# Persistent and transient photoconductivity in oxygen-deficient La<sub>2/3</sub>Sr<sub>1/3</sub>MnO<sub>3-\delta</sub> thin films

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Light illumination produces major, interesting changes of the electrical properties of oxygen deficient  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_{3-\delta}$  thin films. At small oxygen deficiency, the classical insulator-metal (I-M) transition at a temperature  $T_p$  decreases with increasing oxygen deficiency. The low-temperature metallic behavior in darkness shows a persistent increase of the conductivity with light. This photoconductivity increases with oxygen deficiency (from a few to 60%). At large oxygen deficiency, the films are semiconducting in darkness, from helium to room temperature and light induces a transient photoconductivity and a low-temperature I-M transition. The intriguing possibility of collective light induced magnetism is discussed.

DOI: 10.1103/PhysRevB.63.174423 PACS number(s): 72.40.+w, 71.30.+h, 72.80.Ga

## I. INTRODUCTION

LaMnO<sub>3</sub> containing only Mn<sup>3+</sup> and SrMnO<sub>3</sub> containing only Mn<sup>4+</sup> are insulating and antiferromagnetic at low temperatures. Partial substitution of trivalent La ions by divalent Sr ions in  $La_{1-x}Sr_xMnO_{3-\delta}$  (LSMO) compounds induces a mixed Mn<sup>3+</sup>, Mn<sup>4+</sup> valence. For  $0.2 \le x \le 0.5$  this substitution gives rise simultaneously to metallic conduction and ferromagnetism below an ordering temperature  $T_n$  (defined as the temperature at which the electrical resistance is maximum). The transport mechanism in these manganites is usually explained using a double exchange theory based on electron exchange between  $Mn^{3+}$  and  $Mn^{4+}$  ions via the oxygen site.  $T_p$  and the transport properties of these holedoped compounds dramatically depend on the Mn3+/Mn4+ ratio obtained for different relative La<sup>3+</sup>/Sr<sup>2+</sup> concentration. Increased oxygen deficiency in  $La_{2/3}Sr_{1/3}MnO_{3-\delta}$  leads to a negative electric charge deficiency which is compensated by a Mn<sup>4+</sup> decrease to keep charge neutrality. So increased oxygen content also decreases the Mn4+/Mn3+ ratio. Thus the mixed Mn valence can be changed by oxygen deficiency.  $T_p$  decreases with oxygen deficiency and for high oxygen deficiency, this manganite is semiconducting in the whole temperature range. Around  $T_p$  (or even when the manganite is semiconducting), an applied magnetic field decreases the electrical resistance by several orders of magnitude,<sup>3</sup> the socalled colossal magnetoresistance (CMR). Instead of the magnetic field, application of x rays<sup>4</sup> and electric field,<sup>5</sup> induce a large decrease of the electrical resistance in manganites. Moreover, a fast ( $\sim$ nsec) *I-M* transition triggered by infrared photocarrier injection into the charge-ordered state of a thin slice of a Pr<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> single crystal was reported.6

Many examples exist in the literature in which light may induce changes in the transport properties of solids including semiconductors  $^{7.8}$  and materials close to an insulator-metal (I-M) transition.  $^{9.10}$  In particular a related class of materials, the high-temperature superconducting cuprates exhibit in their oxygen deficient state, persistent photoconductivity

(PPC) (Ref. 11) due to the photoinduced increase in the carrier density. Perhaps more interestingly, they also exhibit persistent photosuperconductivity (PPS),<sup>12</sup> i.e., a light induced collective behavior. The above mentioned low-temperature effects relax at room temperature with long (hours to days) characteristic times. The interesting question arises whether it is possible to induce PPC and a collective magnetic effect in the manganites.

