

Optical and Magneto-Optical Studies of a Multiferroic GaFeO_3 with a High Curie Temperature

A. M. Kalashnikova¹, R. V. Pisarev¹, L. N. Bezmaternykh², V. L. Temerov²,
A. Kirilyuk³, and Th. Rasing³

¹ Ioffe Physicotechnical Institute, Russian Academy of Sciences, Politekhnicheskaya ul. 26, St. Petersburg, 194021 Russia
e-mail: kalashnikova@mail.ioffe.ru

² Kirenskiĭ Institute of Physics, Siberian Division, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia

³ IMM, Radboud University of Nijmegen, 6525 ED Nijmegen, The Netherlands

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Single crystals of a noncentrosymmetric orthorhombic pyroelectric ferrimagnet $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$ with a Curie temperature within 260–345 K have been grown by the flux method. It has been found that the electrical properties of the single crystals varied over a broad range from 10^5 to 10^{13} Ω cm depending on the presence of transition-metal oxide impurities. The dispersion relations for all three principal dielectric functions of orthorhombic GaFeO_3 have been determined in the range 0.7–5.4 eV by spectroscopic ellipsometry. The spectra of the dielectric functions of the orthorhombic $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$ crystals are compared with the spectra of the trigonal crystals. The Faraday effect and second-harmonic generation are studied, and the law of the transition to the paramagnetic state has been determined. The crystallographic and magnetic contributions to the second-harmonic generation are analyzed. © 2005 Pleiades Publishing, Inc.

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Materials and multiphase heterostructures characterized by several coexisting order parameters are referred to as multiferroics [1] and have been known since the 1960s [2, 3]. Although they demonstrate interesting physical phenomena such as magnetoelectric and piezomagnetic effects, attempts at designing devices based on these effects proved to be unsuccessful because of the small values of their cross susceptibilities between different order parameters. However, some works have recently reported about “giant” cross susceptibilities in multiferroics [2–5]. This would open up real possibilities for the practical use of these materials in magneto- and optoelectronics. At present, the inquiries into multiferroics are based, on the one hand, on a more advanced technological base and, on the other, on the possibility of theoretical and *ab initio* predictions of materials and structures with predetermined physical properties. It is also worth noting that, since early works on multiferroics, the physical methods of investigation have become much more elaborated, so that there is a real possibility to study phenomena that were inaccessible and even unknown 30–40 years ago. As an example, we mention the spectroscopic studies of optical harmonic generation in multiferroics [6].

In this work, we report optical and magneto-optical properties of a multiferroic $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$ [7] that is an interesting object for physical study and can become a basis for new promising materials because of its high transition temperature to the paramagnetic state and, as

a consequence, because the electric and magnetic order parameters interact in it at room temperature. The specific feature of this material is that, depending on the value of x , its crystal structure and physical properties change. Of the greatest interest are the compositions with concentration $0.7 \leq x \leq 1.4$, which crystallize in the noncentrosymmetric pyroelectric $Pc2_1n$ structure [8] with the spontaneous polarization directed along the y axis. Such materials are ferrimagnets (magnetic space group $Pc2_1n$) [9, 10] with the ferrimagnetic moment directed along the z axis. The Curie temperature T_C significantly depends not only on the concentration of magnetic iron ions Fe^{3+} , increasing with x , but also on the preparation technique [9–11]. For instance, the Curie temperature of the single crystals grown by the “flux” method is considerably higher than for crystals grown by the floating zone method.

