$$\varkappa_{1,2}=\langle\varphi_{1,2}L_{12}\varphi_{2,1}\rangle-\langle\varphi_{1,1}L_{12}\varphi_{2,2}\rangle,\ \varkappa_{2,1}=\langle\varphi_{2,1}L_{21}\varphi_{1,2}\rangle-\langle\varphi_{2,2}L_{21}\varphi_{1,1}\rangle.$$

When the symmetry of the operator $L_{ij}$ is taken into account, the symmetry of the coefficients $\varkappa$ becomes obvious. A similar procedure can be employed also in more complicated cases.

The explicit expressions obtained by us for the kinetic coefficients are convenient for the use of the variational method with a variable functional

$$I={}^1/_2\langle\varphi_i L^{ij}\varphi_j\rangle-\langle D_i\varphi^i\rangle. \tag{32}$$

The solution of the kinetic equations (6) corresponds to a minimum of this functional without any additional conditions. Indeed, let $\varphi_i$ be the solutions of Eqs. (6), and let $(\varphi=\psi)_i$ be a certain trial function. Then

$$\begin{aligned}I(\varphi-\psi)&={}^1/_2\langle(\varphi-\psi)_i L^{ij}(\varphi-\psi)_j\rangle-\langle D_i,(\varphi-\psi)^i\rangle\\&={}^1/_2\langle\varphi_i L^{ij}\varphi_j\rangle+{}^1/_2\langle\psi_i L^{ij}\psi_j\rangle-\langle\psi_i L^{ij}\varphi_j\rangle-\langle D_i\varphi^i\rangle\\&\quad+\langle D_i\psi^i\rangle={}^1/_2\langle\varphi_i L^{ij}\varphi_j\rangle+{}^1/_2\langle\psi_i L^{ij}\psi_j\rangle-\langle D_i\varphi^i\rangle\\&=I(\varphi)+{}^1/_2\langle\psi_i L^{ij}\psi_j\rangle.\end{aligned}$$

By virtue of the self-adjoint character of $L$

$$\langle\psi_i L^{ij}\psi_j\rangle\geqslant 0,$$

and consequently the functional is minimal at $\psi=0$. The absence of any additional conditions when this functional is used constitutes its substantial advantage over the functional proposed by Kohler.[4]

The connection of the functional $I$ with the Kohler functional $\Phi=\langle\varphi_i L^{ij}\varphi_j\rangle$, which was introduced by him for the case of a single-component system, lies in the fact that variation of the latter subject to the additional condition $\langle D_i\varphi^i\rangle=\langle\varphi_i L^{ij}\varphi_j\rangle$, which is taken into account with the aid of Lagrange method, leads precisely to the functional $I$.

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# Magneto-optical spectra of 3*d* ions in spinel ferrites and weak ferromagnets

G. S. Krinchik, A. P. Khrebtov, A. A. Askochenskiĭ, E. M. Speranskaya, and S. A. Belyaev

*Moscow State University*

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The equatorial Kerr effect method was used to investigate the magneto-optical reflection spectra ($\delta(\omega)$ in weak ferromagnets—orthoferrites and hematite—and ferrimagnets—spinel ferrites and chromite ferrites—in the range from 1 to 5.4 eV. It is shown that the threshold of intense absorption in magnetically ordered crystals occurs in the region of the first two-exciton transition $2\times T_{1g}$. As a result of measurements of the chromite ferrites $CoCr_xFe_{2-x}O_4$ and $NiCr_xFe_{2-x}O_4$, in which the $Fe^{3+}$ ions were located either in octahedral or tetrahedral positions, it is revealed that the decisive role is played by optical transitions with participation of ions from both sublattices. In spinel ferrites, optical transitions were observed in the divalent ions $Ni^{2+}$ and $Co^{2+}$. In the region of the transition ${}^4A_2({}^4F)\to{}^4T_1({}^4P)$ in the $CO^{2+}$ ions, values $\sim 10\%$ were obtained for the equatorial Kerr effect at room temperature.

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## INTRODUCTION

The magneto-optical properties of spinel ferrites, garnet ferrites, and certain weak ferromagnets in the infrared and visible regions of the spectrum are determined mainly by the character of the optical transitions, the frequencies of which lie in the near ultraviolet region. The reason is that the first intense optical transitions in the $Fe^{3+}$ ions lie in this band, whereas the visible and infrared regions of the spectrum contain spin-forbidden, and frequently additionally parity-forbidden transitions between the levels of the 3*d* ions in the internal crystal field (crystalline transitions). Ultraviolet optical and magneto-optical spectra of iron garnets have been under intensive study in recent years because new crystals with high magneto-optical quality factors were found, containing bismuth, praseodymium, and neodymium.[1–4] It was established that in the region 2.8–3.3 eV, as well as weak crystalline transitions, there are two or three intense transitions, the origin of which was not finally determined, although it is precisely their enhancement under the influence of bismuth which causes the anomalously high magneto-optical effects in bismuth-containing garnets. Worthy of attention are the following mechanisms whereby the indicated transitions are produced: 1) Charge-transport processes in complexes, from the anions $O^{2-}$ to the cations $Fe^{3+}$ (molecular-orbital transitions in the complexes $FeO_4$ and $FeO_6$); 2) charge-transfer processes between $Fe^{3+}$ ions situated in the octahedral and tetrahedral sublattices; 3) two-ion crystalline transitions (simultaneous excitation of transitions in two $Fe^{3+}$ ions). At the present time there are no reliable grounds for exactly identifying the singularities in the optical and magneto-optical spectra with definite optical transitions. To solve this problem, it is expedient to enlarge the group of investigated crystals containing magnetoactive 3*d* ions. In this paper we attempt, by a purposeful choice of the composition of the investigated ferrites, to help explain the character of the optical transitions of 3*d* ions in the ultraviolet part of the spectrum. The chosen ferromagnetic dielectrics make it possible to trace the variation of the character of the optical transitions in $Fe^{3+}$ ions in different coordinations, estimate the role of the divalent cations $Co^{2+}$, $Ni^{2+}$, and $Fe^{2+}$, and finally, for the purpose of assessing the role of two-ion transitions, create situations in which the magneto-active $Fe^{3+}$ ions are arranged in sequence either in a tetrahedral or in an octahedral sublattice.

