RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 60, NUMBER 2 1 JULY 1999-II

Charge disordering induced by electron irradiation in colossal magnetoresistant manganites

M. Hervieu,* A. Barnabé, C. Martin, A. Maignan, and B. Raveau
Laboratoire CRISMAT, UMR 6508 associée au CNRS, ISMRA et Université de Caen, 6, Boulevard du Maréchal Juin,
14050 Caen Cedex, France

(Received 22 January 1999)

The electron microscopy investigation of $Pr_{0.7}Ca_{0.3}MnO_3$ shows that a complete charge disordering is induced in this phase by electron irradiation at 92 K, the disordered state remaining stable at this temperature, even in the absence of irradiation. A model is proposed for this transition, according to which an electron jumping into the manganite matrix creates a local charge disordered state and extends to the whole matrix through a chain mechanism, leading to a ferromagnetic metallic state. This model is supported by the fact that the charge ordered state (evidenced by the doubling of the a parameter) is restored by heating the material above 120 K ($\sim T_C$) and then disappears above 150 K ($\sim T_{CO}$). Similar results are obtained for $Nd_{0.7}Ca_{0.3}MnO_3$, whereas $Pr_{0.5}Ca_{0.5}MnO_3$ is not sensitive to electron exposure, in agreement with the larger stability of its 1:1 Mn^{3+}/Mn^{4+} charge ordering. [S0163-1829(99)50626-7]

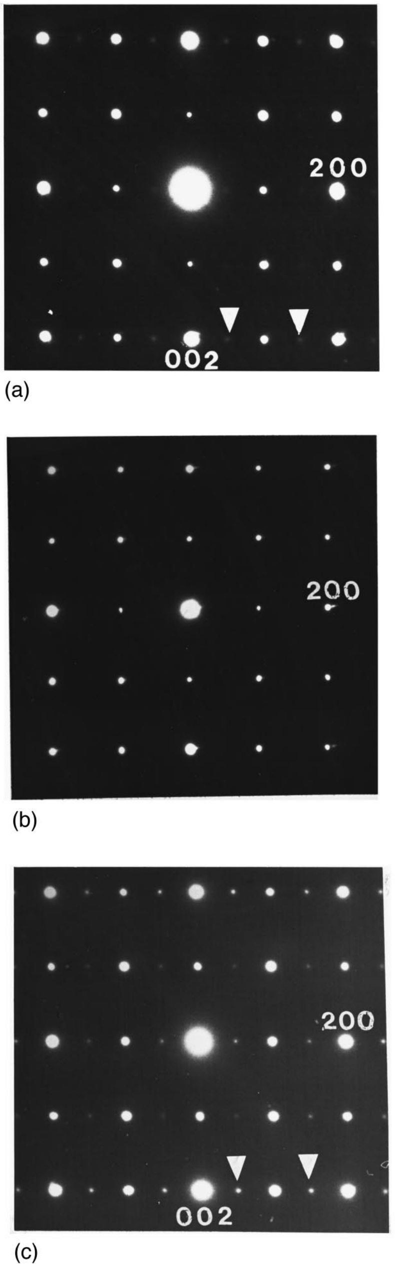
The discovery of negative giant magnetoresistance in manganites with the perovskite structure (see, for instance, Refs. 1–7) has resuscitated a renewed interest in this class of materials. Some of those oxides are insulators and exhibit a decrease of resistance by several orders of magnitude by applying a magnetic field and are called for this reason colossal magnetoresistant (CMR).[8–10] This CMR effect, which appears by applying a magnetic field to such insulating perovskites, originates from a competition between ferromagnetism (FM) and antiferromagnetism (AFM). In those $Ln_{1-x}A_xMnO_3$ oxides (A being an alkaline-earth ion), ferromagnetism coincides with a carrier delocalization leading to a metallic state in agreement with the double exchange mechanism,[11] whereas antiferromagnetism is closely related to charge ordering (CO) phenomena.[12] It has been shown that the transport and magnetic properties of these oxides and especially the magnetoresistance are controlled by the doping level (hole or electron concentration) and the size of the A-site cation, providing the cation radius is beyond a certain size.[7–10] For small A-cations, the carrier delocalization tends to disappear, and for a particular doping level, charge ordering is observed. This is the case of the manganites $Pr_{1-x}Ca_xMnO_3$, which are insulating whatever x and exhibit 1:1 Mn^{3+}/Mn^{4+} charge ordering combined to a CE type AFM structure for $x=0.50$.[13]

