Light-induced antiferromagnetic-ferromagnetic phase transition in $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ thin films

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The effect of light of He-Ne ($\lambda = 633$ nm) and Ar ($\lambda = 488$ nm) lasers on the magnetization of epitaxial films of manganite $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ was studied. It has been found that the illumination stimulates the antiferromagnetic-ferromagnetic phase transition observed in this manganite in a magnetic field at low temperature. In a magnetic field, the light induces the magnetization increase that apparently is related to a partial transformation of an antiferromagnetic phase into a ferromagnetic one and a formation of ferromagnetic clusters within the antiferromagnetic phase. It was observed that a linearly polarized light effects stronger on the magnetic state of $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ films than an unpolarized light. A relaxation of the light-induced state was not detected. The photoexcited state is stable or a long-lived metastable one.
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Among the perovskite manganites showing colossal magnetoresistance, the manganite $Pr_{0.7}Ca_{0.3}MnO_3$ arouses a great interest due to the recent discovery in this compound of photoinduced phase transition from an insulating to a metallic state.[1–4] The insulator-metal phase transition was induced by the light of Nd-YAG pulse laser with the wavelength of 532 nm (second harmonic) in a surface layer of $Pr_{0.7}Ca_{0.3}MnO_3$ single crystal at temperature $T = 30$ K.[1,2] The phase transition from the insulating to the metallic state in $Pr_{0.7}Ca_{0.3}MnO_3$ was also induced by x-ray irradiation.[4] As it was shown by means of x-ray and neutron-diffraction methods,[4,5] significant changes of lattice parameters and unit-cell volume occur under x-ray illumination. Photoinduced phase transition in $Pr_{0.7}Ca_{0.3}MnO_3$ is related to the melting charge-ordered state and the formation of metallic ferromagnetic clusters under irradiation.

In this paper the results of magnetic measurements of the effect of visible light illumination on the magnetic-field-induced phase transition from antiferromagnetic (AFM) to ferromagnetic (FM) state in thin transparent films $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ are presented and discussed. He-Ne and Ar continuous work lasers were used for the illumination of samples in our experiments as distinct from earlier papers.[1–3] The light flux density was 5 orders of magnitude less than the threshold flux density in experiments described in Refs. 1–3. It has to be stressed that in our experiments the dose of illumination necessary to saturate the light-induced effect was higher than 8–9 orders of magnitude. An important feature of our experiments was also the absence of electrical current in the samples.

The $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ films were prepared by single source metal-organic chemical-vapor deposition technique with flash evaporation of the precursor powder of 2,2,6,6-tetramethylheptanedionato complexes of La, Pr, Ca, and Mn.[6] The films were deposited on $SrLaGaO_4$ substrates cut in the (001) plane. The deposition temperature was 860 °C. After the deposition the films prepared were annealed in oxygen at temperature 860°C for 0.5 h. The cation composition and homogeneity of the films were controlled with the secondary neutrals mass spectrometry using high-density ceramic standards. According to x-ray-diffraction study, the $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ films obtained are epitaxial and have no contribution of polycrystalline material. The lattice parameters of films are in a good agreement with the values for bulk materials of the same composition and correspond to the orthorhombic *Pnma* structure. The x-ray-diffraction study has revealed effective relaxation of the lattice strains in the films. The thickness of the studied films is about of 350 nm whereas the substrate thickness is about of 0.5 mm. Both the film and the substrate are transparent for a visible light. According to the spectral measurements a transmission of the films at low temperatures is about 10% and 8% for wavelengths $\lambda = 633$ nm and $\lambda = 488$ nm, respectively.

The magnetization of the films was measured by means of a commercial superconducting quantum interference device magnetometer (MPMS-5 Quantum Design) using fiber-optic sample holder. The measurements were performed in the temperature range 5–300 K in magnetic fields up to 50 kOe. The film studied has a shape of a circle with the diameter of about 3 mm. The magnetic field was applied perpendicularly to the surface of film.