## EXPERIMENTAL PROCEDURE AND INVESTIGATED SAMPLES

From among the known magneto-optical effects we chose for the investigation of the 3*d*-ion spectra the equatorial Kerr effect. Kerr effects are observed in reflected light and have different experimental geometries. In the measurement of the equatorial Kerr effect $\delta$, the vector $\mathbf{I}_s$ is parallel to the surface of the sample and is perpendicular to the plane of incidence of the light. The effect is observed in a light component polarized in the plane of incidence of the light beam ($p$ component). After reflection from the magnetized surface, the intensity of the $p$ component changes, whereas the perpendicularly polarized $s$ component is independent of the ferromagnet magnetization in first-order approximation. We measured the effect $\delta = (I - I_0)/I_0 = \Delta I/I_0$, where $I_0$ and $I$ are the intensities of the reflected light from the demagnetized sample and the sample magnetized to saturation. We investigated the spectra $\delta(\omega)$ in the region from 1 to 5.4 eV.

The maximum amplitude of the alternating field in the gap of the electromagnet, in which the investigated sample is placed (the gap width is 5 mm) was 8 kOe. The light was modulated after reflection from the sample at a frequency 70 Hz and focused on a photoreceiver. An M-95 galvanometer registered the dc component of the photomultiplier current. To decrease the photomultiplier noise level, the synchronous detector operated with a large time constant (10 to 60 sec). As a result, the operators made it possible to measure ratios $\Delta I/I_0 \sim 10^{-5}$.

We investigated spinel-ferrite single crystals $NiFe_2O_4$ and $Li_{0.5}Fe_{2.5}O_4$, grown by the method of solution in the melt; $Ni_x^{2+}Fe_{1-x}^{2+}Fe_2^{3+}O_4$ obtained by the Verneuil method; natural magnetite $Fe_3O_4$ single crystals; the orthoferrites $YFeO_3$, $GdFeO_3$, $YbFeO_3$ and $TmFeO_3$, and the hematite $\alpha$-$Fe_2O_3$ (method of solution in the melt); single-crystal epitaxial films $NiFe_2O_4$, $Fe_3O_4$ and $MgFe_2O_4$, obtained by the transport-reaction method, and also polycrystalline spinels $MgFe_2O_4$ and chromite ferrites $CoCr_xFe_{2-x}O_4$ (at $x=0$; 0.25; 0.5; 0.75; 1) and $NiCr_xFe_{2-x}O_4$ (at $x=0$, 0.5, 1), obtained by the standard ceramic technology. The final annealing of the chromite ferrites was carried out at 1300 °C, with the sample kept at this temperature for ten hours in air. An x-ray structure phase analysis has shown that all the samples of the systems are single-phase, and the lattice constants of the system $NiCr_xFe_{2-x}O_4$ and of the ferrite $CoFe_2O_4$ agree with the published data.[5]

To remove the distorted surface layer prior to the measurements, the samples were etched, after the final mechanical polishing, in orthophosphoric acid for an average of 20 seconds at temperature near 200 °C.

## MEASUREMENT RESULTS

*Orthoferrites and hematite.* In rare-earth orthoferrites, the magnetically active ions $Fe^{3+}$ are located in oxygen octahedra. The rare-earth ions have practically no effect on the magneto-optical spectra, and the $\delta(\omega)$ curves of the orthoferrites of yttrium, gadolinium, ytterbium, and thulium, obtained at room temperature, agree in their main outlines. On the $\delta(\omega)$ spectra for Y-orthoferrite (Fig. 1) there is observed a number of clearly pronounced peaks, among which, at $\varphi = 65°$, one

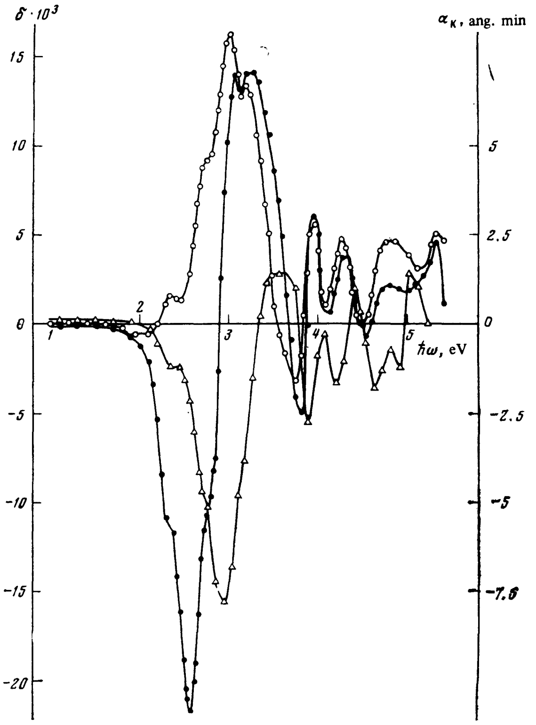

FIG. 1. Equatorial and polar Kerr effects for the single-crystal orthoferrite $YFeO_3$ ((100) plane): ○—light incidence angle $\varphi=65°$, ●—light incidence angle $\varphi=70°$, Δ—polar Kerr effect ($\varphi=0°$).

