Anomalous magnetooptical properties of bismuth-containing iron garnets

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The equatorial and polar Kerr effects are investigated for two bismuth-containing garnet systems in the 2.0–3.4 eV region. Record values for the equatorial Kerr effect of the order of 16% are obtained, the samples having an almost vanishing saturation magnetization. It is shown that the anomalously high magnetooptical characteristics of the bismuth-containing garnets are due to enhancement of the $t_2(\pi, \sigma) \rightarrow e^*(\pi)$ optical transition in the FeO_4 tetrahedral complexes induced by Bi ions.

Sharply pronounced singularities were observed in[1] on the plots of the equatorial Kerr effect δ against the frequency for yttrium, terbium, and europium iron garnets in the region 2.4–2.9 eV. These singularities were attributed to the two lowest-energy transitions in tetrahedral molecular complexes of FeO_4, namely $t_1(\pi) \rightarrow e^*(\pi)$ (A) and $t_2(\pi, \sigma) \rightarrow e^*(\pi)$ (B). It is important that in this case we are dealing with the first allowed molecular-orbital transitions of the charge-transfer type, which are responsible for infrared magneto-optical properties of iron garnets, and it is therefore just their behavior which can explain the origin of the previously observed[2,3] anomalously large Faraday effect in bismuth-containing garnets.

Wittekoek and Lacklison[4] have connected, on the basis of measurements of the polar Kerr effect α_K in a bismuth-calcium-vanadium garnet with composition $Bi_{0.8}Ca_{2.2}V_{1.1}Fe_{3.9}O_{12}$, the increase of the Faraday effect with the two aforementioned tetrahedral transitions. They have assumed, however, that these transitions are magneto-optically inactive in a simple yttrium garnet, and become active only under the influence of the bismuth-containing garnets, since the transitions A and B were not observed on the $\alpha_K(\omega)$ curves of yttrium garnet in[4], nor were they observed in earlier studies by Kahn et al.[5]. In[1], the tetrahedral transitions $t_1(\pi) \rightarrow e^*(\pi)$ and $t_2(\pi, \sigma) \rightarrow e^*(\pi)$ could be displayed even in pure yttrium and rare earth garnets, so that it was possible to trace the variation of these transitions in the garnet following introduction of bismuth ions, starting with low concentration up to complex compositions.

We present here the results of measurements of the equatorial and polar Kerr effects in two systems of bismuth-containing garnets, $Y_{3-x}Bi_xFe_5O_{12}$ ($x = 0.07$, 0.22, 0.3) and $Bi_{3-2y}Ca_{2y}V_yFe_{5-y}O_{12}$ ($y \approx 1$, the region near the compensation point). It is shown that the anomalously high magneto-optical activity of the bismuth-containing garnets is connected with the enhancement of the transitions A and B in the tetrahedral iron ions under the influence of the bismuth.

The equatorial and polar Kerr effects were measured by a dynamic method with a ZMR-3 monochromator. A schematic diagram of the setup used to measure the polar effect is shown in Fig. 1. When the equatorial effect was measured, one mirror and the analyzer were removed and the electromagnet was replaced. The samples were placed between the poles of the electromagnets so constructed that alternating fields up to 15 kOe in the case of the polar effect and 8 kOe in the case of the equatorial effect could be obtained with little stray induction in the receiver. In the measurement of the equatorial Kerr effect, the angle at which the light was incident on the sample was set in the range from 10 to 80°, with accuracy no less than 5′ in the center of the beam at a beam aperture ±30′. The error in the measurement of δ was $\pm 5 \times 10^{-5}$. In the measurement of the polar effect, the light-incidence angle was 3–5°. The measurements were performed on the p- and s-components of linearly polarized light.

