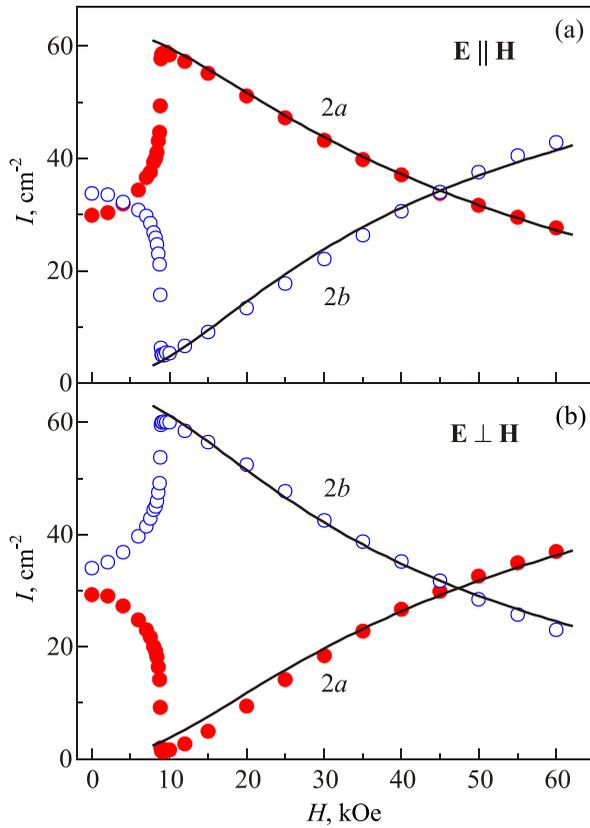


Fig. 4. Dependences of the intensities of lines 2a and 2b on the magnetic field $\mathbf{H} \perp C_3$ in two polarizations. The solid curves show the approximations by Eqs. (5) and (6).

The presence of a local effective magnetic field at the rare-earth center disrupts the uniaxial symmetry of its optical properties, leading to the appearance of a local axis of the polarizability anisotropy in the basal plane of the crystal. It is natural to relate this axis to the direction of the magnetic moment. Here, however, lies the main difficulty of the description, since, as mentioned above, in the ground and excited states the magnitudes of the exchange field turn out to be different. Moreover, their directions in the ground state and state “2” under consideration are different. However, formally it is not important how the local axis is related to

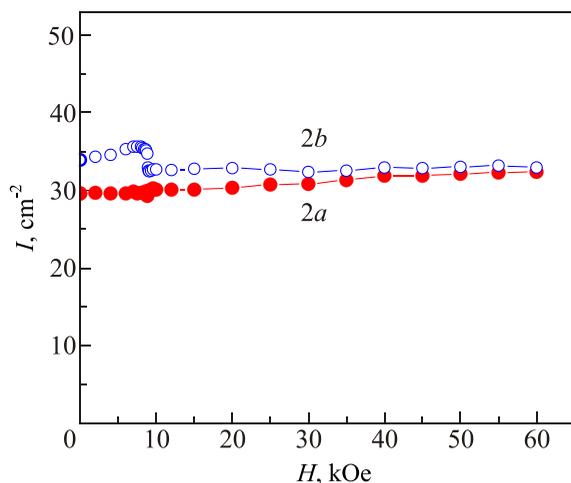


Fig. 5. Magnetic field dependences of the experimental total intensities $I(\mathbf{E} \parallel \mathbf{H}) + I(\mathbf{E} \perp \mathbf{H})$ of lines 2a and 2b.

the magnetic moments in the ground and excited states; it is important that this relation is the same for two sublattices of rare-earth ions, on the basis of the symmetry of the problem. The local axes of different sublattices are tilted from the \mathbf{H} direction by an angle $\pm\theta$. This angle is also a function of the external field. If we characterize the absorption for each sublattice by its “partial” absorption coefficients $k_p(\omega)$ and $k_s(\omega)$, where the subscript p denotes the polarization of light along the local axis of the sublattice and s is perpendicular to it, it can be shown that the global absorption coefficients for the crystal as a whole are expressed through them as follows:

$$\begin{aligned} k_X(\omega) &= 2(k_p(\omega)\cos^2\theta + k_s(\omega)\sin^2\theta), \\ k_Y(\omega) &= 2(k_p(\omega)\sin^2\theta + k_s(\omega)\cos^2\theta). \end{aligned} \quad (2)$$