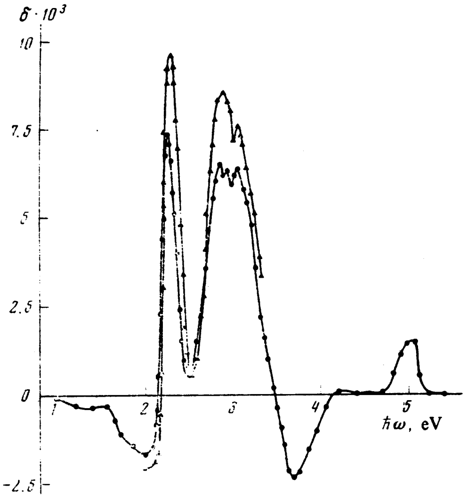

FIG. 2. Equatorial Kerr effects for single-crystal hematite $\alpha$-$\mathrm{Fe_2O_3}$ in the planes (111) and (100) at $\varphi = 70°$: ●—(111) plane ▲—(100) plane.

can note a weak maximum near 2.3 eV and strong maxima in the region 2.7, 3.0, 3.2, 3.9 and 4.2 eV. The low-frequency peaks at 2.35, 2.7, 3.0, and 3.2 eV correspond to the maxima *A*, *B*, *a* and *C* of the imaginary part of the off-diagonal component of the dielectric tensor $\varepsilon_2'$ as determined by Kahn, Pershan, and Remeika[6] from measurements of the polar Kerr effect ($\alpha_K$). Figure 1 shows also the $\alpha_K(\omega)$ plot measured by us, which shows good agreement with[6], and also demonstrates that in this case, just as for iron garnets, measurements of the equatorial Kerr effect have significant advantages over measurements of the polar effect.

The low-frequency sections of the spectra $\delta(\omega)$ for the hematite $\alpha$-$\mathrm{Fe_2O_3}$ (Fig. 2), measured in the (111) and (100) planes, correspond in general outline to the curves for the orthoferrites. However, in the region 2.2–2.4 eV, one can distinguish for the orthoferrites only a weak maximum, which becomes much stronger in hematite.

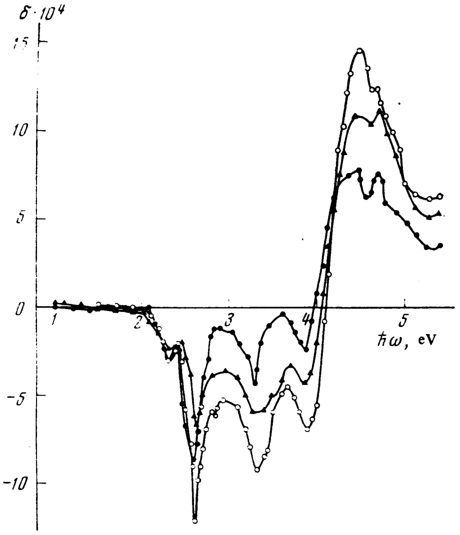

FIG. 3. Equatorial Kerr effect for the spinels $\mathrm{MgFe_2O_4}$ and $\mathrm{Li_{0.5}Fe_{2.5}O_4}$ at $\varphi = 65°$: ●—single crystal $\mathrm{Li_{0.5}Fe_{2.5}O_4}$ ((110) plane), ▲—polycrystal $\mathrm{MgFe_2O_4}$, o—single-crystal film $\mathrm{MgFe_2O_4}$ ((100) plane).

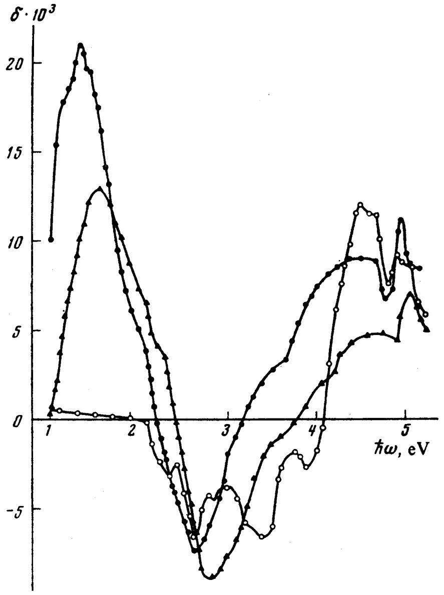

FIG. 4. Equatorial Kerr effect for magnetite $\mathrm{Fe_3O_4}$: ●—bulky single-crystal sample of $\mathrm{Fe_3O_4}$ at $\varphi = 65°$, (110) plane; ▲—the same at $\varphi = 70°$; o—single-crystal film of $\mathrm{Fe_3O_4}$ at $\varphi = 65°$ ((100) plane).

