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The magneto-optical activity of rare-earth ion in Y-substituted erbium and neodymium iron garnets

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Abstract

The magnetic and magneto-optical (MO) properties of $Er_xY_{3-x}Fe_5O_{12}$ ($x = 0.4$, 1.0, 1.5, 2.5 and 3.0) (ErYIG) and $Nd_xY_{3-x}Fe_5O_{12}$ ($x = 0.5$, 0.96, 1.39 and 1.72) (NdYIG) single crystals have been presented. Faraday rotation (FR) spectra obtained in energy region 5500–13,000 cm^{-1} for the erbium garnets and in energy region 6000–17,000 cm^{-1} for the neodymium garnets with a high optical resolution have been presented here, in contrast to other researches of the FR performed only at 1152 nm (8696 cm^{-1}). The investigations at 5, 130 and 295 K temperatures under magnetic field up to 20 kOe applied parallel to the [1 1 1] crystallographic axes of the crystals have been provided.

Anomalous great MO activity is the result of joint action of similar in sign and approximately equal in quantity of paramagnetic and diamagnetic mechanisms in NdYIG.

It has been shown that proportional to magnetic field and independent of temperature contribution of the mixing of the ground state multiplets mechanism exceeds paramagnetic contribution. Concentration dependence of MO coefficients confirms one-ion nature of MO activity of ErYIG.

Keywords: Magnetically ordered materials; Exchange and superexchange; Magnetic measurements

1. Introduction

In recent years, the optical and magneto-optical (MO) properties of ferrimagnetic garnets have attracted increasing interest, from the physical or the applicational points of view. The garnet structure can accommodate a great variety of cations. It is, therefore, an excellent crystal host to be used in the study of the crystal field effects on various cations. It has been known for a long time, that yttrium iron garnet (YIG), for example, is highly transparent between 1200 and 4500 nm ($\alpha \leq 0.03\,cm^{-1}$). Generally speaking, substitution of Y^{3+} by either Bi^{3+}, Pr^{3+} or Nd^{3+} has been one of the methods to increase FR. On the other hand, Scott and Lackleson have shown that an increase in intensity of the lowest energy crystal field transition of the octahedral Fe^{3+} ions occurs as the lattice constant increases [1]. This mechanism has not been fully investigated yet. Garnet structure with its interconnectivities between all three types of cation polyhedra adds further complexities to the study of crystal field effects. Strong correlations seem to exist between ions at various sites and in the literature there are, in fact, several studies of optical spectrum in YIG.

However, the least one can say is that the problem is an extremely complex one and that no simple model has been proposed so far. Nevertheless, some general ideas have been developed, which indicate that the electric dipole transitions arise in the $Fe^{3+}O_6{}^{2-}$ and $Fe^{3+}O_4{}^{2-}$ ligand complexes and borrow their intensities from the exchange coupled nearest neighbor Fe^{3+} ions. Therefore, in this work, we propose to investigate the mixed rare-earth garnets, trying to draw some coherent conclusions from the results obtained and from their comparisons.

Dispersive MO effects in pure and substituted rare-earth iron garnets (RIG) have been the subject of numerous experimental and theoretical investigations [1–12]. To the best of our knowledge, despite the abundant literature, few results concerning the FR in the RIG have been published [5–8].

The aim of this article is to clarify the origin of the MO activity of the rare-earth ion in RIG.

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The typical representatives of two RIG groups: (1) with heavy rare-earth element Er and (2) light rare-earth element Nd, have been studied.

When discussing the experimental results, it is usually supposed that MO effects in RIG can be mainly explained in the frame of a one-ion model [7] considering that the magnetic contributions sublattices can be independent and proportional to their magnetic moments.

Such interpretation of FR in the $Er_3Fe_5O_{12}$ and in the $Er_{2.2}Y_{0.8}Fe_5O_{12}$ [3] has resulted in the fact that the contribution of Er sublattice to FR has turned out to be dependent on the temperature much more than its magnetic moment.

The sign and the absolute value changes of the coefficient of MO activity, with decreasing temperature from 300 to 80 K, obtained in these reports, contradict our representation about relative constancy of physical properties of rare-earth ions in the crystals.

