We report on optical studies of the thin films of multiferroic hexagonal rare-earth orthoferrites $R\text{FeO}_3\ (R=\text{Ho, Er, Lu})$ grown epitaxially on a (111)-surface of ZrO$_2$(Y$_2$O$_3$) substrate. The optical absorption study in the range of 0.6-5.6 eV shows that the films are transparent below 1.9 eV; above this energy four broad intense absorption bands are distinguished. The absorption spectra are analyzed taking into account the unusual fivefold coordination of the Fe$^{3+}$ ion. Temperature dependence of the optical absorption at 4.9 eV shows anomaly at 124 K, which we attribute to magnetic ordering of iron sublattices.
In the last decades materials based on transition-metal (TM) and rare-earth-metal (RE) oxides have attracted much attention because of their importance for multiple applications as well as for fundamental studies. A rich variety of interesting physical properties of TM oxides is determined by different types of TM ion and their local coordinations. The distinct place among the TM oxides belongs to the compounds based on iron ions, as they possess the largest magnetic moments and highest temperatures of magnetic ordering. It is well known that iron ions in oxides prefer to occupy either octahedral or tetrahedral positions and the examples of such materials are numerous. By contrast, the five-fold coordination of iron ions is unstable and only recently several groups reported successful synthesis of powders, fine particles and thin films of hexagonal rare-earth orthoferrites $RFeO_3$. This new type of ferrites remains scarcely investigated. Such an important property as multiferroicity of these compounds was under question till very recently. In early studies no magnetic ordering was identified in ultrafine hexagonal EuFeO$_3$ and YbFeO$_3$ particles. On the contrary, ferrimagnetic ordering for both iron and rare-earth sublattices was later proposed in hexagonal YbFeO$_3$ thin films while recent magnetic measurements have indicated a weak ferromagnetic ordering in hexagonal $RFeO_3$ ($R$=Lu, Er-Tb) and YbFeO$_3$ films below the Néel temperature $T_N \sim 120$ K. Several claims of ferroelectricity in hexagonal $RFeO_3$ were made and confirmed recently by the comprehensive studies of electric polarization in YbFeO$_3$, which revealed two ferroelectric transitions at 470 and 225 K. Despite of the progress in understanding the magnetic and ferroelectric properties of hexagonal $RFeO_3$, until now no theoretical or experimental investigations of their electronic structure has been reported.

In this Communication we report on the studies of optical properties and electronic structure of thin epitaxial films of hexagonal $RFeO_3$ ($R$=Ho, Er, and Lu). In particular, optical absorption of these films was studied in the range of 0.6-5.6 eV and analyzed in terms of the crystal field theory. This allowed us to disclose the features of electronic structure of hexagonal orthoferrite related to the Fe$^{3+}$ ion in the unusual coordination. Furthermore, temperature study of absorption suggests an onset of magnetic ordering of iron sublattices at 124 K, in agreement with recent magnetic studies.

Epitaxial films of hexagonal iron oxides $RFeO_3$ ($R$=Ho, Er, Lu) were grown by metal-organic chemical vapor deposition (MOCVD) on single-crystalline (111)-substrates of cubic yttria-stabilized zirconia ZrO$_2$(Y$_2$O$_3$) (YSZ) using $R$(thd)$_3$ and Fe(thd)$_3$ as volatile precur-
sors, where thd is 2,2,6,6-tetramethylheptane-3,5-dionate. The deposition temperature was 900°C, the precursor evaporator temperature 250°C, the total gas pressure in the reactor was 7 mbar, and the partial oxygen pressure 3.5 mbar. The deposition rate was 5 nm/min and the final thickness of films was 50-70 nm.

A detailed X-ray diffraction (XRD) study using 4-circle diffractometer revealed a highly epitaxial growth resulting in (0001)-oriented films. A characteristic (002)-reflection of the hexagonal $6mm$ phase was found in the $2\theta/\omega$-scans for all samples (see Inset in Fig.1(a)). The in-plane XRD study revealed (300)-reflections in $2\theta/\chi\varphi$-scans at (220)-YSZ reflection accompanied sometimes by a weak (110)-peak indicating $<110>$ preferable in-plane orientation with respect to the $<110>$ axis of YSZ. The corresponding 6 reflections were observed in $\varphi$-scans. Scanning electron microscopy and atomic force microscopy studies showed a very smooth surface of the films with the RSM (root mean square) roughness of 1-2 nm over the $10 \times 10 \mu m^2$ area.