*Spinel ferrites*. The investigated spinel ferrites with monovalent and divalent ions $\mathrm{Ni^{2+}}$ $\mathrm{Li^{1+}}$, $\mathrm{Co^{2+}}$, and $\mathrm{Fe^{2+}}$ have an inverted structure, while those with $\mathrm{Mg^{2+}}$ ions have an almost inverted structure. In the $\delta(\omega)$ spectra for

$$\mathrm{MgFe_2O_4}\ (\mathrm{Mg^{2+}_{0.1}Fe^{3+}_{0.9}[Mg^{2+}_{0.9}Fe^{3+}_{1.1}]O_4})$$

and

$$\mathrm{Li_{0.5}Fe_{2.5}O_4}\ (\mathrm{Fe^{3+}[Li^{+}_{0.5}Fe^{3+}_{1.5}]O_4})$$

attention is called to four negative maxima in the region 2.0–4.0 eV, and in addition, a broad maximum is observed in the region 4–5 eV (Fig. 3).[1)] A weak peak was also observed in an $\mathrm{MgFe_2O_3}$ film at 2.1 eV. An analogous $\delta(\omega)$ curve for lithium ferrite was obtained by Édel'man and co-workers.[7] The negative maxima observed by them on the experimental $\delta(\omega)$ curves at 2.31, 2.58, 2.92, 3.33, and 3.84 eV correspond to the maxima on the $\varepsilon_2'(\omega)$ curves—the imaginary part of the off-diagonal component of the dielectric tensor $\varepsilon' = -i\varepsilon_{xy} = \varepsilon_1' - i\varepsilon_2'$. The measurements on the single-crystal Li-ferrite samples were made in three planes, (100), (111), and (110), at different orientations of the field relative to the crystallographic axes. The effect turned out to be isotropic in first-order approximation.

The plot of $\delta(\omega)$ for natural magnetite crystal $\mathrm{Fe_3O_4}$ ($\mathrm{Fe^{3+}[Fe^{2+}Fe^{3+}]O_4}$) (Fig. 4) is similar in character to the magneto-optical spectra for semiconductors and even metals, this being probably due to the presence of $\mathrm{Fe^{2+}}$ ions, which increase the conductivity. In the $\delta(\omega)$ spectrum obtained in reflection from the (110) plane of single-crystal magnetite one can distinguish four broad maxima: a negative maximum with center at 2.65 eV,

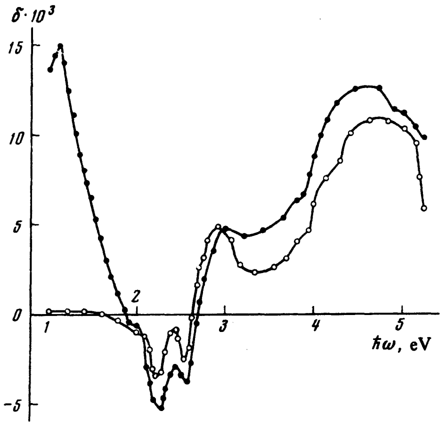

FIG. 5. Equatorial Kerr effect for single-crystal spinels $Ni^{2+}_{0.69}Fe^{2+}_{0.31}Fe_2O_4$ and the film $NiFe_2O_4$ ($\varphi=65°$): ●—single crystal $Ni^{2+}_{0.69}Fe^{2+}_{0.31}Fe_2O_4$, (110) plane; o—$NiFe_2O_4$ film, (100) plane.

two positive maxima at 4.45 and 4.9 eV, and a positive maximum with center at 1.3 eV. We note that no maximum is observed at 1.3 eV, on the $\delta(\omega)$ curve of the epitaxial $Fe_3O_4$ film, this being due to its transparency in this region. Attention must also be called to the appearance, in the spectrum of the $Fe_3O_4$ film sample, of negative maxima which are typical of Mg and Li spinels in the region 2–4 eV.

The $\delta(\omega)$ spectrum for single-crystal $Ni^{2+}_{0.69}Fe^{2+}_{0.31}Fe_2O_4$ ((110) plane) (Fig. 5), grown by the Verneuil method, agrees in general outline with the magnetite spectrum. Attention is called to the presence of a positive peak at 1.1 eV.

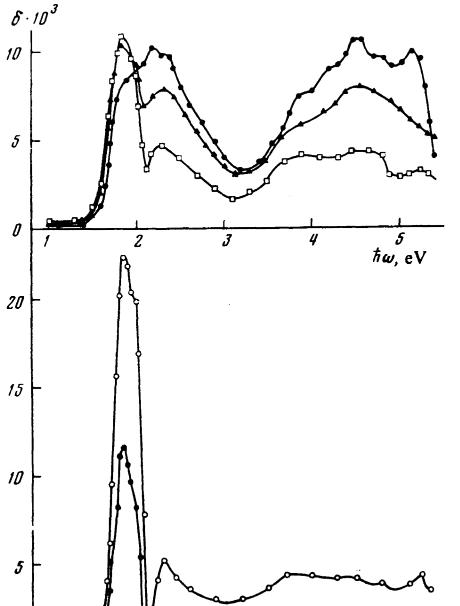

FIG. 6. Equatorial Kerr effect for the system of polycrystalline spinels $CoCr_xFe_{2-x}O_4$ ($x=0$, 0.25, 0.5, 0.75, 1.0), $\varphi=60°$; ●—$x=0$; ▲—$x=0.25$; □—$x=0.5$ (top figure). o—$x=0.75$; ●—$x=1.0$ (bottom figure).

This maximum is not observed in the spectra of polycrystalline and film $NiFe_2O_4$ samples (Figs. 5 and 8). In the case of a film, the reason for the vanishing of this peak may be the transparency of the film in the long-wave region. We note that in spectra of the Kerr effect for $NiFe_2O_4$, in comparison with the previously considered spectra of Li and Mg ferrites, the two negative peaks at 3.3 and 3.9 eV do not appear, and a positive maximum appears in the region of 3 eV.