It is assumed here that the external field \mathbf{H} is directed along the X -axis of the laboratory coordinate system, the Y axis is perpendicular to \mathbf{H} and C_3 axis of the crystal. The appearance of a factor of two in the right-hand sides of Eq. (2) is due to the fact that each of the sublattices has a half-density of rare-earth ions compared to the crystal as a whole. In particular, it is clear from Eq. (2) that to calculate the intensities of the polarized components of the absorption bands of a crystal on the basis of ideas about the behavior of local (sublattice) dipole moments of the transitions, it is necessary to determine the moduli squared of their projections on the X and Y axes of the laboratory coordinate system.

Let us assume that due to isotropy of the g -factor in the XY basal plane of the crystal, the magnetic moments are collinear to the total effective magnetic field on the ion, which consists of the “exchange” and external components perpendicular to each other. The doublet structure of the spectrum of states of the Kramers ion allows us to describe it using a pseudospin variable $\mu = 1/2$. We represent this quantity in the form of a classical vector of fixed length with the same orientation as the magnetic moment associated with it. Figure 6 shows a diagram depicting the directions of the angular moments of the ground state μ_0 and the excited split doublet of the state “2,” μ_a and μ_b , for one of the sublattices. It also shows the directions of the local axes as well as their notation and that of the angles used in the calculations.

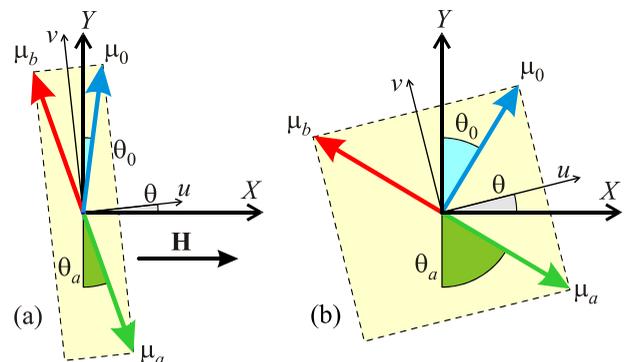


Fig. 6. Mutual orientation of the angular moments of the ground state (μ_0), the components of excited state “2” (μ_a and μ_b), the external magnetic field \mathbf{H} , the axes of the laboratory coordinate system (X , Y) and the local axes (u , v).

When the external field is small [Fig. 6(a)], all the angular moments are essentially collinear, and almost unbroken Zeeman geometry is realized in the local axes of the rare-earth ion. The transition $\mu_0 \rightarrow \mu_a$ corresponds to a transition with a change in the angular momentum projection, i.e., to the Zeeman σ -component, the polarization of which in the transverse geometry of the observation is perpendicular to the direction of the magnetic field. Furthermore, it is close to the direction of the X axis. For the second component $\mu_0 \rightarrow \mu_b$, there is no change in the projection of the angular momentum, so this is the case of the π -component polarized along the Y axis. As the external field intensity increases, the angles between the directions of the moments in the ground and excited states change significantly [Fig. 6(b)]. To fix the local coordinate system uv to the directions of the angular moments of states “0” and “2” we used the bisectors of the angles between the moments μ_0 - μ_a and μ_0 - μ_b , respectively.

In what follows, the transitions $\mu_0 \rightarrow \mu_a$, $\mu_0 \rightarrow \mu_b$ are denoted by the corresponding indices a and b . The dipole moments of the transitions corresponding to the main components (i.e., those following the Zeeman polarization rule) are expressed as

$$d_{a,u} = d_a \cos \frac{\theta_a + \theta_0}{2}, \quad d_{b,v} = d_b \cos \frac{\theta_a + \theta_0}{2}. \quad (3)$$

The deviation from collinearity in the mutual orientation of the moments μ_0 and μ_a (μ_b) should lead to the violation of strictly Zeeman polarization selection rules, i.e., to the appearance of a perpendicular component, the amplitude of which increases with increasing the skew:

$$d_{a,v} = e^{i\varphi} d_a \sin \frac{\theta_a + \theta_0}{2}, \quad d_{b,u} = e^{i\psi} d_b \sin \frac{\theta_a + \theta_0}{2}. \quad (4)$$

This assumption is of an empirical nature, which is related, as will be seen later, with the experimentally observed conservation of the total intensity of the absorption bands in two mutually perpendicular polarizations. In Eqs. (3) and (4), the phase shifts between the u - and v -polarizations of the transitions are introduced.

