Linear and Quadratic Magneto-Optical Effects Observed in La$_{0.7}$Sr$_{0.3}$MnO$_3$ Thin Films in Transmitted Light

Yu. E. Greben'kova[a], *, A. E. Sokolov[a], I. S. Edelman[a], N. V. Andreev[b], V. I. Chichkov[b], and Ya. M. Mukovskii[b]

[a] *Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*
* e-mail: uliag@iph.krasn.ru
[b] *National University of Science and Technology MISiS, Leninskii pr. 4, Moscow, 119049 Russia*

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Magnetic linear dichroism (MLD) is observed in polycrystalline La$_{0.7}$Sr$_{0.3}$MnO$_3$ films in transmitted light. The spectral and temperature dependences of the MLD are determined for the energy E of the light wave ranging from 1.5 to 3.5 eV. The experimental spectra are fitted by a sum of Lorentzian curves. The MLD spectrum exhibits more features in comparison to the spectra of magnetic circular dichroism (MCD), which we measured earlier using the same film samples. Various temperature behaviors of the intensities of the Lorentzian components centered at different E values have been revealed. This can be related to the effect of the surface states on the magneto-optical characteristics of the samples.

Doped manganites attract a considerable amount of current interest owing not only to the promising applications of the colossal magnetoresistance effect observed in them but also to the demand to understand the mechanisms underlying their unusual magnetic and transport characteristics [1–3]. Numerous works deal with the magneto-optical effects (see, e.g., [4–7]) since the magneto-optical investigations provide valuable information on the electron and spin structures of the samples. The studies of the materials in transmitted light by such magneto-optical techniques as magnetic linear dichroism (MLD) and magnetic circular dichroism (MCD) provide more information than the methods based on the Faraday effect. The MLD and MCD spectra exhibit peaks within the range of absorption bands, whereas the Faraday effect is observed far away from these bands. Earlier, we studied the spectral dependence of MCD in La$_{0.7}$Sr$_{0.3}$MnO$_3$ film structures [8]. In these spectra, we revealed the bands characterized by different temperature dependences of their intensity. Such a behavior is of interest for in-depth understanding of the features of the electronic structure of manganites and the origin of the magneto-optical effects in these materials.

Similarly to the Kerr effect, the MCD exhibits a linear dependence on magnetization. It is also used, although not often, in the studies of manganites in transmitted light [5, 9, 10]. At the same time, the MLD, being an effect quadratic in magnetization, was not applied earlier to the studies of manganites. The MCD and MLD spectra can differ from each other. Therefore, the simultaneous studies of both effects can provide new data on the electron transitions and on their sensitivity to the polarization of the incident light wave. This work is focused on the spectral and temperature dependences of MLD and MCD in polycrystalline La$_{0.7}$Sr$_{0.3}$MnO$_3$ films of different thicknesses.

Films with the thickness ranging from 20 to 100 nm were prepared by the dc magnetron sputtering technique. Before the sputtering, the residual pressure in the vacuum chamber was 3×10^{-6} Torr. The operating total pressure of the Ar and O$_2$ gas mixture (4 : 1) was 3×10^{-3} Torr [11, 12]. As the substrates, we used yttrium-stabilized zirconia oxide (YSZ) single crystals. In the course of sputtering, the substrate temperature was 750°C. The studies of the magnetic properties of the samples [8] demonstrated that the Curie temperature T_C of the films under study was about 300 K (for the bulk material, $T_C = 350$–360 K).