The goal of this paper is to study the influence of light on the dc electrical properties of manganite thin films. We find low-temperature PPC on slightly oxygen deficient thin films and transient photoconductivity (TPC) on samples with high oxygen deficiency. These results are compared with those obtained in cuprates. This opens up the possibility for the observation of a particularly intriguing phenomenon, the induction of ferromagnetic behavior by light. <sup>13</sup>

## II. EXPERIMENTAL RESULTS

### A. Sample preparation and measurements

 $La_{2/3}Sr_{1/3}MnO_{3-\delta}$  (LSMO) films were prepared in situ with a multitarget Riber Pulsed Laser Deposition (PLD) apparatus using a frequency tripled Nd:YAG laser (B.M. Industries 503 DNS) with a pulse length of 5 ns at a repetition rate from 1 to 5 Hz. This delivers a 355 nm wavelength laser beam with a 50 to 600 MW/cm<sup>2</sup> power density depending on the laser beam focussing on the target. A deposition rate at 0.26 nm/s at a repetition rate of 2.5 Hz and a substratetarget distance of 35 mm was obtained using a stoichiometric LSMO target (with a density higher than 0.9 of the theoretical one) which is continuously moved to ensure a uniform ablation rate. Before growth, the (100) SrTiO<sub>3</sub> substrates are cleaned by heating in pure oxygen (at a pressure of 45 Pa) up to 800 °C for 10 min. RHEED is used to monitor the flatness and substrate cleanliness before growth. A growth temperature around 700 °C is measured at the surface of the substrate holder. The growth is carried out in pure oxygen at pressures in the range 6 to  $10^{-3}$  Pa depending on the desired oxygen content (Table I). The sample is then cooled to room temperature within 45 min including an intermediate tempera-

TABLE I. Growth conditions of the  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_{3-\delta}$  thin films.  $T_S=$  substrate temperature,  $P_G=$  growth pressure,  $P_C=$  cooling pressure, Tp= resistive peak position, c= hole concentration,  $\delta=$  oxygen deficiency, t= layer thickness.

Sample	$T_S(\mathbf{C})$	$P_G$ (Pa)	$P_C$ (Pa)	$T_p$ (K)	c	$\delta$	t(nm)
		6					
1504	695	$1.7 \times 10^{-2a}$	$4 \times 10^{4}$	121	0.089	0.12	55
1482	670	0.27	$4 \times 10^4$	116	0.087	0.122	50
1498	670	$2 \times 10^{-2}$	$4 \times 10^4$	94	0.075	0.128	45
1611	670	$1 \times 10^{-3}$	$1 \times 10^{-3}$		0.02	0.16	95

<sup>&</sup>lt;sup>a</sup>Oxygen activated by an ECR plasma source.

ture plateau at  $400\,^{\circ}$ C for 15 min under an oxygen pressure as given in Table I. The sample thicknesses are also listed in Table I where one can see that all samples are in the 45–95 nm thickness range.

High resolution x-ray diffraction was utilized to assess the microstructure of the manganite thin films. High angle diffraction with the scattering vector perpendicular to the film plane (i.e., in the growth direction), otherwise known as theta-two theta scans, were performed from 20° to 90°. Alignment was performed by reference to the [200] SrTiO<sub>3</sub> substrate reflection and the miscut angle was deduced to be <0.2°. Only the [110], [220], and [330] reflections were observed from the LaSrMnO<sub>3</sub> films with full widths at half maxima consistent with textured growth in the [110] orientation. Transverse or "rocking" scans were performed at these peak positions, to obtain information on the mosaic spread. The data indicate peak widths slightly larger than the substrate ones, implying no increase in mosaic spread beyond that of the substrate. In summary, the layers are [110] oriented with diffraction widths indicating good texture in the growth direction.

Broad wavelength (250 nm $<\lambda<$ 900 nm) white light, is provided by a 70 W Hg-Xe lamp, which illuminates the whole sample through a window of the optical closed cycle He cryostat. Reproducible four lead, current-voltage characteristics are measured at different temperatures before and after illumination. After one hour relaxation at temperature

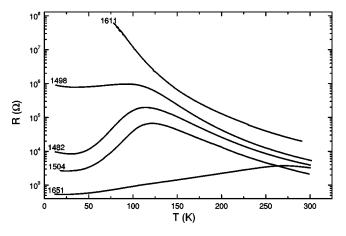


FIG. 1. Resistance versus temperature in darkness for different oxygen content  $La_{2/3}Sr_{1/3}MnO_{3-\delta}$  thin films.

