Pressure effect on magnetic and insulator–metal transition of La$_{0.67}$Pb$_{0.33}$Mn$_{0.9}$Co$_{0.1}$O$_{2.97}$ ceramic


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In our paper, we study the effect of hydrostatic pressure on the magnetic and insulator–metal transitions of La$_{0.67}$Pb$_{0.33}$Co$_{0.1}$Mn$_{0.9}$O$_{2.97}$ manganite. The insulator–metal transition does not coincide with the magnetic transition in this ceramic. The compound undergoes the paramagnetic–ferromagnetic phase transition at $T_C = 260$ K and the insulator–metal transition at $T_p = 184$ K at ambient pressure. We have found that both characteristic temperatures $T_C$ and $T_p$ increase with increasing hydrostatic pressure with $\Delta T_C / \Delta p = 11.2$ K/GPa and $\Delta T_p / \Delta p = 20.1$ K/GPa, respectively.

Keywords: magnetic transition; insulator–metal transition; hydrostatic pressure; manganite

Introduction

Recent works performed on the mixed-valence perovskite manganese oxides have been driven by a desire to understand and exploit the large negative magneto-resistance and magnetocaloric effects. Ca-doped lanthanum manganites were first reported during a study of ionic ferromagnets with the general composition La$_{1-x}$M$_{x}$MnO$_3$, where M is a divalent cation, e.g. Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Cd$^{2+}$ or Pb$^{2+}$ [1]. Both, the mixed-valence state Mn$^{3+}$/Mn$^{4+}$ and the double exchange (DE) interaction are needed for metallic behaviour and ferromagnetism in these materials [2]. Our recent study [3] was focused on the effect of Co substitution on crystal structure, magnetic and electrical transport properties of La$_{0.67}$Pb$_{0.33}$(Mn$_{1-x}$Co$_{x}$)O$_3$ ceramics. The ferromagnetic (FM) character of the un-doped compound still remains after Co-doping for the whole concentration range. With respect to the un-doped composition, the Curie temperature $T_C$, the paramagnetic (PM) Curie temperature $\Theta$, the effective magnetic moment $\mu_{\text{eff}}$ and the saturated magnetization $\mu_s$ decrease with increasing Co-doping. The high-temperature insulator–metal (I–M) transition at $T_p$, observed for all compounds decreases with Co-doping and the re-entrant temperature $T^*$,
observed at low temperatures, increases with Co-doping. The insulator–metal transition does not coincide with the FM transition which allows the possibility to study the pressure effect on both the I–M transition and the magnetic transition; hence, \( \text{La}_{0.67}\text{Pb}_{0.33}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_{2.97} \) represents an example of materials which is desirable for the study of the effect of pressure on \( T_p \) as well as on \( T_C \).

**Experimental procedures**

The single-phase samples of composition \( \text{La}_{0.67}\text{Pb}_{0.33}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_{2.97} \) was prepared by the malic acid gel method. Finally, the obtained powders were compacted into discs and sintered at 1000°C in flowing air for 10 h [3]. All magnetization measurements were performed by a SQUID magnetometer MPMS XL-5. The sample was placed in a pressure cell during all magnetization measurements. A piston cylinder type of the CuBe pressure cell was filled up by a mixture of mineral oils serving as hydrostatic pressure transmitting medium and operating up to 1.2 GPa [4]. Actual pressure was determined *in situ* from the pressure dependence of the superconducting transition temperature \( T_c(p) \) of an inserted high-purity lead sample. Pressure in the clamped CuBe cell increases with increasing temperature and a correction on actual pressure at the actual temperature was made. The pressure CuBe cell is permanently present in all detecting coils of the SQUID magnetometer and hence it practically does not contribute to overall magnetization of the studied samples [4]. Experimental data presented in our paper were not corrected for a signal of the pressure cell. The pressure was changed at room temperature only and the experiments were started at the highest pressure that was then gradually decreased in two or three steps. All pressure-induced changes of magnetization were reversible. Electrical resistance measurements were performed by the four-probe method. Hydrostatic pressure up to 0.9 GPa was generated by a standard Cu−Be piston cylinder device filled again by the mixture of mineral oils as a pressure transmitting medium. The pressure inside the chamber was determined using a manganin pressure sensor and the known change of the manganin resistance under pressure. In this case the temperature in the range from 3.5 to 300 K was varied by a two-stage close-cycle helium refrigerator.

