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Effects of illumination on the electrical properties of oxygen deficient cuprates and manganites

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ABSTRACT

We report the analogies between the electrical properties at low temperatures of oxygen deficient cuprates and manganites thin films under illumination by UV or visible light. For the cuprates, a decrease of the oxygen content decreases the critical temperature of the transition from the normal to the superconducting state while for the manganites it decreases the transition temperature at which the insulator-metal transition occurs. For full oxygenated cuprates and manganites thin films there is no effect of the illumination on the electrical properties of the films. For small oxygen deficient cuprates (in the normal state) and manganites thin films, light increases substantially the conductivity leading to a persistent photoinduced conductivity (PPC) and the effect of persistent photoconductivity increases with oxygen deficiency. For high oxygen deficiency, the cuprates and the manganites are insulating. In that case, a transient photoconductivity is observed in the cuprates and manganites. Moreover, a photoinduced insulator-metal (I-M) transition appears in these insulating thin films.

Keywords: cuprate, manganite,photoconductivity.

1.INTRODUCTION

There are many analogies in the structural and physical properties of manganese and copper based perovskites. Both have rich doping phase diagram and they are mixed valence compounds with Mn^{3+} /Mn^{4+} for the manganese perovskites and Cu^{2+} /Cu^{3+} (or even Cu^{+} /Cu^{2+} for high oxygen deficiency) for the copper perovskites.

The perovskite cuprates like $YBa_2Cu_3O_y$ are superconductors for $6.4 < y < 7$ and semiconductors for $y < 6.4$ with a transition from the normal to the superconducting state at a critical temperature increasing from 0 for $y \sim 6.4$ to 90 K for $y = 7$. The manganese perovskites have the typical formula $Ln_{1-x}D_xMnO_{3-\delta}$ where Ln = La, Pr,.... is the trivalent rare earth element and D = Sr, Ca, Ba... is a divalent element. For $0.2 < x < 0.5$ they exhibit at a Curie temperature Tc, a transition from a ferromagnetic metallic state at low temperature to a paramagnetic semiconducting state at temperatures greater than Tc.

The CuO_2 planes, responsible for the transport properties in the cuprates, are similar to the MnO_2 planes in the manganites. However, the transport mechanism is different. In the cuprates, the CuO chains are assumed to be a charge reservoir which transfers charges to the CuO_2 planes. Thus a superconducting cuprate is assumed to consist of CuO_2 planes separated by a charge reservoir. Charge carriers are added by doping (substitution of trivalent La by Sr in $La_{2-x}Sr_xCuO_4$ or by adding oxygen in $YBa_2Cu_3O_6$). To maintain charge neutrality, electrons are removed from the copper oxide planes and the remaining holes (i.e. missing electrons) are mobile leading to conduction and superconductivity below the critical temperature.[1]

In the manganites, the transport mechanism is usually explained with the 'double-exchange' theory[2, 3] based on the exchange of electrons between Mn^{3+} and Mn^{4+} ions. Thus the transport properties of these hole-doped compounds dramatically depend on the Mn^{4+} /Mn^{3+} ratio, given by the doping amount. Thus the I-M transition at a temperature Tp (corresponding to the maximum resistance) can be changed by modifying the Mn^{4+} /Mn^{3+} ratio obtained for different relative Ln^{3+} /D^{2+} ratio. This mixed Mn valency can be changed also by oxygen deficiency. Increased oxygen deficiency leads to a negative electric charge deficiency which is compensated by a Mn^{4+} decrease, to keep the charge neutrality. So increased oxygen content decreases also the Mn^{4+} /Mn^{3+} ratio.

The goal of this paper is to present the analogies between the effect of illumination by UV or visible light on the electrical properties of oxygen deficient cuprates (principally oxygen deficient thin films of $YBa_2Cu_3O_y$ or $GdBa_2Cu_3O_y$) and manganites thin films (principally $La_{2/3}Sr_{1/3}MnO_{3-\delta}$).