To prepare single crystals with the highest T_C , we applied the flux method. To reduce the possible variations in the basic composition of the grown single crystals, we chose fluxes based on sodium tetramolybdate 90 wt % ($\text{Na}_2\text{O} + 4\text{MoO}_3$) + 10 wt % $\text{Ga}_{0.5}\text{Fe}_{1.5}\text{O}_3$. In this case, the iron distribution coefficient between the crystal and the flux is close to unity. Depending on the growth temperature and the additions of bivalent (Co, Ni, Cu, Zn) or trivalent (Cr, Sc, La) metal oxides, T_C of the grown crystals varied in the range from 260 to 345 K. An unexpected fact was that, upon the introduction of bivalent metal oxides into the flux, the electrical

resistivity increased from 10^6 – 10^7 to 10^{13} Ω cm. Upon the introduction of titanium dioxide (TiO_2), the resistivity decreased to 10^5 Ω cm. The impurities of trivalent metal oxides showed no effect.

The structure of prepared single crystals was monitored by the x-ray method, and the obtained unit-cell parameters were in agreement with the literature data [8, 11]. The fact that the crystal structure is noncentrosymmetric was also confirmed by analyzing the temperature dependences of the damping of elastic vibrations excited by the electrical (sample inside capacitor) and magnetic (sample inside coil) methods in polished spheres with a diameter of 1–2 mm [12]. Figure 1 shows the temperature dependences obtained for the relative amplitudes of piezoelectric (A^{piezo}) and magnetic (A^{mag}) signals, for the reciprocal Q factor Q^{-1} of the piezoelectric signal, the logarithm of resistance $\log R$, and the frequency f of the elastic oscillations of one of the samples obtained from the flux with additions of cobalt oxide (Co/Fe = 6 at. %). The magnetic signal disappears in the region of T_C , while the amplitude of the piezoelectric signal rapidly decreases at temperatures above 400 K. The disappearance of the piezoelectric signal is accompanied by the deterioration of the Q factor of elastic vibrations.

We now discuss the optical properties. The linear polarization $P_i(\omega)$ in the electric field $E_j(\omega)$ of the light wave can be written in the form

$$P_i(\omega) = [\alpha_{ij}^{(i)}(\omega) + i\beta_{ij}^{(c)}(\omega) + \gamma_{ijk}^{(c)}(\omega)k_k(\omega)]E_j(\omega), \quad (1)$$

where the tensors $\hat{\alpha}^{(i)}$, $\hat{\beta}^{(c)}$, and $\hat{\gamma}^{(c)}$ describe the optical and magneto-optical susceptibilities and the linear magneto-optical spatial dispersion, respectively. The superscripts (i) and (c) indicate that the tensor is invariant or noninvariant under time reversal, respectively [13]. For the magnetic point group $m'2'm$, the $\alpha_{xx}^{(i)} \neq \alpha_{yy}^{(i)} \neq \alpha_{zz}^{(i)}$ and $\beta_{xy}^{(c)} \neq \beta_{yx}^{(c)}$ components are nonzero.

The result that the $\hat{\alpha}^{(i)}$ has three independent tensor components is quite obvious for a biaxial crystal. The fact that $\beta_{xy}^{(c)} \neq \beta_{yx}^{(c)}$ indicates that the spontaneous magneto-optical effect should be observed for the light propagation along the z axis, along which the ferrimagnetic moment is aligned. However, in contrast to the Faraday effect in isotropic media, where the natural waves are circularly polarized, the natural waves propagating along the z axis in orthorhombic crystals are polarized elliptically below T_C . Note that the magnetic symmetry allows for the magnetoelectric effect with the tensor components of the $xy \neq yx$ type, which was observed in [14] and interpreted as the manifestation of the toroidal momentum. The possibility of new nonreciprocal optical effects in GaFeO_3 was pointed out in [15]. The observation of the optical magnetoelectric effect was reported in [16].

