| ESRF | **Experiment title:**<br>**THE STRUCTURE OF THE RECONSTRUCTION(S) OF MGO(111) BY GRAZING INCIDENCE -RAY DIFFRACTION (GIXD)** | **Experiment number**:<br>SI-591 |
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**Report:**

The present experiment aimed at determining the structure of the reconstructions stabilising the MgO(111) polar oxide surface. Similarly to previous experiments on NiO(111) [1-3] we have used grazing incidence X ray diffraction. We have shown that a single crystalline NiO(111) surface exhibits the predicted octopolar reconstruction [4] after air-annealing and a spinel configuration after UHV annealing under a partial pressure of oxygen.

Indeed the MgO(111) polar surface was long believed to be unstable because of the divergence of the electrostatic potential. Recently several reconstructions of MgO(111) were reported and a structural model based on cyclic ozone was proposed [5,6] that is very different from the octopolar reconstruction. Since this results were surprisingly different from the NiO case and since MgO is a simple oxide and is thus well suited to perform calculations we have undertaken the measurement of the MgO(111) surface in collaboration with theoreticians in order to get insight in the mechanisms stabilising MgO(111) and not only a structural determination.

We were able to produce a single crystal with a very high crystalline quality up to the surface (micron-sized terraces, a few 1/1000 of degree mosaicity) which showed strong p(2x2) reconstruction peaks. No other periodicity was found. The sample was first measured at room temperature. All accessible in plane reconstruction peaks over the whole reciprocal space were measured with a systematic error level of about 8%. 4 reconstruction rods and 6 crystal truncation rods were also measured. Since the in-plane scattering was very like the NiO(111) scattering at higher temperature (i.e. a mixture of spinel and octopole configurations) we have made two other measurements in order to determine the relative surface concentrations at 150°C and 250°C under partial O pressure. In the MgO case the transformation was found reversible in situ.

The coupling of atomic-scale simulations, based on the density functional theory, with grazing x-ray diffraction experiments provide a unique opportunity to achieve a precise description of the (2x2) reconstructions observed on the (111) polar orientation of magnesium oxide. The calculations are carried out by Fabio Finocchi and Claudine Noguera, in the surface theory group at Orsay.

In the calculations, starting from a realistic configuration, the surface geometry, corresponding to stable or metastable configurations at the actual surface composition can be obtained. The models so obtained can be compared to the structures proposed to fit the x-ray data. The comparison is worth for two reasons: on one side, the calculations are carried out on model systems (flat surfaces, in the micro-canonical ensemble, often at zero temperature), so that the relevant factors governing the evolution of the surfaces can be extracted much better from a critical comparison with the measured data. On the other hand, the fitting procedure of surfaces with a large number of degrees of freedom is a big task, and the outcome of the numerical simulations is often very useful, either as starting point or as a better refinement of a class of fitted structures.

Effectively, as expected from the very qualitative first interpretation during the experiment, a spinel like configuration could be determined and refined theoretically with help of the data taken at 250°C (pure spinel configuration). This spinel configuration is a metastable state since its surface energy is higher than the octopolar reconstruction, but on the other hand it does not spontaneously transform in the octopolar reconstruction. A major difficulty is the mixture of configurations already at low temperatures. With the refined structural model we could determine that at room temperature the surface contains already 55% of the spinel configuration and 100% at 250°C. The corresponding in-plane experimental and calculated structure factors are given in figure 1. However the lack of situations with larger amounts of the octopolar reconstruction does not allow yet evaluating the relaxations of the octopolar reconstruction nor the transition order. Low temperature measurements will thus become mandatory before a coherent and complete understanding of the MgO(111) can be provided. On the other hand the similar behaviour observed for NiO(111) in an other temperature range allows thinking that the observed two structure combination is a general rule for polar oxide surfaces with respect to the O potential and the temperature.

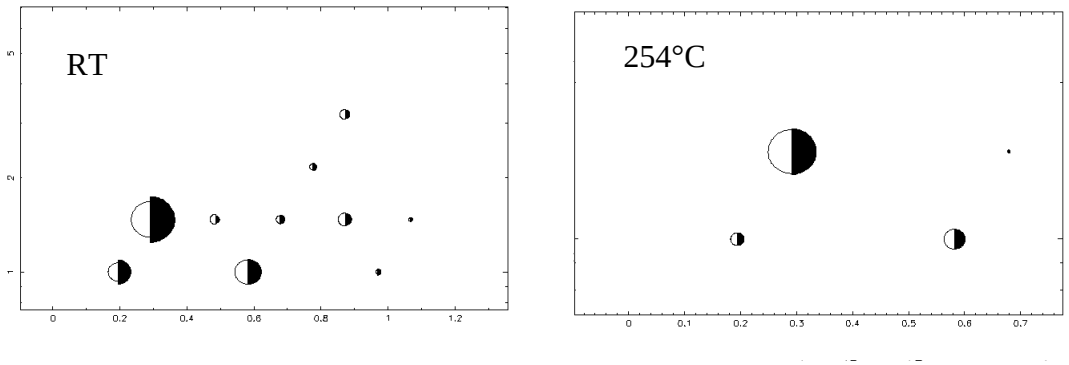


Figure 1: Measured and calculated structure factors for the MgO(111) surface with a model containing 55% (100%) spinel configuration at RT (254°C).

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