Magneto-optical properties of hematite

V. E. Zubov, G. S. Krinchik, and V. A. Lyskov

Moscow State University
(Submitted 24 April 1981)
Zh. Eksp. Teor. Fiz. **81**, 1489–1497 (October 1981)

The off-diagonal elements of the permittivity tensor of hematite in the 1 to 5.5 eV range have been determined by the magneto-optical method. A new magneto-optical transition at $E = 1.5$ eV was found and corresponds to the crystalline transition ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$. The temperature dependence of the equatorial Kerr effect (EKE) was measured in the range $300 < T < 900$ K. The temperature dependence of the EKE peaks turned out to be the same: they all drop rapidly in amplitude and shift to the low energy region by about 0.15 eV. It was deduced from the temperature variation of the EKE that over the range studied it is determined by pair transitions in the exchange-coupled Fe^{3+}ions. The quadratic magneto-optical effect (linear birefringence) was measured in hematite for the first time in reflected light in the range from 2 to 5 eV. The mechanisms (transitions) responsible for the spectral dependence of the linear and circular birefringence are different. The automatic magneto-optical apparatus, with a sensitivity of $\sim 10^{-7}$, used for the measurements is described.

PACS numbers: 78.20.Ls

1. INTRODUCTION

The magneto-optical properties of hematite (α-Fe_2O_3) were first studied by Pisarev *et al.*[1] The magnitude of the linear magnetic birefringence (LMB) at a wavelength $\lambda = 1.15$ μm, for light propagating along the crystallographic c-axis, is independent of the orientation of the sponteneous magnetization in the basal plane, and is surprisingly large, exceeding the circular birefringence (the Faraday effect) by an order of magnitude. It is suggested that the LMB in hematite is determined primarily by exchange interaction, and this gives a qualitative explanation of the large observed values.

A study of the magneto-optical properties of hematite in reflected light was first carried out by Krinchik *et al.*[2] using the equatorial Kerr effect (EKE). It was found that the EKE in hematite is comparable to magnitude with the EKE in ferromagnetic dielectrics, although the spontaneous magnetization in hematite is a thousandfold less than the sum of the magnetization of its sublattices. In an earlier work[3] it was shown, by recognizing two physically different types of magnetization of a hematite crystal, that the anomalously large magneto-optical effects in weak ferromagnets were produced neither by the absolute magnitude of the resulting magnetic moment nor by its reorientation, but by the reorientation of the antiferromagnetism vector accompanying the magnetic reversal of a weak ferromagnet.

An LMB odd with respect to the field was observed in the single domain antiferromagnetic state of hematite[4] and was related to the deviation of the antiferromagnetism vector for the trigonal axis which was linear with field.

In the present work the study of the magneto-optical properties of hematite have been continued in the spectral range from 1 to 5.5 eV. The off-diagonal elements of the permittivity tensor for hematite have been determined by measuring the equatorial and polar Kerr effects, the temperature dependence of the EKE has been measured in the range $300 < T < 900$ K, and the magneto-optical effect in reflected light, quadratic in the magnetization, has been measured.

2. AUTOMATIC MAGNETO-OPTICAL APPARATUS OF INCREASED SENSITIVITY

Measurements both in the dynamic (magnetic reversal of the specimen in an alternating magnetic field) and static regimes can be carried out in the apparatus. Since the measuring sensitivity is mainly limited by fluctuations in the intensity of the light source, a compensation method is used in both the dynamic and static modes of operation to reduce them. A high-pressure DKsSh-1000 xenon lamp is used as light source. The light beam is split in two past a DMR-4 monochromator; the main beam falls on the specimen placed between the poles of an electromagnet, the other is the reference beam. The light is recorded by a pair of identical photodetectors (photomultipliers or photodiodes for different parts of the spectrum). A diaphragm in the reference channel controls the light intensity in it, and is driven by an electric motor with a tracking (servo) system to equalize the light fluxes in both channels.

Operational amplifiers (OA) in the form of integrated microcircuits[6] are used as the basic components in the measuring system. By using up-to-data OA's it was possible to construct the basic components (input differential amplifiers, selective amplifier, dividing unit) satisfying the exacting demands made on the measuring channel: low noise level and drift, high input impedance, stable transmission coefficient etc.