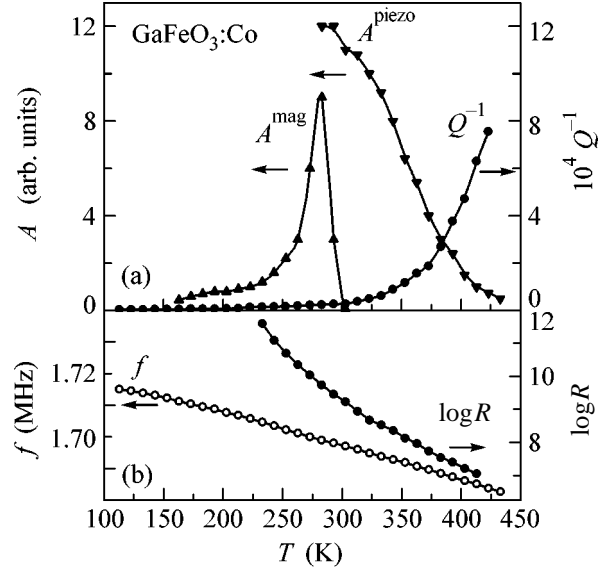


Fig. 1. Temperature dependences of the (a) relative amplitudes of piezoelectric A^{piezo} and magnetic A^{mag} signals, the reciprocal Q factor Q^{-1} of the piezoelectric signal, and (b) logarithm of resistance $\log R$ and frequency f of elastic vibrations in the GaFeO_3 single crystal prepared from a melt with additions of cobalt oxide.

The expression for the nonlinear polarization $P_i(2\omega)$ can be written in the form

$$P_i(2\omega) = [\chi_{ijk}^{(i)}(\omega) + i\chi_{ijk}^{(c)}(\omega)]E_j(\omega)E_k(\omega), \quad (2)$$

where the tensors $\hat{\chi}^{(i)}$ and $\hat{\chi}^{(c)}$ account for the optical second harmonic generation of the crystalline and magnetic nature, respectively. These tensors have nonzero components of the type [11, 13, 17]

$$\chi_{ijk}^{(i)} \begin{cases} a = yxx, b = yyy, c = yzz, \\ d = xxy = xyx, e = zzy = zyz; \end{cases} \quad (3)$$

$$\chi_{ijk}^{(c)} \begin{cases} A = xxx, B = xyy, C = xzz, \\ D = yyx = yxy, E = zzx = zxz. \end{cases} \quad (4)$$

Note that the occurrence of the magnetic second-harmonic components directly follows from the noncentrosymmetry of the crystal structure. The tensor $\hat{\chi}^{(c)}$ has only odd components in the x indices and is identical to the tensor of the piezomagnetic effect [13], which is probably responsible for the appearance of the magnetic acoustic signal A^{mag} (Fig. 1).

In the general case, the linear and nonlinear properties of transition-metal oxides in the optical range are determined by the electronic transitions in magnetic ions in the crystal field, by the charge-transfer transition, and by interband transitions. In order to reveal the main features of the electronic structure of the multiferroic $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$, we carried out an ellipsometric study in the range 0.7–5.4 eV for several differently oriented

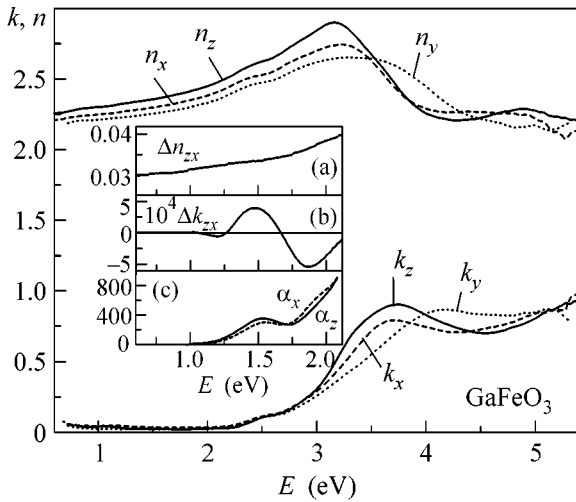


Fig. 2. Absorption coefficients k and refractive indices n vs. the photon energy E for three principal light polarizations. Inset: the spectral dependences of (a) birefringence $\Delta n_{zx} = n_z - n_x$, (b) dichroism $\Delta k_{zx} = k_z - k_x$, as calculated from transmission ellipsometry, and (c) absorption.

