MAGNETO-OPTICS OF Eu^{3+} IONS IN A FERROMAGNETIC CRYSTAL

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The effect of an external magnetic field on the optical properties of europium ferrite garnet was investigated in the infrared region of the spectrum. An anisotropy was found in the fine structure of the $^7F_0 \rightarrow {}^7F_4$ absorption line. Some components of the fine structure in circularly polarized light could be interpreted as the "Raman" excitation of spin waves during optical transitions in rare-earth ions of the ferromagnetic crystal. The temperature dependence of the $^7F_0 \rightarrow {}^7F_4$ line structure was studied and the Faraday effect was measured in this region of the spectrum.

1. ANISOTROPY OF THE FINE STRUCTURE OF THE $^7F_0 \rightarrow {}^7F_4$ ABSORPTION LINE OF Eu^{3+} IONS IN A MAGNETIC FIELD

1. An intense absorption line, which could be identified with the $^7F_0 \rightarrow {}^7F_4$ transition in Eu^{3+} ions, was discovered in the region of 3100 cm^{-1} during an investigation of the absorption spectrum of europium ferrite garnet. We studied the fine structure of this line in polarized infrared light in an external magnetic field.

The measurements were carried out using an IKS-12 spectrograph with an LiF prism and a 0.15 mm (≈ 10 cm^{-1}) slit. A globar was used as the source of light. The light was modulated by means of a mechanical chopper at 200 cps. A PbS photoresistor cooled to the temperature of liquid nitrogen was used as the receiver. After amplification, the signal was fed to an automatic recorder. The sample was magnetized by a field of 2000 Oe in the gap of an electromagnet.

The samples on which the measurements were carried out were polished plates $100\,\mu$ thick, cut parallel, to within 7°, to the crystallographic planes of a europium ferrite garnet single crystal.

The crystal was magnetized transversely (the light was propagated at right angles to the spontaneous magnetization vector of the sample) and the measurements were carried out in linearly polarized light using both the π-component (the electric vector parallel to the sample polarization) and the σ-component (the electric vector perpendicular to the sample magnetization).

Figures 1 and 2 give examples of recorded spectra of the $^7F_0 \rightarrow {}^7F_4$ absorption line for a sample cut along the (110) plane and the magnet-

ization directed along the axes [111] and [110], respectively.

Figure 3 shows schematically how the intensities of the separate components of the $^7F_0 \rightarrow {}^7F_4$ absorption line of the same sample varied with the relative orientation of the magnetizing field and the crystallographic axes of the sample. The positions of the components are indicated by the absorption maxima, and the height of each line is proportional to the absorption coefficient of the sample at a given wavelength [$I = I_0 \exp(-kx)$]. For example, the spectrograms of Figs. 1 and 2
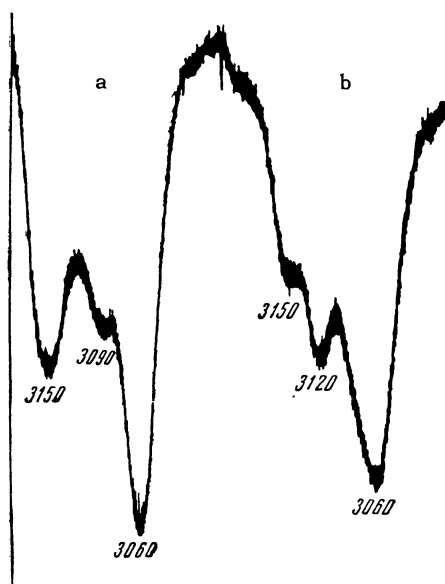

FIG. 1. $^7F_0 \rightarrow {}^7F_4$ absorption line of Eu^{3+} ions for transverse magnetization of a europium ferrite garnet plate cut along the (110) plane; H || [111]: a) $\bar{e} \perp H$; b) $\bar{e}$ || H. Positions of the maxima are given in cm^{-1}.