The geometry of the experiment schematically represented in Fig. 1 was chosen to observe either a linear (MCD) (Fig. 1a) or a quadratic (MLD) effect (Fig. 1b). In both cases, the samples were magnetized up to saturation by the applied magnetic field H with the direction lying in the film plane. At the measurements of MCD, the angle of incidence for light was 12°. This ensured a sufficient value of the magnetization component along the direction of the light propagation. We used the technique reported in [13] involving the modulation of the light-wave polarization from right circular to left circular. The magnitude of the effect was measured as the difference of the signals corresponding to two opposite directions of the
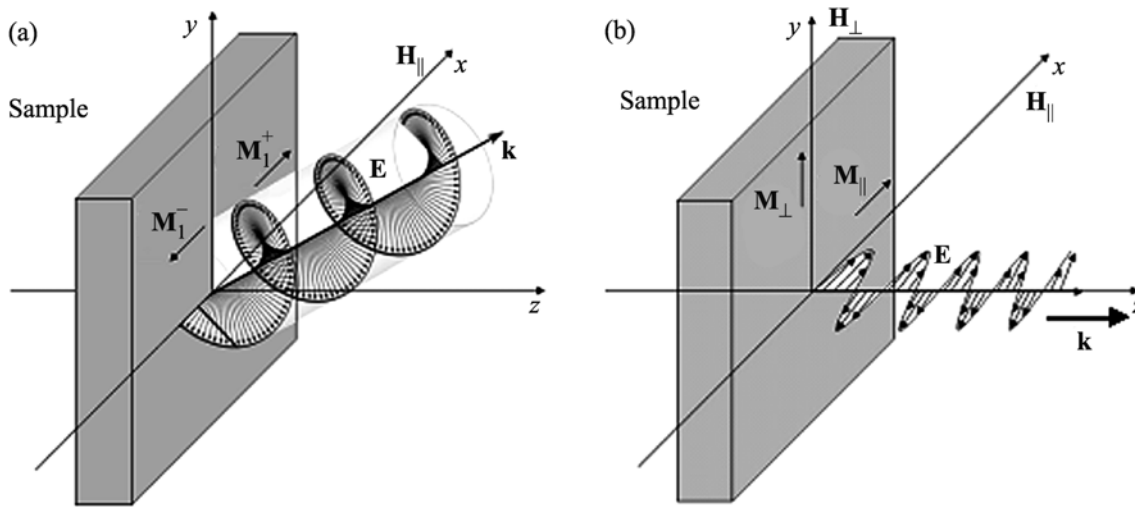
Fig. 1. Geometry of the experiment: (a) the scheme illustrating the measurements of MCD and (b) the scheme illustrating the measurements of MLD.

applied magnetic field. In the course of MLD measurements, the samples were placed perpendicularly to the light beam. The magnetic field was applied in turn along two mutually perpendicular directions in the film plane. As in the case of MCD, the magnitude of the effect was measured as the difference of the signals corresponding to two directions of the applied magnetic field. The magneto-optical measurements were performed at the applied magnetic field equal to 3 kOe at the temperature ranging from 90 to 300 K and within the 1–4 eV energy range.

In Fig. 2a, we show the magnetic field dependence of MCD and MLD for a 90-nm-thick sample. In the case of MCD, the magnetization reversal along the x axis (see the scheme in Fig. 1) corresponds to a symmetric hysteresis loop since, as mentioned above, the effect is odd with respect to the magnetization. In the course of the MLD measurements, the magnetic field component H_x along the x axis varied similarly to the case of MCD. At the same time, the y component H_y of the magnetic field had a constant value. Thus, when H_x was equal to zero, the sample was magnetized along the y axis. In Fig. 2a, we see that the measured effect turns out to be an even function of the applied magnetic field; i.e., it is indeed the MLD.

The general form of the spectra for the two effects under study at $T = 90$ K observed for the 90-nm-thick sample is illustrated in Fig. 2b. Similar spectra are observed for the 50- and 20-nm-thick samples. It can be seen that the MLD magnitude in the spectral maxima is appreciably lower than that of MCD. The shape of both spectra is nearly the same at first glance. Within the range from 1 to 3 eV, the spectral dependence of the effects under study exhibits one positive and two negative peaks. These peaks have an asymmetric shape. At the same time, in the case of MLD, we