The information lack of the physical properties of Nd–Y iron garnet can be explained by principle technological difficulties of their synthesis. Nd^{3+} ion has large radius and "readily" substitutes Y ion in dodecahedral positions in crystals; Nd^{3+} concentration in RIG with the formula $Nd_xY_{3-x}Fe_5O_{12}$ cannot exceed 2.0 [9]. It has been shown [12] that the superexchange interaction influences on the mixing of wave functions in the $ErO_8{}^{13-}$ molecule.

The examination of MO properties of $Er_xY_{3-x}Fe_5O_{12}$ ($x = 0.4$, 1.0, 1.5, 2.5 and 3.0) have been presented in this work; in addition to the result [12], two more samples ($x = 1.0$ and 3.0) and $Nd_xY_{3-x}Fe_5O_{12}$ ($x = 0.5$, 0.96, 1.39 and 1.72) single crystals have been studied in energy regions of 5500–13,000 cm^{-1} and 6000–17,000 cm^{-1} respectively.

2. Experimental

Using the method of flux growth under 10 bar of oxygen pressure, single crystals of $Er_xY_{3-x}Fe_5O_{12}$ ($x = 0.4$, 1.0 and 2.5) were synthesized. X-ray diffraction measurements were in agreement with the garnet Ia 3d structure. Polished platelets – 100–250 μm thickness – oriented perpendicular to [1 1 1] and [1 0 0] axes were obtained from the same "as grown" crystal to avoid the slight Y concentration difference which can occur between different crystals of the same batch. NdYIG samples were grown from the $PbO:PbFe_2:B_2O_3$ flux melts by spontaneous nucleation.

The compositions of the samples have been determined from the published relationship between the compositions and the lattice constant. Polished plates (30–35 μm thickness) were oriented perpendicular to [1 1 1] axes.

FR measurements Φ were performed at temperatures 5, 82, 130 and 295 K under a magnetic field of up to 20 kOe applied parallel to [1 1 1] direction. Faraday rotation spectra obtained in energy region 5500–13,000 cm^{-1} for $Er_xY_{3-x}Fe_5O_{12}$ crystals and in 6000–17,000 cm^{-1} for $Nd_xY_{3-x}Fe_5O_{12}$ with a high optical resolution has been presented here in contrast to other researches of the Faraday rotation performed at 1152 and 1064 nm [1,3,5].

The experimental accuracy is estimated to ±2% for Φ. It is noted that the samples are cooled at the lowest temperature in the absence of a magnetic field prior to FR measurements. Field dependencies of the FR and the differential FR susceptibility $d\Phi/dH$ were measured using the statical compensation method at two wavelengths 1152 and 1064 nm (for comparison with other researches). The angle of rotation was measured with 0.1° accuracy.

This wavelength is in the transparency window of the garnet – the nearest Er absorption lines are located at about 6700 cm^{-1} ($^4I_{15/2}$–$^4I_{13/2}$ transition) and at about 10,000 cm^{-1} ($^4I_{15/2}$–$^4I_{11/2}$ transition) – (the nearest Nd absorption lines are located at about 11,500 cm^{-1} ($^4I_{9/2}$–$^4I_{3/2}$ transition), about 12,500 cm^{-1} ($^4I_{9/2}$–$^2H_{9/2}$ transition), about 13,500 cm^{-1} ($^4I_{9/2}$–$^4S_{3/2}$ transition), 15,000 cm^{-1} ($^4I_{9/2}$–$^4F_{9/2}$ transition), about 15,800 cm^{-1} ($^4I_{9/2}$–$^2H_{11/2}$ transition) and others) and the MO properties presented in this article are mainly dispersive.

Crystallographic directions [1 1 1] are the easy magnetization axes at three studied temperatures (82, 130 and 295 K) (above the compensation point). The direction of light propagation and the direction of applied magnetic field coincide with one of them—with [1 1 1], for example. In this geometry of the experiment, the effects of magnetic birefringence are absent and crystals are uniaxial.

3. Results and discussion

Absorption spectra of two samples of $Er_xY_{3-x}Fe_5O_{12}$ ($x = 1.5$ and 2.5) at 5 and 295 K temperatures are plotted in Fig. 1. They present the fine structure of one of the above-mentioned Er absorption lines ($^4I_{15/2}$–$^4I_{11/2}$ transition).