In fact, the magnetotransport properties of these materials are greatly influenced by the high metastability of the charge ordered state. This property is exemplified by $Pr_{0.7}Ca_{0.3}MnO_3$, which shows three transition temperatures T_C, T_N, and T_{CO} at ~120, ~140, and ~180 K, respectively.[14] In this oxide, melting of the charge ordered state by application either of high magnetic[9] or high electric fields[15] has been demonstrated, so that an insulator to metal (I-M) transition was obtained. Recently, a similar I-M transition was induced in the same compound via photoabsorption of visible-infrared light[16] and of x-ray.[17] This exceptional behavior of $Pr_{0.7}Ca_{0.3}MnO_3$ suggests that a similar effect should be obtained with other radiations. In this paper, we show that complete charge disordering is induced in this oxide via electron irradiation at 92 K in an electron microscope. We also demonstrate that the so obtained disordered state remains perfectly stable at this temperature in the absence of irradiation, and that the charge ordered state is remarkably restored by heating above ~120 K (T_C) and definitively redisappears above T_{CO} (~180 K).

The ceramic $Pr_{0.70}Ca_{0.30}MnO_3$ was prepared from the adequate mixture of Pr_6O_{11}, CaO, and MnO_2 heated up to 1500 °C according to the experiment previously described for this compound.[8] The phase purity and its cationic composition were checked by x-ray powder diffraction and x-ray energy-dispersive spectroscopy, respectively. Electron diffraction investigation was carried out as a function of the temperature with a JEOL 2010 electron microscope equipped with a LINK analyzer.

The electron-diffraction (ED) patterns of this perovskite phase, registered at room temperature, confirm that the sample exhibits the expected *Pnma* orthorhombic cell with $a\approx a_p\sqrt{2}$, $b\approx 2a_p$, and $c\approx a_p\sqrt{2}$.[13]

The sample was then cooled down to 92 K in ≅30 min without any electron beam. The ED patterns were recorded at this temperature, with a constant current density (estimated at 80 pA cm^{-2} at the level of the crystallite). In these conditions, additional reflections at 1/2 0 0 are observed in the [010] ED patterns [Fig. 1(a)], and the reconstruction of the reciprocal space confirms the supercell "$a\cong 2a_p\sqrt{2}, b\cong 2a_p, c\cong a_p\sqrt{2}$," previously established from neutron powder diffraction (NPD) data at low temperature for $Pr_{1-x}Ca_xMnO_3$ with $0.30\leqslant x<0.50$.[13] The doubling of the a parameter is correlated to a |:| ordering, namely $[Mn^{3+}]:[Mn^{3+},Mn^{4+}]$. The corresponding lattice images recorded at 92 K [Fig. 2(a)] confirm the doubling of the a parameter, showing a system of gray and bright fringes, alternating with a periodicity of 11 Å throughout the whole crystallite. Thus for these experimental conditions, the $Pr_{0.7}Ca_{0.3}MnO_3$ phase is 1-1 type charge ordered, and its ideal structure can be described as the alternation along **a** of Mn^{3+} stripes with mixed Mn^{3+}/Mn^{4+} stripes, containing 40% of Mn^{3+} species [Fig. 3(a)]. However, the brightness of the fringes is not regular along **c**, sometimes varying strongly over a few tens Å distance [Fig. 2(a)]. This suggests that, though the "$2a_p\sqrt{2}$" periodicity along **a** is respected, there

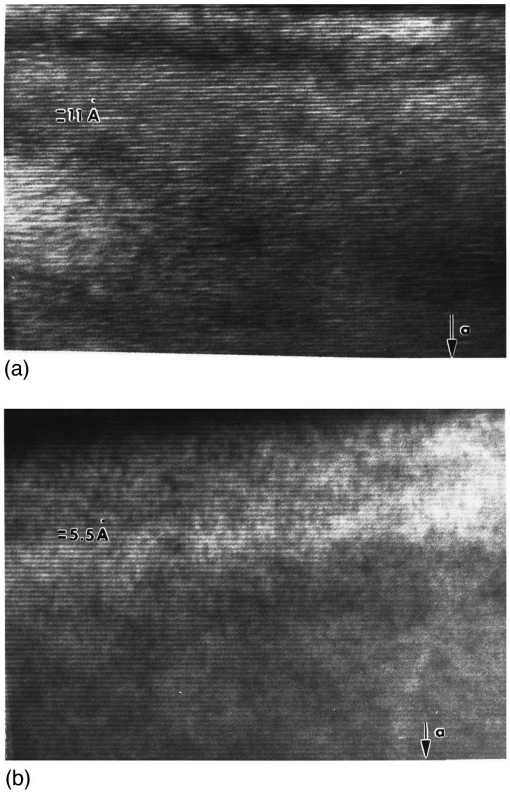


(a)