observe bends. The bend near 2.4 eV is particularly pronounced.
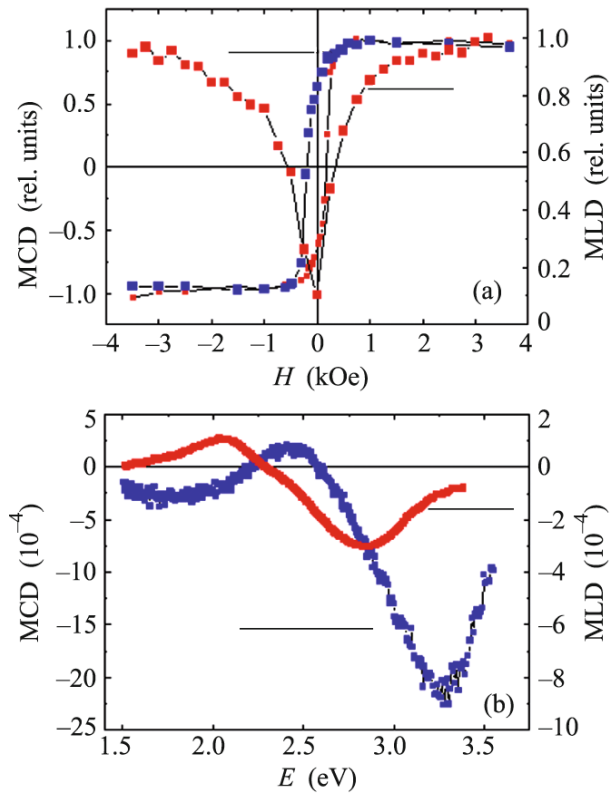
Fig. 2. (a) Magnetic field dependence at $\lambda = 400$ nm and (b) spectral dependence at magnetic field $H = 3$ kOe of magnetic linear dichroism (MLD) and magnetic circular dichroism (MCD) for the film with the thickness $d = 90$ nm measured at $T = 90$ K.
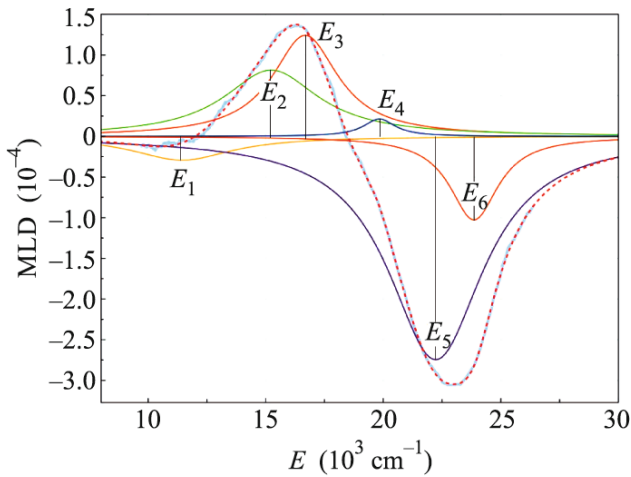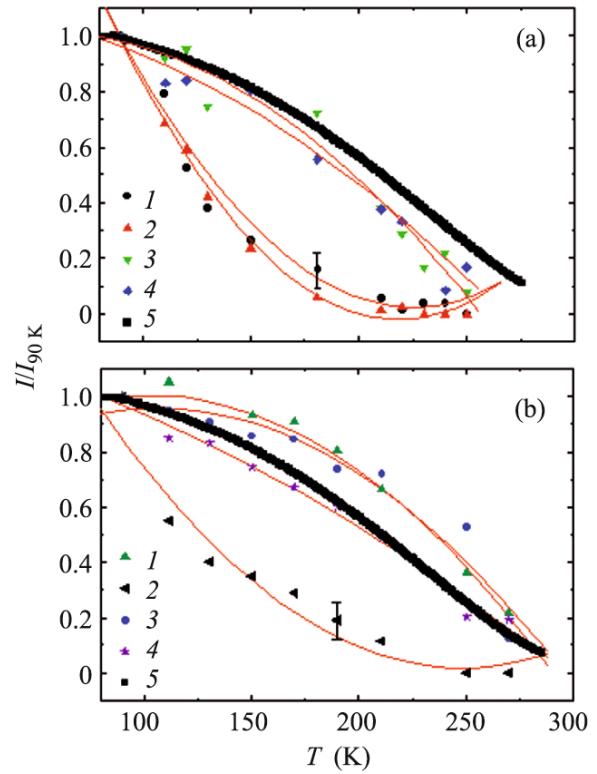
Fig. 3. (Dashed line) Magnetic linear dichroism (MLD) spectrum measured for the film with the thickness $d = 90$ nm at $T = 90$ K and (solid line) its approximation by the sum $E_1 - E_6$ of Lorentzian components.

The asymmetry of the peaks and the existence of bends can be caused by a superposition of several resonances. Therefore, we fitted the MLD spectra by Lorentzian curves following the approach of [14, 15], where the optical conductivity spectrum of $LaMnO_3$ was represented as a sum of Lorentzian-type oscillators. The fitting parameters are the magnitude (amplitude) of the effect, as well as the position and width of the line. The best agreement between the calculated and measured MLD spectra is achieved if we assume the existence of six bands centered at energies $E_1 - E_6$ equal to 1.4 eV (11441 cm^{-1}), 1.9 eV (15233 cm^{-1}), 2.1 eV (16682 cm^{-1}), 2.46 eV (19833 cm^{-1}), 2.75 eV (22231 cm^{-1}), and 3 eV (23858 cm^{-1}), respectively (Fig. 3).