GaFeO₃ samples. This allowed us to determine the dielectric functions $\epsilon = \epsilon' - i\epsilon''$ for the three principal axes of the orthorhombic crystal (Figs. 2, 3). Figure 2 shows the spectra of the absorption coefficients k_i and refractive indices n_i . Two maxima are clearly seen in the region of weak absorption (inset in Fig. 2). They are typical for the majority of trivalent iron oxides and can reliably be assigned to the localized transitions from the ground 6A_1 state to the 4T_1 (~1.5 eV) and 4T_2 (~2.0 eV) levels [18]. The feature near 1.25 eV is likely due to the splitting of the 4T_1 level by the trigonal component arising in the crystal field as a result of displacement of the Fe³⁺ ions along the polar axis y [16]. The feature in the region of 2.5 eV was assigned to the ${}^6A_1 \rightarrow {}^4A_1, {}^4E$ transition.

The dielectric functions ϵ' and ϵ'' and their decomposition in several oscillators are shown in Fig. 3 for the three principal directions. The decomposition is performed in the Lorentz model according to the formula

$$\epsilon = \epsilon_0 + bE + \sum \frac{f_j}{E_j^2 - E^2 - iE\gamma_j}, \quad (5)$$

where the term bE is introduced to take into account the transitions occurring at energies higher than the energy range under study. With the object of revealing trends in the variations of dielectric functions of the Ga_{2-x}Fe_xO₃ system with changes in the gallium/iron ratio, the ellipsometric study was carried out for single crystals of the composition Ga_{0.25}Fe_{1.75}O₃ that crystallize in the trigonal structure of the α -Fe₂O₃ hematite type. The dielectric functions of this uniaxial material and their decomposition in the main oscillators for two principal light polarizations are shown in Figs. 4b and 4c. The comparison of these results with the dielectric functions for GaFeO₃ (Fig. 3) allows the following conclusions to be drawn.

(i) The spectral decomposition for Ga_{0.25}Fe_{1.75}O₃ gives a more structured pattern than for GaFeO₃. This result is understandable because the iron ions in trigonal Ga_{0.25}Fe_{1.75}O₃ are situated in the equivalent crystallographic positions, while, in the orthorhombic GaFeO₃, they occupy three nonequivalent octahedral positions [8]. The results of calculation of the electronic structure of the iron ion in the octahedral cluster of oxygen ions in the cubic-field approximation [19] are presented in Fig. 4a.

(ii) An increase in the concentration of iron ions results in a noticeable low-energy shift of the main absorption maximum and an increase in its intensity. In Ga_{0.25}Fe_{1.75}O₃, the main maximum is situated near 3.0 eV and has intensity $\epsilon'' \sim 6.2$ ($E \parallel z$) and 8.2 ($E \perp z$), whereas the main maximum in GaFeO₃ is positioned at 3.6 eV ($E \parallel x, z$) and 3.9 eV ($E \perp y$) and has intensity $\epsilon'' \sim 4.5$ –5.

(iii) Noteworthy also is a considerable increase in the intensity of localized ${}^6A_1 \rightarrow {}^4A_1, {}^4E$ transitions