The operating system of the measuring part of the apparatus is shown in Fig. 1. The signals from the photodetectors are fed to the input amplifiers A_1–A_3. The alternating components of the signals in both channels go to the differential amplifier A_1, which amplifies the useful signal ($I_\sim$), thereby suppressing the noise in the light. $I_\sim$ is then amplified by a narrow-band amplifier A_5, is rectified by the phase-sensitive detector 6 and reaches the dividing unit 7 (the numerator input). The d.c. components I_1 and I_2 are fed to

 0038-5646/81/100789-05$02.40

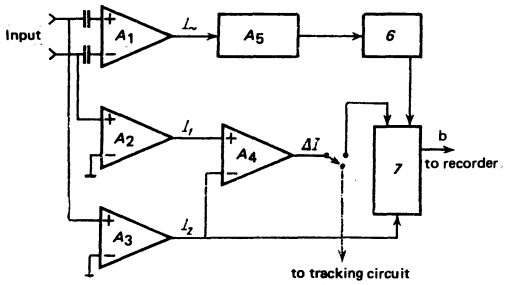

FIG. 1. Operating system of the measuring part of the apparatus; A_1—input differential amplifier; A_2, A_3—input constant current amplifiers; A_4—differential constant current amplifier; A_5—narrow-band amplifier; 6—V9-2 phase-sensitive detector; 7—dividing unit.

amplifiers A_2 and A_3 and then to the differential amplifier A_4 and the dividing unit (the denominator input). Amplifier A_4 only lets through the difference signal $\Delta I = I_1 - I_2$ which characterizes the unbalance of the channels. This signal is governed by the tracking circuit which equalizes the light intensities in both channels with the aid of a diaphragm which limits the light flux in the reference channel.

When operating in the static mode the tracking circuit is disconnected after equalizing the light fluxes with $H = 0$. The difference signal ΔI which appears when a constant magnetic field is turned on is proportional to the change in the light intensity reflected from the specimen and is fed to the numerator input of the dividing unit.

The dividing unit produces the magneto-optical signal $\delta = I_\sim / I$ or $\delta = \Delta I / I$ ($I_1 \approx I_2 = I$), which goes to the x–y chart recorder. The sweep voltage, proportional to the energy of the light quanta or to the strength of the magnetic field in the electromagnet gap etc., is supplied to the second input of the recorder.

The input amplifiers A_1–A_3 are based on low-noise 544UD2A field effect OA's, selected according to their drift. The coefficient of suppression of the in-phase signal of the differential amplifier A_1 is 70 dB. A precision K14OUD13 integrated circuit is used at the input in the differential amplifier A_4 and has a sufficiently large suppression coefficient for the in-phase signal, ~120 dB, so that a difference signal $\Delta I \sim 10^{-5} I$ can be recorded.

The narrow-band amplifier A_5 consists of amplifier U2-6 and an additional selective amplifier (SU) based on K1UT402A integrated circuits with a balanced twin-T network in a feedback loop.[7] The Q of the SU at resonance frequencies in the operating range from 30 to 300 GHz is about 500, which is about 30 times greater than the Q of the commercial U2-6. The high Q value is caused by the higher frequency stabilization requirements of the master oscillator. A G3-49A oscillator with frequency stability 10^{-7} was used for this. The noise at the input of the phase-sensitive detector could be reduced by more than an order of magnitude by using the SU.

The analog-signal dividing system 7 was constructed on the "logarithm-antilogarithm" principle[8] using a 544 UD1A OA. Matched 159NT1V monolithic transistors with transdiode connection were used as the logarithmic components. The counter has a nonlinearity 0.2% for input signals from 0 to ±10V; the resulting error does not exceed 1% in a denominator dynamic range 60 dB.

The sensitivity of the apparatus is $\delta \sim 10^{-7}$ in the dynamic regime and $\sim 10^{-5}$ in the static regime.

The magneto-optical effect (δ_q), quadratic in the magnetization, measured in this work is the relative difference in the intensity of light reflected from the specimen in the two cases: $\mathbf{e} \perp \mathbf{m}_s$ and $\mathbf{e} \parallel \mathbf{m}_s$, where $\mathbf{e}$ is the electric vector in the light wave and $\mathbf{m}_s$ is the spontaneous magnetization vector. Measurements were made on the basal face of hematite for the light incident at an angle close to zero. In the region of strong attenuation δ_q is caused by a difference in complex refractive indices ($\hat{n}$) for the two cases of the relative orientations of the vectors $\mathbf{e}$ and $\mathbf{m}_s$ mentioned above. To a first approximation δ_q is determined by the terms in the expansion of $\hat{n}$ in the components of the vector $\mathbf{m}_s$ which are quadratic in the magnetization.