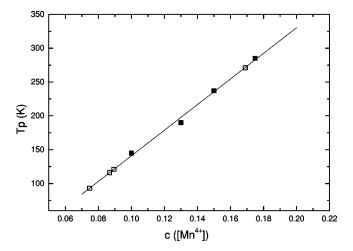


FIG. 2.  $T_p$  versus  $\mathrm{Mn^{4+}}$  concentration. Dark squares from Ref. 16. Open squares: our measurements.

around 100 K in darkness, the illuminated manganites recover the original properties they had before illumination.

# **B.** Experiments

Figure 1 shows the resistance versus temperature for various oxygen deficient  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_{3-\delta}$  films. The resistance peak temperature,  $T_p$  decreases from 271 K for the smallest oxygen deficient sample to less than 10 K for the highest one. The  $T_p$  are well correlated with the oxygen pressure during preparation in agreement with the literature. The resistivity (which in  $\Omega$ cm is roughly  $10^{-4}R(\Omega)$  the measured resistance) also increases with decreasing oxygen content. The resistance upturn below 33 K for the sample 1498, is probably related to localization effects. The resistance upturn below 35 K for the sample 1498, is probably related to localization effects.

To determine the oxygen deficiency we compare our measured  $T_p$  with the correlations between  $T_p$  and hole concentration c of  $\mathrm{Mn}^{4+}$  ions determined from thermogravimetric analysis.  $^{14,16}$  In this range of values,  $T_p$  depends linearly on c as shown in Fig. 2. For  $\mathrm{La}_{2/3}\mathrm{Sr}_{1/3}\mathrm{MnO}_{3-\delta}$  samples, c is related to the oxygen deficiency  $\delta$  by c=1/3-2  $\delta$  both reported in Table I.

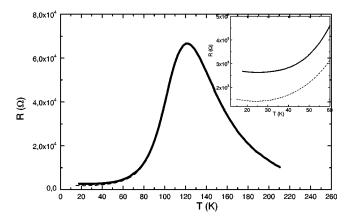


FIG. 3. Resistance versus temperature of a slightly oxygen deficient  $La_{2/3}Sr_{1/3}MnO_{3-\delta}$  thin film. (Sample 1504) in darkness (solid line) and after illumination (dashed line). The inset shows behavior at the low temperature on a larger scale.

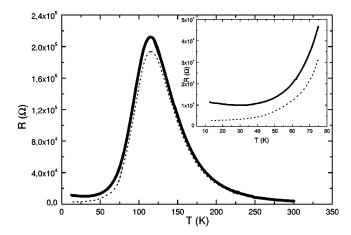


FIG. 4. Resistance versus temperature of a slightly oxygen deficient  $La_{2/3}Sr_{1/3}Mn_{3-\delta}$  thin film. (Sample 1482) in the darkness (solid line) and after illumination (dashed line). The inset shows the low-temperature behavior on an expanded scale.

Motivated by the results from the ceramic oxide superconductors, we have investigated the behavior of oxygen deficient manganites for samples whose oxygen deficiency places them close to the *I-M* transition. Figures 3 and 4 show the resistance versus temperature of two slightly oxygen deficient La<sub>2/3</sub>Sr<sub>1/3</sub>MnO<sub>3- $\delta$ </sub> thin films. (sample 1504 with  $T_p$ = 121 K and sample 1482 with  $T_p$  = 116 K) before and after illumination. Under illumination, the low-temperature metallic state resistance decreases (inset of Figs. 3 and 4). This decrease of the resistance is persistent at low temperature (i.e., remains after the light is turned off) as shown in Figs. 5 and 6 where the resistance R is displayed versus illumination time. The original state may be recovered, but long time annealing above 100 K is needed. The small step observed after the light is turned off is probably related to heating effects. The persistent photoconductivity increases with increasing oxygen deficiency in a similar fashion to the PPC and PPS in high-temperature superconductors. 17-20 The low-temperature decrease of the resistance is 3% for sample 1651 (not shown here), 42% for sample 1504 (Fig. 5), and

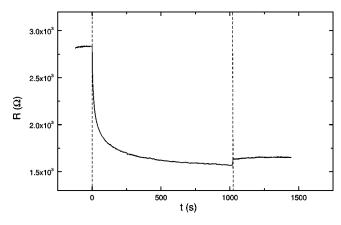


FIG. 5. Resistance versus illumination time for the sample 1504 showing persistent photoconductivity. The small increase at 1020s may be due to a heating effect as the light is turned off.  $T = 10 \, \text{K}$ .