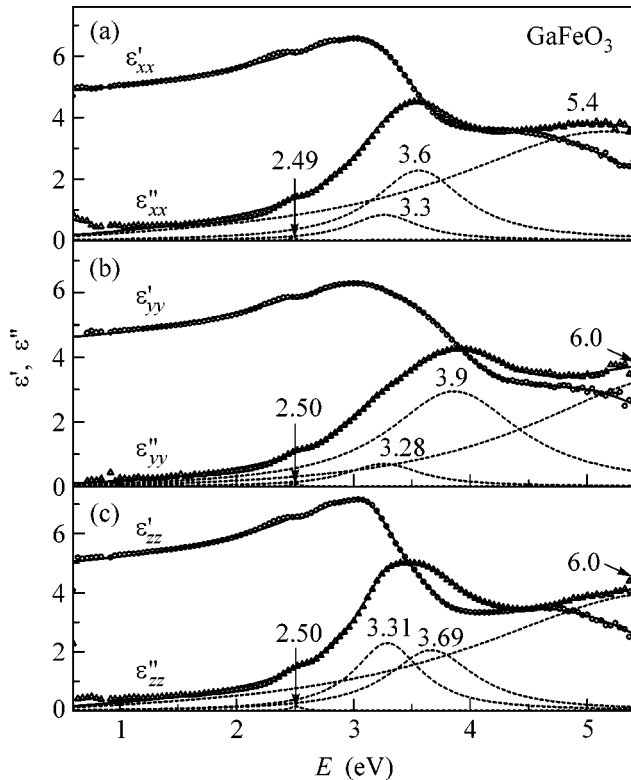


Fig. 3. (Points) Spectral dependences of the dielectric functions ϵ' and ϵ'' of GaFeO₃ for three principal polarizations and (dotted lines) their decomposition into main oscillators. Numerals indicate the positions of the main transitions in electron volts.

near 2.5 eV in $\text{Ga}_{0.25}\text{Fe}_{1.75}\text{O}_3$. This is caused by the strengthening of mixing of the 3d-states with the allowed electric-dipole charge-transfer transitions because of their high intensity and proximity to the localized transitions.

The study of spontaneous optical rotation was carried out on a plate 60- μm thick whose normal was directed along the y axis. The wave vector was perpendicular to the x axis and made an angle $\alpha \sim 20^\circ$ with the y axis (the direction of the light beam in the sample was $\sim 10^\circ$), and the magnetizing field was directed along the z axis. Due to birefringence, the rotation of the polarization plane observed in this geometry is not the true Faraday effect that is determined by the $\beta_{xy} \neq \beta_{yx}$ components. The temperature dependences of the residual rotation angle θ_F of the polarization plane are shown in Fig. 5. The effect disappears at $T \approx 260$ K, which we identify as the Curie temperature of the sample. The hysteresis loops for θ_F for several temperatures are presented in the inset in Fig. 5.

The second-optical-harmonic generation, which is related to the crystallographic and magnetic contributions by formula (2), was studied on the same sample and in the same geometry as for the Faraday effect. Earlier, the second-harmonic generation was studied only for GaFeO_3 crystals prepared by the floating zone method and having $T_C \sim 200$ K [17, 20]. A change in the magnetic contribution to the second-harmonic generation is clearly seen from the temperature dependence of

the magnetic contrast $\frac{I^{2\omega}(+H) - I^{2\omega}(-H)}{I^{2\omega}(+H) + I^{2\omega}(-H)}$ of the sec-

ond-harmonic signal (Fig. 5). One can see that the temperature dependences of the linear rotation of the polarization plane and the nonlinear magnetic contrast obey the power law $(1 - T/260.0(4))^{0.37(4)}$; i.e., this sample undergoes transition to the paramagnetic state at $T_C \approx 260$ K. The azimuthal dependences for a photon energy of ~ 1.54 eV are shown in Fig. 6 for the opposite field directions $\pm H \parallel z$ and two polarizations of the second harmonic. Using Eq. (2) and Eqs. (3) and (4) for the tensor components of nonlinear susceptibility and performing appropriate coordinate transformations [21], we arrive at expressions describing the dependences of the second-harmonic intensities on the azimuth φ of pump polarization:

$$I_{\parallel x}^{2\omega} \propto |A \cos^2 \varphi + (B \sin^2 \alpha + C \cos^2 \alpha) \sin^2 \varphi + d \sin 2\varphi \sin \alpha|^2; \quad (6)$$

$$I_{\perp x}^{2\omega} \propto |[a \cos^2 \varphi + (b \sin^2 \alpha + c \cos^2 \alpha) \sin^2 \varphi + D \sin 2\varphi \sin \alpha] \sin \alpha \quad (7)$$

$$+ [e \sin^2 \varphi \sin 2\alpha + E \sin 2\varphi \cos \alpha] \cos \alpha|^2.$$

