Effects of nanocracks on the magnetic and electrical properties of La$_{0.8}$Sr$_{0.2}$MnO$_3$ single crystals

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An investigation of the physical properties of La$_{0.8}$Sr$_{0.2}$MnO$_3$ single crystals grown by the molten zone technique is realized close to the metal-to-insulator transition temperature ($T_{MI}$). In this paper, we review the effect of the structural defects through magnetotransport and local magnetic microstructures. From electron microscopy observations, some ‘nanocrack’ defects (i.e. defects at a nanometer scale) were found, essentially in the center part of the single crystals. At room temperature, magnetic force microscopy measurements have shown that the absence of defects allowed a magnetic ordering of the domains at the crystal edge, which is the best-crystallized region. In addition, the magnetization loops have permitted us to verify that the crystal was ferromagnetically weaker in the center. On analyzing the electrical resistivity data, we observed in the linear current regime a sensitive variation of the resistivity due to defects, by comparing the center and the edge of the material at $T_{MI}$. Additionally, at strong current, non-linearity phenomena have been supposed to be related to local heating. Finally, we discuss the structural disorder effect on the relaxation of the ferromagnetic domains.

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1. Introduction

Mixed-valence manganites of general formula A$_{1-x}$B$_x$O$_3$ (A = La, Pr, Nd, B = Sr, Ca, Ba) have undergone a resurgence of interest during the last decade due to the newly discovered important properties such as colossal magnetoresistance (CMR), percolative phase separation and spin/charge/orbital ordering [1–7]. The CMR effect is usually interpreted by the double exchange (DE) interaction model [8], which is based on the exchange of (3d) band $e_g$ electrons between Mn$^{3+}$ and Mn$^{4+}$ ions. Doped compounds of the family La$_{1-x}$Sr$_x$MnO$_3$, from $x = 0.2$, have a Curie temperature higher than room temperature [9], which allows one to develop new technological applications. There are many such applications: for example, metal–ferroelectric/insulator–semiconductor field-effect transistors (FETs), magnetic field sensors, and magnetic random access memories (MRAMs). As indicated in Ref. [10], the physical properties are strongly dependent on structural defects. In this work, we pursue a previous study of La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSMO) single crystals [11], where nanodefect patterns imaged by high-resolution electron microscopy are represented in evidence along the twinned structure, preferentially in the material center. So as to discuss their possible influence on interactions between magnetic domains and transport properties of the crystal, we measured the local magnetic structure using magnetic force microscopy (MFM), to investigate the magnetization and electrical properties from the resistivity around the metal–insulator region near $T = 300$ K.

2. Experimental

Oxide powders were prepared by the sol–gel method as described by Douy et al. [12]. Polycrystalline rods were synthesized from Mn, SrCO$_3$ and La$_2$O$_3$ conductive precursors which had undergone several heat treatments. The growth of single crystals was carried out by means of a feed rod and a crystal used as a seed.
rod put into contact in an image furnace. X-ray diffraction (XRD) and energy dispersive X-ray spectrometry (EDXS) revealed that the samples obtained were single phased, oriented along the [001] direction, and presented a homogeneous chemical composition. Their microstructure, examined by electron microscopy, was single crystalline and with good quality. Note that no grain boundaries were found, but rather a twin density that was almost homogeneous over the whole crystal. Nevertheless, some defects of nanometric size, of 'nanocrack' type, due to the large stress gradient during the growth, appeared more numerous in the rod center of the single crystals \[11\] along the twin boundaries.

The magnetotransport measurements were carried out using a Physical Property Measurements System (Quantum Design cryostat PPMS 6000) from 5 to 400 K by using a standard four-probe method with the AC current applied perpendicular to the magnetic field \(H\). Rectangular single crystals of equal dimensions of length \(\times\) width \(\times\) thickness \(= 1.2 \times 1 \times 0.6 \text{ mm}^3\) (edge part of the rod) and \(1.1 \times 0.96 \times 0.7 \text{ mm}^3\) (center part) were extracted for measurements. We also imaged the surface topography of the crystal with atomic force microscopy (AFM) (NT-MDT society, solver P7-LS type) at room temperature (300 K) and used MFM in order to probe the local magnetic properties. The sample used for the experiment was cut from the crystallized rod (diameter = 4.5 mm, thickness = 1.5 mm) (Fig. 1, left bottom part) so as to observe the effect of mechanical strains as a function of the tip position from the center toward the edge. We utilized a commercial tip of silicon magnetically coated with Co/Cr of nominal spring constant \(~ 5 \text{ N/m}\). Topography and MFM patterns were simultaneously acquired in the non-contact AC-AFM mode under the application of a magnetic field of 3000 G.