There are two absorption maximums in the absorption spectra of two samples of $Nd_xY_{3-x}Fe_5O_{12}$ ($x = 0.5$ and 1.72) in Fig. 2. The first maximum in energy region 10,500 cm^{-1} is identified with $^6A_{1g}(^6S)$–$^4T_{1g}(^4G)$ transition in Fe^{3+} ions occupying octahedral sites in the garnet structure, the second

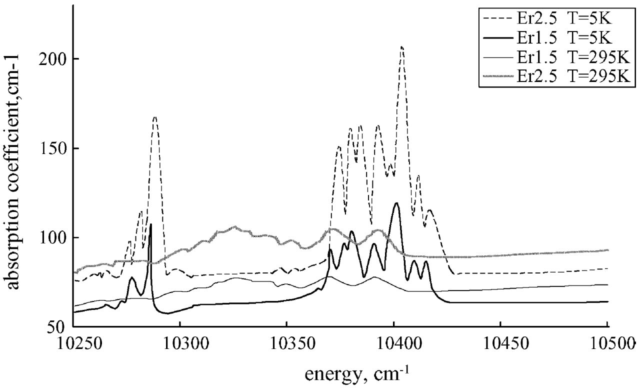

Fig. 1. Absorption spectra of two samples of $Er_xY_{3-x}Fe_5O_{12}$ ($x = 1.5$ and 2.5).

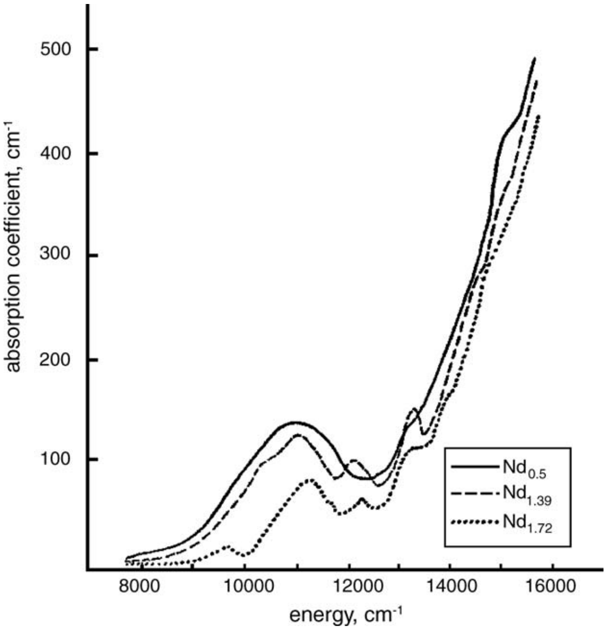

Fig. 2. Absorption spectra of three samples of $Nd_xY_{3-x}Fe_5O_{12}$ ($x = 0.5$, 1.39 and 1.72), $T = 295$ K.

maximum in energy region 16,000 cm^{-1} is identified with $^6A_1(^6S)$–$^4T_1(^4G)$ transition in Fe^{3+} ions occupying tetrahedral sites.

A number of narrow optical transitions in Nd^{3+} ions whose intensity increases with increasing Nd^{3+} concentration in crystals and which much more exactly resolute in FR spectra are put on these transitions.

To study these transitions was not our aim that is why absorption spectra have been presented here only at room temperature for convenient practical usage.

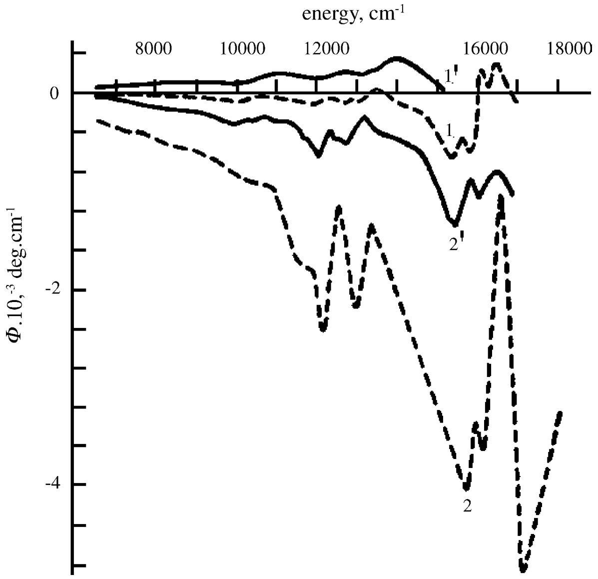

Fig. 4. Frequency dependences of FR of $Nd_xY_{3-x}Fe_5O_{12}$; $x = 0.5$ (1, 1′) and 1.39 (2, 2′). 1, 2—130 K; 1′, 2′—295 K.

