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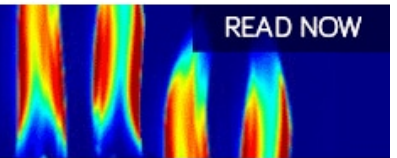
Visible magnetic circular dichroism spectroscopy of the Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ and Pr$_{0.6}$Sr$_{0.4}$MnO$_3$ thin films

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Visible magnetic circular dichroism (MCD) in Pr$_{1-x}$Sr$_x$MnO$_3$ with $x = 0.2$ and 0.4 was investigated for the first time. Samples for the investigation – polycrystalline films with thickness from 20 to 150 nm were prepared with the dc magnetron sputtering. MCD spectra obtained in the energy interval 1–4 eV at temperatures 100–300 K consist of several maxima with different intensities: very strong one near 3.25–3.4 eV and a broad essentially weaker band near 2 eV. An additional maximum of opposite sign arises in the samples with $x = 0.4$ MCD spectrum at 2.33 eV. Experimental spectra were decomposed to several Gaussian components, and their amplitudes temperature dependences were analyzed. In the case of $x = 0.2$, all four Gaussian components are characterized by the identical temperature dependence of their amplitudes. In the case of $x = 0.4$, maxima observed in different spectral intervals demonstrate different temperature dependences of their amplitudes. One more unexpected phenomenon is associated with the different MCD value change in different spectral intervals when coming from $x = 0.2$ to $x = 0.4$: high-energy maximum increases more than twice while low-energy maxima intensity stays at that, practically, unchanged. *© 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4879818]

History of the explosive development of the doped manganites investigations goes back to the works of Jonker and Van Santen,[1,2] who revealed, probably for the first time, ferromagnetic ordering and unusual transport properties in mixed perovskite compounds La$_{1-x}$M$_x^{2+}$MnO$_3$ where M^{2+} was Ca, Sr, Ba. Numerous subsequent studies of the perovskite manganites, R$_{1-x}$M$_x^{2+}$MnO$_3$ where R is La or trivalent Rare Earth element, have shown that their magnetic and electric properties were governed by the R and M^{2+} elements nature and their relative concentrations.[3] In particular, for the R$_{1-x}$M$_x^{2+}$MnO$_3$ system doping of Sr^{2+} leads to formation of a series of magnetic phases including the ferromagnetic (FM) insulator (at $0.1 \leq x < 0.25$) and metallic FM (at $0.25 < x < 0.5$).[3,4] Compounds Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ and Pr$_{0.6}$Sr$_{0.4}$MnO$_3$ studied here represent two types of magnetic phases mentioned above.

The origin of metallic ferromagnetic state in the low-doped manganites is one of the questions under debate: the double exchange mechanism suggested by C. Zener[5,6] and generally accepted now supposes a strong interatomic exchange between localized spin and delocalized electron, so that the electrons spin is always built parallel to the ion spin. Thus, double exchange involves two simultaneous electron transfers: one electron from Mn^{3+} to an overlapping O$_{2p}$ orbital and a second electron from O$_{2p}$ orbital to the adjacent Mn^{4+} ion. However, authors of Ref. 7 considered the double exchange interaction to play an important role in determining the magnetic and electrical properties even for low doped insulating ferromagnetic manganites.

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Magneto-optical effects in combination with optical absorption spectroscopy offer great opportunities for the in-depth study of the manganite magnetic and electronic states (see, for example, Ref. 8 and references therein). Numerous works were dealing with the magneto-optical effects in $La_{1-x}M_xMnO_3$, mainly, with the polar and transverse Kerr effects (KE),[9–12] rarely with the Faraday effect (FE),[13,14] and also with magnetic circular[15,16] and linear[17] dichroism (MCD and MLD, correspondingly). However, we failed in seeking any magneto-optical data for $Pr_{1-x}Sr_x^{2+}MnO_3$ system neither for bulk samples nor for thin films. Comparative magneto-optical study of two FM compounds with similar elemental compositions but belonging to the different electric phases could give new information on the manganites fundamental properties.