The magnetic measurements have showed that the *H-T* phase diagram of $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ film is similar to the phase diagram of $Pr_{0.7}Ca_{0.3}MnO_3$.[7] At low temperatures, *T*

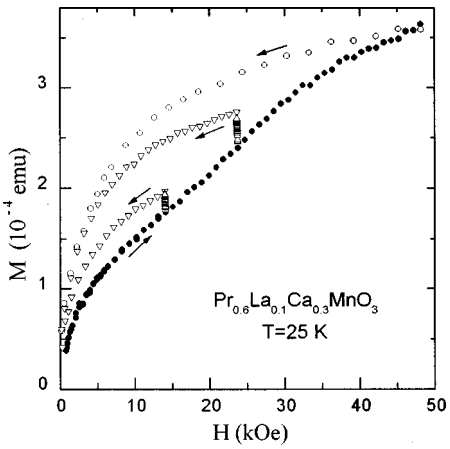

FIG. 1. The field dependences of magnetization measured at $T = 25$ K in the unilluminated film (full and open circles) and after illumination of the film (down triangles). Up triangles show the change of magnetization under illumination at $H = \text{const}$.

<50 K, the magnetic field induces in the film the magnetic phase transition from AFM to FM state. As an example, the field dependences of magnetization *M(H)* at $T = 25$ K in fields $0<H<50$ kOe are presented in Fig. 1. In the dependences shown, the contribution of the substrate has been subtracted and demagnetization fields of sample have been taken into account (*H* denotes an internal field in Fig. 1). At first the virgin *M(H)* (full circles in Fig. 1) was measured after cooling the sample from room temperature to $T = 25$ K in zero magnetic field (zero-field-cooling regime: ZFC). The obtained virgin curve *M(H)* is to some extent similar to the virgin magnetization curve measured in $Pr_{0.7}Ca_{0.3}MnO_3$.[8] Analyzing the slope dM/dH vs *H* in the virgin *M(H)* curve one can find that its behavior is nonmonotonic. There are two kinks in the *M(H)*—first at $H\approx19$ kOe and second at $H\approx32$ kOe. After the first kink the slope increases by about 20% and after the second one decreases by about 50%. Thus the phase transition from AFM to FM state seems to be observed at $19<H<32$ kOe. As a magnetic field decreases from 50 kOe–0, the *M(H)* curve lies distinctly higher (open circles in Fig. 1) than the initial magnetization curve and the reversal phase transition from FM to AFM phase is not observed. After remagnetization of the sample in field up to -50 kOe, the *M(H)* curve measured once more in fields from 0–50 kOe practically coincides with that obtained for lowering the field from 50 kOe–0. Thus the field induced phase transition from AFM to FM state in our films is irreversible at $T = 25$ K similarly to the transition in $Pr_{0.7}Ca_{0.3}MnO_3$.[7,8]

The source of illumination used in our experiments was the He-Ne laser with the wavelength $\lambda=633$ nm and the power of about 25 mW. The direction of light was perpendicular to the surface of film. These experiments were carried out as follows. At first, the sample was cooled from room temperature to $T = 25$ K. Then, the magnetic field increased slowly up to 25 kOe and the *M(H)* was measured (full circles in Fig. 1). The external field $H = 25$ kOe corresponds approximately to the middle of the region in which the phase transition from AFM to FM state occurs. At this field the illumination of the sample was turned on. Under illumination the increase of magnetization of $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ film is clearly demonstrated.