In the projections on the axis of the laboratory coordinate system, the dipole moments of the transitions have the following representation:

$$\begin{aligned} d_{a,X} &= d_{a,u} \cos \theta - d_{a,v} \sin \theta \\ &= d_a \left(\cos \frac{\theta_a + \theta_0}{2} \cos \theta - e^{i\varphi} \sin \frac{\theta_a + \theta_0}{2} \sin \theta \right), \\ d_{a,Y} &= d_{a,u} \sin \theta + d_{a,v} \cos \theta \\ &= d_a \left(\cos \frac{\theta_a + \theta_0}{2} \sin \theta + e^{i\varphi} \sin \frac{\theta_a + \theta_0}{2} \cos \theta \right), \\ d_{b,X} &= d_{b,u} \cos \theta - d_{b,v} \sin \theta \\ &= d_b \left(e^{i\psi} \sin \frac{\theta_a + \theta_0}{2} \cos \theta - \cos \frac{\theta_a + \theta_0}{2} \sin \theta \right), \\ d_{b,Y} &= d_{b,u} \sin \theta + d_{b,v} \cos \theta \\ &= d_b \left(e^{i\psi} \sin \frac{\theta_a + \theta_0}{2} \sin \theta + \cos \frac{\theta_a + \theta_0}{2} \cos \theta \right). \end{aligned}$$

For the intensities of the transitions we obtain

$$\begin{aligned} I_{a,X} &= I_a \left(\cos^2 \frac{\theta_a + \theta_0}{2} \cos^2 \theta + \sin^2 \frac{\theta_a + \theta_0}{2} \sin^2 \theta \right. \\ &\quad \left. - \frac{1}{2} \cos \varphi \sin (\theta_a + \theta_0) \sin 2\theta \right), \\ I_{a,Y} &= I_a \left(\cos^2 \frac{\theta_a + \theta_0}{2} \sin^2 \theta + \sin^2 \frac{\theta_a + \theta_0}{2} \cos^2 \theta \right. \\ &\quad \left. + \frac{1}{2} \cos \varphi \sin (\theta_a + \theta_0) \sin 2\theta \right), \\ I_{b,X} &= I_b \left(\cos^2 \frac{\theta_a + \theta_0}{2} \sin^2 \theta + \sin^2 \frac{\theta_a + \theta_0}{2} \cos^2 \theta \right. \\ &\quad \left. - \frac{1}{2} \cos \psi \sin (\theta_a + \theta_0) \sin 2\theta \right), \\ I_{b,Y} &= I_b \left(\cos^2 \frac{\theta_a + \theta_0}{2} \cos^2 \theta + \sin^2 \frac{\theta_a + \theta_0}{2} \sin^2 \theta \right. \\ &\quad \left. + \frac{1}{2} \cos \psi \sin (\theta_a + \theta_0) \sin 2\theta \right). \end{aligned} \quad (5)$$

It follows from Eq. (5) that the sum of the intensities of the X and Y components for each of the transitions is conserved, which is observed experimentally with good accuracy. It is also seen that the behavior of the X and Y components for the two transitions is complimentary, corresponding to the replacement of X by Y and vice versa. Further transformations are associated with the transition from angles to magnetic field. Let us denote the effective exchange field in the ground state as $H_{\text{Fe}0}$ and that for the excited doublet as $H_{\text{Fe}2}$. In addition, we recall that the angle θ in the expressions above is related to the angles θ_0 and θ_a through the relation $\theta = (\theta_a - \theta_0)/2$. Furthermore, $\text{tg} \theta_0 = H/H_{\text{Fe}0}$, $\text{tg} \theta_a = H/H_{\text{Fe}2}$.