The graphs show the averaged values of $\alpha_K = (\alpha_K^s + \alpha_K^p)/2$, corresponding to normal incidence of light. The angle between the polarization planes of the polarizer and analyzer was 45°. The error in the measurement of the rotation angle of the polarization plane was ±0.08′ in this case. The values of δ and α_K; shown in the figure correspond to variation of the sample magnetization from zero to I_S. The receiver was an FÉU-39A photomultiplier, the ac component of the signal (f = 70 Hz) was amplified by a V6-2 selective amplifier and recorded with a V9-2 synchronous detector. The samples were polished plates cut from a bulky single crystal. The compositions of the measured samples, the saturation magnetizations, and the values of the Faraday effect α_F at a wavelength $\lambda = 0.63\ \mu$ are listed in the table. The serial numbers of the samples in the table correspond to the numbers on the curves in the figures.

Figures 2 and 3 show the frequency dependences of the equatorial effect δ for light-incidence angles $\varphi = 65°$ and $\varphi = 70°$. The following features of the experimental curves could be noted: the intensity of the positive maxima at $\hbar\omega = 2.57$ eV (transition A) and $\hbar\omega = 2.75$ eV (transition B) increases sharply when even a small amount of bismuth ($x = 0.07$) is introduced, and continues to increase with increasing bismuth content. The increase of the second maximum (B) is much greater, so that conceivably the intensity of the first maximum (A) may not even increase.

The amplitude of the negative effect at $\varphi = 70°$ in

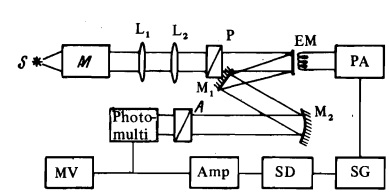

FIG. 1. Schematic diagram of setup: S–light source; M–monochormator; L_1, L_2–objectives; P, A–polarizers; EM–electromagnet; M_1, M_2–mirrors; PA–power amplifier; SG–sound generator; Amp–selective amplifier; SD–synchronous detector; MV–microvoltmeter.

bismuth-calcium-vanadium garnet reaches 0.08, corresponding to a 16% change in the light intensity when the field is reversed, although the magnetization of this garnet is approximately one-fiftieth of the yttrium garnet. It should be emphasized that the value of δ increases sharply for this garnet in the entire visible band. Thus, at the helium-neon laser wavelength $\lambda = 0.63\ \mu$ the commutation Kerr effect reaches 5%. It is seen from the plots of δ for yttrium-bismuth garnets with relatively small bismuth content at $\varphi = 65^\circ$ (Fig. 2) that the increase of the equatorial Kerr effect is indeed due to an enhancement of the magnetic-optical activity of the tetrahedral transitions A and B in the Fe^{3+} ions. According to Crossley et al.[6], the Faraday effect in yttrium garnet in the visible and near-infrared regions is determined by predominance of the contribution of the octahedral sublattice of Fe^{3+} ions over the tetrahedral one. The sharp increase of the magneto-optical activity of the tetrahedral transitions following introduction of the bismuth ions ensured a predominance of the contribution of the tetrahedral sublattice, and thus guarantees a reversal of the sign of rotation of the plane of polarization of α_F.

Sample number	Composition	I_s, G	α_F, deg/cm
1	$Y_3Fe_5O_{12}$	140	750
2	$Y_{2.93}Bi_{0.07}Fe_5O_{12}$	134	−1400
3	$Y_{2.78}Bi_{0.22}Fe_5O_{12}$	144	−2000
4	$Y_{2.7}Bi_{0.3}Fe_5O_{12}$	138	−5900
5	$Ca_{1.96}Bi_{1.04}V_{0.98}Fe_{4.02}O_{12}$	2,8	−11400

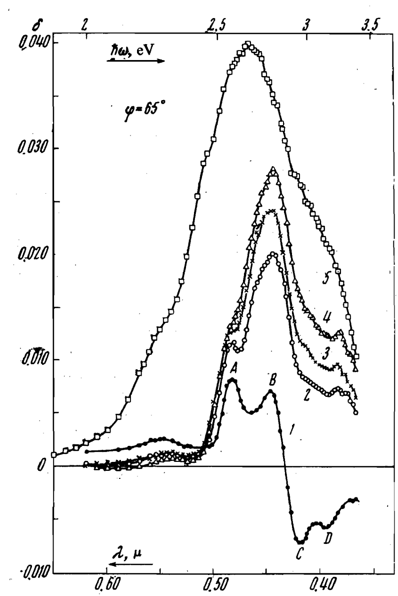

FIG. 2. Equatorial Kerr effect for light incident on the sample at an angle $\varphi = 65^\circ$, $H_\sim \approx 4500$ Oe.