For observing the quadratic effect, periodic tilting of the magnetic moment in the specimen plane by 90° from the equatorial to the polar directions of magnetization was carried out. Since a uniaxial surface anisotropy with an effective field of ~1 kOe is observed on natural basal faces of hematite,[8] an alternating magnetic field is applied perpendicular to the easy anisotropy axis (EA) to tilt the magnetization vector. Measurement of the alternating component of the intensity of the light reflected from the specimen was carried out at the frequency of the change in the projection of the magnetization on the EA and HA (hard axis), which is double the frequency of the magnetization reversal field. The sign of the effect was determined from measurements in the static regime.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Measurements were carried out on natural basal (111) and non-basal (100) faces of synthetic hematite single crystals grown from a molten solution. The magneto-optic spectra taken for different specimens practically coincide (the scatter in the magnitude of the effect at the maxima did not exceed 10 to 15%).

The components of the permittivity tensor $\hat{\varepsilon}$ are written in the following form

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon = \varepsilon_1 - i\varepsilon_2, \quad \varepsilon_{zz} = \varepsilon_0,$$
$$\varepsilon_{xy} = -\varepsilon_{yx} = -i\varepsilon' = -i(\varepsilon_1' - i\varepsilon_2').$$

The EKE was measured for very different angles of incidence of the light onto the specimen ($\varphi_1 = 15°$ and $\varphi_2 = 70°$) in order to obtain linearly independent equations for ε_2' and ε_1' for determining the imaginary and real parts of the off-diagonal components of $\hat{\varepsilon}$ for hematite. Figure 2 shows the spectral dependence of the EKE for the two angles given. When compared with Ref. 9, a new spectral maximum was found at $E = 1.5$ eV and the existence of the peak in the region of 4.1 eV was reliably established. Figure 3 shows the spectral

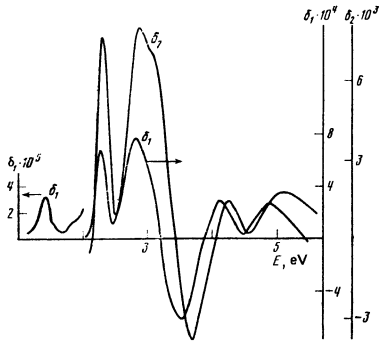

FIG. 2. The equatorial Kerr effect in hematite for two angles of incidence of the light on the specimen: $\delta_1 - \varphi_1 = 15°$; $\delta_2 - \varphi_2 = 70°$.

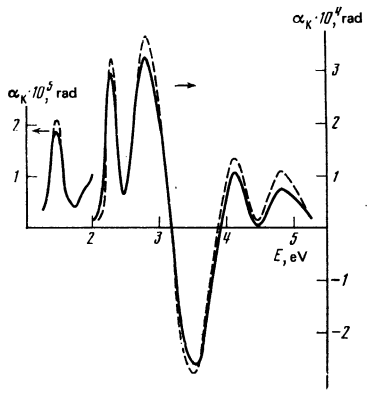

FIG. 4. The meridional Kerr effect. Solid curve, experimental; dashed curve, calculated.

dependences of ε_1' and ε_2' calculated, with the aid of a computer, according to equations given earlier by one of the authors.[10] Values of the diagonal components of the $\hat{\varepsilon}$ tensor, required for the calculation, were taken from Ref. 11 for the near infrared region and from Ref. 12 for the visible and ultraviolet parts of the spectrum. Analysis of the formulae for EKE shows that for $\varepsilon_2 \ll \varepsilon_1$ the value of the EKE is determined by the imaginary part (ε_2') of the off-diagonal component of $\hat{\varepsilon}$ and, as a result, an accurate measurement of ε_1' using the EKE is not possible in the region of relatively weak attenuation. For the same reason ε_1' cannot be determined over the same region from the meridional (MKE) and polar Kerr effects and the intensities of the magneto-optical effects.[10] For this reason, values of ε_2' are shown in Fig. 3 over the whole range studied but of ε_1' for $E > 2.3$ eV.