In this paper, we report the study of the MCD spectral and temperature dependences in polycrystalline $Pr_{1-x}Sr_xMnO_3$ (PSMO) thin films where x is 0.2 and 0.4. The MCD spectroscopy was chosen for the investigation as this technique provides information to be easier for interpretation comparing to methods based on FE and KE. On the other hand, MCD is one of the higher resolution power techniques comparing to the optical absorption spectroscopy because it allows observing of the weak bands on the background of strong ones. Besides, in the case of MCD, nonmagnetic substrate gives, as a rule, no contribution to the measured effect. As concerns manganites, MCD was used earlier only to study the hole-doped $La_{0.7}Sr_{0.3}MnO_3$ structure.[15,16]

The samples fabrication technique was analogous to that presented in Ref. 18. The single-phased $Pr_{0.8}Sr_{0.2}MnO_3$ and $Pr_{0.6}Sr_{0.4}MnO_3$ targets were prepared by solid-state synthesis using stoichiometric Pr_2O_3, SrO and MnO_2 powders as the starting materials. The relevant thin films were grown on the Y stabilized zirconium oxide substrates by magnetron sputtering using radio frequency power and off-axis sputtering scheme with double cathodes. Such scheme allows transferring the elements from a target to the substrate without element content changing. Before the sputtering, the residual pressure in the vacuum chamber was 3×10^{-6} Torr. The mixture of Ar and O_2 (4:1) was used as working atmosphere. The mixture pressure during the growth process was 3×10^{-3} Torr. The substrates temperature during the sputtering was 750 °C. The thickness of the films was controlled by the deposition time, was determined ex-situ by the X-ray fluorescence analysis, and changed from 20 to 150 nm for $Pr_{0.8}Sr_{0.2}MnO_3$ and from 20 to 130 nm for $Pr_{0.6}Sr_{0.4}MnO_3$.

Powder X-ray diffraction data were obtained by Bruker D8 ADVANCE diffractometer with Cu Ka radiation at 40 kV and 40 mA. The data for Rietveld refinement were collected in a step mode (the step size 0.016^o and 10 s counting time per step) over the range from $10°$ to $140°$. The X-ray beam was controlled by a 0.6 mm fixed slit.

The optical absorption spectra were obtained at room temperature in the range of 0.5 – 4.5 eV with the SHIMADZU-3600 instrument. MCD was measured in the normal geometry: the magnetic vector and the light beam were directed normal to the film plane. Polarization state of the incident light wave was modulated from the right-hand to the left-hand circular polarization using optical piezoelectric modulator. In the case of a sample possessing MCD, its absorption coefficients were different for the right- and left-hand circular polarized light waves relative to the direction of a sample magnetic moment. As a result, the light flux having passed through the sample and reaching a photomultiplier had a modulated intensity. The MCD value was measured as the difference between the photomultiplier voltages for two opposite directions of an applied magnetic field up to 0.35 T in the spectral range 1.0–4.0 eV at temperatures from 100 to 300 K. The measurement accuracy was about 10^{-4}, and the spectral resolution was 0.005 eV.

The difference Rietveld plots for two PSMO films (Figure 1) show large peaks corresponding to the substrate and series of relatively narrow peaks with small intensities corresponding to only one polycrystalline phase without pronounced texture. The Rietveld refinements have been performed by program TOPAS 4.2. Reflections from the substrate were simulated by individual peaks with the Pearson VII profile; other peaks were accounted by corresponding phase using Rietveld refinement. $Pr_{0.7}Sr_{0.3}MnO_3$ was taken as the original structure.[19] Phases $Pr_{0.6}Sr_{0.4}MnO_3$ and $Pr_{0.8}Sr_{0.2}MnO_3$ were obtained from it by changing occupancy of Pr/Sr positions. The reflexes association with the interplanar spacing coincides with that presented in Ref. 7 for the bulk $Pr_{0.8}Sr_{0.2}MnO_3$ polycrystalline sample.