2.EXPERIMENTAL RESULTS

2.1 Cuprates

The superconducting transition temperature of oxygen-deficient superconducting $YBa_2Cu_3O_y$ thin films increases considerably with illumination. This photo-induced change persists, after the light is switched off if the sample is kept at low temperatures (typically lower than 100K). This persistent photoinduced superconductivity (PPS) is more pronounced for oxygen deficient thin films and vanishes for fully oxygenated $YBa_2Cu_3O_7$. Kudinov et al[4] discovered earlier that illumination of normal or semiconducting $YBa_2Cu_3O_y$ increases substantially the conductivity, leading to a persistent photoinduced conductivity (PPC). An insulating thin film close to the metal - insulator transition ($y\approx6.4$) can even become superconducting by illumination.[5]

The PPC effect is shown figure 1 with the resistivity of a $GdBa_2Cu_3O_y$ thin film displayed as a function of illumination time. The initial resistivity change is large and has a long slowly varying tail at long times. The figure 1 shows also the relaxation time of the persistent photoconductivity of the $GdBa_2Cu_3O_y$ thin film at 300K. The resistivity relaxation or excitation as a function of time is usually described by a stretched exponential law:

$$\rho(t) = \rho(\infty) + [\rho(0) - \rho(\infty)].\exp[-(t/\tau)^{\beta}]$$

where $\rho(\infty)$ is the resistivity at saturation and $\rho(0)$ the initial resistivity, τ a relaxation time and β a dimensionless dispersion parameter. The relaxation time τ follows a thermal activation process $\tau = \tau_0 \exp[\Delta/k_BT)$.

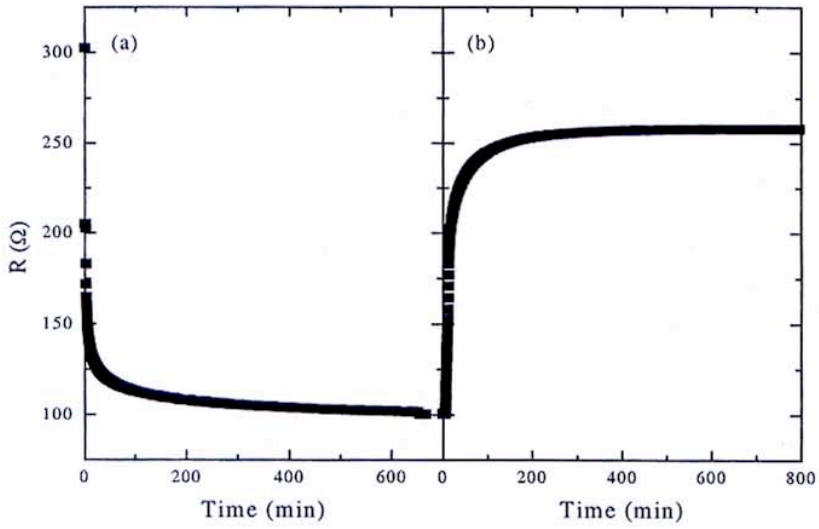

Figure 1: Resistance versus (a) illumination time at 95 K and (b) relaxation time at 300 K for $GdBa_2Cu_3O_y$

A transient increase in the conductivity together with a delayed response was also found in more oxygen deficient $YBa_2Cu_3O_y$. For insulating $YBa_2Cu_3O_{6.3}$, Yu et al.[6] have observed clear signatures of a transient photoinduced transition to metallic behavior below 100 K. Unfortunately after the few initial experiments[6], no further results appeared on this very interesting transient effect.

Two classes of models have been proposed to explain photodoping experiments in high-Tc superconductors. In one case, the PPC and PPS are due to an increase in the CuO chain order by light irradiation. This has been claimed to be supported by Raman measurements of photoexcited $YBa_2Cu_3O_y$ thin films[7].

In the other scenario, Kudinov et al[4] suggested that illumination causes photoexcitation of electron-hole pairs with the subsequent trapping of electrons by defects. For $YBa_2Cu_3O_y$ these defects are the oxygen vacancies in the CuO chains where normally an oxygen ion would be located in a fully oxygenated sample. This capture process creates excess mobile holes transferred into extended states in the CuO_2 planes with the consequent enhancement of the transport properties. This effect is more pronounced for oxygen deficient films because more electrons can be trapped by the increased oxygen vacant sites. The electron trapping mechanism is also supported by other experiments . For example the spectral dependance of the PPC shows peaks in the photoinduced magnitude and the illumination with IR light which can quench partially the persistent photoconductivity. The wavelength dependence of the IR quenching suggests that the average trap depth of the potential well is near 1eV in agreement with the value determined from the activation energy of the relaxation time. Moreover, the presence of PPC and PPS in the Tl and Bi based compounds (where CuO chains are absent) leads further support to this second scenario. Nevertheless, it is probably fair to state that to date no unique explanation has emerged and that further theoretical work is needed to explain the large amount of systematic data available. For a review article on the PPC and PPS effect in the cuprates see for example A.Hoffmann et al[8] and A.Gilabert et al.[9]