The values of ε_1' and ε_2' obtained were used to calculate the MKE. Experimental and calculated spectral dependences of the MKE for $\varphi = 45°$ are shown in Fig. 4. The agreement between calculation and experiment is entirely satisfactory.

The temperature dependence of the EKE in the temperature range $300 < T < 900$ K was measured in order to explain the mechanism of the magneto-optical transitions in hematite. EKE curves for $\varphi = 35°$ for a number of temperatures are shown in Fig. 5. It can be seen that the spectral maxima are rapidly reduced in magnitude on raising the temperature and shifting the spectrum to the low energy part by about 0.15 eV. The band broadening with increasing temperature is small. Figure 6 shows the temperature dependence of the value of the EKE for $E = 2.3$ and $E = 2.8$ eV. For comparison, the temperature dependence of the magnetization (dashed curve) of hematite, according to the data of Néel and Pauthenet,[14] is shown. The fall-off in the EKE with increasing temperature takes place considerably faster than the fall-off in magnetization [the $\delta(T)$ dependence for $E = 1.5$ eV could not be measured up to 900 K because of thermal radiation at high temperatures]. The temperature dependence of the magnitude of the EKE spectral maxima at different energies are approximately the same and only the spectral maximum at $E = 4.1$ eV falls faster than others in the region $T \lesssim T_N$.

It was shown by Krebs and Maisch[14] that the strength of the optical attenuation for a number of crystal line transitions in Fe^{3+} ions in $Al_2O_3:Fe^{3+}$, which is isomorphous with hematite, is connected with pair excitation of the Fe^{3+} ions. The spin and parity restrictions which exist for electric dipole crystalline d–d transitions in Fe^{3+} ions are lifted for pair (exciton-magnon and two-exciton) transitions.[15] The rate of pair transitions is very sensitive to the relative orientations of the spins of the Fe^{3+} ions which take part in the transition. Petrov and Gaididei[16] showed that the transition rate in an exchange-coupled pair of ions is proportional

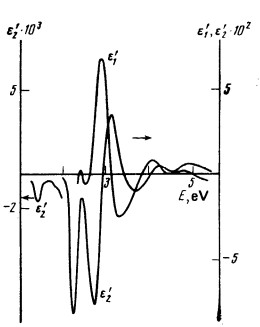

FIG. 3. The real and imaginary parts of the off-diagonal elements of the permittivity tensor for hematite.

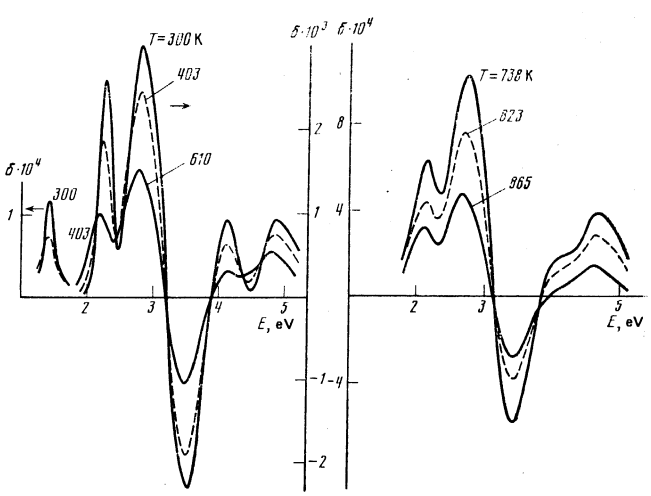

FIG. 5. The equatorial Kerr effect at different temperatures.

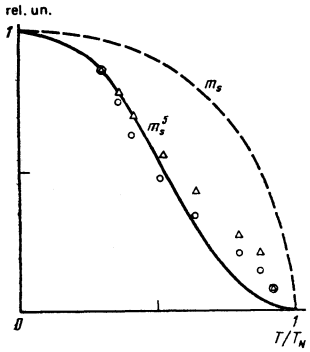

FIG. 6. The temperature dependence of the magnitude of the EKE; ○—E = 2.3, △—2.8 eV.