Anisotropic broadening of reflections of PSMO phase was used during the Rietveld refinement. This is because crystallites of PSMO have different sizes in two directions (Table I). The cell
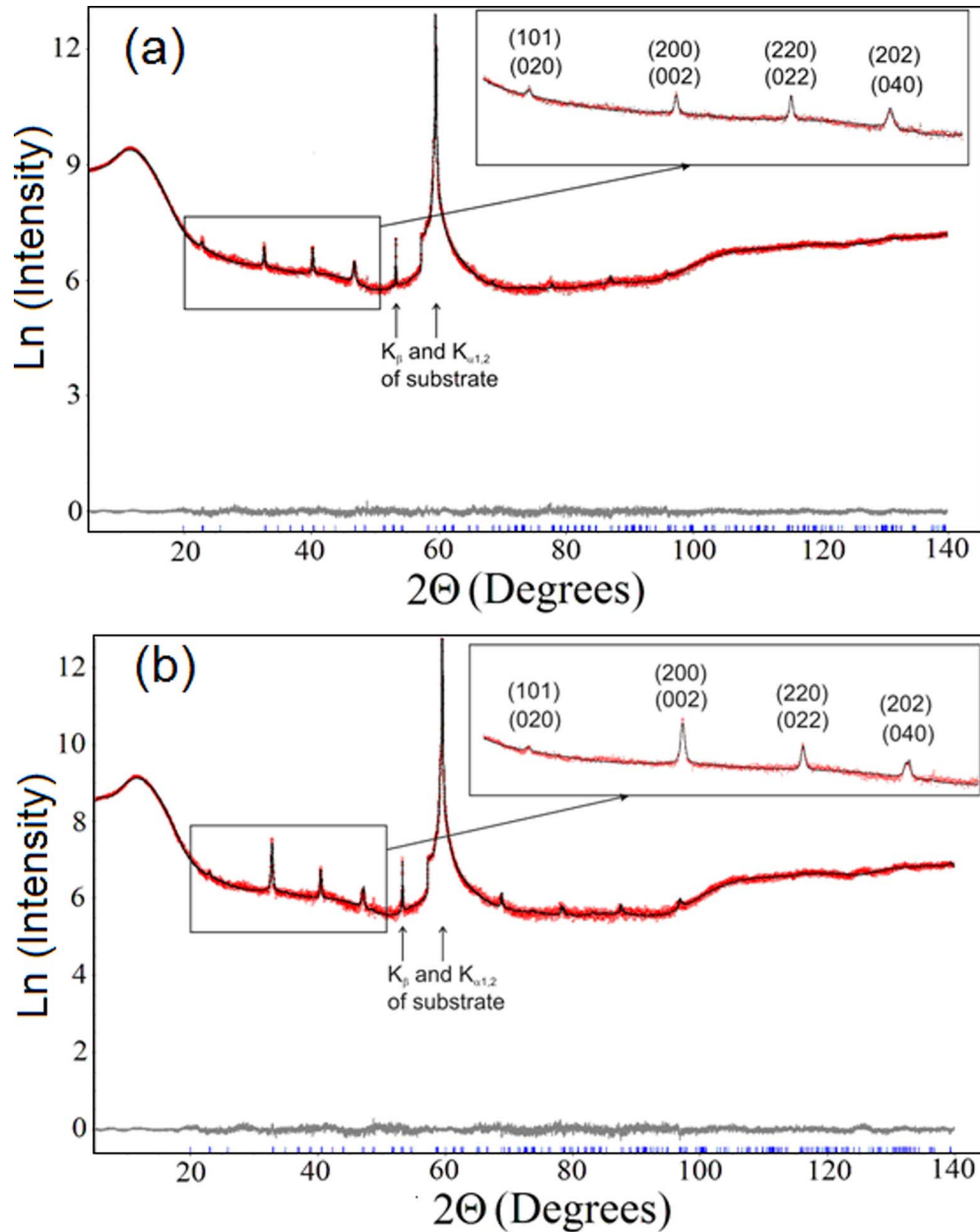
FIG. 1. The difference Rietveld plot of (a) $Pr_{0.8}Sr_{0.2}MnO_3$ (d = 150 nm); (b) $Pr_{0.6}Sr_{0.4}MnO_3$ (d = 130 nm). The reflections from the substrate are indicated by arrows.

parameters of PSMO phases after refinement are presented in Table I. The linear dependence of the cell volume of PSMO compounds on the concentration x taken from databases[4, 19–22] is shown in Figure 2. Cell volume of investigated films lays very well on this linear dependence. This indicates that the estimated Pr/Sr proportion is very close to reality.

Typical room temperature absorption spectra of two PSMO films of the same thickness are presented in Figure 3. A weak relatively narrow peak in the vicinity of 1.5 eV and the strong increase in the absorption with an increase of the photon energy higher than 3 eV are the main characteristics of the spectra. Similar shape of the absorption spectra as well as the optical conductivity spectra were observed by many authors for manganites both undoped $RMnO_3$ and doped $R_{1-x}M_xMnO_3$, with different x values (e.g. Refs. 9, 14, 23). Discussing the spectral dependence of the optical

TABLE I. Structural parameters and crystallites size of two PSMO films.