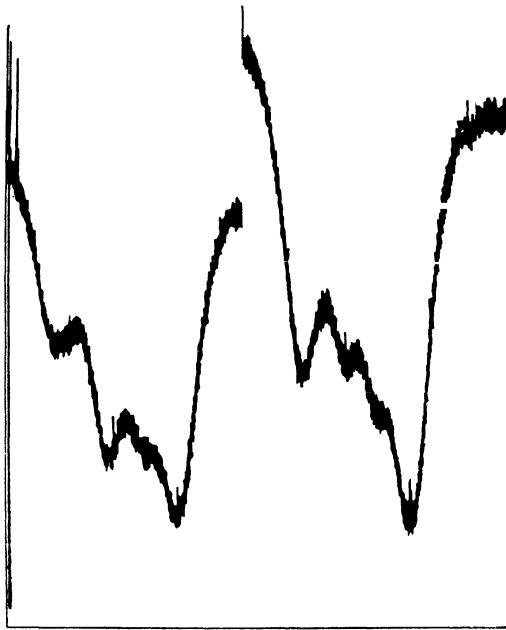FIG. 2. $^7F_0 \rightarrow {}^7F_4$ absorption line for transverse magnetization of a plate cut along the [110] plane; H || [110].

are represented by the first and second diagrams in Fig. 3. Figure 4 gives similar results for a sample cut along the (111) plane.

The results obtained illustrate well the controlled optics effects in a ferromagnetic crystal.[1] The rotation of the magnetization vector of
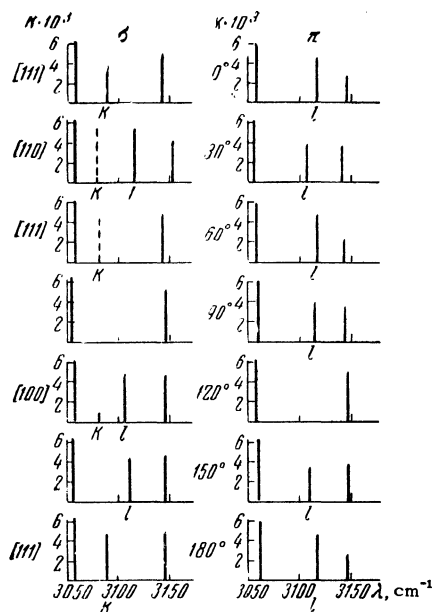

FIG. 3. Diagram showing how the intensity of individual components of the $^7F_0 \rightarrow {}^7F_4$ absorption line varies with the relative orientation of the external magnetic field and the crystallographic axes of sample No. 1 magnetized transversely. The sample was cut along the (110) plane. The uppermost pattern corresponds to H || [111].
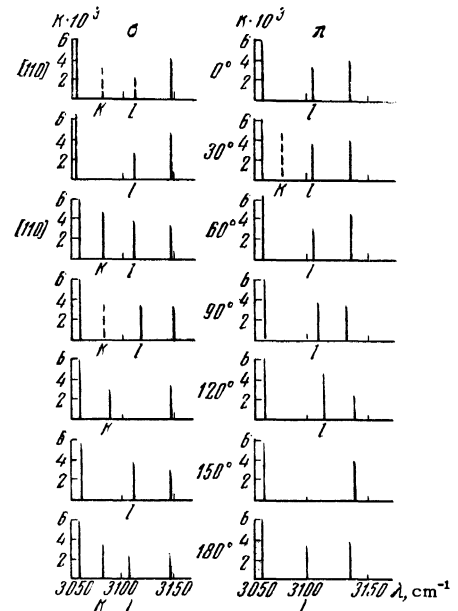

FIG. 4. Diagram showing how the intensity of individual components of the $^7F_0 \rightarrow {}^7F_4$ absorption line varies with the relative orientation of the external magnetic field and the crystallographic axes of sample No. 3 magnetized transversely. The sample was cut along the (111) plane. The uppermost pattern corresponds to H || [110].

the ferrite garnet by 90° causes the appearance, disappearance and change of the intensity of the polarized lines in the absorption spectrum of the crystal. Thus, for example, it is evident from Fig. 1 that a weak external magnetic field may change the absorption coefficient of a crystal in the region of a given component from 5×10^{-3} to 10^{-3}, which corresponds to a change of the transmission coefficient of a $100\,\mu$ thick plate from 3 to 50%.

Some of the complexities of the observed pattern compared with the $^7F_0 \rightarrow {}^7F_4$ transition[2] may be explained by the fact that this transition is neither purely electric dipole nor purely magnetic dipole, i.e., in no case do we observe a clear pattern characteristic of a Zeeman triplet: one π-component and two σ-components for the electric dipole transition, two π-components and one σ-component for the magnetic dipole transition.

