

X-ray Crystal Truncation Rod Analysis of the Surface Structure of LaAlO₃ As a Function of Temperature

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Beamline(s): X22C

Introduction: The structure, composition and termination of the surface of LaAlO₃ is of major interest due to its extensive use as a substrate for thin film growth,¹ in particular for the growth of superconducting oxide films. Previous studies have suggested that surface termination of LaAlO₃ is dependent on temperature, and changes from aluminum to lanthanum termination between 150 and 250°C.² Furthermore the change was found to be fully reversible. It was suggested that this surprising observation may be related to the formation of surface oxygen vacancies, but to date there is no direct structural information regarding this surface transformation. Hence, we have applied the technique of x-ray crystal truncation rod (CTR) analysis³ to directly and sensitively probe the surface structure and terminations of single crystals of LaAlO₃.

Methods and Materials: The CTR profiles were recorded on station X22C of the NSLS. CTR profiles in a number of different lattice directions were measured on highly polished [001] oriented single crystals of LaAlO₃ at both room temperature and ca. 400°C. Transverse scans were taken at each point along the rod enabling the subtraction of the diffuse scattering contribution from the integrated intensities.

Results: The CTR profiles recorded at room temperature and ca. 400°C showed small but significant differences above and below the transition temperature indicative of the surface structure change suggested by earlier experiments. Figure 1 shows the 00L CTR profiles for room temperature and 400°C. 10L and 20L profiles were also recorded. Various structural models and techniques (simulated annealing, least-squares fitting and energy minimization) were used to simulate the experimental data. Using aluminum terminated model in which the top 4 surface layers are allowed to relax it proved possible to simulate the experimental data at both room and high temperature with a chemically sensible model. Figure 2 shows representations of the calculated room and high temperature structures. At room temperature a fairly minor rearrangement of topmost two layers occurs (relative to the ideally terminated structure), mostly involving a relaxation of the surface oxygen atoms away from the surface, together with a small relaxation of the aluminum atom into the surface. Thus the Al coordination changes from five coordinate pseudo-octahedral (in the ideally terminated case) to square-pyramidal. The second (La-O) layer also shows some small vertical movements. At high temperature a much more significant structural rearrangement involving all of the top four surface layers occurs. In particular, the aluminum atoms move a considerable distance into the bulk (~0.16c) while the surface oxygen atoms move a considerable distance out of the bulk (~0.25c). Additionally, there are significant lateral movements of the oxygen atoms in the top two layers. This has the effect of changing the aluminum atom coordination from square pyramidal to pseudo-tetrahedral geometry, as was suggested by previous studies. However, no evidence for a complete reversal of surface termination from Al-O to La-O or the formation of surface oxide vacancies is seen, as was previously reported.

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References: ¹ E. McDaniel and J. W. O. Hsu, J. Appl. Phys. **80**, 1085 (1996); ² J. Yao, P. B. Merrill, S. S. Perry, D. Marton, and J. W. Rabalais, J. Chem. Phys. **108**, 1645 (1998); ³ I. K. Robinson, Phys. Rev. B **33**, 3830 (1986).

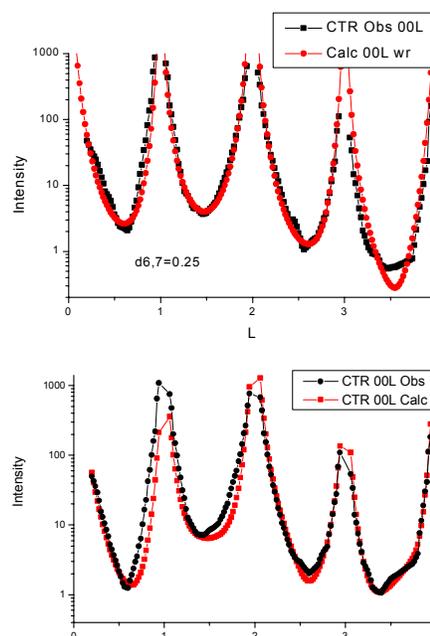


Figure 1: Observed (black) and calculated (red) 00L CTR profiles recorded on LaAlO₃ at a) room temperature and b) ca. 400°C

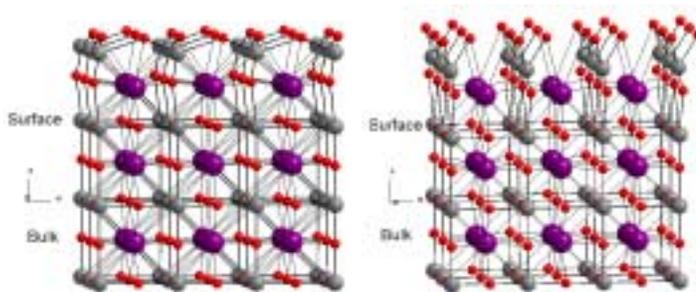


Figure 2: Representations of the calculated room temperature and high temperature surface structures of LaAlO₃ viewed near parallel to the b-axis. La is shown in purple, Al in grey, O in red.