When calculating, we consciously excluded those regions of absorption spectra on which the absorption lines of rare-earth ion were put.

The FR dispersion in all studied samples is characterized by monotonous, with frequency increasing, rise of the FR due to the contribution of allowed electric transitions in Fe^{3+}, Er^{3+} and Nd^{3+} ions (or associated molecular complexes) which frequencies are in the far ultraviolet region. These spectra are shown for two concentrations as an example in Figs. 3–5.

The peculiarities of the FR involving narrow intraconfigurational f–f absorption bands $^4I_{15/2}$–$^4I_{13/2}$ (~6700 cm^{-1}), $^4I_{15/2}$–$^4I_{11/2}$ (~10,300 cm^{-1}), $^4I_{15/2}$–$^4I_{9/2}$ (~12,500 cm^{-1})

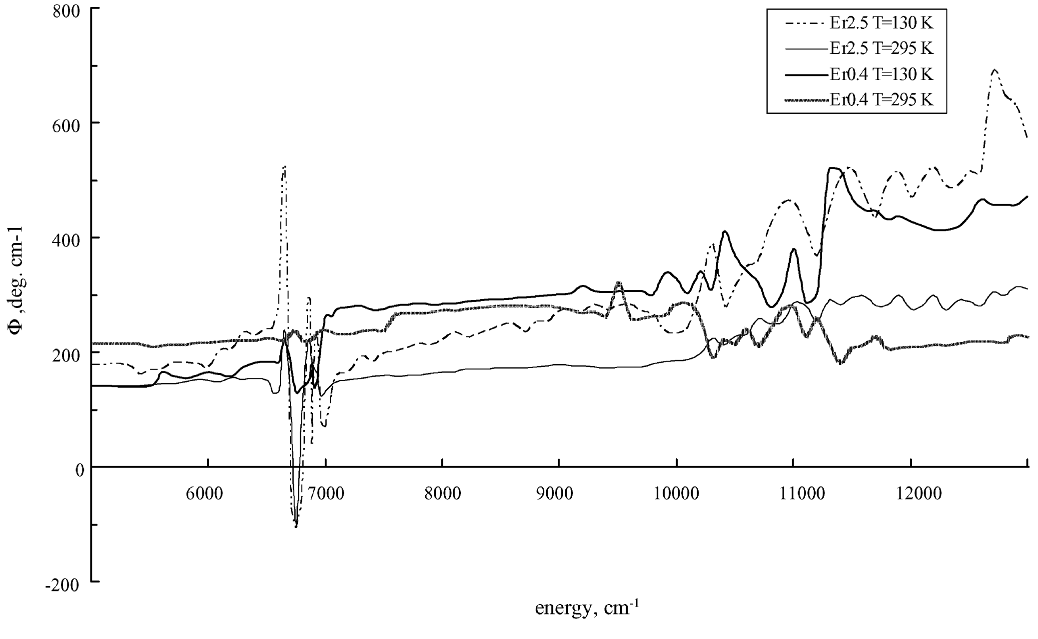

Fig. 3. Frequency dependences of Faraday rotation of $Er_xY_{3-x}Fe_5O_{12}$ ($x = 0.4$ and 2.5).

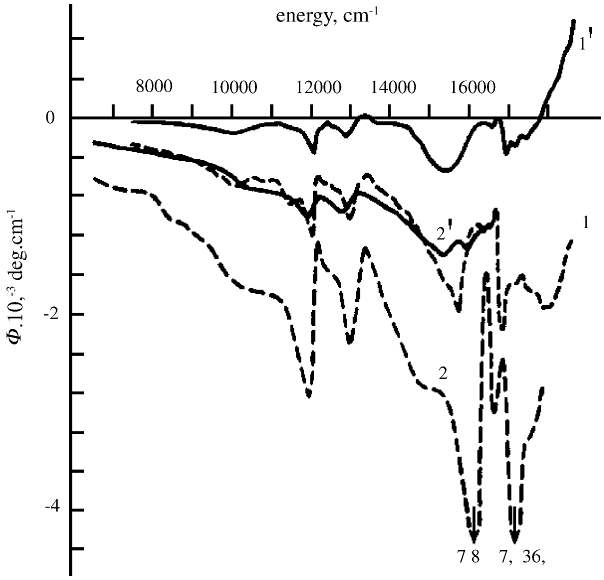

Fig. 5. Frequency dependences of FR of $Nd_xY_{3-x}Fe_5O_{12}$; $x = 0.96$ (1, 1′) and 1.72 (2, 2′). 1, 2—130 K; 1′, 2′—295 K.