A situation in which the magneto-active ions $Fe^{3+}$ in crystals with spinel structure are located predominantly in tetrahedral or octahedral positions was realized by us in chromite ferrites. Thus, for $CoCrFeO_4$, $(Co^{2+}[Cr^{3+}Fe^{3+}]O_4)$ with a normal distribution of the cations, the $Co^{2+}$ ions are arranged in tetrahedra, while $Cr^{3+}$ and $Fe^{3+}$ are in octahedra. At the same time, in the inverted spinel $NiCrFeO_4$, $(Fe^{3+}[Ni^{2+}Cr^{3+}]O_4)$ in a tetrahedral environment there are only $Fe^{3+}$ ions.[5] When the $Cr^{3+}$ content in the system $CoCr_xFe_{2-x}O_4$ is increased from $x=0$ to $x=1$, the $Co^{2+}$ ions go over from octahedral to tetrahedral positions, and the iron content in the octahedra remains constant, while the spinel structure gradually changes from inverted to normal.

From a comparison of the $\delta(\omega)$ curves for the samples $CoCr_xFe_{2-x}O_4$ ($x=0$, 0.25, 0.5, 0.75, 1) at $\varphi=60°$ (Fig. 6) and for $CoCrFeO_4$ at three different incidence angles of the light (Fig. 7) it is seen that when the Cr content is increased the magnitude of the measured magneto-optical effect in the 2.6–5.4 eV range decreases sharply, and for the $CoCrFeO_4$ sample the effect practically vanishes in this region. Simultaneously, an intense positive maximum first appears in the region 1.9 eV and then increases.

The maximum value of the effect ~5% (~10% in the case of field switching) was obtained at $\varphi=65°$ for the sample $CoCr_{0.75}Fe_{1.25}O_4$. The reason why the optimal conditions for obtaining maximal effects at room tem-

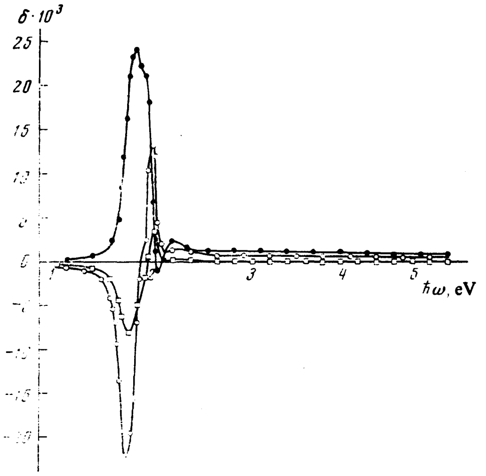

FIG. 7. Equatorial Kerr effect for single-crystal spinel $CoCrFeO_4$ at different light-incidence angles: ●—$\varphi=65°$, o—$\varphi=70°$, □—$\varphi=75°$.

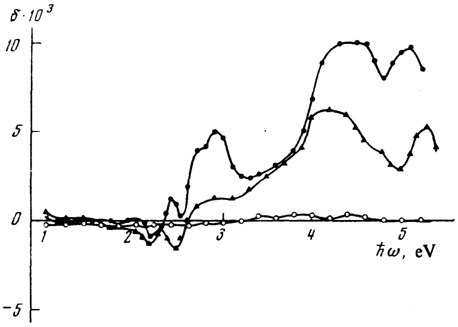

FIG. 8. Equatorial Kerr effect for the system of polycrystalline spinels $NiCr_xFe_{2-x}O_4$ ($x=0$, 0.5, 1.0), $\varphi=60°$; ●—$x=0$; ▲—$x=0.5$; ○—$x=1.0$.

perature occurred for a composition with $Cr_{0.75}$ and not $Cr_{1.0}$ is that with increasing Cr content the Curie temperature decreases. So large a value of the effect is observed at the He–Ne laser wavelength (0.63 $\mu$), a fact that makes promising the use of ferrite chromites of cobalt in systems for modulation of laser radiation. The saturation magnetization in a field 10 kOe is half as large for $CoCr_{0.75}Fe_{1.25}O_4$ at room temperature and one-third as large for $CoCrFeO_4$ at liquid-nitrogen temperature.

Figure 8 shows plots of $\delta(\omega)$ for the Ni–Cr spinel system. The effect of introducing $Cr^{3+}$ ions is qualitatively similar to that observed for cobalt chromite ferrites, but the very sharp decrease of the effect for samples with $x=1$ can be due not only to a decrease of the number of $Fe^{3+}$ ions in the octahedral sublattice, but also to the sharper decrease of the Curie temperature with increasing $Cr^{3+}$ content. The magnetization of $NiCrFeO_4$ at room temperature is lower by a factor ~10 than the magnetization of $NiFe_2O_4$. The magnetization of cobalt chromite ferrites decreases under the same conditions by only a factor ~4.

## DISCUSSION OF RESULTS

In the discussion of the results we shall pay attention mainly to the region 1.0–4.0 eV. First, it is precisely here that the intense optical transitions, which determine the magneto-optical characteristics of ferrodielectrics in the infrared region, are located. Second, the extrema on the experimental $\delta(\omega)$ curves in this region of the spectrum are mainly connected with the corresponding extrema on the plots of the imaginary part $\varepsilon_2'$ of the off-diagonal components of the dielectric tensor ($\varepsilon'=-i\varepsilon_{xy}=\varepsilon_1'-i\varepsilon_2'$) against the frequency. The equatorial Kerr effect is given by

