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Investigations of Domain Structures in $La_{0.7}Ca_{0.3}MnO_3$ Single Crystals

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One of the key elements in the research of manganese oxides is the issue of an intrinsically inhomogeneous or phase-separated electronic ground state [1]. The question is linked to the occurrence of chemical or crystalline disorder. Fäth et. al. [2] have studied samples of $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) in single-crystalline bulk and thin-film forms. Below the transition temperature T_C, coexistence of metallic and insulating areas was found strongly field dependent in their size and structure. In order to understand the inhomogeneous properties and also to elucidate the relationship between the microstructure and CMR behavior, we have investigated the microstructure of single crystals of LCMO by high resolution electron microscopy and find abundant twinning on submicron length scales.

Single crystals of LCMO were grown by the floating zone technique [2]. They were crushed into smaller pieces and electron-transparent areas were obtained by ion milling. High resolution electron microscopy was performed with a Philips CM300UT electron microscope with a field emission gun operated at 300 kV. At the crystal growth temperature LCMO adopts a cubic structure. During cooling to room temperature a phase transformation occurs to an orthorhombic structure (Pnma). The room temperature structure can be described with a $\sqrt{2}a_p$, $2a_p$, $\sqrt{2}a_p$ enlarged unit cell, where p is the unit cell axis of the cubic phase [3]. The transformation from cubic to orthorhombic leads to six possible variants, as was discussed by Wang et al. [4]. All variants are observed in the crystals. Twin domain structures in which the b-axis is changed (90° rotation of the twin relations) can be most easily observed along the <100>c cubic direction. Fig. 1a is a low resolution image with a lamella microstructure commonly observed, which is formed of twins with widths that range from 300 nm to 1 µm. Mostly the twin boundaries (TB's) are parallel to the (100)c plane. Figs. 1b,c show high resolution images of these 90° TB's. In Fig. 1b the b-axes of neighboring lamellae are perpendicular to each other as indicated, the [101]o directions of both twins are along the twin plane, which is very flat and without any dislocations. However, in Fig. 1c the b-axis of one domain and the [-101]o direction of its twin are parallel to the twin plane, and dislocations are found along the boundary (marked by white arrows). These dislocations are logical given the difference between the spacings d(020)o and d(101)o. In both kinds of twin relations as shown in Figs. 1b,c the twin walls are very narrow, typically 0.2 to 0.4 nm wide.

Twin domain structures in which a_o and c_o are interchanged (a-c twinning) can be seen best in the <110>c direction, because of the symmetry difference for the [100]o and [001]o zones. Fig. 2a shows a low - resolution image with a typical pattern of narrow lamellae. The width of the twins is 30-100 nm. Electron diffraction of this area indicates that these lamellae are indeed due to a-c twinning. The most frequently occurring a-c twin plane is the (101)o plane. No high resolution image of this twin is shown because no features of special interest are observable. The (101)o TB's are mostly straight. Another observed a-c twin is the (010)o plane; as shown in Fig. 2b. The local structure near the twin boundary can be seen from the HREM image in Fig. 2b. The TB's are only roughly parallel to (010)o since they contain steps of several

unit cells. The twin walls are again very narrow. The microstructural features of the various observed twins are summarized in Table 1. The most common twinning is the a-c twinning. Such twinning was observed in all areas of the different crystals. Thus, true single crystalline areas can only be found with very small size, of the order of 50 nm or even less.

References
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TABLE 1. Summary of the various twin relations and their microstructural features

Twin	Twin plane Orthorhombic	Twin plane Cubic	Twin width [nm]	Shape of twin plane
90° rotation	(010) (101)	{100} {100}	300-1000 300-1000	straight straight
a-c twinning	(010) (101)	{100} {100}	30-60 30-60	wavy straight

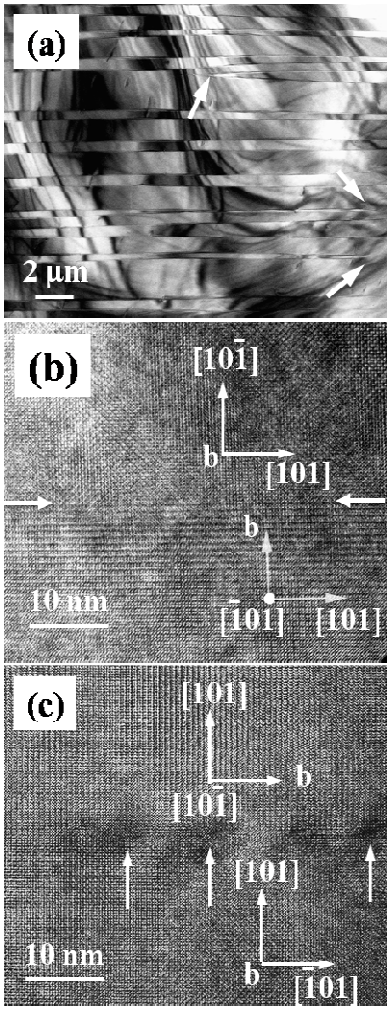

FIG. 1. (Left) TEM images of a LCMO single crystal in [100]c orientation. (a) shows a low resolution image with a pattern of narrow twinning lamellae. Some lamellae that end as a sharp tip (white arrows). (b) and (c) HREM images showing various kinds of twin boundaries.

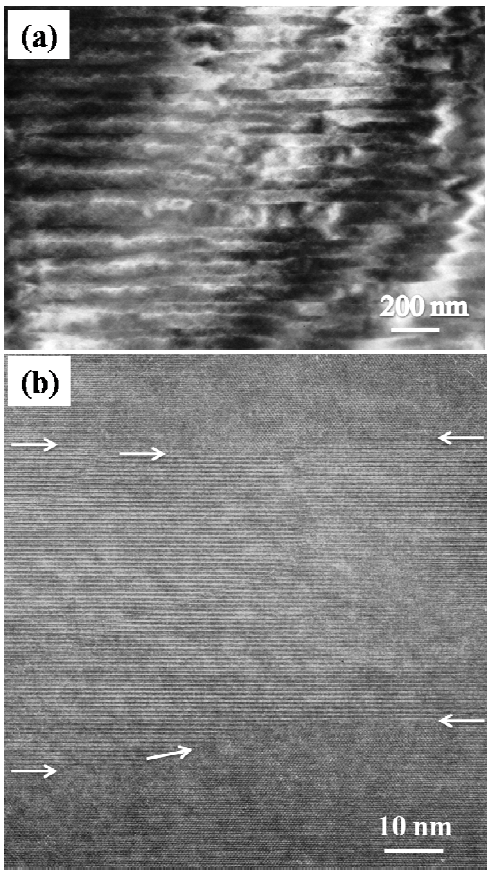

FIG. 2. (Right) TEM images of a LCMO single crystal in [110]c orientation. (a) shows a low resolution image of a twin domain structure due to a-c twinning. (b) shows a HREM image of such twin boundaries. The twin boundaries are marked by white arrows. In both twins the b-axis is perpendicular to the twin boundary planes. In the top and bottom of the image a [100]o orientation is presented and in the middle a [001]o orientation.