We described the spectral dependence of MCD in [8]. Good agreement with the experimental data was achieved if we decomposed the experimental curve into four bands centered at energies $E_1 - E_4$ equal to 1.7, 2.4, 3.1, and 3.3 eV [8]. A positive peak in the vicinity of 2.4 eV and a negative peak at 3 eV are common features for both MLD and MCD spectra. Thus, in the MLD spectrum in the energy range from 1.4 to 2.75 eV, we reveal additional features in comparison to those observed in the MCD spectrum.

Since the spectra can be represented by a lot of resonance peaks of different signs, we analyzed the temperature behavior of the intensity separately for each Lorentzian component. The fitting of the temperature dependence of the spectral band intensities is performed with the use of the polynomial regression technique, which allows us to provide a clearer representation for the behavior of each component. As can be seen in Fig. 4a, the intensities of different bands changes differently at the temperature decrease. The temperature behavior of the bands with the negative

Fig. 4. Temperature dependences of the band intensities (a) in magnetic linear dichroism (MLD) spectra (curves $1-4$ correspond to bands $E_3 - E_6$ in Fig. 3) and (b) in magnetic circular dichroism (MCD) spectra (curves $1-4$ correspond to bands $E_1 - E_4$ in Fig. 3) in comparison to (line 5) the temperature dependence of the magnetization at $H = 3$ kOe and $d = 90$ nm. The error in the determination of the band intensities is shown by the error bars in the centers of the panels.

sign (curves 3 and 4 in Fig. 4a) nearly reproduces the temperature dependence of the magnetization of the sample (curve 5 in Fig. 4a). At the same time, the intensities of the bands with the opposite sign (curves 1 and 2 in Fig. 4a) obey another law. We have not managed to find any clearly defined regularity, possibly because these bands are located too close to the boundary of the spectral range under study. However, for the band at E_1, we can observe a tendency characteristic of the bands at E_5 and E_6, whereas, for the E_2 band, we have a tendency characteristic of the bands at E_3 and E_4. For comparison, in Fig. 4b, we show a similar temperature dependence for the bands that we observed earlier in the MCD spectra [8]. In the case of MCD, the temperature dependence for the bands of the same sign centered at 1.7, 3.1, and 3.3 eV also nearly reproduces that of the sample magnetization. At the same time, the changes in intensity of the band with the opposite sign centered near 2.4 eV is described by a curve similar to curves 1 and 2 in Fig 4a.

In many works concerning the band structure calculations for undoped $LaMnO_3$ manganite [6, 14, 15],

the authors give the measured spectra of the optical conductivity, which exhibit several bands in different spectral ranges. In particular, all researchers observed a broad peak centered at 2 eV. In [6, 15], additional features were found in the background of this peak. These features suggest the existence of several peaks. In addition, in [6], the polar Kerr effect was studied for the surface of a $La_{0.7}Sr_{0.3}MnO_3$ single crystal, whose spectrum demonstrates many more features in comparison to those observed in the spectra of the optical conductivity for $LaMnO_3$. Similar spectra for the Kerr effect were observed by several other researchers (see, e.g., [16, 17]). Earlier, we mentioned the similarity between the MCD and Kerr effect spectra in $La_{0.7}Sr_{0.3}MnO_3$ [8]. This similarity is quite natural, because these effects are described by the analogous relations [18]

$$\Theta_{MCD} = \frac{4\pi}{\lambda}\left(\frac{n}{k^2+n^2}\varepsilon''_{xy} - \frac{k}{k^2+n^2}\varepsilon'_{xy}\right) \qquad (1)$$

and

$$\Theta_K = \frac{B}{B^2-A^2}\varepsilon''_{xy} - \frac{A}{B^2-A^2}\varepsilon'_{xy}, \qquad (2)$$

where Θ_{MCD} is the MCD magnitude; Θ_K is the Kerr effect magnitude; n is the refractive index; k is the absorption coefficient; λ is the wavelength; ε'_{xy} and ε''_{xy} are the real and imaginary parts of the off-diagonal component of the permittivity tensor, respectively; $A = n^3 - 3nk^2 - n$; and $B = 3n^2 - k^3$. The MLD spectrum is described by another relation [19]

$$\Theta_{MLD} \approx \frac{n_0}{2}\left[\frac{n^2-k^2}{(n^2+k^2)^2}\Delta\varepsilon'' - \frac{2nk}{(n^2+k^2)^2}\Delta\varepsilon'\right], \qquad (3)$$

where Θ_{MLD} is the MLD magnitude, and $\Delta\varepsilon''$ and $\Delta\varepsilon'$ are the real and imaginary parts of the difference of the diagonal components (ε_{zz} and $\varepsilon_{yy} = \varepsilon_{xx}$) of the permittivity tensor. Hence, one should expect different forms of the MLD and MCD spectra. This is indeed observed. The MLD spectrum exhibits a larger number of peaks. Thus, it can give additional information on the electronic structure of the sample.