$$\delta=a(n,k,\varphi)\varepsilon_1'+b(n,k,\varphi)\varepsilon_2',$$

where $a$ and $b$ are complicated functions of $n$ and $k$[$\varepsilon=\varepsilon_{xx}=\varepsilon_{yy}=\varepsilon_1-i\varepsilon_2=(n-ik)^2$] and of the light-incidence angle $\varphi$; $\varepsilon_1'$ and $\varepsilon_2'$ are the real and imaginary parts of the off-diagonal components of the dielectric tensor. Inasmuch as $k\ll n$ in the region 2.0–4.0 eV, it follows that at angles $\varphi$ smaller than the Brewster angle, $a$ is smaller than $b$ by approximately one order of magnitude and the character of the dependence of $\delta(\omega)$ is determined mainly by the frequency dependence of $\varepsilon_2'$. For the so-called paramagnetic rotation mechanism, due to the difference between the oscillator strengths $f_+$ and $f_-$ of right- and left-polarized light, the maxima on the $\varepsilon_2'(\omega)$ curves should be observed at the natural frequencies $\omega_0$ of the optical transitions.[4,6] For the diamagnetic mechanism of the rotation due to the difference between the natural frequencies $\omega_0^+$ and $\omega_0^-$ of the transitions for circularly polarized components, the optical transitions should correspond to the zero point on the dispersion curve $\varepsilon_2'(\omega)$, and the interpretation of the spectra becomes somewhat more complicated. In an investigation of iron garnets,[2] Scott and Lacklison have shown that in the range from 1 to 4 eV practically all the transitions are of the paramagnetic type. We shall therefore identify henceforth the natural frequencies of the transitions with the maxima on the $\delta(\omega)$ curves, obtained at $\varphi=60$ or 65°.

We begin the analysis with the transitions at 2.7, 3.0, and 3.2 eV, observed in orthoferrites and hematite. Investigations of iron garnets, particularly measurements of the dependence of the intensity of the absorption bands on the concentration of the $Fe^{3+}$ ions,[2,4] and also the results obtained by us for chromite ferrites (see below), show that the indicated transitions cannot be connected with single-ion (single-exciton) crystalline transitions, since they are all spin-forbidden, and consequently have a low intensity.

In antiferromagnetic crystals,[8] to remove the spin forbiddeness, one considers two-particle exciton-magnon transitions, at which an exciton is produced in one sublattice and a magnon in the other. It is possible to consider in similar fashion also a two-particle transition consisting of simultaneous excitation of molecular-orbital transition and a magnon.

Of greatest interest in our case, however, are the still more intense two-exciton transitions connected with simultaneous excitation of two excitons in the same or in different sublattices.[2,9] The term "two-exciton transition" will automatically include also the case of simultaneous excitation of two exciton-magnon transitions by the light.

The energy of the first two-exciton transition $2\times[{}^6A_{1g}({}^6S)-{}^4T_{1g}({}^4G)]$ (we shall henceforth, for brevity, designate such a transition by $2\times T_{1g}$) amounts to 2.5 eV, if we use for the $T_{1g}$ transition the value 1.25 eV, which was obtained by Wood, Remeika, and Kolb.[10]

Thus, from among the low-energy transitions in orthoferrites, the 2.3-eV transition must be identified with the exciton magnon transition ${}^6A_{1g}({}^6S)\to{}^4E_g({}^4G)$, which agrees also with its low intensity.

The higher-energy and more intense transitions at 2.7, 3.0, and 3.2 eV (see Table I) can be identified with two-exciton transitions for the two lowest of the excited levels of the $Fe^{3+}$ ions in the orthoferrite: 1) $2\times T_{1g}$, ($\hbar\omega_1$), 2) $T_{1g}+T_{2g}$, ($\hbar\omega_2$), 3) $2\times T_{2g}$, ($\hbar\omega_3$). For the energies of the two-particle transitions $\hbar\omega_1=2.73$ eV and $\hbar\omega_3=3.38$ eV, which were observed in the experiment, it is necessary that the levels $T_{1g}$ and $T_{2g}$ be separated from $A_{1g}$ by 1.36 and 1.74 eV, respectively. The val-

TABLE I. Energy (in eV) of optical transitions in magneto-active ions.