(b)

(c)

FIG. 1. [010] ED pattern of $Pr_{0.7}Ca_{0.3}MnO_3$. (a) At 92 K, just after cooling. The extra reflections which attest of the doubling of a parameter are indicated by white arrows. (b) At 92 K, after a 30 min exposure, keeping constant T and the electron current density. The extra reflections have disappeared. (c) After warming up to 125 K, the extra reflections have reappeared and are still observed upon cooling back to 92 K. The cycle has been carried out several times on the same crystallite.



(a)

(b)

FIG. 2. [010] lattice image, recorded at 92 K. (a) Just after cooling [ED pattern in Fig. 1(a)]: charge ordered state. (b) After a 30 min exposure [ED pattern in Fig. 1(b)]: charge disordered state.

exists short-range ordering along **c** within the ''$Mn^{3+}-Mn^{4+}$'' stripes. The sample at this temperature is insulating and weakly FM as shown from the T-dependent resistivity and magnetization curves [Fig. 3(b)], and can be considered as biphasic, i.e., consists of FM clusters embedded in an AFM matrix as described from NPD studies.[14]

Keeping the sample at 92 K under the same constant electron current density (80 pA cm^{-2}) leads to a progressive weakening of the satellites which disappear after ≅30 min exposure [Fig. 1(b)]. In the same way, the corresponding lattice image [Fig. 2(b)] confirms a periodicity of 5.5 Å in agreement with the loss of charge ordering. This experiment, carried out several times and for different crystallites, is reproducible. More importantly, this transition from a charge ordered to a charge disordered state is very sensitive to the current density of the electron beam: a density of 80 nA cm^{-2} allows the transition to be reached in a much shorter time of few seconds. Moreover, after cutting off the electron beam during several hours, electron-diffraction observation of the previously characterized crystallites shows that the extra reflections have not reappeared, proving that the transition to the so-formed disordered state is stable at 92 K, even in the absence of electron irradiation.

The fact that the temperature of the sample is maintained at 92 K all during this experiment strongly suggests that the transition is not due to the Joule effect, but is induced by electron irradiation. Different from x-ray[4,17] or from visible IR radiation,[16] this transition is not photoinduced, but can be described by an extra electron at a Mn^{4+} site in the matrix of $Pr_{0.7}Ca_{0.3}MnO_3$, creating locally a distortion of the lattice. The latter is then relaxed, as the electron jumps to the next Mn site. It results in a complete disordering of the Mn^{3+} and Mn^{4+} species, due to a kind of chain mechanism. Most probably, the so-formed charge disordered state is ferromagnetic and metallic, but unfortunately measurements cannot be carried out in the present conditions.

In this model, the electron induced FM metallic charge disordered state should only be stable below T_C (120 K). In order to check this point, the complete charge disordered sample (observed after prolongated exposure at 92 K) was

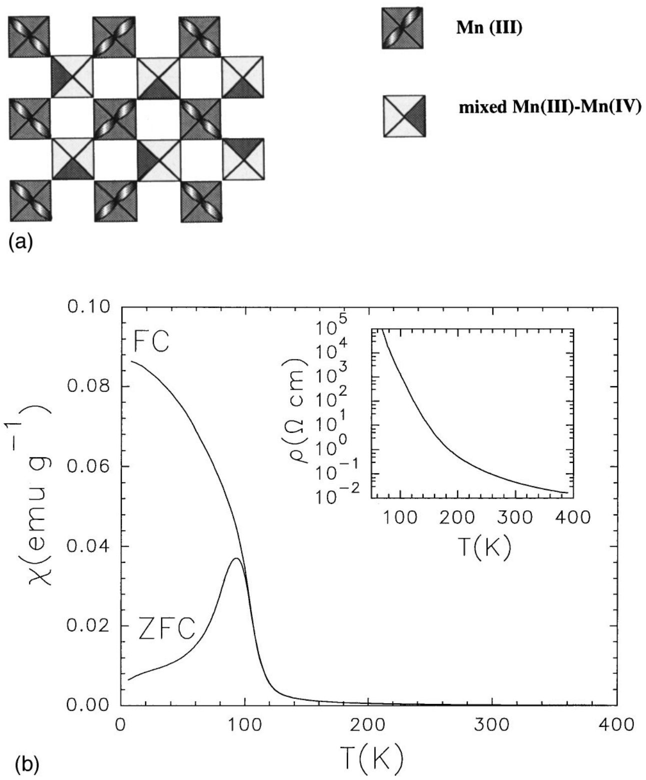


FIG. 3. (a) Ideal structure of a 1-1 type ordered structure for $Pr_{0.7}Ca_{0.3}MnO_3$. (b) *T*-dependent magnetization curves registered in 10^{-2} T [field-cooling: FC, zero-field-cooling: ZFC, and zero-field *T*-dependent resistivity (inset)].