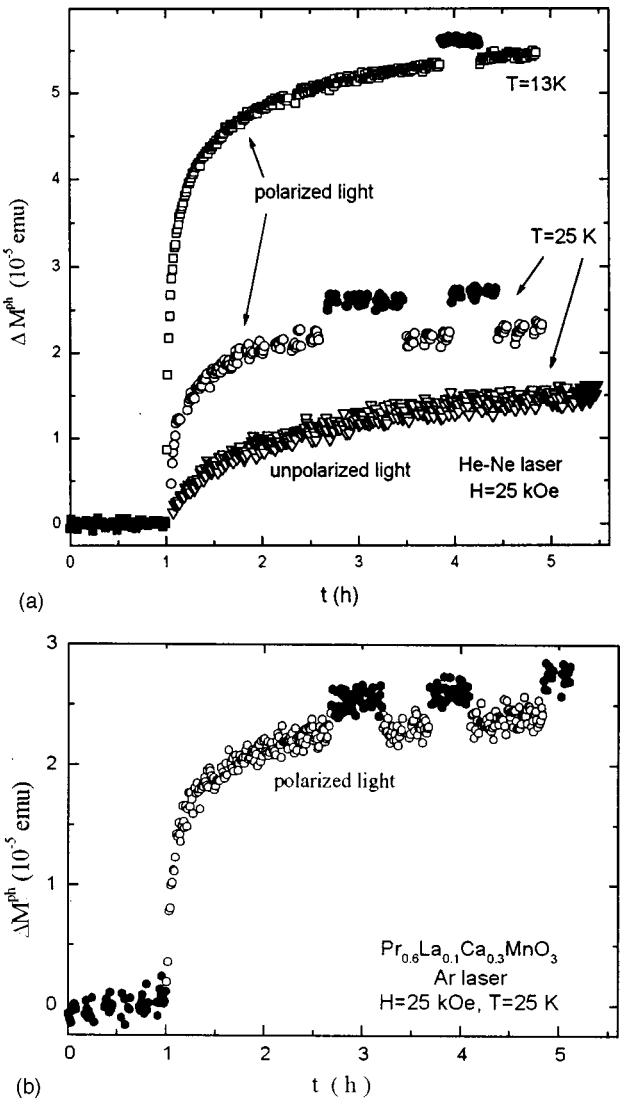

FIG. 2. The time evolution of magnetization at 25 kOe (illumination was turned on at $t=1$ h). Open and full dots represent data obtained under and without illumination, respectively. (a) Illumination by He-Ne laser: linearly polarized light (circles: 25 K, squares: 13 K), unpolarized light (triangles: 25 K). (b) Illumination at 25 K with linearly polarized light of Ar laser.

In Fig. 2(a), the time evolution of magnetization of the film under illumination by He-Ne laser at 25 and 13 K is shown (open circles and squares, respectively). At first the magnetization of film was measured without illumination for one hour [full circles and squares in Fig. 2(a)]. Magnetization change was not detected. Then the illumination was turned on at $t = 1$ h. As it can be seen, the magnetization increases under illumination and achieves the saturation value after approximately 1 h of exposure [$t\approx2$ h in Fig. 2(a)].

This increase of magnetization is not related to the sample heating. The heating of the sample by the laser light was evaluated using the magnetization in the FM state in which the light-induced effect was not detected. As an effect of illumination by He-Ne laser the temperature of the sample was raised from 25 K about 3–4 K. Such increase of temperature corresponds to an increase of ZFC magnetization by about 4×10^{-6} emu (see Fig. 3) which is distinctly less than

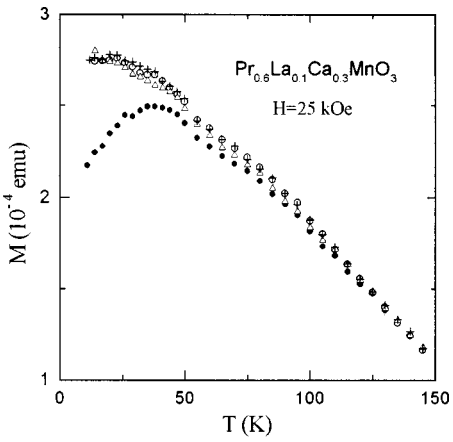

FIG. 3. Temperature dependences of magnetization measured in the field $H = 25$ kOe in the unilluminated film (full and open circles show ZFC and FC dependences, respectively) and in the film under illumination (crosses and triangles show ZFC and FC dependences, respectively).

the observed increase of magnetization under illumination [see Fig. 2(a)]. Moreover, the temperature of the sample reached the equilibrium value as the illumination was turned on (or turned off) significantly faster than the light-induced change of magnetization reached the saturation in the experiment. As the illumination was turned off, the fast small increase of magnetization was observed [full dots in Fig. 2(a)]. The magnitude of magnetization returned rapidly to the previous value as illumination was again turned on. These fast changes of magnetization can be related to the small decrease or increase of sample temperature at the turning off and turning on the illumination, respectively.

In Fig. 1, the light-induced increase of magnetization is shown by up triangles. As it can be seen, at 25 K the magnetization under illumination does not reach the value for the FM phase at 25 kOe (open circles). However, the magnetization of $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ film significantly increases under illumination. After turning off the illumination the *M(H)* in the field decreasing from 25 kOe–0 is shown in Fig. 1 by the down triangles. The increase of magnetization under illumination has been also observed in magnetic fields below the field required to induce the transition from AFM to FM phase. For the film illuminated at 15 kOe the *M(H)* in the field decreasing to zero is shown in Fig. 1 by the down triangles. Similar effect of film illumination on the *M(H)* were observed at 13 K. The time evolution of magnetization of the film under illumination by He-Ne laser at 13 K is shown in Fig. 2a (squares). The magnitude of light-induced increase of magnetization is larger for lower temperature. It should be noted that at low temperatures the relaxation of magnetization was not detected even during 20 h after the illumination was turned off.