Fig.1(a) shows optical density spectra of the films at temperatures $T=293$ and 20 K. All samples show negligible absorption below $\sim 1.9$ eV. Above this energy the absorption begins to increase gradually and could not be measured above $\sim 4.8$ eV at $T = 293$ K and above $\sim 5.1$ eV at $T = 20$ K. The averaged absorption index $k$ for HoFeO$_3$ and ErFeO$_3$ at room temperature is shown in Fig.1(b). The uncertainty in the films thickness yields the accuracy for the absorption index of $\pm 30\%$. The absorption spectrum of hexagonal RFeO$_3$ differs significantly, on one hand, from those of perovskite orthoferrites and related iron oxides, and, on the other hand, from hexagonal manganites.

In order to identify the position of the absorption bands contributing to the spectra in Fig.1 we decomposed the absorption index spectrum to the set of Lorentz oscillators according to

$$k = \text{Im}\sqrt{\varepsilon}; \quad \varepsilon = a + bE + icE + \sum_n \frac{f_n}{E_n^2 - E^2 - iE\gamma_n},$$

where $\varepsilon$ in the complex dielectric function, $E$ is the photon energy; $a$, $b$ and $c$ are coefficients describing collective contribution from all transitions above the experimental spectral range. $E_n$, $f_n$ and $\gamma_n$ are the resonance energy, oscillator strength and relaxation parameter of the $n$-th oscillator, respectively. This analysis yielded four broad bands in the range above 1.9 eV as shown Fig.1(b).

We analyze the possible origin of the observed absorption bands in hexagonal RFeO$_3$
FIG. 1. (Color online) (a) Experimental optical density spectra of hexagonal $R$FeO$_3$ ($R$=Ho, Er, Lu) films at $T = 293$ K (solid lines) and $T = 20$ K (dashed lines). No corrections for reflection losses were taken. Inset shows $2\theta/\omega$ scans. (b) Optical spectrum of the mean value of the absorption indexes of HoFeO$_3$ and ErFeO$_3$ at $T = 293$ K (symbols) and its fit using Eq. 1 (line). Color-shaded areas show single Lorentz oscillators as obtained from the fit.

on the basis of the crystal field (CF) theory for the 3$d^5$ ion with octahedral and trigonal bypyramidal oxygen coordinations, shown in Fig. 2(a). The ground state of the Fe$^{3+}$ ion is the high-spin singlet (Fig. 2(b)), with any crystal field excitation being a transition between majority- and minority-spin 3$d$ orbitals. The energies of the excited states in the Fe$^{3+}$O$_{5,6}^2$ complex (Fig. 2(c)) can be expressed in terms of the crystal field parameters $\Delta_0$, $D_s$ and $D_t$ and exchange splitting parameter $\varepsilon_0$. We calculated the CF parameters in the Fe$^{3+}$O$_5^2$ complex in hexagonal $R$FeO$_3$ using the known values of these energies for the octahedral complex Fe$^{3+}$O$_6^2$ in perovskite orthoferrites (Fig. 2).

Here we took an advantage of the unequivocal relation between $\Delta_0$ parameters in different Fe$^{3+}$O$_{5,6}^2$ complexes and the dependence of the CF parameters on the Fe$^{3+}$-O$_2^-$ bond lengths. The resulting CF parameters for the hexagonal orthoferrite are $\Delta_0 = 1.76$ eV, $D_s = 0.149$ eV and $D_t = 0.157$ eV.