The results of calculations by formulas (6) and (7) are shown in Fig. 6 by hatched regions. When calculating,

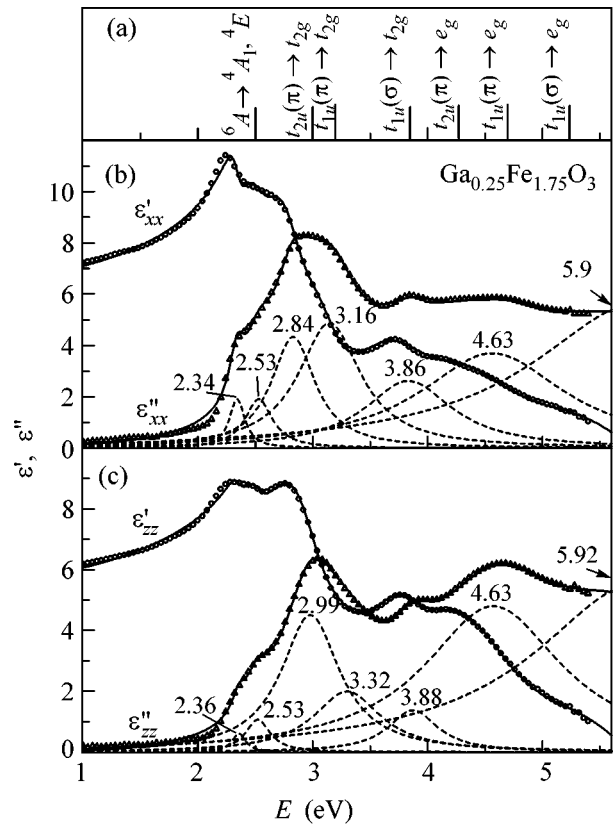


Fig. 4. (a) Main transitions in iron oxides calculated in the cubic-field approximation [19] and (b), (c) (points) spectra of the dielectric functions ϵ' and ϵ'' of the uniaxial crystal $\text{Ga}_{0.25}\text{Fe}_{1.75}\text{O}_3$ and (dotted lines) their decomposition into main oscillators for the principal light polarizations.

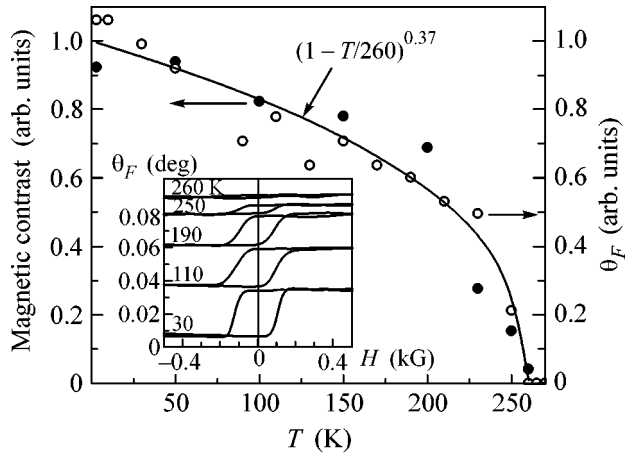


Fig. 5. Temperature dependences of (open circles) the rotation θ of the polarization plane and (closed circles) the magnetic contrast of the second harmonic. The solid line is the function $(1 - T/260.0(6))^{0.37(4)}$. Inset: the field dependences of the rotation of the polarization plane for several temperatures.