It is worth noting that in the transition $^7F_0 \rightarrow {}^7F_4$ the central components (Figs. 3 and 4), corresponding to the dipole transitions with ΔM = 0, are grouped about two different frequencies. It is possible that this is due to the presence in the ferrite garnet lattice of at least two types of nonequivalent site l and k for rare-earth ions.[3] This explanation is supported by the fact that the central component position is independent of temperature (cf. Sec. 4).

From this point of view, the diagrams shown in Figs. 3 and 4 can be interpreted as follows. The π-component exhibits only the short-wavelength central line, i.e., the electric dipole transitions occur in Eu^{3+} ions of l-type. The magnetic dipole transitions occur in ions of types l and k, and in this case there is a marked anisotropy of the intensity of the transition.

Obviously, the increased importance of the magnetic dipole transitions and the related strong anisotropy of the fine structure of the $^7F_0 \to {}^7F_4$ absorption line are due to a reduction of the transition energy. For example, an additional study of the $^7F_0 \to {}^7F_6$ transition confirmed the conclusion that it was a purely electric dipole transition, i.e., one π-component and two σ-components were observed and the line was approximately isotropic. A similar increase of the role of the magnetic dipole transitions on reduction of the transition energy was discovered earlier for other rare-earth ions.[4]

2. "RAMAN" SPIN-WAVE LINES OF THE ABSORPTION OF LIGHT IN A FERROMAGNETIC CRYSTAL

The $^7F_0 \to {}^7F_4$ absorption line was also investigated in circularly polarized light in the case of longitudinal magnetization (the light was propagated along the spontaneous magnetization vector of the sample). The circular polarization was obtained by means of an NaCl Fresnel rhomb.

Figure 5 shows examples of records of the $^7F_0 \to {}^7F_4$ line profile for the longitudinal magnetization of a plate cut along the (111) plane. The profiles show that the components A and D have the highest intensity for the right-handed and left-handed circular polarizations, respectively. These components can be identified with the transitions to the levels M = −1 and M = +1 of an exchange Zeeman triplet with splitting of the order of 95 cm^{-1}.

The origin of the less intense lines A and B for the left-handed circular polarization, and C and D for the right-handed circular polarization, is not yet clear. One can suggest that the additional absorption lines, for example A and B in Fig. 5b, are due to the excitation in a ferromagnet of the collective types of oscillation of the spin system under the action of infrared light during optical electronic transitions. For example, if the line A in Fig. 5a is considered[1] as due to a transition to the level F_{+1} in the state with the magnetic moment oriented parallel to the magnetization vector of the rare-earth sublattice of the fer-
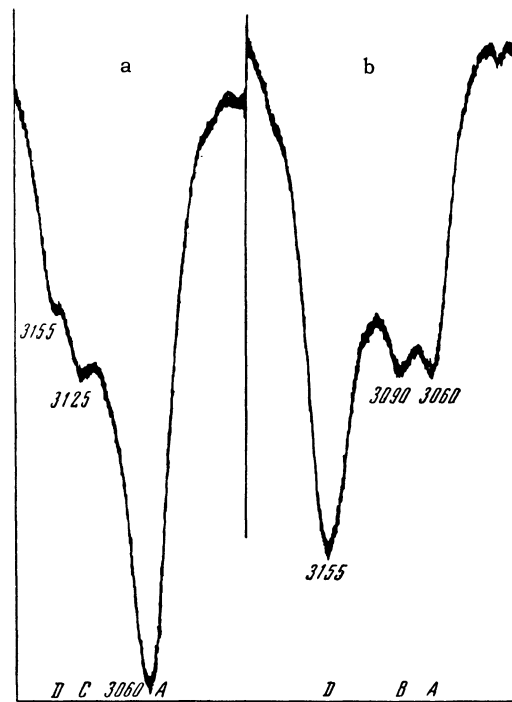

FIG. 5. $^7F_0 \to {}^7F_4$ absorption line for longitudinal magnetization of a plate (sample No. 3) cut along the (111) plane in right-handed (a) and left-handed (b) circularly polarized light.