2.2. Manganites

Figure 2 shows the resistance versus temperature for three different typical oxygen deficient $La_{2/3}Sr_{1/3}MnO_{3-\delta}$ thin films. The maximum resistance Tp decreases from room temperature for full oxygenated sample down to low temperatures for oxygen deficient thin films and even disappears for the highest oxygen deficient samples. This is in agreement with measurements reported in litterature[10]. De Leon-Guevara[11] has measured Tp versus the hole concentration c due to Mn^{4+} ions. From this curve we can estimate c : c(n°1)=0.02; c(n°2)=0.07; c(n°3)=0.09. For $La_{2/3}Sr_{1/3}MnO_3$ samples, this concentration is related to δ by $c=1/3 - 2\delta$. From this relation we can estimate the oxygen deficency δ in the different films and find: δ(n°1)=0.16; δ(n°2)=0.13, δ (n°3) = 0.12. The resistivity of the thin films increases also with decreasing oxygen content. An upturn of the resistivity is usually observed at low temperatures and it has been related to localization effects.[12]

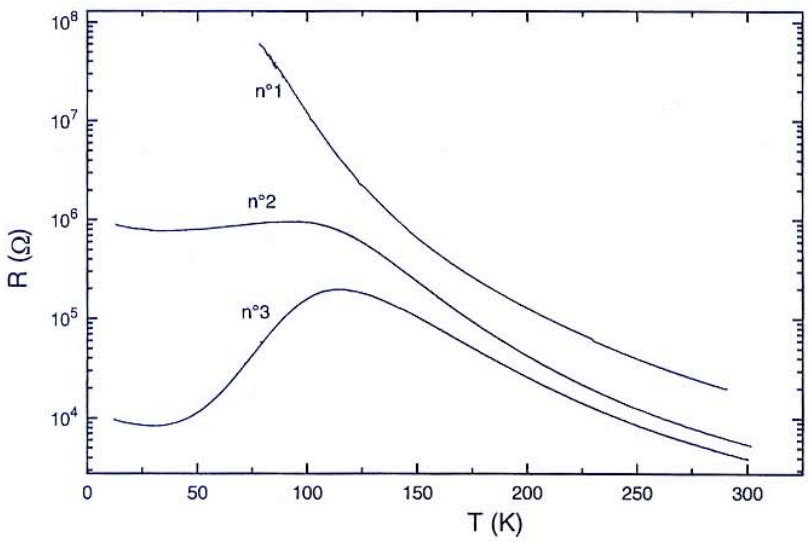

Figure 2: Resistance versus temperature, in the darkness, of three different oxygen content $La_{2/3}Sr_{1/3}MnO_{3-\delta}$ thin films

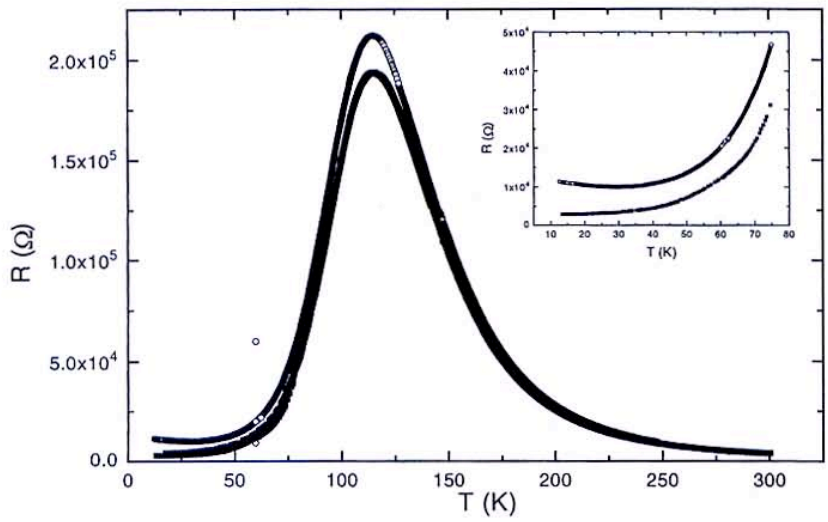

Figure 3: Resistance versus temperature of a weakly oxygen deficient $La_{2/3}Sr_{1/3}MnO_{3-\delta}$ thin film (sample n° 3) in the darkness (open circles) and under illumination (solid squares)