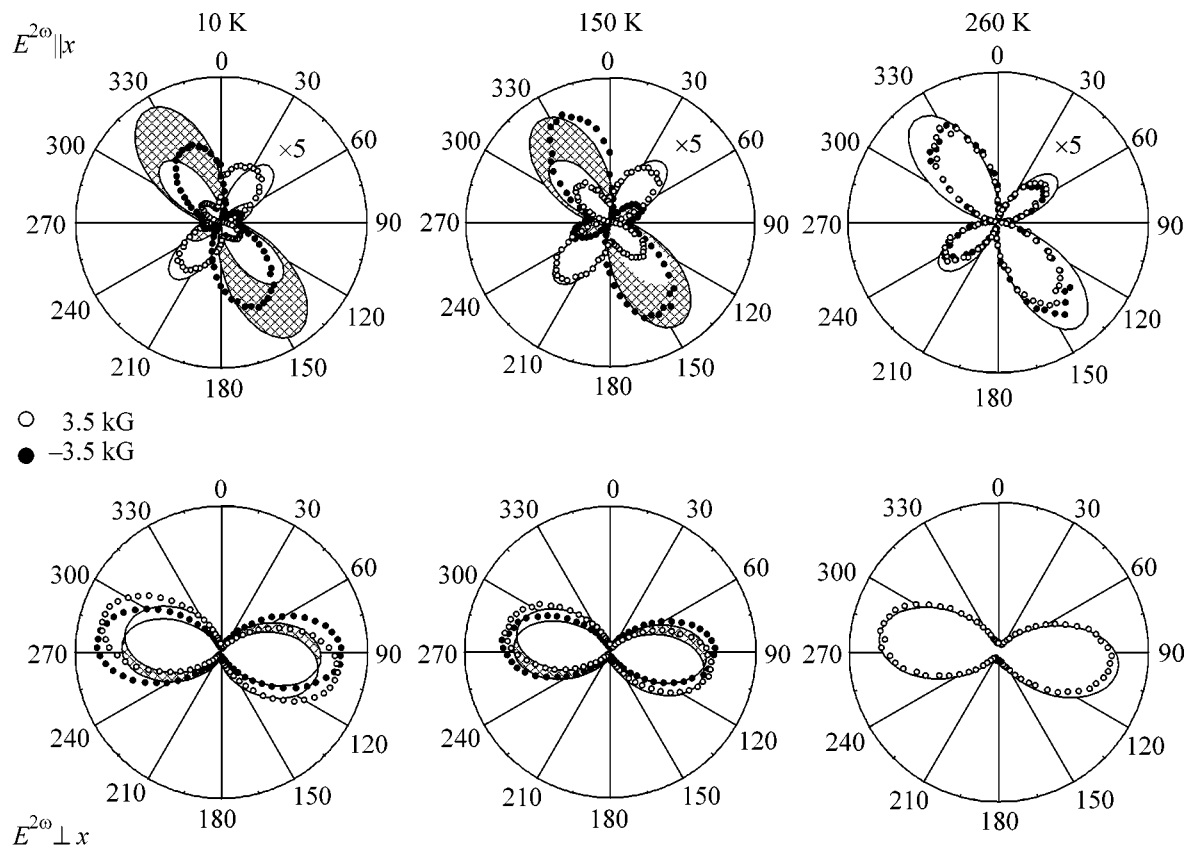


Fig. 6. Azimuthal dependences of second-harmonic intensities for the $E^{2\omega} \parallel x$ and $E^{2\omega} \perp x$ polarizations in a field $\pm H \parallel z$ for several temperatures. The solid lines are calculations by formulas (6) and (7).

we took into account a small misorientation of the crystal axes about the laboratory coordinate systems. We attribute the discrepancy between the experimental and calculated dependences to the disregard of the influence of strong birefringence.