PSMO	$Pr_{0.8}Sr_{0.2}MnO_3$	$Pr_{0.6}Sr_{0.4}MnO_3$
Space group	*Pnma*	*Pnma*
a, Å	5.480 (1)	5.4465 (7)
b, Å	7.761 (1)	7.721 (1)
c, Å	5.462 (5)	5.422 (1)
V, Å^3	232.3 (2)	228.00 (6)
Average crystallites	31 (3) along b axis	45 (7) along b axis
size, nm	54 (4) along a and c	62 (3) along a and c
	axes	axes
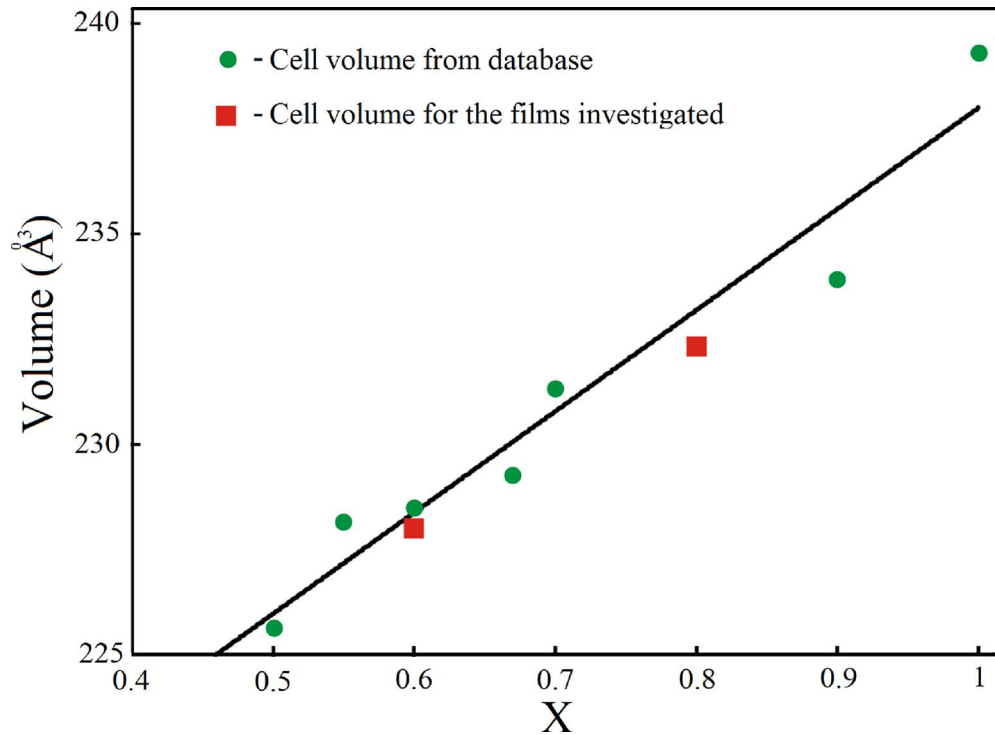
FIG. 2. The cell volume dependence on the concentration x in PSMO films.

conductivity, the authors of[8,24–26] 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. On doping of $LaMnO_3$, the distribution of the band intensities can change and the bands themselves can move toward lower or higher energies.[26] Such a band shift can be related to the contribution of the bands coming from the transitions involving the states of Mn^{4+} ions. In our case, the main difference between the spectra is a shift of the spectral weight of $Pr_{0.6}Sr_{0.4}MnO_3$ a little bit to the lower energies comparing to $Pr_{0.8}Sr_{0.2}MnO_3$ that can be associated with the different ratios Mn^{3+}/Mn^{4+} in these two compounds.

The MCD spectra of PSMO films with the difference doping ions concentration are presented in Figure 4. It is worth noting that the films thickness does not affect in the MCD spectra shape, the peaks amplitude is the only value depending on the film thickness. Two main features characterize MCD spectra of PSMO films: a strong broad peak in the region of 3.25–3.4 eV and significantly weaker asymmetric broad band in the region of 1.7–2 eV. Besides, the relatively weak peak of the opposite sign (Figure 4(b)) appears near 2.3 eV in the $Pr_{0.6}Sr_{0.4}MnO_3$ film MCD spectrum by analogy with that observed at low temperatures in the case of the $La_{0.7}Sr_{0.3}MnO_3$ films.[16] Similar peak absents in the case of $Pr_{0.8}Sr_{0.2}MnO_3$ in the whole temperature interval used (compare insets