Figure 3 shows the resistance versus temperature of a weakly oxygen deficient $La_{2/3}Sr_{1/3}MnO_{3-\delta}$ thin film. (sample n°3) with a Tp = 116 K before and after illumination with UV or visible light. Under illumination, the resistance decreases only at low temperaure in the metallic state. This decrease of the resistance is persistent as shown by figure 4 where the resistance R is displayed versus illumination time. After illumination, the resistance which has decreased by around 62 %, stays in the excited state . To recover the original state at low temperature, the film must be heated to room temperature.

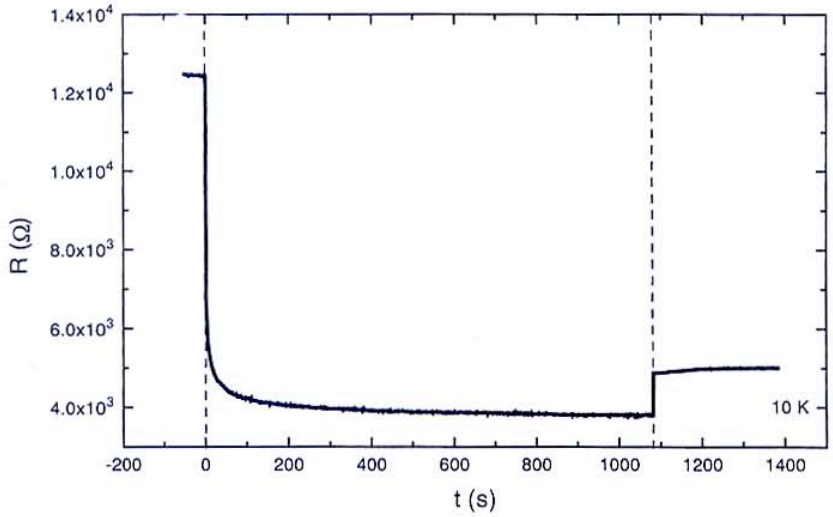

Figure 4: Resistance versus illumination time (0 <t<1080 s) for the sample n°3 showing the persistent photoconductivity

The small increase of the resistance at 1080 s is due to a small heating effect of the light. Such persistent photoconductivity (PPC) at low temperatures on manganites have been reported by Cauro et al.[13] in $La_{0.7}(CaBa)_{0.3}MnO_3$ thin films and by A.Gilabert et al.[14] on $Pr_{2/3}Sr_{1/3}MnO_3$ thin films. This effect, which shows a decrease of the resistivity of the manganites after illumination by UV or visible light, persists even after the light is switched off if the temperature is kept at low temperatures (< 100 K). This enhanced conductivity relaxes towards the original properties when the temperature of the sample is risen back to room temperature. This effect is similar to the PPC effect observed in high critical temperature superconductors as described in the first subsection.

Figure 5 shows the resistance R(T) versus temperature T measured in the darkness and under illlumination for the less oxygenated sample (n°1). In the darkness the film is always semiconducting and the transport properties are described by a three dimensional variable range hopping as shown in the inset of figure 5 where Ln(R) is linear with $T^{-1/4}$. There is no I-M transition on the whole temperature range. Under illumination, an I-M transition is induced. This I-M transition is transient, contrary to what is seen in the weakly deficient sample where we observe a persistent decrease of the resistance in the metallic state. The photoinduced I-M transition occurs at a temperature Tp which decreases from 91 K for high optical power down to 75 K for low optical power.

