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COMMENT

Comment on ‘The controlled charge ordering and evidence of the metallic state in $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ films’

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Abstract

In a recent letter (Lee Y P, Prokhorov V G, Rhee J Y, Kim K W, Kaminsky G G and Flis V S 2000 *J. Phys.: Condens. Matter* **12** L133), Lee *et al* have studied the transport properties of $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ thin films. They claimed that they are able to control the charge-ordered state by means of the lattice strains. We propose herein another alternative, since another indexation of the orientation of the film can be found leading to almost no distortion of the cell, as compared to that of the bulk compound.

In a recent letter dealing with the study of $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ thin films, Lee *et al* [1] have shown that the ‘appearance of the charge-ordered (CO) state at 205 K can be controlled via the lattice strains accumulated during the film growth’.

While few papers have been published up to now on the particular compounds showing the charge-ordering state [2–5], the manganite thin films have been extensively studied in the past few years due to their property of colossal magnetoresistance: a huge decrease in resistance on applying a magnetic field [6–9]. The authors of [1], Lee *et al*, present the results of their x-ray and resistivity measurements on $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ thin films grown by pulsed laser deposition. They obtained x-ray diffraction (XRD) patterns with highly resolved peaks. Considering that these peaks correspond to the $00l$ reflections (002 and 004 respectively) of the $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ -type structure, they have demonstrated that the as-grown thin film of the manganite is tetragonal with $a = b = 5.432 \text{ \AA}$ and $c = 7.74 \text{ \AA}$, i.e. fundamentally different from the bulk material with the same composition, $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$, which is orthorhombic with $a = 5.42 \text{ \AA}$, $b = 5.46 \text{ \AA}$ and $c = 7.67 \text{ \AA}$ [10]. Unfortunately, for the determination of the structure, they also used weak reflections of the perovskite (103, 113 and 312) which appear in their XRD patterns, but which belong to a secondary phase with a different orientation and possibly with a different composition (note that the cationic composition of the film has not been checked and that a small change in composition can drastically modify the parameters of the cell and therefore the properties). Nevertheless, the authors conclude that lattice strains lie at the origin of the unusual behaviour of this thin film which exhibits, according to them, a metallic-like behaviour with an incredibly high resistivity of 10^5 \Omega cm below 120 K! After

a brief summary regarding charge ordering, we will show that another conclusion can be proposed involving no distortion of the cell as compared to that of the bulk material.

Hole-doped manganites, with the general formula $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$ (RE = rare earth, A = alkaline earth) exhibit a rich phase diagram as a function of the doping concentration x . As the average size of the cations at the lanthanide site is reduced, a tilt of the MnO_6 octahedra is induced which favours localization and ordering of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ cations [11]. Moreover, below a certain temperature (T_{CO}), the metallic state becomes unstable and the material goes to an insulating state. Such a charge-ordering transition is associated with antiferromagnetic, insulating properties and large lattice distortions. Another amazing feature is that the application of a magnetic field results in the melting of the CO state (i.e. the material becomes ferromagnetic and metallic). This phenomenon has been observed in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (with $0.35 < x < 0.65$) [12]. Thus, the composition $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ studied in the letter by Lee *et al* shows, in the bulk, a CO state at low temperature.

We propose another alternative for the crystallographic nature of this $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ thin film. It has been shown previously [13, 14], using electron diffraction, that many manganite thin films with a $Pbnm$ space group (such as $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$), are often [110] oriented when grown on LaAlO_3 (as used by Lee *et al*). Thus, it can alternatively be proposed that these peaks in the XRD pattern correspond not to the $00l$ reflections but to the $hk0$ reflections (i.e. 110 and 220 respectively). As a consequence, the observed values of d_{220} and d_{004} and those deduced from the data obtained by the authors ($d_{220}^{obs} \cong 1.93 \text{ \AA}$ and $d_{004}^{obs} \cong 1.92 \text{ \AA}$ for the as-grown film and $d_{220}^{obs} \cong 1.92 \text{ \AA}$ and $d_{004}^{obs} \cong 1.96 \text{ \AA}$ for the annealed film) are perfectly compatible with those calculated from the parameters of the cell of the corresponding bulk compound ($d_{220}^{cal} \cong d_{004}^{cal} \cong 1.92 \text{ \AA}$ [10]). In other words, the XRD pattern of the $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ thin film suggests that the film is identical to the bulk, and this does not provide any proof of the accumulation of the lattice strains during the film growth, contrary to the statement of Lee *et al*.

In conclusion, the assumption regarding the orientation of the film of $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ made by Lee *et al* is purely speculative. This demonstrates that the thin films must be correctly characterized from the crystal structure viewpoint before proceeding to physical measurements, using electron diffraction to reconstruct the reciprocal space. For this reason, all of the physics which is developed in the letter by Lee *et al* might be incorrect.

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