rite garnet crystal, and the D line in Fig. 5b is regarded as due to a transition to the level with the antiparallel orientation of the magnetic moment F_{-1}, then the line B in Fig. 5b can be considered as due to a transition involving the excitation of a spin wave with the exchange resonance frequency and the line A in Fig. 5b as due to a transition with the excitation of a spin wave of the ordinary ferromagnetic resonance frequency. The exchange resonance frequency[5] is given by the expression

$$\omega_{exc} = \lambda \, (\gamma_2 I_1 - \gamma_1 I_2)$$

(λ = 1900 Oe, $\gamma_1 = 1.76 \times 10^7$ Oe^{-1} sec^{-1}, $I_1 = 135$, $\gamma_2 = 2.61 \times 10^7$ Oe^{-1} sec^{-1}, $I_2 = 43$), where γ_1 and γ_2 are the gyromagnetic ratios of the ions in the sublattices, I_1 and I_2 are the spontaneous magnetizations of the sublattices, λ is the molecular field coefficient. Substituting the numerical values into the above formula, we find that $\hbar\omega_{exc} \approx 28$ cm^{-1}, which corresponds in order of magnitude to the separation of the lines A and B, C and D (g, the factor for the ground level of Eu^{3+} ions, determined from the experimental value of the gyromagnetic Faraday effect,[2] was, according to our measurements, 31 deg/cm).

The physical meaning of this explanation is as follows: in a ferromagnetic crystal, the action of light may produce not only the transitions to the

lower energy state of the excited level with the magnetic moment parallel to the sublattice magnetization, but also to the state with the opposite magnetic moment. The magnetic moment reversal may require various energies, exciting one or the other type of oscillation of the spin system of the ferromagnet which gives rise to various "Raman" lines in the absorption spectrum. Thus, like the usual Raman scattering of light which allows us to study the fundamental frequencies of molecules or crystals, the appearance of the "Raman" frequencies of magnetic origin may be used to study the fundamental frequencies of the magnetic spin system of a ferromagnetic crystal.

3. FARADAY EFFECT IN EUROPIUM FERRITE GARNET FOR THE $^7F_0 \rightarrow {}^7F_4$ ABSORPTION LINE

In the region of the $^7F_0 \rightarrow {}^7F_4$ absorption line, we measured the frequency dependence of the specific rotation of the plane of polarization of light. The apparatus used to carry out these measurements was similar to that described above. A germanium mirror served as the polarizer, and a pile of AgCl plates was the analyzer. An LiF prism with a 0.6 mm slit was used, corresponding to a spectral interval of approximately 30 cm^{-1}.

The results of the measurements are given in Fig. 6. The curve has the characteristic resonance shape. It is interesting to note that the Faraday effect has a different sign for the transitions $^7F_0 \rightarrow {}^7F_4$ and $^7F_0 \rightarrow {}^7F_6$.[2] The same figure shows the theoretical dependence of the Faraday effect on the wavelength in the region of the absorption line. The latter curve was plotted from the experimentally determined (using the same slit width) absorption coefficients of the left-handed and right-handed polarized light, from which we then calculated the refractive indices of the circularly polarized waves and the Faraday effect.[1] The Faraday effect was calculated for
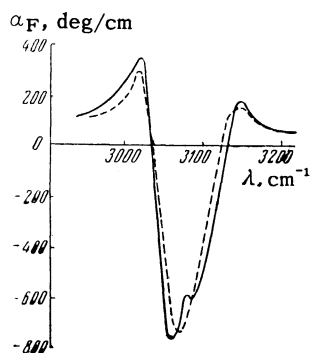
the following parameters:

I. $\nu_A^r = 9.165 \cdot 10^{13}$ sec^{-1},

   $a_A^r = 4.4 \cdot 10^{-3}$, $\gamma_A^r/2 = 2\pi \cdot 0.6 \cdot 10^{12}$ sec^{-1};

II. $\nu_C^r = 9.310 \cdot 10^{13}$ sec^{-1},

   $a_C^r = 1.45 \cdot 10^{-3}$, $\gamma_C^r/2 = 2\pi \cdot 0.1 \cdot 10^{13}$ sec^{-1};

III. $\nu_B^l = 9.195 \cdot 10^{13}$ sec^{-1},

   $a_B^l = 1.86 \cdot 10^{-3}$, $\gamma_B^l/2 = 2\pi \cdot 0.8 \cdot 10^{12}$ sec^{-1};

IV. $\nu_D^l = 9.400 \cdot 10^{13}$ sec^{-1},

   $a_D^l = 2.65 \cdot 10^{-3}$, $\gamma_D^l/2 = 2\pi \cdot 0.7 \cdot 10^{12}$ sec^{-1}.