The effect of the light illumination on the temperature dependence of magnetization *M(T)* in $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ films was also studied. In Fig. 3 the *M(T)* at 25 kOe of the unilluminated sample after zero-field cooling (full circles) and field cooling (FC) (open circles) are presented. The difference between ZFC and FC curves at $T<50$ K evidences the existence of nonuniform magnetic state in the sample that contains AFM and FM phases. The ZFC and FC magnetizations were also measured under continuous illumination of the sample (triangles and crosses, respectively, in Fig. 3). The measurements were begun after 1 h illumination of the sample at 10 K when the light-induced change of magnetization achieved the saturation value [see Fig. 2(a)]. Both ZFC and FC $M(T)$ curves after illumination coincide approximately with the FC magnetization before the illumination. This result additionally proves that the He-Ne laser light illumination stimulates in $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ films the phase transition from AFM to FM phase. It should be noted that the change of ZFC magnetization after illumination cannot be explained by the heating of sample. As a result of heating the ZFC magnetization can never reach the FC magnetization value at temperatures below $T = 50$ K (see Fig. 3).

Ar laser with wavelength $\lambda = 488$ nm and power of about 160 mW was also applied as a source of light illumination for the study of light-induced AFM-FM phase transition. In this case, the light-induced increase of magnetization at $T = 25$ K and $H = 25$ kOe was also observed [Fig. 2(b)]. The magnitude of magnetization change and the time of saturation achievement were approximately the same for He-Ne and Ar laser illuminations.

The results described above were obtained for linearly polarized light. Because the light which passed through optical wave guide is unpolarized the polarizer was placed between the light output and the sample. The experiment without the polarizer was also carried out at 25 K. In this case, the saturation of magnetization change was not reached after the exposition of 5 h [Fig. 2(a), triangles] although the intensity of the unpolarized light was larger by factor 2 than that of the polarized one in the previous experiments. Thus the linearly polarized light stronger influences magnetic state of $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ films than unpolarized one.

The performed studies allow to formulate the following main results:

(i) The illumination by visible light of He-Ne or Ar laser induces the phase transition from AFM to FM state and results in the increase of magnetization in $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ films. However, only a part of the AFM phase is transformed by the light into the FM phase that can be related to the formation of FM clusters into the AFM phase under illumination.

(ii) The time necessary for saturation of magnetization change under illumination by He-Ne and Ar laser is quite long. The saturation was reached only after 1–2 h of illumination with polarized light and was not reached after 5 h illumination with unpolarized light of He-Ne laser.

(iii) The relaxation of light-induced magnetization change at 13 K was not detected at least for 20 h after the turning off the illumination. Apparently, the light-induced phase transition from AFM to FM phase is irreversible similarly AFM-FM phase transition induced in $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ films by a magnetic field.

(iv) Under the same conditions, linearly polarized light induced the AFM-FM phase transition in $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ films considerably faster than unpolarized light.

The nature of the observed effect seems to be similar to that proposed for the explanation of photoinduced insulator-metal phase transition in $Pr_{0.7}Ca_{0.3}MnO_3$.[1–5] Light illumination of the $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ films at $T<50$ K leads to the formation of FM clusters in the AFM phase and conse-

quently to AFM-FM phase separation responsible for the increase of magnetization. However, the mechanisms of formation of FM phase should be different in our experiments and those in which the sample was illuminated by the Nd-YAG pulse laser. The flux density of light in our experiments was by 5 orders of magnitude less than the threshold flux density of light in experiments described in Refs. 1–3. Assuming the same physical mechanisms in both kinds of experiments, photoinduced phase transition in experiments described in this paper should not be observed due to relaxation. Moreover, the partial transition of the $Pr_{0.6}La_{0.1}Ca_{0.3}MnO_3$ film from AFM to FM state requires significantly larger dose of illumination which exceeds by 8–9 orders of magnitude the dose of illumination inducing the insulator-metal phase transition in the experiments described in Refs. 1–3. Apparently in our case, significantly slower processes are responsible for light-induced phase transition than in the case of power pumping by pulse Nd-YAG laser. As distinct from the power pumping inducing the high density of current carriers exceeded the threshold one, in our experiments the accumulation processes are important to produce the photoinduced AFM-FM phase transition. Such processes are possible at low temperature when the reverse charge transfer between Mn ions can occur very slowly.

It is interesting to elucidate the reason of dependence of velocity of formation of FM phase on the polarization of light. It is possible that linearly polarized light induces the directional charge transfer between Mn^{3+} and Mn^{4+} ions in the crystal lattice. This could promote faster reconstruction of magnetic and crystal structures.

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