In summary, the optical and magneto-optical properties of a noncentrosymmetric orthorhombic orthoferrite GaFeO_3 that has T_C in the range 260–345 K and is grown by the flux method have been studied in this work. The dielectric functions for the three principal crystallographic axes have been obtained over a broad spectral range. The comparison of these spectra with the spectra of trigonal $\text{Ga}_{0.25}\text{Fe}_{1.75}\text{O}_3$ has shown that an increase in the concentration of the Fe^{3+} ions gives rise to the low-energy shift of the fundamental absorption edge. Since the iron ions in orthorhombic GaFeO_3 occupy three nonequivalent crystallographic positions, the pattern of charge-transfer transitions is more pronounced in trigonal $\text{Ga}_{0.25}\text{Fe}_{1.75}\text{O}_3$, where Fe^{3+} ions occupy only equivalent positions. The study of the magneto-optical Faraday effect and second-harmonic generation in a magnetic field allows for the determination of the transition law to the paramagnetic state for GaFeO_3 .

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REFERENCES

1. K. Aizu, *Phys. Rev. B* **2**, 754 (1970).
2. G. A. Smolenskii and I. E. Chupis, *Usp. Fiz. Nauk* **137**, 415 (1982) [*Sov. Phys. Usp.* **25**, 475 (1982)].
3. H. Schmid, in *Introduction to Complex Mediums for Optics and Electromagnetics*, Ed. by W. S. Weigliger and A. Lakhtakia (SPIE Press, Bellingham, 2003), pp. 167–195.
4. T. Kimura, T. Goto, H. Shintani, *et al.*, *Nature* **429**, 392 (2004).
5. J. Wang, J. B. Neaton, H. Zheng, *et al.*, *Science* **299**, 1719 (2003).
6. M. Fiebig, V. V. Pavlov, and R. V. Pisarev, *J. Opt. Soc. Am. B* **22**, 96 (2005).
7. J. P. Remeika, *J. Appl. Phys.* **31**, 263S (1960).
8. S. C. Abrahams, J. M. Reddy, and J. L. Bernstein, *J. Chem. Phys.* **42**, 3957 (1965).
9. R. B. Frankel, N. A. Blum, S. Foner, *et al.*, *Phys. Rev. Lett.* **15**, 958 (1965).

10. B. F. Levin, C. H. Nowlin, and R. V. Jones, *Phys. Rev.* **174**, 571 (1968).
11. T. Arima, D. Higashiyama, Y. Kaneko, *et al.*, *Phys. Rev. B* **70**, 064426 (2004).
12. R. G. LeCraw and R. L. Comstock, in *Physical Acoustics. Principles and Methods*, Ed. by W. P. Mason (Academic, New York, 1965; Mir, Moscow, 1968), Vol. 3, Part B.
13. R. R. Birss, *Symmetry and Magnetism* (North-Holland, Amsterdam, 1966).
14. Yu. F. Popov, A. M. Kadomtseva, G. P. Vorob'ev, *et al.*, *Zh. Éksp. Teor. Fiz.* **114**, 263 (1998) [*JETP* **87**, 146 (1998)].
15. A. K. Zvezdin, *Kratk. Soobshch. Fiz.*, No. 6, 35 (2000).
16. J. H. Jung, M. Matsubara, T. Arima, *et al.*, *Phys. Rev. Lett.* **93**, 037403 (2004).
17. K. Eguchi, Y. Tanabe, T. Ogawa, *et al.*, *J. Opt. Soc. Am. B* **22**, 128 (2005).
18. R. V. Pisarev, *Fiz. Tverd. Tela (Leningrad)* **7**, 207 (1965) [*Sov. Phys. Solid State* **7**, 158 (1965)].
19. A. I. Likhtheim, A. S. Moskvina, and V. A. Gubanov, *Fiz. Tverd. Tela (Leningrad)* **24**, 3596 (1982) [*Sov. Phys. Solid State* **24**, 2049 (1982)].
20. Y. Ogawa, Y. Kaneko, J. P. He, *et al.*, *Phys. Rev. Lett.* **92**, 047401 (2004).
21. V. N. Gridnev, V. V. Pavlov, R. V. Pisarev, *et al.*, *Phys. Rev. B* **63**, 184407 (2001).

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