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Quenching effects on correlation between electrical and magnetic properties in $Pr_{0.5}Sr_{0.5}MnO_3$ polycrystalline manganites

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ABSTRACT

In this work, we studied the effect of quenching on the magnetocaloric effect and the correlation between electrical and magnetic properties of two samples polycrystalline manganites $Pr_{0.5}Sr_{0.5}MnO_3$. Sample I (quenched in water) exhibits a negative maximum of magnetic entropy change ΔS around its Curie temperature with $\Delta S = -4.61$ J kg^{-1} K^{-1} at a magnetic applied field of 8 T. Sample II (quenched in air) is characterized by the presence of two extrema of magnetic entropy change with a great positive value reaching 5.17 J kg^{-1} K^{-1} for only 2 T magnetic field around its Neel temperature. Resistivity and magnetization were found to be related with the different relations $\rho = \rho_0 \exp(-M/\alpha)$ and $\rho = \rho_0 \exp(-M^2/\alpha)$ for samples I and II respectively. From these relations associated to Maxwell–Weiss relation, we found the way to evaluate ΔS from resistivity and the obtained results were discussed.

1. Introduction

The manganites having the general formula $Re_{0.5}Ae_{0.5}MnO_3$, where Re is a rare earth (La, Pr, Nd…) and Ae is an alkaline earth (Ca, Sr, Ba…) are very interesting compounds. They are characterized by a colossal magnetoresistance [1–6] which gives several technological applications (hard drives, magnetic random access memories MRAM, spin valves, magnetic field sensors…), and they are the seat of relevant physical phenomena like charge ordering and phase separation [6–12]. $Pr_{0.5}Sr_{0.5}MnO_3$ compound is one of the most studied compounds in the last years [6,7,13–19]. This compound exhibits when cooled a magnetic transition from paramagnetic PM to ferromagnetic FM state at $T_C = 265$ K, this transition is followed by another one to an antiferromagnetic AFM state at $T_N = 130$ K. The first ordered transition from FM to AFM state seems to be accompanied by a structural transition from tetragonal I4/mcm to orthorhombic Fmmm space group [19]. At low temperature, no evidence of charge ordering was observed and the AFM state was reported to be A-type (FM metallic layers with parallel alignment of spins in the same layer but the layers are antiferromagnetically arranged) with an orbital ordering of $d_{(x^2-y^2)}$ orbitals yielding to a two-dimensional characteristics in electrical and magnetic behavior at low temperature [20]. The compound $Pr_{0.5}Sr_{0.5}MnO_3$ was reported to be phase-separated with the appearance of AFM clusters just below Curie temperature and the persistence of around 22% of high-temperature FM I4/mcm phase at low temperature [17]. Both electrical and magnetic behavior seems to be strongly dependent of elaborating conditions, especially the quenching effect [6,7]. A great difference was observed in magnetic and magneto-transport properties for the compound $Pr_{0.5}Sr_{0.5}MnO_3$ once it was quenched in water or in air. Although, the magnetocaloric study of these samples is not yet performed and the relation between electrical and magnetic properties is not studied. Thus, we tried in this work to evaluate the magnetocaloric effect of the two differently quenched samples $Pr_{0.5}Sr_{0.5}MnO_3$ from magnetization data and discuss the behavior of temperature dependence of magnetic entropy change, and to find a correlation between electrical and magnetic behaving in these two samples.

2. Experimental techniques

The two samples $Pr_{0.5}Sr_{0.5}MnO_3$ were prepared using traditional solid state route at high temperature from high purity Pr_6O_{11}, $SrCO_3$ and MnO_2. The starting materials were mixed in stoichiometric proportions and heated in air for 60 h. After that, several cycles of pressing, annealing and grinding were performed to ensure that the reaction took place. The samples were annealed at 1400 °C for 60 h. And finally, a pellet was rapidly quenched in water (sample I), however, another pellet is quickly quenched in air (sample II). Phase purity was checked out through X-ray powder diffraction using Guinier–Hagg cameras with Cr K_α radiation for sample I and diffractometer with Cu K_α radiation for sample II. Crystal structure and cell parameters were determined using standard Rietveld technique [21]. Magnetization measurements

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were recorded by an extraction magnetometer in the temperature range 10–350 K up to 8 T magnetic applied field. Magnetocaloric effect was deduced from isothermal magnetization dependence of magnetic field based on thermodynamical equations. The standard four-probe technique was used to perform resistivity measurements on the dense ceramic pellets.

3. Results and discussion

Structural, electrical and magnetic studies of the samples I and II were well detailed in previous works [6,7]. The sample I was indexed in rhombohedral system with $R\bar{3}c$ space group and the sample II was reported to crystallize in orthorhombic structure with Imma space group. In the most recent works, the compound $Pr_{0.5}Sr_{0.5}MnO_3$ was indexed at room temperature with tetragonal I4/mcm space group [15,17,19,20,22–24], the difference between these works and our results can be attributed to the difference in elaborating conditions. Temperature dependence of magnetization under a magnetic applied field of 0.05 T shows that sample I (quenched in water) exhibits a PM–FM transition when temperature decreases at T_C=280 K with the presence of canted spin state at low temperature. However, sample II exhibits two magnetic transitions with decreasing temperature: the first one from PM to FM state at T_C=265 K and the second one from FM to AFM at T_N=160 K [7]. The results for sample II are in agreement with several works performed on $Pr_{0.5}Sr_{0.5}MnO_3$ compound. Resistivity evolution as a function of temperature at 0 T field showed that sample I has a metallic behavior between T_{FC} and T_ρ but, outside this temperature range, the electrical behavior is semiconducting-like one. Sample II has a semiconducting behavior in the whole temperature range with two small anomalies corresponding to T_C and T_N [6]. Thus, it is obvious that quenching has a great effect on electrical and magnetic properties in $Pr_{0.5}Sr_{0.5}MnO_3$ compound. In order to study its effect on magnetocaloric properties, temperature dependence of magnetic entropy change at several values of magnetic applied field for the two samples was represented in Fig. 1. The values of magnetic entropy change ΔS were calculated using isothermal $M(H)$ curves and the Maxwell–Weiss relation

$$\Delta S_M(T,H) = S_M(T,H) - S_M(T,0) = \int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH \quad (1)$$