Discussing the spectral dependence of the optical conductivity, the authors of [6, 14, 15] mentioned that the electron transition with the lowest energy in undoped $LaMnO_3$ manganite is the indirect $d–d$ transition in Mn^{3+} ions at about 2 eV corresponding to the e_g band split by the Jahn–Teller interaction. At doping of $LaMnO_3$, the distribution of the band intensities can change and the bands themselves can move toward lower or higher energies. Such a band shift can be related both to the neighboring bands arising and affecting the spectrum owing to the possibility of the existence of other permitted transitions and to the

contribution to the formation of the bands coming from the transitions involving the states of Mn^{4+} ions. Thus, the bands observed in the magneto-optical spectra at 1.4 eV (MLD) and at 1.7 eV (MCD) should be related to the $e_g–e_g$ transitions in Mn^{3+} and Mn^{4+}.

The formation of octahedral complexes $(Mn^{4+}O_6)^{8-}$ is another consequence of the manganites doping. The magneto-optical characteristics of $(Mn^{4+}O_6)^{8-}$ were studied in [20] using the Kerr effect in $A_2Mn_2O_7$ pyrochlore. In its spectrum, the authors of [20] observed bands at 2.6 eV and 3.1 eV, which they attributed to $^4A_{2g}–^4T_{2g}$ and $^4A_{2g}–^4T_{1g}$ $d–d$ transitions in Mn^{4+} ions. Using the results obtained in [20], the authors of [4] attributed the asymmetric shape of the Faraday rotation peak to the close positions of two $d–d$ electronic transitions at 2.7 and 3.1 eV in Mn^{4+} ions. We should also take into account that no peaks are observed within the 2–3 eV range in $LaMnO_3$ containing only Mn^{3+} ions. Thus, the bands with close energies observed in the MLD and MCD spectra are obviously related to the transitions characteristic of Mn^{4+} ions. Probably, in the case of MCD, the band centered at 3.3 eV is related to the $O(2p)–Mn(3d)$ charge transfer since it has the highest intensity in comparison to other bands.

The MLD and MCD peaks discussed above are characterized by the temperature dependence of intensity similar to that of the sample magnetization. However, the bands exhibiting a temperature dependence different from that of the magnetization are of special interest (Fig. 4). Earlier, a similar picture was reported in [5] for MCD observed in one of two epitaxial $La_{0.7}Sr_{0.3}MnO_3$ films deposited onto different substrates. The authors related it to the mechanical stresses in the film. In our case, we observe two different temperature dependences of the band intensities attributed to the magneto-optical effect in one sample. Such behavior can be caused by the contribution of conduction electrons appearing on doping to the magneto-optical effects. Since the conduction electrons are spin-polarized owing to the magnetic field produced by the ion cores [21, 22], they should affect the magneto-optical characteristics. Here, the degree of spin polarization must be different at the surface of the sample and within its bulk [21]. In Fig. 4, curves 1 and 2 for MLD and curve 2 for MCD have a shape similar to that for the temperature dependence of magnetization at the surface of the $La_{0.7}Sr_{0.3}MnO_3$ film shown in Fig. 4 of [21]. Therefore, the $E_2–E_4$ bands in the MLD spectrum and the E_2 band in the MCD spectrum can be caused by the contribution of the surface states in the film, whereas the other bands are related to the bulk magnetization.

In conclusion, we have observed the quadratic magneto-optical effect in transmitted light for $La_{0.7}Sr_{0.3}MnO_3$/YSZ film structures. In contrast to the linear effect, it exhibits a larger number of the spectral

features revealed by the fitting of the spectra by Lorentzian curves. We have analyzed the of the intensities of the Lorentzian components in the spectra of the linear and quadratic effects in comparison to the temperature dependence of the magnetization. It has been shown that the temperature behavior of the intensity for some components corresponds to the temperature dependence of the magnetization, whereas several other components demonstrate another behavior. The latter can be caused by the difference in the degree of spin polarization of the conduction electrons at the surface of the sample and within its bulk. This is confirmed by the observation that, in the magneto-optical spectrum of the thinnest film (20 nm thick), the band with the temperature dependence of its intensity different from that of the magnetization is already seen at room temperature, whereas such bands in the spectra of the thicker samples appear only at lower temperatures.

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