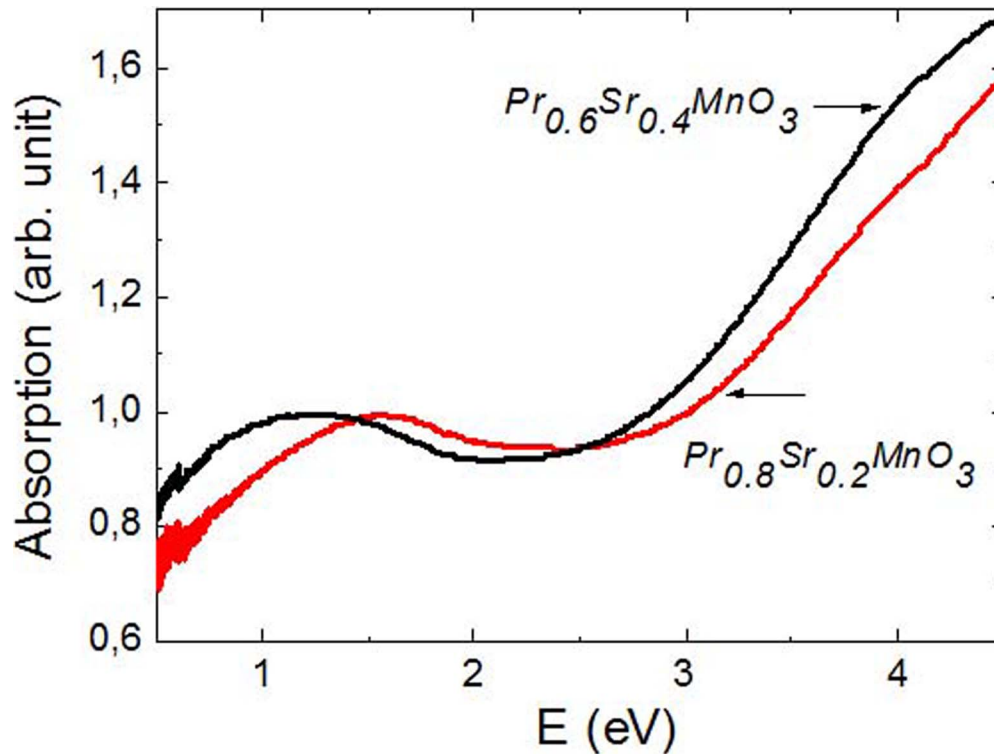FIG. 3. Room temperature absorption spectra for the $Pr_{0.8}Sr_{0.2}MnO_3$ and $Pr_{0.6}Sr_{0.4}MnO_3$ films both of the same thickness 50 nm.

in Figures 4(a) and 4(b)). This peak appearance is not the only difference between two compounds. Another one is associated with the strong MCD value increase in the higher energy region when coming from $Pr_{0.8}Sr_{0.2}MnO_3$ to $Pr_{0.6}Sr_{0.4}MnO_3$, i.e., from sample with lower to sample with higher Sr concentration. At that, the MCD value in the lower energy interval remains almost the same for the both compounds. This behavior is clearly seen in Figure 4(c).

In order to extract meaningful information from the MCD data, we have carried out the spectra decomposition to several Gaussians. The typical example is shown in Figure 5. The best fit was obtained under the assumption of the four bands existence for $Pr_{0.8}Sr_{0.2}MnO_3$ and five bands for $Pr_{0.6}Sr_{0.4}MnO_3$, whose energies (E) are presented in Table II. The temperature dependence of amplitude of each Gaussian component was analyzed separately. For all components, the amplitude at 100 K was taken as a unit. Results are presented in Figure 6 for the $Pr_{0.6}Sr_{0.4}MnO_3$ and $Pr_{0.8}Sr_{0.2}MnO_3$ films. Similar behavior was observed for all samples.

For the sample with the lower Sr^{2+} concentration ($x = 0.2$), the amplitudes of all peaks change, practically, identical with the temperature, Figure 6(a); trend of the curves is close to the bulk $Pr_{0.8}Sr_{0.2}MnO_3$ magnetization temperature dependence.[7] However, for the sample with the higher Sr^{2+} concentration ($x = 0.4$) the picture is more complex: amplitudes of the peaks situated in different parts of the spectrum change with temperature in different way (Figure 6(b)). The highest energy peak (E_5) amplitude follows approximately to the magnetization temperature dependence.[27] The opposite sign peak (E_3) amplitude increases almost linearly with the temperature decrease. The E_1, E_2, and E_4 amplitudes demonstrate a kink at 140–160 K after that they diminish slowly. Such a behavior is the third difference between two compounds investigated.