The exchange splitting $5\varepsilon_0$ between the majority- and minority-spin orbitals defines solely the transition $^6A_1' \rightarrow ^4A_1'$, $^4A_2'$, $^4E'$ and is similar in a vast majority of iron oxides (see e.g. Ref. 12, Table 5.15). Therefore, we take this energy to be close to that in the perovskite orthoferrite (2.67 eV). Knowing this value and the crystal field parameters $D_s$ and $D_t$ we
FIG. 2. (Color online) (a) Schematic presentation of the Fe\(^{3+}\)O\(_6^2^-\) complex in a perovskite orthoferrite and the Fe\(^{3+}\)O\(_5^2^-\) complex in a hexagonal orthoferrite. The bond lengths are given in Å.\(^{17,20}\) (b) Splitting and occupation of the Fe\(^{3+}\) ion ground state in the spherically-symmetric, octahedral (\(O_h\)), distorted octahedral (\(D_{4h}\)) and trigonal-bipyramidal (\(D_{3h}\)) complexes. Numbers show the energies of the orbitals (in eV) with respect to the ground state in the spherical coordination. (c) Ground and the four lowest excited states of Fe\(^{3+}\) in distorted octahedron and trigonal bipyramid. Arrows with numbers show the CF transitions and their energies (in eV). Also shown (in the middle) is the lowest CT transition from the valence to the conduction band.

Calculated the energies for other three low lying excited states, as shown in Fig.2(c).

No features in the absorption spectra of hexagonal orthoferrites are observed below 1.9 eV (Fig.1), while our calculations predict appearance of two bands in this range. Their absence in the spectra is easily understood because the \(d-d\) transitions in Fe\(^{3+}\) compounds are spin-forbidden. Therefore, we expect these bands to be too weak for detection in the samples as thin as 50 nm. An estimate gives optical density \(D\) for these bands to be of the order of \(10^{-2}\), even assuming the absorption coefficient for them being 10 times higher than the one for the \(6A_{1g} \rightarrow 4T_{1g}\) transition in perovskite orthoferrite TmFeO\(_3\).\(^{19}\) On one hand, two broad bands centered at 2.23 and 2.94 eV, respectively, can be assigned to the \(d-d\) transitions \(6A_1' \rightarrow 4A_1''\) and \(6A_1' \rightarrow 4A_1', 4A_2', 4E''\), respectively (Fig.2(c)). On the other
hand, from the numerous studies of 3$d$ metal oxides it is known that the strength of some $d-d$ absorption bands can be considerably enhanced due to admixture of the electric-dipole-allowed charge transfer (CT) transitions from the valence band formed predominantly by the occupied $2p$ oxygen orbitals to the conduction band formed by unfilled $3d$ iron orbitals. In perovskite orthoferrites the typical photon energy for the lowest CT transition is $\sim 3$ eV. In hexagonal orthoferrites one can expect a red-shift of the fundamental absorption edge due to the somewhat shorter Fe$^{3+}$-O$^{2-}$ distances. Therefore, the absorption bands at 2.27 and 2.97 eV may have a combined CF and CT origin. The absorption bands at 3.77 and 5.08 eV should be purely CT transitions from $2p$ oxygen to the $3d$ iron orbitals. We add that no absorption lines associated with the rare earth ions were detected.

High-energy optical absorption of hexagonal $R$FeO$_3$ is characterized by a sharp band centered at 5.08 eV at $T=293$ K. The absorption edge associated with this band is noticeably blue-shifted at $T=20$ K (Fig. 1). Fig. 3 shows the temperature dependence of the absorption at 4.9 eV in HoFeO$_3$. It is seen, that the absorption sharply decreases when temperature is going down. A well defined anomaly is observed at 124 K (see inset). We relate the overall decrease of absorption in the temperature range 150-300 K to the freezing of phonons contributing to the broadening of the absorption band at 5.08 eV. The anomaly at 124 K in the temperature dependence of the absorption is in a very good agreement with recently reported temperature of the magnetic ordering for several hexagonal $R$FeO$_3$. Therefore, we assign the observed anomaly to the exchange splitting of ground and excited states.
responsible for the given absorption band.\textsuperscript{16,22}

