Journal of Magnetism and Magnetic Materials 325 (2013) 29–35

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Evolution of structural phase coexistence in a half doped manganite $Pr_{0.5}Sr_{0.5}MnO_3$: An evidence for magneto-structural coupling

A.K. Pramanik [a,*,1], Rajeev Ranjan [b,2], A. Banerjee [a]

[a] UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452001, Madhya Pradesh, India
[b] School of Materials Science and Technology, Banaras Hindu University, Varanasi-221005, Uttar Pradesh, India

ARTICLE INFO

Article history:
Received 11 June 2012
Available online 13 August 2012

Keywords:
Manganite
Magnetic phase transition
Phase coexistence
Crystallographic structure
X-ray diffraction

ABSTRACT

Temperature dependent x-ray diffraction measurements have been performed to understand the implications of magnetic phase coexistence on crystallographic structure in a half-doped manganite $Pr_{0.5}Sr_{0.5}MnO_3$. The compound shows a structural phase transition from high-temperature tetragonal-*I4/mcm* to low-temperature orthorhombic-*Fmmm* symmetry around the ferromagnetic to antiferromagnetic transition. Rietveld analysis shows the coexistence of these two structures emerges at high temperature within the ferromagnetic state, and persists down to lowest temperature. Below around 40 K, however, this structural evolution stops, and a significant fraction ($\sim$22%) of untransformed high-temperature phase remains. This agrees with earlier magnetization study, thus establishing its magneto-structural coupling.

1. Introduction

Magnetic phase coexistence (PC) is a very commonly observed phenomenon in many materials of interest. In manganites, the signature of PC was shown long back by Wollan and Koehler [1], but the intense activities were started about a decade ago with the simulation work by Moreo et al. [2] which is followed by many theoretical and experimental investigations [3–18]. In spite of plenty of studies, the clear understanding about the origin of PC is still lacking whereas the dynamics and thermodynamics of the coexisting phases has accrued many interesting concepts [3,10–14,19,20]. The strong interrelation between spin–orbit and lattice parameters in manganites manifests in magneto-structural coupling which is expected to play a significant role for the observed PC in this class of materials. Moreover, this PC and the magneto-structural coupling is considered to be of significant importance for the functionality in materials of current interest such as, magnetocaloric materials [21] or shape memory alloys [22].

Manganites around half doping are quite interesting where the two competing phases viz. ferromagnetic (FM)–metallic and antiferromagnetic (AFM)–insulating share the similar energy scale [23], hence suggesting a possible coexistence of these phases. Half doped manganites with intermediate bandwidth are in fact found at the boundary of FM and AFM phases [24], and they usually exhibit first order phase transition (FOPT) associated with these two phases as a function of temperature (T) and magnetic field (H). Around the broad FOPT, a thermal hysteresis (TH) is observed due to supercooling and superheating of high-T and low-T phases, respectively. This results in natural coexistence of both these phases. However, the PC at low temperature below the closure of broad FOPT, where the high-T phase continues to be present as an untransformed one (not as a supercooled state), remains to be of significant interest. It has been shown that this PC arises due to arrested kinetics of FOPT, and has been evidenced in many materials of current interest [10,11,22,25,26,12–14,19,27]. Therefore, it is necessary to investigate the evolution of characteristic crystallographic structures related to these distinct magnetic and electronic phases to comprehend the PC phenomenon, and to establish some connection between the spin–charge–orbital degrees of freedom with the phenomenon at mesoscopic and microscopic level. Such interrelation between magnetic and structural phases at low temperature has been shown previously for $La_{0.5}Ca_{0.5}MnO_3$ using neutron powder diffraction measurements [28], however this has been shown later as an outcome of arrested phase transformation [19].

Here we present a detail study of temperature dependent x-ray diffraction (XRD) measurements on a half-doped manganite $Pr_{0.5}Sr_{0.5}MnO_3$ (PSMO). The PSMO is a medium bandwidth compound, and shows second-order paramagnetic (PM) to FM transition followed by a first-order FM to AFM transition on cooling from room temperature [16,29,30]. The AFM state at low temperature in PSMO is of A-type where the $d_{x^2-y^2}$ orbitals order along the plane and gives

* Corresponding author. Tel.: +91 731 2463913; fax: +91 731 2462294.
E-mail address: ashpramanik@gmail.com (A.K. Pramanik).
[1] Present address: Department of Physics, Indian Institute of Science, Bangalore-560012, India.
[2] Present address: Department of Materials Engineering, Indian Institute of Science, Bangalore-560012, India.

0304-8853/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jmmm.2012.08.006

rise to double exchange (DE) mediated planner ferromagnetism and metallic behavior [31,32]. Interestingly, recent studies have revealed that magnetic states in this compound is inhomogeneous showing different types of PC at different temperature regimes. For instance, within the PM state close to room temperature, there has been FM fluctuations giving rise to Griffiths phase like behavior [33]. Just below the PM to FM transition temperature T_C, PC arises in this compound with the formation of AFM clusters within the FM matrix which are, notably, not due to superheating effect of low-T FM-AFM transition [16]. With further cooling, a broad FOPT paired with a large TH is observed. This yields a natural coexistence of FM and AFM phases around the transition temperature T_N. Then at low temperature, PC is realized with the presence of kinetically arrested, untransformed high-T (FM) phase within the host AFM phase [16,13]. Thus, there are four regions having different types of magnetic PC, presumably of different origins [13,16,30,33]. Structural study shows that while there is no change in structural symmetry at PM-FM magnetic transition, the low-T FM-AFM transition in PSMO is accompanied by a structural transition where the system transforms from the high-T tetragonal-*I4/mcm* to the low-T orthorhombic-I*Fmmm* structure [34]. Therefore, in the scenario of above discussed magnetic PC, there is a strong need to thoroughly investigate the structural details of this material over a wide temperature range.