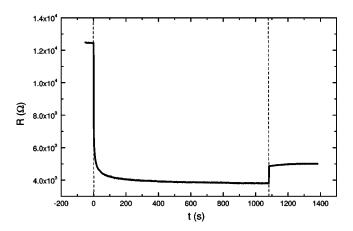


FIG. 6. Resistance versus illumination time for the sample 1482 showing persistent photoconductivity.  $T=10\,$  K.

60% for sample 1482 (Fig. 6). Percent values of PPC and TPC are tabulated in Table II along with the quenching temperature for the PPC effects. Figure 7 shows the resistance versus illumination time for sample 1482 at fixed optical power for three different temperatures: 10, 60, and 110 K. Note that the effect is large enough that it is appreciable (10%) even at 110 K. In addition to the persistent photoconductivity, transient photoconductivity (TPC) (Ref. 21) is also observed. At 110 and 60 K, as the light is switched off (at, respectively, 3500 and 1600 s) a sharp resistance increase is found, which cannot be connected to heating. Since the resistance increases with increasing temperature, heating would increase the resistance. Therefore turning off the light, would decrease the resistance contrary to observations. At 10 K the situation is more complicated due to the small low temperature resistance upturn which could also produce a similar resistance increase due to surface heating. This TPC increases with increasing oxygen deficiency and will be discussed below.

Figure 8 shows the R(T) in darkness and under illumination for the least oxygenated sample 1611, with  $\delta$ =0.16. In darkness the film is always semiconducting (no *I-M* transition) and the transport properties are well described by three dimensional variable range hopping, <sup>22</sup> i.e.,  $\ln(R)$  linear with  $T^{-1/4}$ , as shown in the inset of Fig. 8. Above 125 K the

TABLE II. Photoconductivity properties of the 5 samples. (to 10 K unless otherwise indicated). PPC = persistent photoconductivity (i.e., percentage persistent change in conductivity after illumination), TPC = transient photoconductivity (i.e., percentage transient change in conductivity), and  $T_q$  = quenching temperature for the photoconductivity effects.

Sample	PPC(%)	TPC (%)	$T_q(K)$
1651	3.0	0	80
1504	5.0	42	90
1482	12	60	125
1498	8.0	factor of 28	125
1611 <sup>a</sup>	N/A	factor of 12.8	125

<sup>&</sup>lt;sup>a</sup>Value was measured at 82 K as the lower temperature resistance was unmeasurable.

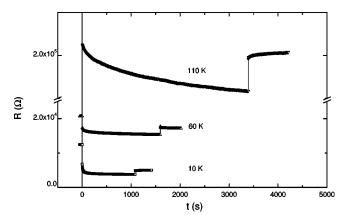


FIG. 7. Resistance versus time (sample 1482) with the same optical power at different temperatures (illumination times: 0–1080 s at 10 K, 0–1600 s at 60 K, and 0–3400 s at 110 K).

resistivity is not affected by the illumination. However, below 125 K, a transient I-M transition is induced by illumination. This photoinduced I-M transition occurs at a temperature  $T_p$  which decreases linearly with power as shown in Fig. 9. The corresponding inverse of the resistance maximum (measured with a higher accuracy than  $T_p$ ) also shows a similar behavior. In this case there is a possibility that heating effects may explain the results. However, the following reasons indicate that this probably is a real effect and not an artifact due to heating: (a) the I-M transition is induced by very low level light irradiation, (b) fixing the light intensity and decreasing the temperature results in a resistivity decrease, and (c) resistivities smaller than the room temperature resistivity can be obtained in this fashion. Perhaps more importantly, above 125 K light has no effect on the resistivity, which probably rules out heating altogether. Further experiments must be performed to rule out, in a unique fashion, the possibility of heating. These include frequency dependence and changing the thermal coupling of the sample to cryogens and exchange gas.