$$\begin{aligned} I_{a,X} &= I_a \frac{1}{2} \left(\cos^2 \theta_a (1 + \alpha) + \cos^2 \theta_0 (1 - \alpha) \right), \\ &= I_a \frac{1}{2} \left(\frac{H_{\text{Fe}2}^2 (1 + \alpha)}{H_{\text{Fe}2}^2 + H^2} + \frac{H_{\text{Fe}0}^2 (1 - \alpha)}{H_{\text{Fe}0}^2 + H^2} \right), \\ I_{a,Y} &= I_a \frac{1}{2} \left(\sin^2 \theta_a (1 + \alpha) + \sin^2 \theta_0 (1 - \alpha) \right), \\ &= I_a \frac{1}{2} \left(\frac{H^2 (1 + \alpha)}{H_{\text{Fe}2}^2 + H^2} + \frac{H^2 (1 - \alpha)}{H_{\text{Fe}0}^2 + H^2} \right), \end{aligned} \quad (6)$$

where the parameter $\alpha = \cos \varphi$. For the line $2b$, we obtain analogously

$$\begin{aligned} I_{b,X} &= I_b \frac{1}{2} \left(\frac{H^2 (1 - \beta)}{H_{\text{Fe}2}^2 + H^2} + \frac{H^2 (1 + \beta)}{H_{\text{Fe}0}^2 + H^2} \right), \\ I_{b,Y} &= I_b \frac{1}{2} \left(\frac{H_{\text{Fe}2}^2 (1 - \beta)}{H_{\text{Fe}2}^2 + H^2} + \frac{H_{\text{Fe}0}^2 (1 + \beta)}{H_{\text{Fe}0}^2 + H^2} \right), \end{aligned} \quad (7)$$

where $\beta = \cos \psi$.

Using Eqs. (6) and (7), a sufficiently correct description of the experimental dependences is achieved, using the same set of parameters for the two polarizations of each component, a and b , of the Kramers doublet (see Fig. 4). In this case, the parameters α and β are small or can even be set equal to zero. The exchange field magnitude $H_{\text{Fe}2} = 28$ kOe of the excited state “2” in Eqs. (6) and (7) is not an adjustable parameter; it was obtained independently from the

experimentally observed splitting pattern of a doublet in a magnetic field (see Sec. 3.2). The magnitude of the exchange field in the ground state $H_{Fe0} = 78.8$ kOe, which also enters into Eqs. (6) and (7), has been obtained in Ref. 16 from the observed splitting of the ground state and the calculated $g_{\perp 0}$. In fact, only two amplitudes I_a and I_b are adjustable.

It is seen from Eqs. (6) and (7) that the role of the parameters α and β is manifested in the renormalization of the weights of the terms of the type $\frac{H^2}{H_{Fei}^2 + H^2}$, where the index $i = 0, 2$ enumerates the exchange fields in the ground and excited states, respectively. If these parameters are set equal to zero, the magnetic field at which the intensities of the two components of lines 2a and 2b become equal correspond to the geometric mean of the exchange fields in the ground and excited state $H_{I_x=I_y} = \sqrt{H_{Fe0}H_{Fe2}}$. For this external field strength, $\mu_0 \perp \mu_{a,b}$.

4. Conclusion

The present work demonstrates an unusual behavior of the polarized components of the absorption bands associated with ${}^4I_{9/2} \rightarrow {}^2H_{11/2}$ optical transition of a Nd^{3+} ion in $NdFe_3(BO_3)_4$ ferroboreate. In the magnetically ordered state, the doublet sublevels of the ground and excited Nd^{3+} states are split due to f - d exchange interaction with the subsystem of Fe^{3+} ions having the “easy plane” type ordering. When an external magnetic field $H > 9$ kOe is applied in this plane, a nontrivial pattern of the magnitudes and directions of the effective magnetic fields for various electronic states of the Nd^{3+} ion is formed within the plane. This pattern is manifested in a complex dependence of the intensities of the polarized components of the absorption bands on the external magnetic field. In our opinion, this phenomenon belongs to a special case of the transverse Zeeman effect, in which the directions of the magnetic moments of the initial and final levels of the electronic transition are not collinear with each other and the direction of the external field. Moreover, the magnitude of the non-collinearity can vary within certain limits by varying the external field.

A semiempirical model was developed allowing the description of the experimental field dependences of the intensities of the polarized components of the absorption lines of the Kramers doublet 15971 – 15978 cm^{-1} . The model equation does not contain any adjustable parameters, except the scale factors. The parameters of the exchange fields of the ground and excited states are determined independently.

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