Because we failed in searching data on the $Pr_{1-x}Sr_xMnO_3$ magneto-optical spectra in literature, the results presented can be compared with magneto-optical properties of other manganite compounds. The MCD spectral dependence of $Pr_{0.6}Sr_{0.4}MnO_3$ (Figure 4(b)) is almost identical to that of $La_{0.7}Sr_{0.3}MnO_3$ films,[16] as well as to the KE[9,28] and to the off-diagonal part of the optical conductivity $\omega\sigma_{xy}$[8] of this compound.
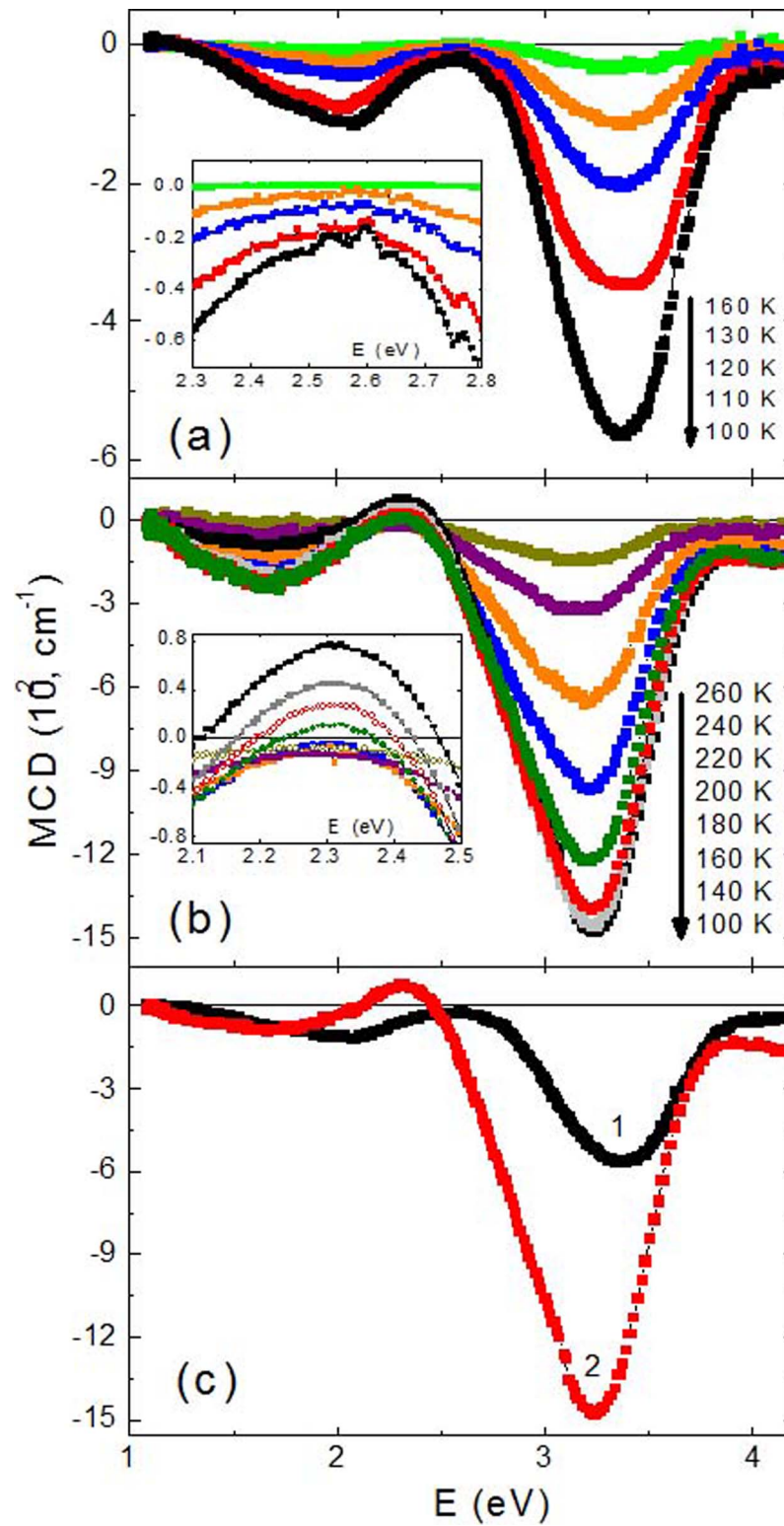