In conclusion, optical absorption was studied in thin films of multiferric hexagonal rare earth orthoferrites $R$FeO$_3$ ($R=$Ho, Er, Lu) grown epitaxially on (111)-oriented YSZ substrates by MOCVD method. We demonstrate that optical absorption spectra of hexagonal orthoferrites differ strongly from those of perovskite orthoferrites and hexagonal manganites. Based on the analysis of the electronic structure in terms of the CF theory, we assign absorption bands in hexagonal $R$FeO$_3$ at 2.27 eV and 2.97 eV to combined CF and CT transitions, whereas the absorption bands at 3.77 eV and 5.08 eV to the purely CT transitions from 2$p$ oxygen to the 3$d$ iron orbitals. We add, that these results unveil the general features of the optical spectra and electronic structure of hexagonal $R$FeO$_3$ and, thus, may serve as a reference for more elaborated theoretical calculations, required for understanding various properties of these compounds. Temperature dependence of absorption within the 5.08 eV band shows an anomaly near 124 K, which is likely to originate from the magnetic ordering of Fe$^{3+}$ ions.

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REFERENCES

1. C. N. R. Rao and B. Raveau, \textit{Transition Metal Oxides: Structure, Properties, and Synthesis of Ceramic Oxides}, Second Edition (Wiley-VCH, NY, 1998).
2. R. M. Cornell, U. Schwertmann, \textit{The Iron Oxides: Structure, Properties, Reactions, Occurrences, and Uses}, Second Edition (Wiley-VCH, Weinheim, 2003).
3. O. Yamaguchi, H. Takemura and M. Yamashita, J. Electrochem. Soc. \textbf{138}, 1492 (1991).
4. Y. Mizoguchi, H. Onodera, H. Yamaguchi, M. Kagawa, Y. Syono, and T. Hirai, Mat. Sci. Eng. A \textbf{217}, 164 (1996).
5. K. Nagashio and K. Kuribayashi, J. Amer. Cer. Soc. \textbf{85}, 2550 (2002).
6. A. A. Bossak, I. E. Graboy, O. Yu. Gorbenko, A. R. Kaul, M. S. Kartavtseva, V. L. Svetchikov, and H. W. Zandbergen, Chem. Mater. \textbf{16}, 1751 (2004).
7. E. Magome, C. Moriyoshi, Y. Kuroiwa, A. Masuno, and H. Inoue, Jap. J. Appl. Phys. \textbf{49},
8H. Iida, T. Koizumi, and Y. Uesu, Phase Transitions 84, 747 (2011).
9A. R. Akbashev and A. R. Kaul, Russ. Chem. Rev. 80, 1159 (2011).
10A. R. Akbashev, A. S. Semisalova, N. S. Perov, and A. R. Kaul, Appl. Phys. Lett. 99, 122502 (2011).
11Y. K. Jeong, J.-H. Lee, S.-J. Ahn, S.-W. Song, H. M. Jang, H. Choi, and J. F. Scott, J. Am. Chem. Soc. 134, 1450 (2012).
12R. R. Burns, Mineralogical Applications of Crystal Field Theory, Second Edition (Cambridge University Press, Cambridge, 1993).
13A. B. P. Lever, Inorganic Electronic Spectroscopy (Elsevier Science Publisher B. V., Amsterdam, 1984).
14F. J. Kahn, P. S. Pershan and J. P. Remeika, Phys. Rev. 186, 891 (1969).
15R. V. Pisarev, A. S. Moskvin, A. M. Kalashnikova, and Th. Rasing, Phys. Rev. B 79, 235128 (2009).
16A. B. Souchkov, J. R. Simpson, M. Quijada, H. Ishibashi, N. Hur, J. S. Ahn, S. W. Cheong, A. J. Millis, and H. D. Drew, Phys. Rev. Lett. 91, 027203 (2003).
17A. M. Kalashnikova and R. V. Pisarev, JETP Lett. 78, 143 (2003).
18F. Palacio, J. Chem. Phys. 82, 837 (1976).
19P. A. Usachev, R. V. Pisarev, A. M. Balbashov, A. V. Kimel, A. Kirilyuk, Th. Rasing, Phys. Sol. State 47, 2292 (2005).
20J.-S. Zhou and J. B. Goodenough, Phys. Rev. B 77, 132104 (2008).
21R. V. Pisarev, A. M. Kalashnikova, O. Schöps, L. N. Bezmaternykh, Phys. Rev. B 84, 075160 (2011).
22H. Terasawa, T. Kambara, K. I. Gondaira, T. Teranishi, and K. Sato, J. Phys. C: Sol. St. Phys. 13, 5615 (1980).