3. Results and discussion

3.1. Magnetic characterization

Topographic images have revealed a more damaged morphology in the center (due to defects) with an average surface roughness of 12 nm. This can be explained by the growth mechanism of material as the strains are more important in the center due to the high temperature gradient (above 1800 °C). The topography images have been raised in plane and smoothened, using a vertical Prewitt filter. The MFM images are the result of a shift in the resonant frequency of the cantilever. One fit in the plane and a uniform filter in a 5 \(\times\) 5 matrix were used. \(H = 0.3 \text{T}\) was applied along the c-axis perpendicular to sample plane and along the long axis of the tip. This was scanned across the surface using the lift mode \([13]\); the magnetic interactions are of long-range nature \((\sim 100 \text{ nm})\). Fig. 1 shows topographic and magnetic images taken at the same time on the crystal from the center (A) toward the edge (D). There is no direct correlation between the surface morphology and the magnetic domain patterns. The MFM images present bright and dark regions corresponding to attractive and repulsive tip–sample interactions, respectively. At the edge, the magnetic domains tend to spread with more facility. Their ordering is realized according to an easy axis of magnetization when the amorphous zones are non-existent (see cross-correlated image (D)). On the other hand, at the center, the screening by the defects shows an absence of the magnetic domain ordering, that can be seen by a ring characteristic of an amorphous state (see cross-correlated image (A)). We also suggest that the defect density plays a preponderant role in the arrangement of the magnetic domains at room temperature, which is independent of the twin boundary density.

LSMO is one of the most typical Mn perovskite compounds which present a transition from a ferromagnetic (FM) phase to
3.2. Electrical properties

3.2.1. Zero magnetic field

In the LSMO compound, the FM-to-PM transition is accompanied by a metallic-to-insulating transition that can be studied from electrical resistivity measurements. Fig. 4(a) illustrates \( \rho(T) \) of the center at \( I = 5 \) mA in zero field for two sweep rates of \( dT/dt = +2 \) K/min and \( +0.1 \) K/min. Note that a relaxation problem has been noticed on both samples (center and edge) in the \( T_{MI} \) region, due to the metallic–insulator phase coexistence. This is not the case at the structural phase transition temperature \( (T_s) \) [14,17] of about \( T = 90 \) K, because of the metallic part of the resistivity that is completely FM at low temperature (see inset of Fig. 4(a)). This \( T_s \) transition is accompanied by a magnetic phase transition of the spin reorientation type, changing the crystal structure from the orthorhombic to rhombohedral phase [18] due to a Jahn–Teller distortion of the \( \text{MnO}_6 \) octahedron. We thus observe that the temperature cycle full width at half maximum (FWHM) in the resistivity field of 290–320 K decreases significantly, and almost vanishes at 0.1 K/min. Measurements in Fig. 4(b) show various successive ramps from 4 K/min by going down until 0.1 K/min. This last ramp corresponds to an optimal threshold for the realization time of experiments. For a better precision of the metal–insulator transition, this will be determined for \( dT/dt = 0.1 \) K/min, from inflection point of \( \rho(T) \) for increasing temperature using \( d\rho/dT \) vs. \( T \). \( T_{MI} = 308.2 \) K (in the center) and \( T_{MI} = 308.8 \) K (at the edge). These values are in good agreement with the \( T_c \) ones and correlate well with those reported by Urushibara et al. [19] and Bebenin et al. [20] in single crystals for \( x = 0.2 \) doping. Moreover, they also confirm that the oxygen content at the edge of the crystal is slightly greater than at the center.

The crystalline defect study with a temperature sweep of \( \rho \) in the linear current regime has not shown differences between the center and the edge. However, as it is interesting to know the current interval in which we could work with this crystal, we chose to carry out measurements at stronger current. Fig. 5 presents the temperature dependence of the resistivity with a sweep rate of \( dT/dt = +2 \) K/min and various currents up to 100 mA. One can examine the effects of high current densities. So as to compare the center and the edge because of their equal section, the \( \rho(T) \) magnitude has been normalized by a multiplicative coefficient. It appears that \( \rho \) drastically increases at the same time as the current for \( I \geq 10 \) mA [21]. We can observe a non-linearity regime which can put in evidence a local heating of the material [22,23]. The results at the edge show a shift of the cooling–heating cycle toward low temperatures from 60 mA and at the center from about 10 mA. According to Palanisami et al., the shift of \( \rho(T) \) at different currents in \( \text{La}_0.7\text{Ca}_{0.3}\text{MnO}_3 \) thin films will be due to Joule heating, \( R^2 \). In spite of the shift of the cooling–heating cycle in the direction of low temperatures in our crystals, FWHM at the edge is the same as at the center (\( \sim 2 \pm 0.1 \) K) for all the currents. At lower temperature, the hysteretic phase transition does not change with the current density. However, the hysteretic cycle is square at the center, characteristic of a ‘pure first-order’ phase transition, and slightly rounded at the edge, representing a degeneration of first-order character of this transition in the presence of a sufficient volume of amorphous zones.