heated progressively, keeping the electron-beam current density at 80 pA cm^{-2}. One indeed observes that at about 125 K the set of extra reflections, characteristic of charge ordering, is restored, as shown from the [010] ED pattern [Fig. 1(c)]. Note that an identical result is obtained by heating the sample in the absence of an electron beam up to 125 K, confirming that the appearance of extra reflections is, in that case, only due to the temperature increase effect, leading to the charge ordered AFM insulating state. The phenomenon is perfectly reproducible: by decreasing again the temperature down to 92 K, the extra reflections are still observed, but keeping the electron beam (80 pA cm^{-2}) at this temperature for 30 min leads again to a disappearance of the extra satellites.

Finally, starting from the charge ordered sample obtained at 125 K, one observes that by heating above 150 K in the presence of or without an electron beam, the extra reflections disappear again, and do not reappear at 160 K after prolongated exposure to the electron beam whatever the current density. This last transition corresponds to the disappearance of the charge ordering above T_{CO}, leading to the paramagnetic insulating disordered state. Note that T_{CO} deduced from the ED investigation ($T_{CO}\equiv 150$ K) is smaller than the value obtained from the NPD data ($T_{CO}\equiv 180$ K).[14] This difference may be due to the fact that close to T_{CO}, the electron irradiation also contributes, together with the temperature increase, to the destruction of the metastable charge ordered state, so that T_{CO} may be artificially lowered with respect to other methods of observation.

In this oxide, the electron induced charge disordering at low temperature is only made possible because of the great metastability of the charge ordered state. Lattice images recorded at 92 K (Fig. 2), before and after electron-beam exposure, support this viewpoint.

In contrast, all attempts to destroy the charge ordered state of $Pr_{0.5}Ca_{0.5}MnO_3$ by electron exposure below T_{CO} (250 K), varying the intensity of the beam, were unsuccessful. This different behavior is easily explained by the fact that the 1:1 Mn^{3+}/Mn^{4+} charge ordering in this phase is more stable than that of $Pr_{0.7}Ca_{0.3}MnO_3$,[13] which implies the alternation of Mn^{3+} and disordered Mn^{3+}/Mn^{4+} stripes.

This electron induced charge disordering is not specific to $Pr_{0.7}Ca_{0.3}MnO_3$, but should appear each time the charge ordered state is at the border of the instability. This explains why we observe a similar effect in $Nd_{0.7}Ca_{0.3}MnO_3$. The ED patterns of this oxide exhibit at 92 K the extra reflections characteristic of a 1:1 Mn^{3+}/Mn^{4+} charge ordering; T_C, T_N, and T_{CO} were obtained from the NPD data.[18] However, the ED patterns registered at 92 K, keeping the same conditions as those described for the praseodymium phase, clearly show that the extra reflections characteristic of charge ordering have disappeared and are restored by warming the crystals at 140 K due to a similar mechanism.

In conclusion, we have shown that a complete charge disordering is induced in $Pr_{0.7}Ca_{0.3}MnO_3$ by electron irradiation. The destruction of the charge ordered state of this manganite by electron injection may be of great interest for applications since, most probably, it allows a ferromagnetic metallic state to be induced in insulating materials which involve a strong competition between FM and AFM interactions. There is no doubt that such an effect will appear in oxides whose charge ordered states are very metastable, i.e., in oxides that are on the border of the charge ordered and charge disordered states. In this respect, this effect is very similar to the chemical pressure induced by the *A*-site substitution. For instance, $Pr_{0.7}Ca_{0.26}Sr_{0.04}MnO_3$ is an insulator whereas $Pr_{0.7}Ca_{0.25}Sr_{0.05}MnO_3$ exhibits an I-M transition.[8] Finally these results show that particular attention will have to be paid to the electron microscopy observations of these manganites, in order to avoid errors, due to a possible sensitivity of the charge-ordered states to an electron beam.

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*Author to whom correspondence should be addressed. Electronic address: hervieu@crismat.ismra.fr

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