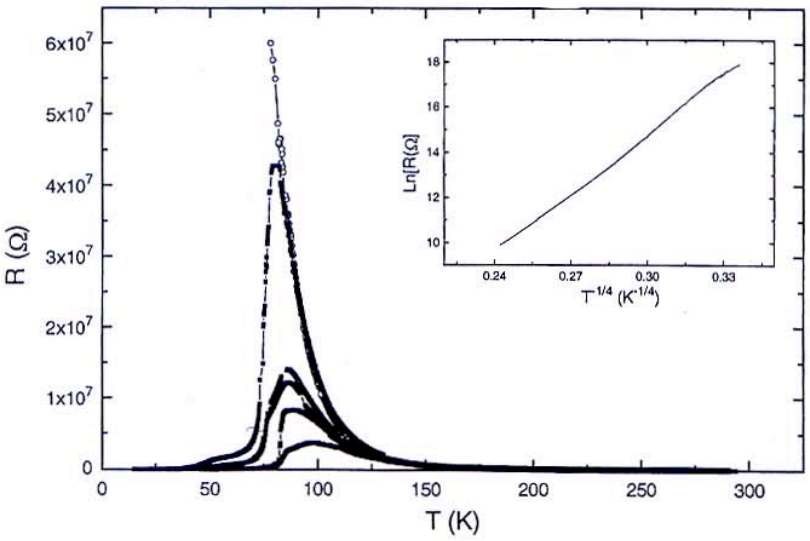

Figure 5: Resistance versus temperature measured in the darkness (open circles) and under illlumination (solid squares for 5 optical powers) for the less oxygenated sample (n°1)

We consider now the case of an intermediate case of oxygen deficiency (sample n°2) between the weakly oxygen deficient sample n°3 and the highly oxygen deficient sample n°1. In figure 6, the resistance versus temperature measured in the darkness, shows that the oxygen content is enough to have a semiconducting state at low temperature with the upturn below the 33K and an I-M transition of small amplitude at 90 K. The illumination of the thin film (figure 6) restores an I-M transition at around 80 K which has been smoothed by oxygen deficiency. A filter which decreases the optical power by ~15% shifts to lower temperatures the I-M by a few K.

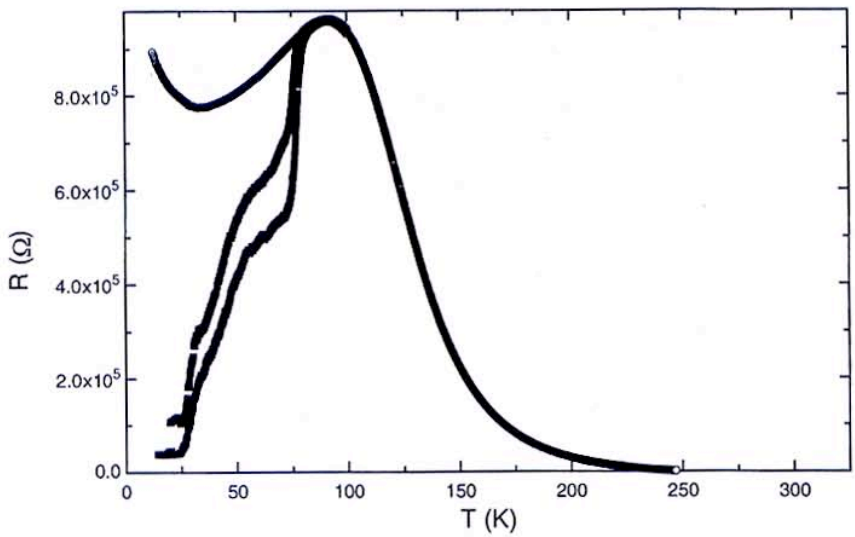

Figure 6: Resistance versus temperature measured in the darkness (open circles) and under illumination (solid squares, for two optical powers) for the intermediate oxygen deficient sample (n°2)

CONCLUSIONS

We have shown that illumination by UV or visible light of slightly oxygen deficient cuprates or manganites gives rise for both to persistent photoconductvity at low temperatures. For high oxygen deficient cuprates or manganites, high optical power may give rise to a transient photoconductivity and to a photoinduced insulator -metal transition.

The effects on the manganites have been observed[13, 14] also in other manganites like $La_{1-x}Ca_xMnO_{3-\delta}$ or $Pr_{2/3}Sr_{1/3}MnO_{3-\delta}$ thin films. Furthermore, for intermediate oxygen deficiency, it is possible to observe both persistent photoconductivity and transient photoconductivity in the metallic state.

The mechanism by which light changes the electrical properties of manganites is not understood at present time. For low oxygen deficient manganites, the behavior of persistent enhancement of the conductivity is very similar to the effect of light on the cuprates. This phenomena could be explained by an electron-hole pair mechanism, with capture of the electrons in the potential wells provided by the oxygen vacant sites.

For highly oxygen deficient samples which are insulating in the darkness, the transient photo-induced I-M transition could be explained by a shift of the Fermi energy through the mobility edge[6].

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