Compressive Strain Effects on Charge and Orbital Ordering in $Pr_{0.6}Ca_{0.4}MnO_3$

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Introduction

The study of manganites is an active area of research in the field of strongly correlated electron systems [1]. Prominent issues surrounding these materials include those pertaining to both basic and applied physics. With regard to the latter, manganite films have been the subjects of research since the first observation of a colossal magnetoresistance (CMR) effect in a $La_{0.67}Ca_{0.33}MnO_x$ film [2]. The magnetoresistance in manganite films, which is more than three orders of magnitude larger than typical values observed in conventional metal multilayers, immediately suggests the potential for applications.

The impetus for manganite film studies also arises from the opportunity they provide to tune the properties through the use of substrate-induced strain and variations in the after-growth processing. Since the complex behaviors exhibited by the manganites result from the interplay of the charge, orbital, spin, and lattice degrees of freedom, small changes in the balances among these four degrees of freedom may result in dramatic differences in the properties of these materials. For example, recent theoretical calculations predict a change in the magnetic ground state as a result of a ~2% strain in $LaMnO_3$ [3]. The goals of such tuning are twofold: to learn about the relationships among the various degrees of freedom and to obtain a material that exhibits a large magneto-resistance at room temperature upon application of a small (tens of Gauss) magnetic field.

In order to investigate the effects of substrate-induced strain in manganite films, we began by considering a well-characterized material: $Pr_{0.6}Ca_{0.4}MnO_3$. In bulk form, this material exhibits CE-type charge and orbital ordering — with associated lattice distortions — below a temperature of ~240K [4]. While the charge order is observed to be long-range, the orbital order is short-range, with a correlation length of 320 Å [5]. For studies of a $Pr_{0.6}Ca_{0.4}MnO_3$ film, the effects of substrate-induced strain on the ordering properties are the primary concern. Specifically, what will the effects of substrate-induced strain be with respect to the type of ordering, ordering temperature, and correlation length of the orbital ordering? With these questions in mind, we carried out an x-ray scattering study of a $Pr_{0.6}Ca_{0.4}MnO_3$ film on CMC-CAT beamline 9-ID at the APS.

Methods and Materials

The (110)-oriented $Pr_{0.6}Ca_{0.4}MnO_3$ film was grown on a lanthanum aluminate (LAO) substrate by using the pulsed laser deposition technique. The nominal, compressive strain on the film due to the lattice mismatch with the LAO substrate was 1.4%, and the film thickness was ~2500 Å.

The x-ray scattering studies were carried out on CMC-CAT beamline 9-ID. The beamline optics consisted of a Si(111) double-crystal monochromator, which was used to select an energy near the Mn K edge (6.539 keV); a Pt-coated focusing mirror; and a flat harmonic rejection mirror. The sample was placed in a closed-cycle cryostat that enabled measurements to be conducted over the temperature range of ~8 to 300K.

Results

At a temperature of 100K, the $Pr_{0.6}Ca_{0.4}MnO_3$ film was observed to exhibit CE-type charge and orbital ordering. Specifically, charge and orbital order peaks were observed at (H00) and (H/2 0 0), respectively, for odd H. The orbital correlation length was measured by using a graphite analyzer; it was determined to be 90 Å.

The temperature dependences of the charge and orbital ordering were studied, and the results are summarized in Fig. 1. The orbital ordering was observed to disappear at a temperature of ~160K. Intriguingly, the scattering intensity at the charge order wave vector also decreased

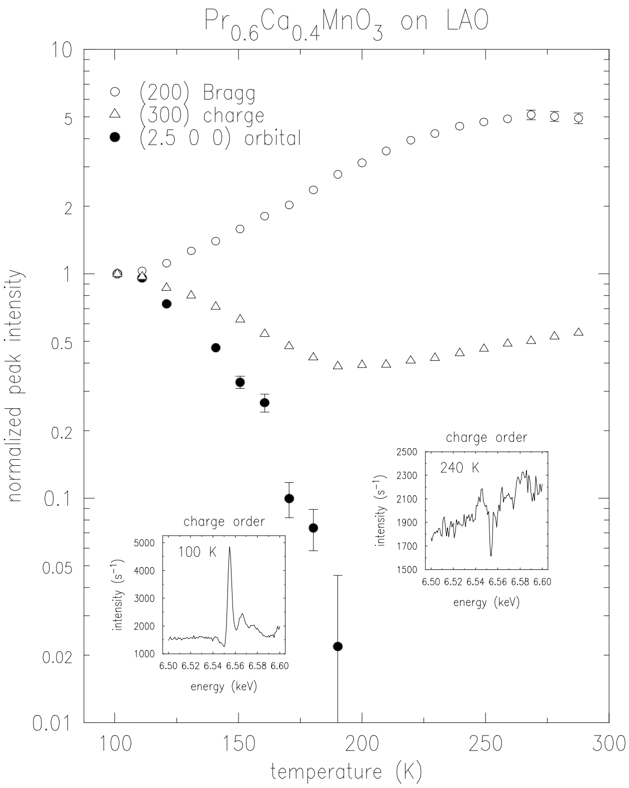

FIG. 1. Temperature dependences of the peak intensities of a Bragg peak (200), charge order peak (300), and orbital order peak (2.5 0 0) normalized to equal 1 at 100K. Insets show the energy line shapes at the charge order wave vector at 100 and 240K.

with increasing temperature, but it did not disappear at 160K. Instead, the energy line shape at the charge order wave vector was observed to change near this temperature (see insets to Fig. 1). In other words, the resonant peak at 6.555 keV observed at low temperatures disappeared above the transition temperature.

Discussion

The $Pr_{0.6}Ca_{0.4}MnO_3$ film grown on a LAO substrate is observed to behave differently than the bulk material. While both exhibit CE-type charge and orbital ordering, the orbital correlation length and the ordering temperature in the film are reduced with respect to bulk values. Possible explanations for these reductions include the change in the Mn-O-Mn bond angle and the clamping of the film by the substrate, which may counteract the formation of the CE-type phase because of its effect on the strain energy. Another difference in the behavior of the $Pr_{0.6}Ca_{0.4}MnO_3$ film is the lattice modulation at the charge order wave vector that was found to persist above the transition temperature. More recently, we have observed this lattice modulation in tensile-strained films of similar thicknesses, which suggests that it is a common feature of $Pr_{0.6}Ca_{0.4}MnO_3$ films.

In conclusion, the intriguing results observed in studies of the $Pr_{0.6}Ca_{0.4}MnO_3$ film indicate that the effects of substrate-induced strain can be quite dramatic. These results also suggest future directions for studies of manganite films involving variations in the magnitude of the strain and after-growth processing. Finally, the robust scattering intensity observed on CMC-CAT beamline 9-ID suggests the feasibility of future studies of manganite films with reduced (e.g., a few tens of nanometers) thicknesses, which are of interest for practical applications.

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