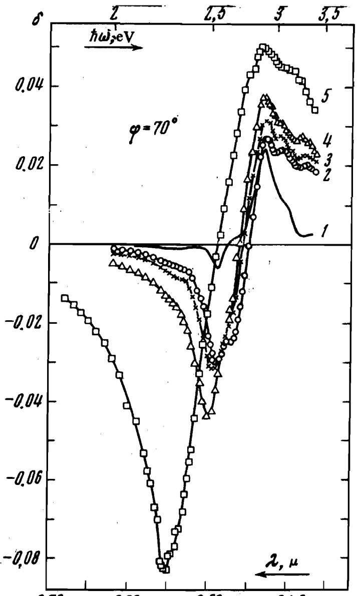

FIG. 3. Equatorial Kerr effect for light incident on the sample at an angle $\varphi = 70^\circ$, $H_\sim \approx 4500$ Oe.

As already noted, the component B (the transition $t_2(\pi, \sigma) \to e^*$) increases particularly sharply in this case, possibly as a result of a difference between the $t_1(\pi)$ and $t_2(\pi, \sigma)$ levels from which the transitions A and B proceed. The molecular orbital $t_1(\pi)$ of the complex FeO_4 consists of atomic $2p(\pi)$ orbitals of oxygen, while the molecular orbital $t_2(\pi, \sigma)$ contains, in addition, an admixture of the atomic orbitals $2p(\sigma)$ of oxygen and $3d(t_2)$ of iron[7]. It is therefore possible that the strong spin-orbit interaction of the 2p electrons of bismuth, which leads to an anomalous increase of the magneto-optical activity of the garnet, is transferred to the molecular orbital $t_2(\pi, \sigma)$ via the indicated additional components $2p(\sigma)$ and $3d(t_2)$. Favoring the assumption that the orbital $t_2(\pi, \sigma)$ is more sensitive to the influence of the ions in the dodecahedral sites of the garnet is also the fact[1] that the intensity of the component B is strongly altered also in the rare-earth terbium and europium garnets. For the bismuth-calcium-vanadium garnet, in which the bismuth content is much larger than in the yttrium-bismuth garnets, and which contains also the ions Ca^{2+} and V^{5+}, one observes more appreciable changes in the δ curves, namely an increase of the effect in the entire visible range and a shift of the singularities by approximately 0.1 eV into the long-wave region.

We note also the possibility of identifying the negative maxima at $\hbar\omega = 2.95$ eV (C) and 3.14 eV (D) on the δ curves at $\varphi = 65^\circ$ for the yttrium garnet. They are attributed in[8] to the transitions $t_{2u}(\pi) \to t_{2g}^*$ and $t_{1u}(\pi) \to t_{2u}^*$ in the octahedral complexes FeO_6. On the

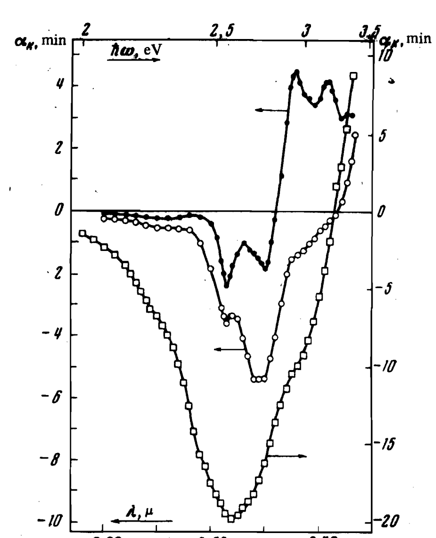

FIG. 4. Polar Kerr effect. $H_\sim \approx 5$ kOe, ●—sample No. 1, ○—No. 2, □—No. 5.