Agreement between theory and experiment is obtained on allowing for four components of the absorption line: two for each circulat polarization, in contrast to the $^7F_0 \rightarrow {}^7F_6$ transition, for which two lines were sufficient. This means that the lines A, B and C, D in Figs. 5b and 5a, respectively, do really exist and are not due to the poor circular polarization of the light. The good agreement obtained between theory and experiment indicates that the Faraday effect in the region of the absorption line is of exchange origin, because the fine structure of the $^7F_0 \rightarrow {}^7F_4$ absorption line is due to the splitting of the Eu^{3+} ion levels in the exchange field of the iron ferrite garnet sublattices.

4. TEMPERATURE DEPENDENCE OF THE FINE STRUCTURE OF THE $^7F_0 \rightarrow {}^7F_4$ ABSORPTION LINE IN LINEARLY POLARIZED LIGHT

The temperature studies of the $^7F_0 \rightarrow {}^7F_4$ absorption line were carried out in a metal cryostat with NaCl windows; the sample temperature was measured with a copper-constantan thermocouple.

The measurements of the temperature dependence of the magnitude of the splitting ΔE of the $^7F_0 \rightarrow {}^7F_4$ line were carried out to check the suggestion that the A–D splitting is of exchange origin (cf. Fig. 5). The measurements were carried out with a slit 0.5 mm wide. In this case, the spectrogram showed clearly two broadened lines, the distance between which could easily be varied. The following results were obtained:

$$\Delta E = 75 \text{ cm}^{-1} \ (T = 373° \text{ K}),$$
$$\Delta E = 85 \text{ cm}^{-1} \ (T = 290° \text{ K}),$$
$$\Delta E = 110 \text{ cm}^{-1} \ (T = 100° \text{ K}).$$

The above table shows that the magnitude of the splitting ΔE corresponds quantitatively to the tem-

α_F, deg/cm

FIG. 6. Dependence of the Faraday effect on the infrared wavelength in the region of the $^7F_0 \rightarrow {}^7F_4$ absorption line: the continuous curve is experimental and the dashed curve is theoretical.
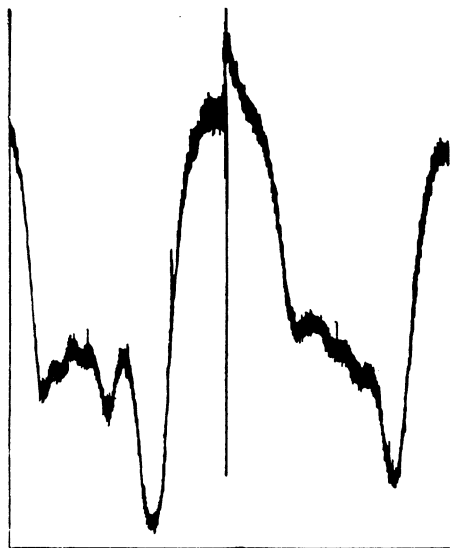
FIG. 7. $^7F_0 \rightarrow {}^7F_4$ absorption line for transverse magnetization of a plate cut along the (110) plane; H $\parallel$ [111] at T = 200°K.

perature dependence of the yttrium ferrite garnet magnetization, i.e., to the value of the exchange field of the iron sublattices of the europium garnet acting on europium ions.

Investigation of the temperature dependence of the $^7F_0 \rightarrow {}^7F_4$ absorption line at a higher resolution (slit width 0.17 mm) showed that the relationships representing the variation of the fine structure of the line are complex and obviously indicate a change of the europium ferrite garnet structure between room temperature and the boiling point of nitrogen.
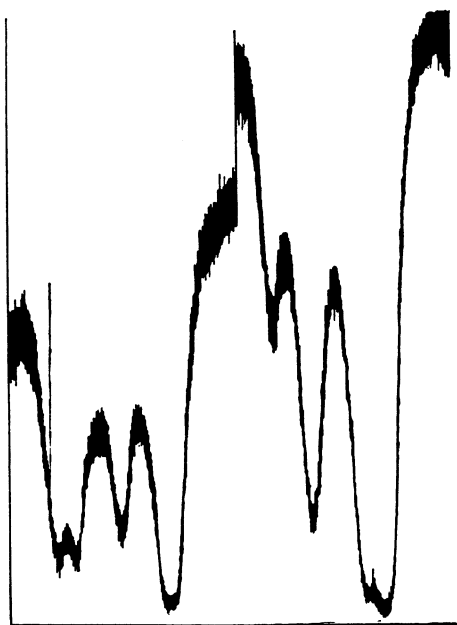