of Er^{3+} ion and a wider d–d band $^6A_{1g}(^6S)$–$^4T_{1g}(^4G)$ (∼10,900 cm^{-1}) of octachedral $FeO_6{}^9$ complexes can be seen against the background of the monotone rise of FR. These spectra obtained with resolution 4 cm^{-1}.

One can easily see a number of extremes of FR connected with electronic transition in ion Nd^{3+}. Y^{3+} ion substitution by Nd ions results initially in decreasing FR in garnet, but when $0.5 \leq x \leq 1$, FR at room temperature equals zero, then the absolute value of FR increases.

Much more influence on the value of FR while entering Nd^{3+} ions in the garnet lattice has been observed with the temperature decreasing. It is obviously shown on transition of $^4I_{9/2}$–$^4F_{9/2}$ in energy region 15,000 cm^{-1}. There is no point of compensation in the temperature range 82–295 K.

Unfortunately, the scale of the article has not allowed us to represent the calculations.

The results of our experimental research have been treated through quantum theory of FR taking into account the influence of effective magnetic fields on splitting the ground and exciting multiplets of rare-earth ions and mixing of wave functions of ground and exciting multiplets of rare-earth ions. The electric dipole transition between the $4f^3$ and $4f^2 5d$ configuration split states are studied taking into account the spin-orbit crystal field and superexchange interaction in developing [7,11].

When analyzing the values of paramagnetic and diamagnetic contributions for some wavelengths the conclusion that paramagnetic and diamagnetic contributions to hiroelectrical FR in Y-substituted neodymium garnets have equal signs, can be made; far from own rare-earth ion transitions paramagnetic rotation can be compared with diamagnetic contribution; diamagnetic contribution begins to predominate over paramagnetic in 4f-transition region.

The magnetic moment of Nd^{3+} ion is parallel to the resulting magnetic moment of Fe sublattices that is common with all light elements with less than half closed f-shell atom in the RIG structure.

That is why paramagnetic contribution to FR has negative value. This contribution being summarized with equal and, in some cases with exceeded in value negative in sign diamagnetic contribution, results in large negative experimentally observed values of FR in Nd^{3+} system (Figs. 4 and 5).

Quantum theory of FR used by us in this work allows us to be confirm in the conclusion, made in [12], concerning the nature of MO activity of Er^{3+} ion in Y-substituted erbium iron garnets. The validity of the single-ion model of Er sublattice contribution to a non-resonant FR shows that we can consider the rare-earth and iron sublattices to the overall rotation within the "transparency range" independently. The FR spectral analysis shows (Fig. 3) that the FR origin within the range of spin and parity forbidden f–f and d–d absorption bands appears to be much more complicated. The fine FR line structure observed within the range of f–f Er^{3+} ion absorption band $^4I_{15/2}$–$^4I_{13/2}$ strongly depends on Er^{3+} ion concentration and FR may be considered to be linear in the first approximation. In the energy range above 10,000 cm^{-1} against FR lines related to d–d iron sublattice absorption bands a number of relatively broad FR lines are observed whose amplitude slightly depends on ion Er^{3+} concentration. The positions of energetic maxima of these lines are shifted with concentration and energy changes. The origin of these is related with combined interactions of rare-earth end iron subsystems.

4. Conclusion

Given measurements of frequency dependence of FR in ErYIG and NdYIG substituted garnets have allowed us to define the essential role of the mechanism of wave functions mixing in FR forming:

1. It has been shown that proportional to magnetic field and independent of temperature contribution of the mixing of the ground state multiplets mechanism exceeds paramagnetic contribution to FR in Y-substituted erbium iron garnets ErYIG. Concentration dependence of MO coefficients justifies single-ion nature of MO activity of ErYIG.
2. Temperature independent diamagnetic mechanism plays an important role in formation of FR in Y-substituted neodymium iron garnets. Anomalous great MO activity is the result of joint action of similar in sign and approximately equal in quantity of paramagnetic and diamagnetic mechanisms in NdYIG.

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