Figure 10 shows the time dependence of the resistance before, during and after illumination for sample 1611. The

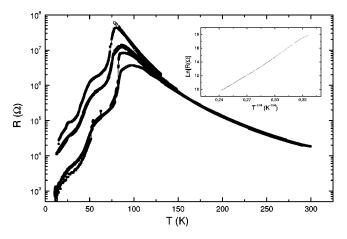


FIG. 8. Resistance versus temperature measured in darkness (open dots) and under illumination (solid dots) with different optical power for the least oxygenated sample (No. 1611).

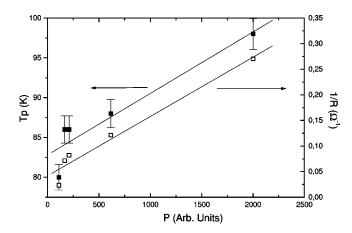


FIG. 9. Linear dependence of  $T_p$  and the corresponding value  $R^{-1}$  versus optical power.

illumination begins at t=0 and ceases at  $t=130\,$  s. Note that the relaxation of the TPC is rather rapid. It is worth noting at this point that it is difficult to establish the magnitude of the PPC in this situation when the TPC is so large (many orders of magnitude at 10 K). Future experiments will involve measurement of the spectral dependence of the photoconductivity to establish the frequency dependence of the PPC and TPC. It is possible that they are dissimilar. We will return to the issue of the existence of the large TPC at a later stage.

The sample with the intermediate oxygen deficiency (sample 1498 with  $\delta$ =0.13) has a very interesting behavior. The R(T) in darkness, shows that the oxygen content is high enough to induce the low-temperature semiconducting state with an upturn below 33 K, while conserving a smoothed I-M transition (of small amplitude) at 90 K. The illumination of the thin film (Fig. 11) restores an I-M transition at around 80 K. Decreasing the optical power by approximately 15% lowers the I-M by a few degrees K. On the other hand, Fig. 12 shows that in darkness an applied magnetic field of 0.48 T is not able to recover the I-M transition. The application of a magnetic field gives rise only to a low-temperature negative magnetoresistance in darkness or under illumination (Fig. 13) where the I-M transition is shifted to lower resistances.

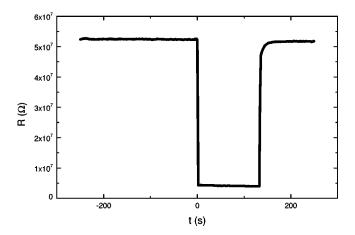


FIG. 10. Time dependence of the resistance of sample 1611 after illumination at t=0 and ceasing illumination at  $t=130\,$  s.

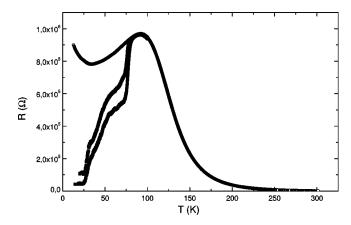


FIG. 11. Resistance versus temperature measured in darkness (open dots) and under illumination (solid dots) for two optical powers for the intermediate oxygen deficient sample (No. 1498).

#### III. DISCUSSION

Illumination of oxygen deficient LSMO gives rise to two effects; PPC in samples with small oxygen deficiency and TPC in highly oxygen deficient ones. For intermediate oxygen deficiency, the same sample can show both PPC and TPC, as shown in Fig. 7. The PPC persists for long periods of time, as long as the sample is kept below 100 K, and it relaxes back to its original state after annealing at higher temperatures. These effects cannot be explained as an experimental artifact, such as heating, as this would give opposite changes in the resistivity to those observed here. Moreover the PPC is enhanced with increasing oxygen deficiency, i.e., by approaching the *I-M* transition. These results are similar to persistent and transient photoconductivity effects which observed in  $La_{0.7}(Ca, Ba)_{0.3}MnO_{3-\delta}$ , <sup>23</sup>  $Pr_{2/3}Sr_{1/3}MnO_{3-\delta}$ , <sup>24</sup> and  $La_{1-x}Pb_xMnO_{3-\delta}$  (Ref. 25) thin films. Therefore these phenomena are of a general nature in this class of materials.