FIG. 4. MCD spectra of samples (a) $Pr_{0.8}Sr_{0.2}MnO_3$ with thickness 150 nm and (b) $Pr_{0.6}Sr_{0.4}MnO_3$ with thickness 130 nm at different temperatures, and (c) MCD spectra of these two samples reduced to the films thickness (curves 1 and 2, correspondingly) at T = 100 K. Magnetic field H = 0.3 T. Insets in (a) and (b): scaled up regions between two main peaks.
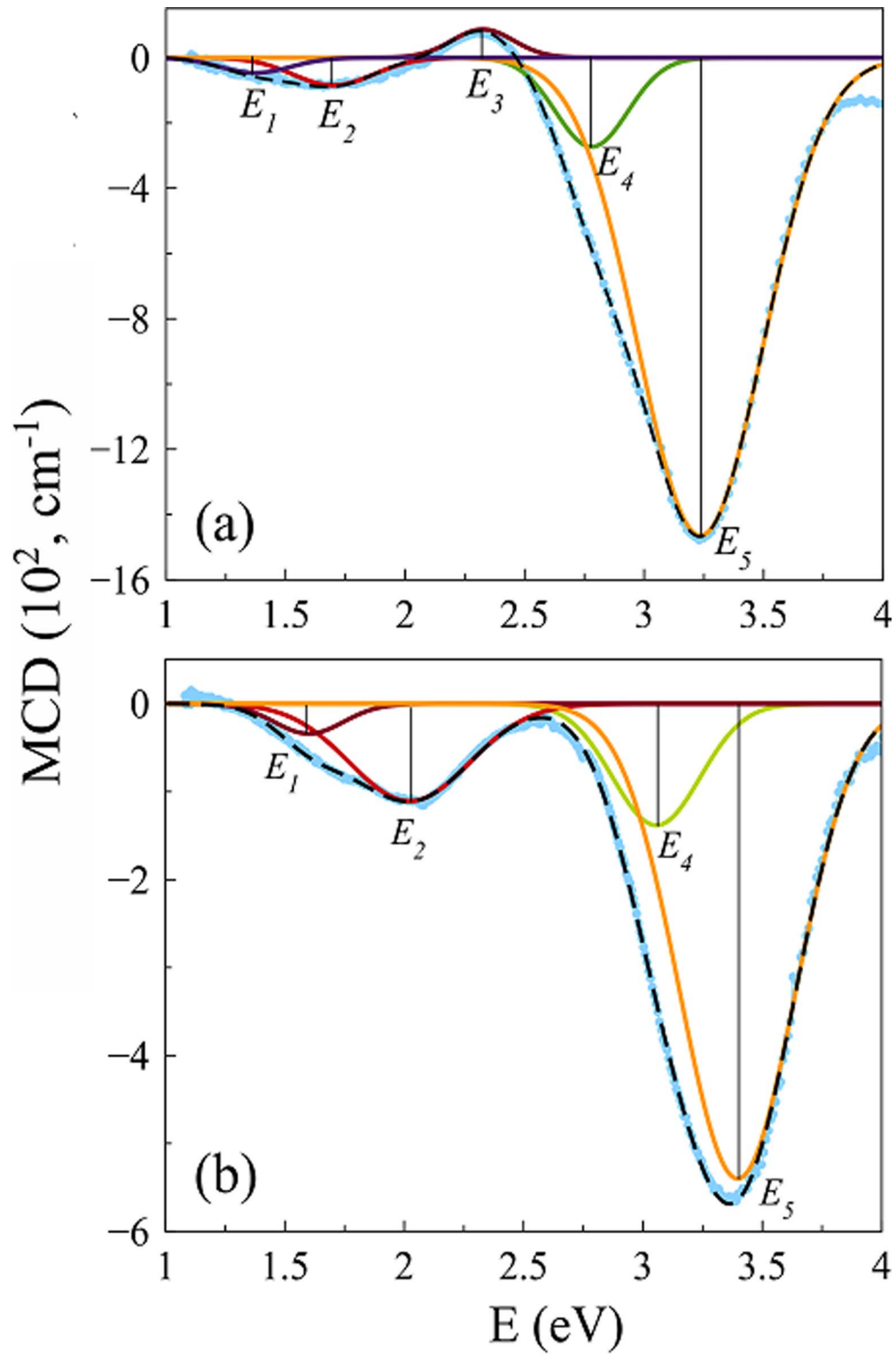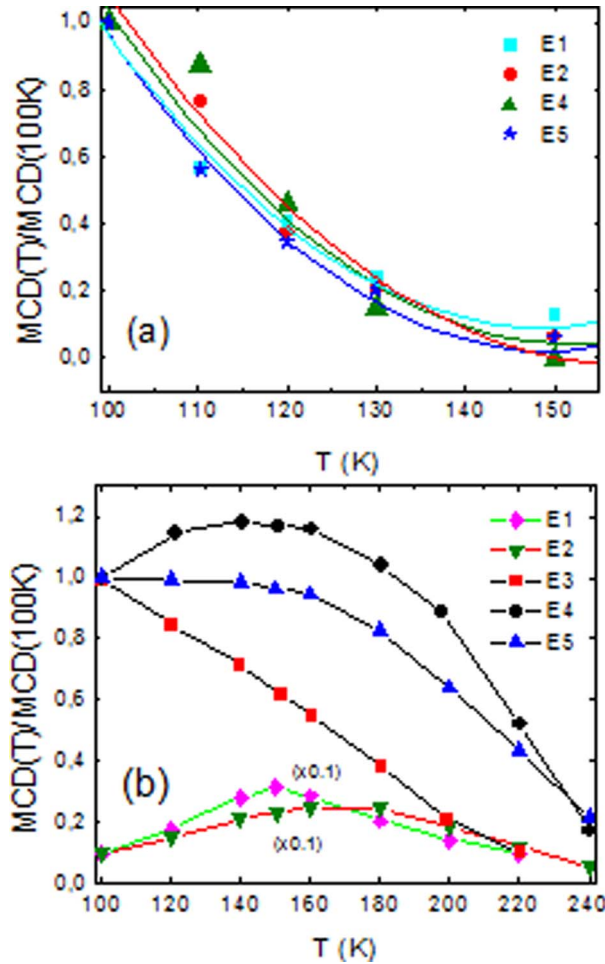
FIG. 5. The MCD spectra decomposition for (a) $Pr_{0.6}Sr_{0.4}MnO_3$ and (b) $Pr_{0.8}Sr_{0.2}MnO_3$. T = 100 K, H = 0.3.