We now focus on the \( T_{MI} \) temperature and study the frequency dependence on \( \rho \) for applied various currents, as shown in Fig. 6(a). No effect in frequency is noticed, but we can observe non-linearities at strong current. The more the current increases, the greater the resistivity becomes as \( I \geq 10 \) mA (see Fig. 6(a) and (b)). The inset of Fig. 6(a) is a measurement of \( \rho(1) \) in linear scale; non-linearities here can be attributed to heating, as previously seen in Fig. 5. In the non-linear regime, the resistivity is the same, thus no role is played by the defects. However, at low current, the defects seem to have an influence as the defect density is stronger in the center. One can measure a slight difference of about 6% for the center and 8% for the edge at \( I = 60 \) mA (by taking as reference the plateau at low current up to \( \sim 10 \) mA). These results are consistent with the variations observed in Fig. 5. The temperature cycles were more shifted at the edge part of the material from \( I = 60 \) mA. The results suggest that the defects have a tendency to dissipate the heating. This heating has a non-negligible effect that can mask or modify the intrinsic properties of the material and it is thus important to limit the study to low current (\( I < 10 \) mA).

3.2.2. Non-zero magnetic field

Using magneto-resistance (MR) measurements, one now investigates the influence of structural disorder between the center and the edge of the material at room temperature. This study specifically shows the effects of the FM metallic domains when they relax at low field and it seems that this phenomenon is slower in the center due to the defects. A representation for different temperature at \( I = 1 \) mA is given in Fig. 7. The MR(%) ratio is given by the expression \( (R(H) - R(0))/R(0) \times 100 \). One can note a \( \sim 45\% \) absolute change of MR for \( H = 80 \) KOe at \( T = 300 \) K and \( T = 350 \) K. The local Jahn–Teller distortion at the Mn\(^{3+}\) sites is very important around the \( T_{MI} \) transition, but close to \( T_s \) we notice the absence of MR. The MR of single crystals and epitaxial films is maximum near \( T_c \) and almost zero at low temperature. On the contrary, some published researches [24,25] indicate that polycrystalline
compounds present a high MR down to low temperature due to the grain boundary effect. The low field MR is associated with spin dependent charge transport across grain boundaries [26]. Although they are totally absent in our crystals, we can guess that the MR measurements imply a flip of the FM metallic domains across percolative conduction channels in the $T_{MI}$ region. From Fig. 7, we can clearly see at low field that the material had no time to find a stable balanced position at $T = 300$ K: the reversal of the magnetic domains is less fast so as to minimize the energy. Consequently, we can notice a weak magnetic hysteresis, as seen in Ref. [27], because of the reorganization time during the magnetic domain relaxation. The ratio defined as $\Delta MR(\%) = MR(H \uparrow) - MR(H \downarrow)$ at $T = 300$ K in zero field is about 3% at the edge and 3.7% in the center. The metal-to-insulator transition temperature is related to the electron–lattice interaction, which is increased by the presence of the structural defects. The slow relaxation is attributed to the coexistence of metallic (FM) and insulating (PM) phases [28]. This effect on the resistance cannot be detected when the percolation of the FM metallic domains is achieved above the $T_{MI}$ region, as can be seen at $T = 350$ K (insulating (PM) phase) as soon as a small increase in the number of disconnected metallic clusters appears, whereas a small increase of the size of the low resistive metallic fil-

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**Fig. 3.** Graphs showing the decrease of $H_s$ and $M_s$ with an increase in temperature for $T = 5, 60, 100, 120$ and $280$ K.

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**Fig. 4.** (a) $\rho(T)$ in the warming–cooling cycles for a sweep rate of $dT/dt = +2$ K/min and $+0.1$ K/min at $I = 5$ mA ($\parallel$ c-axis) (inset: zoom at low temperature), $\Delta \rho(0.1 \text{ K/min}) = 0.38 \text{ m}\Omega\text{ cm}$ at $T = 307$ K. (b) $\rho(T)$ for various sweep rates of $dT/dt$.

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**Fig. 5.** $\rho(T)$ at $I = 1, 25, 60$ and $100$ mA ($\parallel$ c-axis) in the cooling–warming cycles (inset: zoom at low temperature).
aments can be disclosed as soon as the percolation occurs toward $T_{MI}$.

The size of the amorphous zones (of width below 10 nm [11]) must be connected to strains induced during the growth at the rod center. It appears that the relaxation of the magnetic domains is dependent on these defects in the vicinity of $T_{MI}$, whereas the edge part of the material can easily relax the strains due to the better crystallinity. These results obviously show the important role of nanocracks on the low field MR in LSMO crystals.

4. Conclusions

Our results point out the significant role of structural defects on the local magnetic and transport properties in a $La_{0.8}Sr_{0.2}MnO_3$ single crystal. The absence of defects has a certain influence on the magnetic ordering of the domains which takes place because of the stronger magnetic coupling at the edge. As we have seen, the center presents a ferromagnetic character that is globally weaker due to the defects. Electrical measurements clearly showed a non-negligible discrepancy of the resistivity measured between the center and the edge of material that can be due to nanocracks and thus local strains induced by the growth mechanism, for $I \leq 10$ mA at $T_{MI}$. We have also reported that, at strong current, non-linearity phenomena occur, probably due to the Joule effect. In conclusion, we have studied the effect of structural disorder on the relaxation of the FM metallic domains which entails a more marked slowing down close to $T_{MI}$ on the low field MR. We conclude that the defects are tuned to the electron lattice interaction which is linked to $T_{MI}$.

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References