The PPC in LSMO is very similar to what is observed in cuprate superconductors and other systems close to a *I-M* transition. A particularly striking example of PPC occurs in

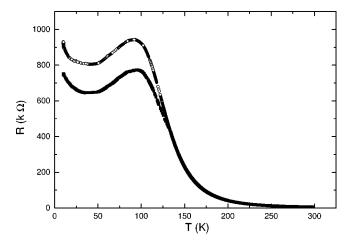


FIG. 12. Resistance versus temperature measured in darkness with an applied magnetic field of B = 0.48 T (solid squares) and without (open circles) for sample 1498.

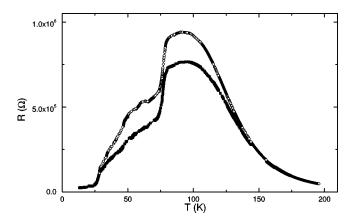


FIG. 13. Resistance versus temperature measured under illumination with applied magnetic field of B = 0.48 T (solid squares) and without (open circles) for sample 1498.

oxygen deficient YBa<sub>2</sub>Cu<sub>3</sub>O<sub>r</sub> where changes of several orders of magnitude in the resistivity may be observed under the appropriate conditions. The increased conductivity relaxes to its original value if the sample is annealed close to room temperature and the effect is enhanced with increased oxygen deficiency, i.e., as one approaches the *I-M* transition. In the case of DX centers in GaAs (Ref. 26) based compounds or for CdMnTe, 10 the PPC has been quite convincingly proven theoretically and experimentally, to be due to an increase in the density of charge carriers. On the other hand, in the cuprates the situation is not as clear. There are two main competing theories used to interpret the existence of PPC effects. The first is based on photoinduced ordering in the CuO chains and is specific to cuprates although "similar" situations could be envisaged in other materials. The second model hypothesizes that incoming photons create electron-hole pairs in the solid which are hindered in their attempts to recombine by a microscopic potential barrier. This barrier is provided by the fact that the electrons are easily trapped at the oxygen vacancies while the holes contribute to the conduction. Given the structure of the manganites it seems clear that the most likely mechanism to be active here is the latter, i.e., creation of the electron-hole pairs with the holes contributing to the conduction process while the electrons are trapped at the oxygen vacancies. This model provides simple explanations for the increase in resistance peak temperature (due to the increase in hole density) and for the experimental observation that the PPC reduces in magnitude as "optimal" doping is approached (the oxygen deficiency decreases meaning that the trapping mechanism for the electrons is destroyed).

Transient photoconductivity has also been observed in high- $T_c$  superconductors. The mixed valence substitution or the partial oxygenation creates disorder which is sufficient to localize the electronic wave functions in the band tails. This weak localization is characterized by the formation of a mobility edge at an energy  $E_c$ , close to the Fermi level. The photodoping which increases the carrier density, can shift the Fermi level through the mobility edge and induce the I-M transition as  $E_F$  moves through  $E_c$ . Parallels can be drawn with work on  $Gd_{3-x}v_xS_4$  (Ref. 29) where magnetic field

application changes  $E_F$ - $E_c$  and induces a *I-M* transition when  $E_F$ = $E_c$ . Further experiments are needed to understand more deeply the origin of  $E_c$  and the dependence of  $E_F$ - $E_c$  on illumination in various regimes.

# IV. CONCLUSIONS

We have shown that illumination gives rise to persistent and transient increases of the low-temperature conductivity of oxygen deficient  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_{3-\delta}$ . Both effects are enhanced with decreasing distance from the *I-M* transition, i.e., with increasing oxygen deficiency. The results are very similar to those observed in a wide range of other materials systems including high-temperature oxide superconductors, narrow band semiconductors, DX centers in GaAs based systems, ferroelectrics, etc. Although the mechanism for this effect has not been uniquely established at this time, it is

likely that it arises from an increase in the charge carrier density by light and the consequent trapping of the electrons in oxygen vacancies. This photodoping effect provides two exciting opportunities for future research: a reproducible and repeatable way for exploring the doping dependent phase diagram of CMR materials and perhaps the more exciting possibility of inducing magnetism<sup>30</sup> with an external driving agent.

#### ACKNOWLEDGMENTS

The authors thank E. Jacquet for his helpful contribution in the film preparation. They are also grateful to Professor A. Revcolevschi (Université Paris-Sud) for supplying the LSMO target used in this study. The work at UCSD is supported by the U.S. Department of Energy and ONR-DARPA.

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