basis of the results of Kahn et al.[5], who measured substituted europium garnets, we have proposed in[1] that these negative maxima are sections of dispersion curves due to the tetrahedral transitions A and B. However, the reversal of the signs of the maxima C and D relative to A and B, and also the fact that they are not enhanced to yttrium-bismuth garnets, makes the first identification more probable, namely, that the negative maxima of C and D are due to the allowed transitions with lowest energies in the octahedral complexes FeO_6. As a result we obtain for the tetrahedral transitions $t_1(\pi) \rightarrow e^*(\pi)$ and $t_2(\pi, \sigma) \rightarrow e^*(\pi)$ in iron garnets the characteristic frequencies 2.55 and 2.75 eV, and for the octahedral transitions $t_{2u}(\pi) \rightarrow t_{2g}^*$ and $t_{1u}(\pi) \rightarrow t_{2g}^*$ the respective frequencies 2.95 and 3.14 eV. We note also that at the indicated identification the eigenfrequencies of the octahedral transitions turns out to be practically the same both for garnets and for orthoferrites[5], whereas in[4] it was necessary to shift these transitions for yttrium garnet in the 4.0 eV region.

Figure 4 shows the frequency dependences of the polar Kerr effect α_K for the yttrium and two bismuth-containing garnets. The α_K curve for the yttrium garnet was obtained with a sample cut from the natural (110) face. It agrees qualitatively with the results of the measurements in[4,5], but our curve revealed two negative peaks (2.55 and 2.75 eV) and two positive peaks (2.95 and 3.15 eV) corresponding to the transitions A, B, C, and D, previously observed on the δ curves. An enhancement of the transition B is seen also on the curve for the yttrium-bismuth garnet.

The maximum value of the polar Kerr effect (approximately 20 min) was obtained with the calcium-bismuth-vanadium garnet at $\hbar\omega = 2.7$ eV. This $\alpha_K(\omega)$ curve also reveals for anomalies corresponding to the transitions A, B, C, and D shifted into the long-wave region. It should be noted that on the δ and α_K curves of all the investigated garnets one observes a weak anomaly in the region of 2.25 eV (0.5 μ), which can be identified in accordance with[5] with the "crystalline" transition ${}^6A_{1g}({}^6S) \rightarrow {}^4E_g({}^4G)$, ${}^4A_{1g}({}^4G)$. The intensity of this transition does not depend on the bismuth concentration (Figs. 2—4), in agreement with the assumption that it is a crystalline rather than a molecular-orbital transition.

[1] G. S. Krinchik and V. A. Krylova, ZhETF Pis. Red. 16, 267 (1972) [JETP Lett. 16, 188 (1972)].
[2] C. F. Buhrer, J. Appl. Phys., 40, 4500 (1969); 41, 1393 (1970).
[3] R. V. Pisarev, E. V. Berdennikova, and R. A. Petrov, Fiz. Tverd. Tela 12, 1547 (1970) [Sov. Phys.-Solid State 12, 1218 (1970)]; Izv. AN SSSR ser. fiz. 30, 1184 (1971).
[4] S. Wittekoek and D. E. Lacklison, Phys. Rev. Lett., 28, 740 (1972).
[5] F. J. Kahn, R. S. Pershan, and J. P. Remeika, Phys. Rev., 186, 891 (1969).
[6] W. A. Crossley, R. W. Cooper, J. L. Page, and R. P. van Stapele, Phys. Rev., 181, 896 (1969).
[7] C. J. Ballhausen and A. D. Liehr, J. Mol. Spectr., 2, 342 (1958).
[8] G. S. Krinchik, V. A. Krylova, G. K. Tyutneva, and A. P. Khrebtov, Proc. 4th All-Union Conf. on Ferrites, Minsk, 1972.

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