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TWINNING MICROSTRUCTURE AND CHARGE ORDERING IN THE COLOSSAL MAGNETORESISTIVE MANGANITE Nd$_{1/2}$Sr$_{1/2}$MnO$_3$

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Charge ordering (C.O.) in the colossal magnetoresistive (CMR) manganites gives rise to an insulating, high-resistance state. This charge ordered state can be melted into a low-resistance metallic-like state by the application of magnetic field. Thus, the potential to attain high values of magnetoresistance with the application of small magnetic fields may be aided by a better understanding of the charge-ordering phenomenon. This study focused on microstructural characterization in Nd$_{1/2}$Sr$_{1/2}$MnO$_3$. In Nd$_{1/2}$Sr$_{1/2}$MnO$_3$, the nominal valence of Mn is 3.5+. On cooling, charge can localize and lead to a charge ordering between Mn 3+ and Mn 4+. The ordering of charge results in a superlattice structure and a reduction in symmetry.$^{13}$

Thin foil specimens were prepared from bulk samples by conventional thinning and ion milling (at LN$_2$ temperature) methods. The TEM work was carried out in a Philips CM30 at 300 kV with a Gatan LN$_2$ cold stage, and a JEM 4000EX with a resolution of 0.17 nm at 400 kV for HREM observation.

The room temperature TEM observation of Nd$_{1/2}$Sr$_{1/2}$MnO$_3$ reveals that it contains a highly twinned microstructure, together with a small number of stacking faults (SFs). Figure 1 shows the same area of the specimen at different zone axes obtained by tilting around two perpendicular directions as indicated. Three grains A, B and C are labeled for each of the zone axes. The room temperature EDPs from the matrix and twins shows an approximate 90° rotation suggesting a 90° twin orientation. These results are further confirmed by C.O. at low temperatures as will be demonstrated below. The twinning planes can be determined by tilting with large angles. In figure 1(a) at the [010] zone axis, the twinning planes 1 and 2 are at the edge-on positions, and the plane 4 formed by shearing is also at the edge-on position, while the SF plane 3 is inclined to the viewing direction. At the [111] zone axis in (b), only the plane 1 remains the edge-on position while all others are inclined. In (c) at the [11̅1] zone axis, all of these planes are inclined. Therefore, the planes 1, 2, 3 and 4 are determined as (10̅1), (101), (1̅10) and (001) respectively.

HREM observation on the twins reveals that the crystalline lattices of the matrix and the twin are not parallel to each other but rotated by a very small angle (−2°), as shown in figure 2. Such a rotation leads to a mismatch along the twin plane that is accommodated by dislocations. The region enclosed by the dotted lines is enlarged at the bottom-left corner, where a simulated image with t = 15 nm and Δf = -30 nm is inserted. Unit cells are outlined by white squares. The predicted dislocation spacing is l = b/φ = 10.9 nm, assuming b = 0.38 nm and misorientation angle φ = 2°. This spacing is consistent with the experimental value determined from observation in figure 2.

Figure 3(a) shows the microstructure at 146 K, just above the C.O. transition temperature. At the temperature of 94 K in (b) and (c), the EDPs exhibit extra reflections from the charge ordered superlattice (2axbxc), from which the near 90° twinning rotations are very clearly revealed. The dynamics and history dependence of C.O. are illustrated by figures 3(b) and (c). The interface between the C.O. and non-C.O. are schematically marked by broken white lines. Figure 3(b) shows the C.O. structure upon initial cooling while figure 3(c) shows the C.O. structure after heating and cooling a second time. From this work, the C.O. is observed as a nucleation and growth transformation, which is influenced by the twin boundaries as shown in (b) and (c). Some regions remain untransformed in (b) and (c). These regions may provide a link to compositional or structural variations.$^4$

Reference:
Figure 1. Microstructure at [010] (a), [111] (b) and [11\overline{1}] (c) zone axes, referred to the matrix orientation.

Figure 2. HREM observation of the twin boundary.

Figure 3. History and structure dependence of C.O. (a) Above C.O. transition; (b) after first cooling to 94 K; (c) after re-heating and second cooling to 94 K.