| Compound | Single-exciton transitions in magneto-active 3*d* ions in the complexes: | | | | Two-exciton transitions in $Fe^{3+}$ ions in the complexes: | | | Maxima on the magneto-optical spectra in the region 3.9–5.4 eV. |
|---|---|---|---|---|---|---|---|---|
| | $Co^{2+}O_4$ | $Co^{2+}O_6$ | $Fe^{3+}O_6$ | $Ni^{2+}O_6$ | $FeO_6$ | | | |
| | ${}^4A_2({}^4F) \to {}^4T_1({}^4P)$ | ${}^4T_1({}^4F) \to {}^4A_{2g}; {}^4T_{1g}(P)$ | ${}^6A_{1g}({}^6S) \to {}^4E_g({}^4G)$ | ${}^3A_{2g}(F) \to {}^3T_{1g}(P)$ | $2\times{}^6A_{1g}({}^6S) \to 2\times{}^4T_{1g}({}^4G)$ | $2\times{}^6A_{1g}({}^6S) \to {}^4T_{1g}({}^4G) + {}^4T_{2g}({}^4G)$ | $2\times{}^6A_{1g}({}^6S) \to 2\times{}^4T_{2g}({}^4G)$ | |
| $YFeO_3$ | | | 2.34 | | 2.70 | 3.00 | 3.20 | 3.94; 4.28; 4.80; 5.30 |
| $GdFeO_3$ | | | 2.35 | | 2.70 | 3.00 | 3.20 | 3.92; 4,30; 4.80; 5,25 |
| $TmFeO_3$ | | | 2.32 | | 2.72 | 3.00 | 3.20 | 3.92; 4.28; 4.78; 5.30 |
| $YbFeO_3$ | | | 2.35 | | 2.70 | 3.00 | 3.20 | 3.94; 4.28; 4.80; 5.30 |
| $\alpha$-$Fe_2O_3$ | | | | | 2.30 | 2.94 | 3.10? | 5.00 |
| $MgFe_2O_4$ (PC) * | | | 2.32 | | 2.64 | 3.32 | 3.88 | 4.50; 4.72 |
| $MgFe_2O_4$ (F) ** | | | 2.34 | | 2.60 | 3.32 | 3.88 | 4.50; 4.70 |
| $Li_{0,5}Fe_{2,5}O_4$ | | | 2.30 | | 2.60 | 3.27 | 3.88 | 4.40; 4.70 |
| $Fe_3O_4$ | | | | | 2.32 | | | 4.40; 4.95 |
| $Fe_3O_4$ (F) | | | 2.34 | | 2.62 | 3.32 | 3.88 | 4.50; 4.94 |
| $NiFe_2O_4$ (EI) *** | | | 2.25 | 3.00 | 2.56 | | | 4,50 |
| $NiFe_2O_4$ (F) | | | 2.24 | 2.95 | 2.54 | | | 4.70 |
| $Ni_{0,69}{}^{2+}Fe_{0,31}{}^{2+}Fe_2O_4$ | | | 2.26 | 3.00 | 2.56 | | | 4.60 |
| $NiFe_2O_4$ (PC) | | | 2.20 | 2.90 | 2.52 | | | 4.50 5,10 |
| $NiCr_{0,5}Fe_{1,5}O_4$ | | | 2.20 | 2.95 | 2.46 | | | 4.30 5,25 |
| $NiCrFeO_4$ | | | | | | | | |
| $CoFe_2O_4$ | | 2.25 | | | | | | 4.50 |
| $CoCr_{0,25}Fe_{1,75}O_4$ | 1.88 | 2.30 | | | | | | 4.50 |
| $CoCr_{0,5}Fe_{1,5}O_4$ | 1.88 | 2.30 | | | | | | 4.20 |
| $CoCr_{0,75}Fe_{1,25}O_4$ | 1.88 | 2.30 | | | | | | 4,20 |
| $CoCrFeO_4$ | 1.88 | | | | | | | |

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*PC—polycrystal.

**F—film.

***EI—with excess of iron.

ues obtained in[10] for the $T_{1g}$ and $T_{2g}$ transitions were 1.25 and 1.77 eV.

The appearance in the hematite spectrum of a strong sharp maximum in the 2.3 eV region can be attributed to the fact that this transition is also of the two-exciton type, although previously[11] this maximum was identified with enhancement of the parity-forbidden molecular-orbital transition $t_{1g}(\pi) \to t^*_{2g}$, and attributed to the displacement of the $Fe^{3+}$ ions relative to the centers of the oxygen octahedra. Lehmann[12] obtained for the energies of the transition ${}^6A_{1g}({}^6S) \to {}^4T_{1g}({}^4G)$ a value 1.17 eV, and for ${}^6A_{1g}({}^6S) \to {}^4T_{2g}({}^4G)$ a value 1.77 eV. Accordingly, the maxima on the $\delta(\omega)$ curves for $\alpha$-$Fe_2O_3$ (see Fig. 2) at 2.3 and 2.94 eV can be ascribed respectively to the two-exciton transitions $2\times T_{1g}$ and $T_{1g}+T_{2g}$.

We note in this connection one interesting possibility of a general formulation of the problem of the threshold of intense absorption of magnetically-ordered crystals, which is of importance in the search for new transparent ferromagnets. It follows from the foregoing that in magnetically-ordered crystals with $Fe^{3+}$ ions this threshold occurs at the frequency of the lowest-energy two-exciton transition, namely, $\hbar\omega_1$ corresponds to $2\times T_{1g}$. This assumption agrees with the experimental fact that in the antiferromagnetic crystals $MnF_2$, $MnCO_3$, and $CsMnF_3$, in which the magnetoactive $Mn^{2+}$ ions are isoelectronic to the $Fe^{3+}$ ions, the energy of the $T_{1g}$ transition is 2.3 eV, and the intense two-exciton transitions should occur at energies higher than $\hbar\omega_1 = 4.6$ eV. This explains the much higher transparency of such antiferromagnetic crystals in the visible and near-ultraviolet parts of the spectrum in comparison with orthoferrites and iron garnets. It appears also that there is a correlation between the transparency and the temperature of the magnetic ordering. Thus, the antiferromagnets $MnF_2$, $MnCO_3$ and $CsMnF_3$ mentioned above have relatively low Néel temperatures, namely 67.5, 32, and 53.5 °K, while the less transparent orthoferrites and iron garnets have Curie temperatures in the range 600–700 K. This statement does not contradict our assumption concerning the energy of the absorption threshold. The increased intensity of the field inside the crystal, which is due to the decreased distance between the ligands and the magnetically active ion, can be accompanied by an increase of the temperature of the magnetic ordering because of the increased overlap of the wave functions of the neighboring ions. On the other hand, the growth of the crystal field leads to a shift of the frequency of the $T_{1g}$ transition towards the long-wave region of the spectrum, decreasing $\hbar\omega_1$ and accordingly decreasing the transparency of the crystal.