TABLE II. The center of gravity energies of the Gaussian components of two PSMO compounds MCD spectra.

PSMO	E_1	E_2	E_3	E_4	E_5
$Pr_{0.8}Sr_{0.2}MnO_3$	1.6	2	-	3	3.4
$Pr_{0.6}Sr_{0.4}MnO_3$	1.3	1.7	2.33	2.8	3.24

FIG. 6. MCD components temperature dependences for $Pr_{0.8}Sr_{0.2}MnO_3$ (a) and $Pr_{0.6}Sr_{0.4}MnO_3$ (b).

Some divergences should be noted between KE spectra characteristics presented by different authors (compare, for example, Refs. [8], [9], and [28]), possibly, being due to the different sample preparation techniques. However many authors have observed in the $La_{0.7}Sr_{0.3}MnO_3$ magneto-optical spectra two peaks of the same sign in the intervals 1–2 and 3–4 eV and a weak peak of the opposite sign near 2.3 eV. Our data are very close to the KE spectrum characteristics of the $La_{0.7}Sr_{0.3}MnO_3$ films of 60 nm in thickness presented in Ref. [28].

The difference between MCD characteristics of two compounds under investigation is evidently due to the differences in their conductivity and in the Mn^{4+} ions concentration. Since the narrow peak near 2.33 eV is not observed in the insulating $Pr_{0.8}Sr_{0.2}MnO_3$ and observed not only in $Pr_{0.6}Sr_{0.4}MnO_3$ but also in other manganites[8,9,11,16,28] with the metal conductivity, it seems to be reasonable to associate this peak with the charge carries spin polarization.

It is generally accepted that the Mn^{4+} ion concentration is proportional to the doping ions concentration,[29] in our case Sr^{2+} concentration. Since the high-energy peak near 3.24 eV demonstrates an increase in the intensity approximately proportional to the increase of the Sr^{2+} ions concentration it can be associated with the electron transitions involving Mn^{4+} ions.

The unusual temperature behavior of the low-energy MCD peaks E_1 and E_2 in the case of $x =$ 0.4 can be associated with the spectral intensity redistribution between the different nature electron transitions as it was observed in Ref. 30 in the optical conductivity temperature dependence for the metal manganites. Authors have shown that in the metallic phase, low-energy spectra consisted of two parts: intraband excitations and Drude peak with different temperature dependences (see Figure 5 in Ref. 30). At this the intraband excitations contribution decreases at temperature lowering. Thus the temperature behavior of the E_1 and E_2 peaks is determined by the competition of two mechanisms: the magnetization increase and intraband excitations decrease that can explain the kink. The kink in the E_4 peak is more difficult for explanation. This question is in progress now.

In summary, we observed MCD spectra of $Pr_{1-x}Sr_xMnO_3$ thin films with $x = 0.2$ and 0.4 and obtained the correlation of the MCD peculiarities in different spectral interval with the x value: high-energy peaks become twice as larger when x changes from 0.2 to 0.4 while in low-energy spectral interval the MCD intensity remains, practically, unchanged, but for $x = 0.4$ new peak of the opposite sign appears near 2.33 eV. Besides, in the case of $x = 0.4$ different temperature dependences have been observed of the MCD peaks centered at different light wave energies. These experimental findings can give an impetus to reconsider the interpretations of the perovskite type manganite's optical and magneto-optical properties.

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