Our study employing Rietveld analysis of XRD data shows a huge TH in structural phases over a wide temperature range, similar to previous magnetization and resistivity studies [13,16]. This coexistence starts well within the FM state much above T_N. Although, with a decrease in the temperature the FM-*I4/mcm* phase converts into AFM-*Fmmm* one but the fully AFM ground state is not attained. Our analysis implies a large amount of untransformed high-T phase ($\sim 22\%$ in terms of molar fraction) is present at low temperature. Moreover, the structural parameters across T_C and T_N show certain anomalies which are justified on the basis of respective coexisting phases.

2. Experimental details

The single phase polycrystalline sample of $Pr_{0.5}Sr_{0.5}MnO_3$ has been prepared by the standard solid state ceramic route. The sample has been characterized by means of XRD and chemical analysis. The details of sample preparation and characterization techniques are given in Ref. [16]. The sample is found to be chemically homogeneous, stoichiometric and around half doping to the experimental accuracy. Temperature dependent powder XRD measurements are performed with a high power (18 kW) copper rotating anode-based Rigaku powder diffractometer fitted with a graphite monochromator in the diffracted beam. Data are collected in temperature range of 300–13 K both during heating and cooling run. A helium closed cycle refrigerator with a cold head is used to achieve the sample temperature. Sufficient wait time has been given to ensure proper stabilization of temperature before the data collection. The data have been collected in the 2θ range of 21–101° at a step of $\Delta 2\theta = 0.02°$ and a scan rate of 2°/min. XRD patterns are analyzed by the Rietveld profile refinement program by Young et al. [35]. DC magnetization (M) data are collected with a physical property measurement system (PPMS) made by Quantum Design.

3. Results and discussions

3.1. Magnetization measurement

Fig. 1 presents the dc magnetization data as a function of temperature measured in 500 Oe for the compound PSMO following

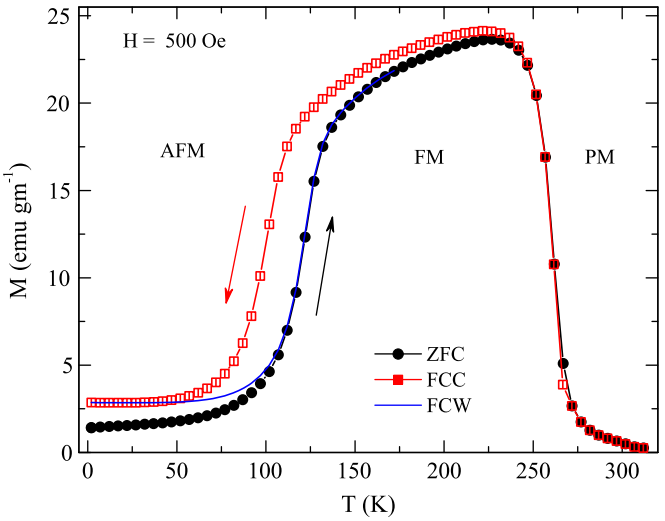

Fig. 1. Temperature dependence of dc magnetization measured in 500 Oe are shown for $Pr_{0.5}Sr_{0.5}MnO_3$. Data are collected following ZFC, FCC and FCW protocols (described in text). The arrows indicate the direction of thermal cycling. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

different protocols, viz., zero field cooled (ZFC), field cooled cooling (FCC) and field cooled warming (FCW). On cooling, $M(T)$ exhibits PM to FM and then FM to AFM transition which are marked by rise and fall in magnetization, respectively. A large TH (~ 20 K) between M_{FCC} and M_{FCW} is evident at low temperature being an indication of broad first order FM-AFM transition. Using the inflexion point in $M(T)$ plot, we obtain T_C around 262 K and T_N around 122 K during heating and 102 K during cooling. It is worth mentioning that a fair amount of TH is also observed just below the T_C between M_{FCC} and M_{FCW} (Fig. 1). This TH has earlier been shown due to the coexistence of FM and AFM clusters arising just below T_C, and continues to persist down to low temperature [16]. It is noteworthy that these AFM clusters in FM state below T_C are not due to superheating effect of broad first-order FM-AFM transition at low temperature, thus highlighting the electronic phase separation phenomenon in wide temperature range [16].

It is observed in Fig. 1 that a fully AFM state is not developed at low temperature. This is evident from the fact that a substantial value of magnetization is obtained in such a low magnetic field as well as from the observed bifurcation between magnetization measured in ZFC and FC paths. Note, that this measurement field is above the anisotropy field of this compound [16], which discounts the fact that this bifurcation arises due to an effect of local anisotropy. Moreover, unlike other systems such as spin-glass (SG) or superparamagnet (SPM), this bifurcation increases with the measuring field [30]. The actual cause of this bifurcation is shown due to a hindrance of FOPT by the arrest of kinetics, yielding an untransformed high-T phase at low temperature in this compound [13]. This complex nature of magnetic states in this compound, indeed, calls for a detailed investigation of structural parameters over the wide temperature range.

3.2. Temperature variation of XRD patterns

3.2.1. High temperature PM and FM phase

Fig. 2 depicts the XRD patterns of PSMO at 300, 193 and 15 K which corresponds to PM, FM and AFM state, respectively (see Fig. 1). Room temperature XRD data show that the material crystallizes in single phase with no other impurity peaks. In Fig. 2(a) and (b), XRD patterns show same experimental feature indicating that there is no structural transition during PM to FM