In stoichiometric spinel ferrites $MgFe_2O_4$ and $Li_{0.5}Fe_{2.5}O_4$, four clearly pronounced transitions are observed in the region from 2.0 to 4.0 eV (see the table). The first and least intense maximum at 2.3 eV can be ascribed, just as in orthoferrites, to the single-ion (exciton-magnon) transition ${}^6A_{1g}({}^6S) \to {}^4E_g({}^4G)$. The 2.6, 3.25, and 3.9 eV transitions agree well with the triplet of two-exciton transitions $2\times T_{1g}$, $T_{1g}+T_{2g}$ and $2\times T_{2g}$, where the energies of the $T_{1g}$ and $T_{2g}$ transitions are 1.3 and 1.95 eV, respectively. The first $T_{1g}$ transition was observed in $Li_{0.5}Fe_{2.5}O_4$ at 1.24 eV.[13]

The presence of divalent magneto-active ions ($Fe^{2+}$, $Ni^{2+}$, $Co^{2+}$) in the spinel ferrites leads to a strong distortion of the magneto-optical spectra of these compounds. It is obvious that the distortion is due to the presence of intense transitions of these ions in the same region of the spectrum as for the $Fe^{3+}$ ion.

The vanishing of the two negative maxima at 2.6 and 3.3 eV in the spectrum of the nickel spinel $NiFe_2O_4$ (see Figs. 5 and 8) in comparison with the Mg and Li spinels is due, in our opinion, to the appearance of the broad positive maximum in the region of 3 eV, due to optical transitions in the $Ni^{2+}$ ions in the octahedral complexes. In the absorption spectra of crystals containing $Ni^{2+}$ ions, an intense broad maximum is observed at this energy, and can be ascribed to the electric dipole transition $^3A_{2g}(F)\to{}^3T_{1g}(P)$ in the $Ni^{2+}$ ions.[14] The two negative peaks of $NiFe_2O_4$ at 2.25 and 2.56 eV are attributed by us, just as in the case of the Mg and Li spinels, to the very same transitions in the octahedral complexes of the $Fe^{3+}$ ion: $^6A_{1g}\to{}^4E_g$ and $2\times T_{1g}$.

The appearance of an intense positive maximum at 1.3 eV (see Fig. 4) on the magneto-optical spectrum of natural magnetite crystal $Fe_3O_4$ can also be explained as being due to optical transitions in the octahedral ions of $Fe^{2+}$. Indeed, in the absorption spectra of the crystals containing $Fe^{2+}$ ions in octahedral positions, a wide band, due to the $^5T_{2g}\to{}^5E_g$ transition, is observed at this energy.[15] A more probable mechanism of the intense optical transitions in magnetite, however, is charge transfer, for example, between the ions $Fe^{2+}$ and $Fe^{3+}$, since as magnetite has a higher quasi-metallic conductivity.

The four negative peaks in the region 2–4 eV for the $Fe_3O_4$ film (see Fig. 4) are due to transitions in the octahedral ions $Fe^{3+}$, just as in the case of $MgFe_2O_4$ and $Li_{0.5}Fe_{2.5}O_4$. The appreciable deformation of the spectrum of the natural magnetite crystal in comparison with the film can be due to the presence of an excess of $Fe^{2+}$ ions located in the free octahedral or tetrahedral voids, which intensify the conduction-type transitions, i.e., the transitions with charge transfer from the $Fe^{2+}$ ions to the $Fe^{3+}$ ions.

In the absorption spectra of crystals containing a $Co^{2+}$ ion in octahedral coordination, a broad band is observed in the visible region (near 2.35 eV) with a complex maximum (a triple maximum with distances ~0.12 eV between the peaks).[16] This absorption band is connected with the transition $^4T_1(^4F)\to{}^4A_{2g};\ {}^4T_{1g}(P)$. The magneto-optical spectrum of the spinel ferrite $CoFe_2O_4$ shows also a broad maximum with a complex structure in the region 1.5 to 3.0 eV (center at 2.35 eV) (Fig. 6), which apparently is connected with the aforementioned absorption band of the $Co^{2+}$ ion. As the $Fe^{3+}$ ions become replaced by $Cr^{3+}$ ions in the system $CoCr_xFe_{2-x}O_4$ ($x=0$; 0.25; 0.5; 0.75; 1.0), the cation distribution changes from inverted (at $x=0$) to normal (at $x=1$). In the magneto-optical spectra of these compounds (see Fig. 6), the peak at 2.36 eV becomes suppressed and the maximum in the region of 1.9 eV, which is connected with the transitions $^4A_2(^4F)\to{}^4T_1(^4P)$ in the $Co^{2+}$ ions in the tetrahedral coordination[17] becomes enhanced (see Fig. 6). The same transition was observed by Ahrenkiel[18] in the spectrum of the magnetic circular dichroism. Thus, in the magneto-optical spectra of the investigated magnetic crystals we can reliably separate, in a number of cases, the anomalies connected with the optical transitions in doubly-charged 3*d* ions, determine the type of these transitions, and by the same token point the way towards the solution of the inverse problem, that of determining the presence and coordination of doubly-charged ions from magneto-optical spectra of crystals.

We emphasize in conclusion that the most interesting result is the abrupt decrease of the intensity of the transitions, as recorded by the magneto-optical spectra, which is observed when one of the sublattices in the chromite ferrites ($CoCr_xFe_{2-x}O_4$ and $NiCr_xFe_{2-x}O_4$) is replaced. These results show directly that the intense optical transitions in two-sublattice ferrimagnets are the results of participation of both sublattices, since the magneto-optical effects in the region of the first intense optical transitions decrease with increasing chromium concentration in both the first and the second systems (in the first system the only intense transitions are those in the region 1.9 eV and are due to the appearance of $Co^{2+}$ ions in the tetrahedral sites).

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1) The ions in the square brackets are in octahedral positions, and those preceding the brackets in tetrahedral positions.

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