**Results and discussion**

Figure 1 shows temperature dependences of the low-field magnetization \( \mu(T) \) of \( \text{La}_{0.67}\text{Pb}_{0.33}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_{2.97} \) ceramic that was measured in the zero field cooling (ZFC) regime and the field cooling (FC) regime under different pressures. The transition from PM to FM state is accompanied by a sharp increase in magnetization. The Curie temperature \( T_C \) was determined as a minimum on the \( d\mu/dT(T) \) curve. A hysteresis observed between the transitions in ZFC and FC regimes is a typical feature of this material and substitution of Co for Mn strengthens this behaviour [3]. The \( M(T) \) curves measured in ZFC regime start to deviate from the \( M(T) \) curve measured in FC regime at the bifurcation temperature \( T_b \), which is close to \( T_C \). The ZFC \( M(T) \) curve exhibits compensation temperature \( T_{\text{comp}} \). Under hydrostatic pressure, \( T_C \) increases almost linearly with the slope of a linear fit \( dT_C/dp = 11.2 \text{ K/GPa} \) and the compensation temperature \( T_{\text{comp}} \) is shifted to higher temperatures. Low-field magnetization \( \mu \) measured in FC regime increases with applied pressure while a decrease in \( \mu \) measured in ZFC regime was observed. Effect of pressure on characteristic physical parameters of the hysteresis loop-saturated magnetization \( \mu_s \), remanent magnetization \( \mu_r \) and coercive field is small and results in an increase in these parameters (Figure 2).

The variations of electrical resistivity \( \rho \) with temperature under different pressures are shown in Figure 3. We associate the first maximum observed with decreasing temperature on the resistivity
Figure 1. Temperature dependences of the magnetization measured in ZFC and FC regime of La$_{0.67}$Pb$_{0.33}$Mn$_{0.9}$Co$_{0.1}$O$_{2.97}$ ceramic for different pressures. The Curie temperature was determined as a minimum of the $d\mu/dT(T)$ curve.

Figure 2. Magnetization curves taken on La$_{0.67}$Pb$_{0.33}$Mn$_{0.9}$Co$_{0.1}$O$_{2.97}$ are plotted for different pressures. The saturated magnetization, remanent magnetization and coercive field increase slightly with pressure.

The characteristic features of this sample are the I–M transition represented by the maximum at $T_p$ and the re-entrant metal–insulator transition (M–I) observed at $T^*$ as the minimum on the resistivity curve at low temperatures. Two characteristic temperatures $T_C$ and $T_p$ decrease with Co-doping. On the other hand, the re-entrant temperature $T^*$ increases with Co-doping [3]. The applied magnetic field $\mu_0 H = 1$ T smears out the anomalies at $T_C$ and $T_p$ and the values of these temperatures increase with field. The re-entrant temperature $T^*$ is reduced by the applied magnetic field [3]. The applied pressure reduces all maxima and shifts the maximum at $T_C$ to higher temperatures with nearly the same rate $\Delta T_C/\Delta p$ as it was determined from magnetization measurements. The maximum at $T_p$ is shifted to higher temperatures with the rate $\Delta T_p/\Delta p = 20.1$ K/GPa. The minimum at about $T^* = 50$ K does not change its position – the re-entrant temperature $T^*$ is not affected by pressure but the upturn in resistivity is a little bit pressed.

The physical properties of interest for this paper are $T_C$ and $T_p$, all determined by bandwidth, band filling and local disorder but with different intensities. Application of external pressure on
the mixed-valence perovskite manganese oxides with induced compression of the unit cell volume leads always to an increase in $T_C$, with $dT_C/dp$ varying in the range 5–50 K/GPa [5]. These effects have been discussed by the majority of authors in terms of a variation of the electronic bandwidth $W$ as a function of chemical and applied pressure, with the main focus being on the influence of the Mn–O–Mn bond angle on $W$. The Mn–O–Mn bond angle is expected to increase both as a function of increasing radius of R ion $\langle r_R \rangle$ and as a function of applied pressure. This would account for our trend in the increase in the $T_C$ temperature with pressure, because the metallic or FM states are stabilized by the pressure-induced increase in the electronic band width $W$ due to increase in the bonding angle and reduction of the bond length of Mn–O–Mn [4,6]. While substitution of divalent ions on La positions has a similar effect on magnetic properties as the application of hydrostatic pressure, the substitution of Co for Mn exhibits an opposite tendency which can be explained by the dilution effect by the Co$^{3+}$ ions leading to the reduction of DE interaction and to the reduction of $T_C$ [7]. As a consequence, while the physical properties are coupled to each other, in general $T_C \neq T_p$. Our study revealed the different pressure effect on I–M transition at $T_p$ and magnetic transition at $T_C$ in La$_{0.67}$Pb$_{0.33}$Mn$_{0.9}$Co$_{0.1}$O$_{2.97}$ ceramic. We can conclude that in this case the effect of pressure on $T_p$ is stronger and $\Delta T_p/\Delta p$ is almost two times higher than $\Delta T_C/\Delta p$.

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References