to the coefficient

$$p=\sin^4[(\theta_A-\theta_B)/2],$$

where θ_A and θ_B are the angles which the spins of neighboring magnetic ions make with some chosen direction. The frequency of a pair transition is a maximum when $\theta_A-\theta_B=\pi$, i.e., when the spins of ions A and B are antiparallel. Thermal motion destroys the strict antiparallel arrangement of neighboring spins in an antiferromagnet. The mean values of $\theta_A(T)$ and $\theta_B(T)$, which are determined by the mean values of magnetization of the antiparallel sublattices of hematite ($I_s^{(1)}(T)$ $=I_s^{(2)}(T)=I_s(T)$) must be substituted into the argument of the sine to evaluate the rate of pair transitions. To this approximation, the rate of pair transitions is proportional to $I_s^4(T)\sim m_s^4(T)$. It is clear that at $T\sim T_N$ the $m_s^4(T)$ dependence decreases the rate compared with the mean value of $\bar{p}$, since $\bar{p}|_{T=T_N}\neq 0$ (the averaging is over all possible values of the angles θ_A and θ_B) while $m_s^4(T_N)=0$. Since the linear magneto-optical effects are proportional to the magnetization, the EKE, produced by pair transitions in magnetic ions, must be proportional to $m_s^5(T)$. Figure 6 shows the $m_s^5(T)$ dependence. It can be seen from the figure that the dependence of the magnitude of the EKE at the spectral maxima is very satisfactorily represented by the $m_s^5(T)$ curve for temperatures not too close to T_N.

The assumption that the observed magneto-optical transitions are of two-particle nature thus explains the temperature dependence of their rate. On the basis of this it can be deduced that the magneto-optical transitions in hematite in the ragne from 1 to 5.5 eV are connected with crystalline d–d transitions in iron ions being permitted, and are not produced by transitions with charge transfer from O^{2-} to Fe^{3+}. (We have not discussed here charge transfer processes between Fe^{3+} ions from different magnetic sublattices,[17] for which the theory is insufficiently developed.)

The shift in the EKE maxima towards lower energies can be explained by the reduction in magnetization of the hematite sublattices with increasing temperature and a corresponding reduction in the effective exchange field. In the molecular field approximation (assuming for simplicity that H_{ex} in the excited state of the Fe^{3+} ion is equal to H_{ex} in the ground state) the maximum energy shift of pair transitions due to the reduction in magnon energy on changing T from 0 to T_N, must be $\Delta E\approx 2g\mu_B H_{ex}=0.24$ eV ($H_{ex}\sim 10^7$ Oe in α-Fe_2O_3, Ref. 18). In the temperature range from 300 to 900 K, m_s and consequently H_{ex} decrease by 60% from the maximum value (Fig. 6) and the energy shift of pair transitions must therefore be 0.14 eV, which is very close to the experimentally observed value (~0.15 eV).[1)]

It is difficult to identify the magneto-optical transitions in hematite by using the data from optical measurements presently available.[12,17] Only the transition at $E=1.5$ eV can be definitely connected with the optical transition at 1.5 eV observed by Bailey[11] and attributed to the crystalline transition ${}^6A_{1g}\rightarrow{}^4T_{1g}$ (^4G) (Ref. 19). There are several reasons for the difficulties in identification. Firstly, the natural frequencies of the magneto-optical transitions are not known; secondly, the optical transitions shift with temperature (the shift in the 1.5 eV transition was observed by Bailey[11]) and all the optical transitions were observed at helium temperatures; thirdly, the number of optical transitions in the visible and ultraviolet regions of the spectrum is rather large and the energies of these transitions are very close together.

The increase in sensitivity of the magneto-optical measurements enabled the spectral dependence quadratic in magnetization of the magneto-optical effect with reflected light to be obtained in the region of strong attenuation. Figure 7 shows a record of the quadratic effect in hematite at an angle of incidence $\varphi\sim 7°$ of the light to the specimen. The calculated effect which is a result of the existence of circular birefringence in hematite is shown by the dashed curve. Calculation of the contribution quadratic in magnetization was carried out in the range from 2.3 to 5.5 eV using the appropriate equations given by Krinchik,[10] making use of the off-diagonal elements of the $\hat{\varepsilon}$ tensor obtained in the present work (Fig. 3). Measurements carried out in the static regime showed that the quadratic effect in the spectral maximum at $E=2.5$ eV for the (111) face does not change

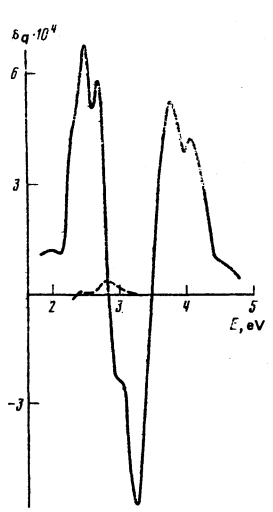

FIG. 7. The quadratic magneto-optical effect in reflected light. Solid curve—experimental, dashed curve—calculated quadratic magneto-optical effect accompanying circular magnetic birefringence.

when the specimen is rotated around the C_3 crystal axis.