For discrete measurements of magnetization, Eq. (1) can be written as

$$\Delta S_M(T,H) = \sum_i \frac{M_{i+1}(T_{i+1},H) - M_i(T_i,H)}{T_{i+1} - T_i} \Delta H \quad (2)$$

Sample I shows a unique negative maximum of magnetic entropy change around T_C, this behavior is characteristic of classic PM–FM transition. The maximum value of negative magnetic entropy change reaches $-4.42\ J\ kg^{-1}\ K^{-1}$ under 8 T magnetic field at T_C=280 K. The absolute value of maximum magnetic entropy change |ΔS| increases with increasing the magnetic applied field due to the enhancement of FM interactions. However, one can notice that sample II behaves differently: a negative maximum is observed near T_C and the maximum value of ΔS reaches $-4.61\ J\ kg^{-1}\ K^{-1}$ for a magnetic applied field of 8 T at T_C=280 K. But a positive maximum is observed in vicinity of T_N, and we can see a great value of positive magnetic entropy change near $5.17\ J\ kg^{-1}\ K^{-1}$ for only 2 T. With increasing the applied field, the value of this maximum did not increase too much, but the pick became wider. This behavior is characteristic of metamagnetic transition (field induced transition from a magnetically ordered state to another ordered one) also called order–order transition, such shape of

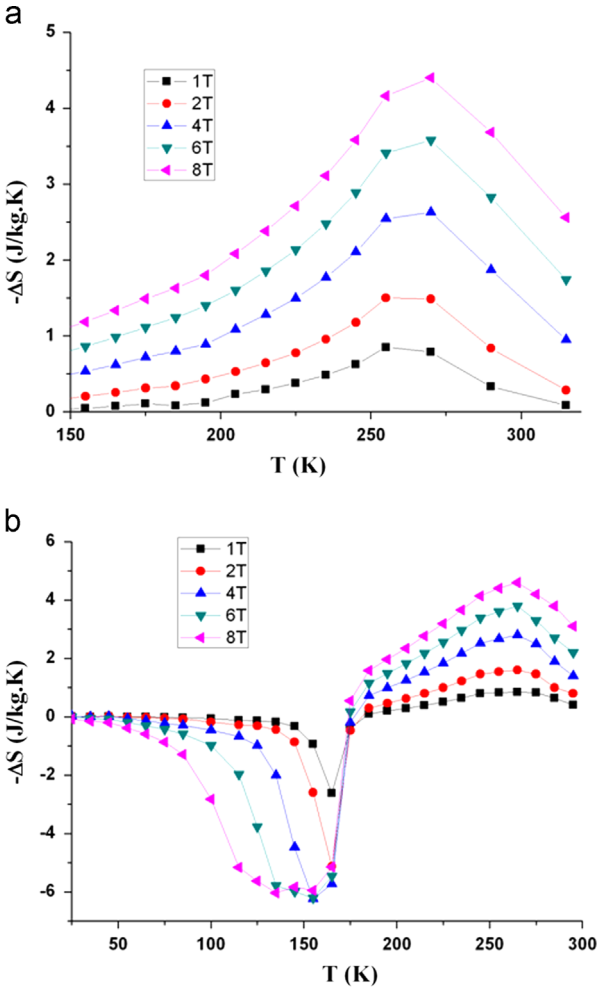

Fig. 1. Temperature dependence of magnetic entropy change at several values of magnetic applied field deduced from Maxwell–Weiss relation for sample I (a) and sample II (b).

magnetic entropy change can be seen for the half-doped manganites like $La_{0.5}Ca_{0.5}MnO_3$ [9]. Generally, the Maxwell–Weiss relation fails to evaluate exactly the magnetic entropy change in the case of metamagnetic transitions; this was the case when studying phase-separated $Eu_{0.45}Sr_{0.55}MnO_3$ and $La_{0.27}Nd_{0.4}Ca_{0.33}MnO_3$ manganites [25] or even $Mn_{1-x}Fe_xAs$ alloys [26]. In order to evaluate exactly the magnetic entropy change for a phase-separated compound, one can use Clausius–Clapeyron equation [27]. However, it was proved that the Maxwell–Weiss relation can successfully evaluate the magnetic entropy change at low temperature for $Pr_{0.5}Sr_{0.5}MnO_3$; this success originates from the fact that the heat capacity of FM domains is more important than that of AFM ones. The values of magnetic entropy change determined from magnetization data are very close to those deduced from specific heat data and the maximum values are positive too [16]. Thus, this fact ensures the credibility of our results. The important value of magnetic entropy change recorded at T_N for sample II can be attributed to the first-ordered nature of the metamagnetic transition. In order to study the order of this transition, we have shown in Fig. 2 the Arrott plots for the sample II for $T < T_N$. When the Arrott plots present a positive slope, this fact testifies that the magnetic transition is second order; but if the slope is negative, we notice the happening of a first-ordered transition [9,28]. In our case, it is obvious that all the Arrott plots show a negative slope for $T < T_N$ which is the signature of a first-ordered metamagnetic transition. So, it is clear that quenching procedure produced a big difference in