FIG. 8. $^7F_0 \rightarrow {}^7F_4$ absorption line for transverse magnetization of a plate cut along the (110) plane; H$\parallel$ [111] at T = 100°K.
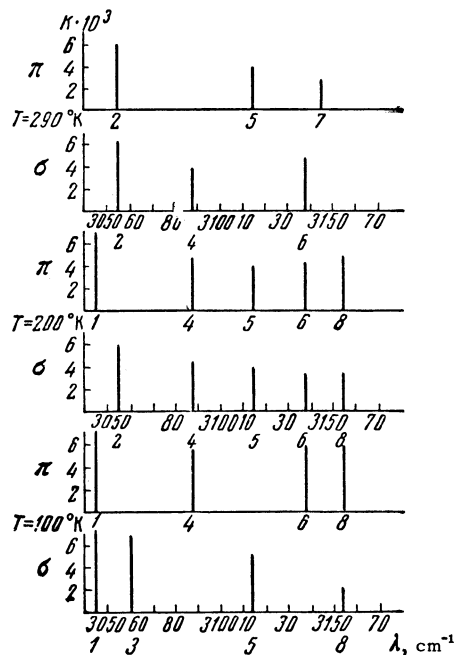

FIG. 9. Diagram showing the variation of the intensity of the individual components of the $^7F_0 \rightarrow {}^7F_4$ absorption line with temperature, for a sample cut along the (110) plane.

Figure 7 shows the profile of the $^7F_0 \rightarrow {}^7F_4$ absorption line at T = 200°K, and Fig. 8 the profile at T = 100°K, in linearly polarized light. The external magnetic field was oriented parallel to the [110] axis, which corresponds to Fig. 1 at room temperature. The system of linearly polarized components then obtained is given in Fig. 9. From the data, it is clear that the patterns for the linearly polarized components vary strongly with temperature in a characteristic way: the extreme lines 2 and 7 at T = 100°K split into two components separated by about 20 cm^{-1}, the splitting of line 2 occurring in the σ-component and of line 7 in the π-component.

The central lines behave somewhat differently. At T = 290°K, the short-wavelength component was observed in the π-polarization and the long-wavelength component in the σ-polarization. At an intermediate temperature of 200°K, both lines were observed in the π- and σ-polarizations. At temperatures close to the boiling point of nitrogen T = 100°K the long-wavelength component was observed in the π-polarization and the short-wavelength component in the σ-polarization, i.e., the central lines seemed to change places. If the assumption is justified (Sec. 1) that the appearance of the two central components is related to the presence of two nonequivalent types of rare-earth ion site in the lattice, the results obtained indicate that in the temperature range T = 290°K to T

= 100°K there is a change of the magnetic or crystal structure of europium ferrite garnet, because in those Eu^{3+} ions in which—at T = 290°K—electric dipole transitions mainly occur, the chief contribution at T = 100°K is that from magnetic dipole transitions, and conversely. At an intermediate temperature of T = 200°K both electric and magnetic dipole transitions occur in l- and k-type ions.

It is noticeable that the magnitude of the splitting of lines 2 and 7 is quantitatively equal to the energy of the transition of an Eu^{3+} ion in the exchange field of the iron sublattices (of the order of 3×10^3 Oe) at which the magnetic quantum number M changes by unity,

$$\Delta E = g\mu_B H_{exc} \sim 18 \text{ cm}^{-1} \text{ for } g = 1.5.$$

An attempt was made to carry out measurements of the temperature variation of the fine structure in circularly polarized light for which the selection rules are more rigid. Unfortunately, because of the increase of the magnetic moment and of the anisotropy, the sample could not be magnetized to saturation in a longitudinal magnetic field at low temperatures.

In conclusion, it should be mentioned that because of the similarity of the quantitative values of many characteristic energies of europium ferrite garnet, the qualitative explanations of the experimental results proposed in the present paper are not unique. Thus, for example, if we use the energy estimates we find that the circular components B and C in Fig. 5 may be of the same origin as the central components l and k in linearly polarized light (Figs. 3 and 4); the lines 4 and 5 in Fig. 9 (T = 100°K) may be related to the "Raman" excitation of spin waves (cf. Sec. 2), etc. These examples are given to indicate the interesting possibilities of the magneto-optical method of investigating ferrite garnets for the purpose of developing a theory of the spectra of rare-earth ions in ferromagnetic crystals.

The single crystals of europium ferrite garnet were grown for us by A. G. Titova, to whom we are greatly indebted.

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