The effect quadratic in magnetization thus has a large anomaly in the visible and ultraviolet part of the spectrum (as it does in the infrared region[1]). The large value of the quadratic effect found immediately in the region of the natural frequencies of the transitions would evidently lead to an anomalously large MLD in the range where hematite is transparent.

[1)] Estimates show that the reduction in the strength of the crystal field due to a change in the crystal lattice parameters of hematite with increasing temperature is small, and cannot explain the observed shifts in the magneto-optical maxima.

[1]R. V. Pisarev, I. G. Siniĭ, and G. A. Smolenskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **9**, 112, 294 (1969); [JETP Lett. **9**, 64, 172 (1969)].

[2]G. S. Krinchik, A. P. Khrebtov, A. A. Askochenskiĭ, and V. E. Zubov, Pis'ma Zh. Eksp. Teor. Fiz. **17**, 466 (1973); [JETP Lett. **17**, 335 (1973)].

[3]G. S. Krinchik and V. E. Zubov, Pis'ma Zh. Eksp. Teor. Fiz. **20**, 307 (1974); [JETP Lett. **20**, 137 (1974)].

[4]V. S. Merkulov, E. G. Rudashevskiĭ, H. Le Gall, and C. Leycuras, Zh. Eksp. Teor. Fiz. **80**, 161 (1981); [Sov. Phys. JETP **53**, 81 (1981)].

[5]G. S. Krinchik and G. M. Nurmukhamedov, Zh. Eksp. Teor. Fiz. **47**, 778 (1964); [Sov. Phys. JETP **20**, 520 (1965)]. G. S. Krinchik and V. S. Gushchin, Zh. Eksp. Teor. Fiz. **56**, 1833 (1969); [Sov. Phys. JETP **29**, 984 (1969)].

[6]V. L. Shilo, Lineĭnye integral'nye skhemy (Linear Integrated Circuits), Sov. Radio, Moscow (1979).

[7]A. E. Znamenskiĭ and I. N. Teplyuk, Aktivnye RC fil'try (Active RC Filters), Svyaz', Moscow (1970).

[8]V. E. Zubov, G. S. Krinchik, and V. A. Lyskov, Zh. Eksp. Teor. Fiz. **80**, 229 (1981); [Sov. Phys. JETP **53**, 115 (1981)].

[9]G. S. Krinchik, A. P. Khrebtov, A. A. Askochenskiĭ, E. M. Speranskaya, and S. A. Belyaev, Zh. Eksp. Teor. Fiz. **72**, 699 (1977); [Sov. Phys. JETP **45**, 366 (1977)].

[10]G. S. Krinchik, Fizika magnitnykh yavleniĭ (The Physics of Magnetic Phenomena), MGU Press, Moscow (1976).

[11]P. C. Bailey, J. Appl. Phys. **31**, 399 (1960).

[12]A. I. Galuza, V. V. Eremenko, and A. P. Kirichenko, Fiz. Tverd. Tela (Leningrad) **21**, 1125 (1979); [Sov. Phys. Solid State **21**, 654 (1979)].

[13]L. Néel and R. Pauthenet, C. R. Acad. Sci. **234**, 2172 (1952).

[14]J. J. Krebs and W. G. Maisch, Phys. Rev. **B4**, 757 (1971).

[15]Y. Tanabe, T. Moriya, and S. Sugano, Phys. Rev. Lett. **15**, 1023 (1965).

[16]E. G. Petrov and Yu. B. Gaididei, Phys. Status Solidi B **46**, 103 (1971).

[17]K. W. Blazey, J. Appl. Phys. **45**, 2273 (1974).

[18]I. S. Jacobs, R. A. Beyerlein, S. Foner, and J. P. Remeika, Int. J. Magn. **1**, 193 (1971).

[19]R. V. Pisarev, Fiz. Tverd. Tela (Leningrad) **7**, 207 (1965); [Sov. Phys. Solid State **7**, 158 (1965)].

Translated by R. Berman