

Experiment Report Form

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- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Beamline: ID03	Experiment title: Investigation of the surface structure of glycine at the pyrite-water interface	Experiment number: SI-1585
	Date of experiment: from: 28 November 2007 to: 04 December 2007	Date of 2nd report: 22.02.2010
	Shifts: 18	Local contact(s): Dr. Didier WERMEILLE
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Report:

In this experiment we investigated the pyrite (100) surface first in dry atmosphere at ambient conditions, then covered with a water film and in contact with aqueous glycine solution with grazing incidence X-ray diffraction methods. For each part of the experiment the specular reflectivity and a data set of non-specular crystal truncation rods (CTRs) were measured. We obtained data sets of 13, 14 and 13 CTRs for the pyrite surface in dry ambient conditions, for the hydrated surface and for the aqueous glycine-pyrite-interface, respectively.

Due to personal reasons (pregnancy and parental leave) the analysis of the data sets is not yet completed. The intensity profiles of the rocking scans were corrected for polarization, lorentz and experimental factors, fitted with a Lorentzian function and integrated after subtracting a linear background. We obtained integrated and corrected intensities for the surface in dry ambient conditions and for the hydrated surface so far. These sets of CTRs were used in a least square fit to obtain the atomic structure of the pyrite surface and pyrite-water-interface. Various surface structure models were tested with different surface terminations (defects), different initial parameters and with and without the glide plane symmetry in the topmost layers of the surface cell. The analysis of both data sets is not yet completely finished, but our results so far are in general agreement with simulation and experimental results published in literature: The surface has an unreconstructed, bulk terminated structure with only small relaxations in the topmost layers, in agreement with [1-4]. The surface is cleaved at the Fe-S bonds, but we also observed structure defects, e.g. S vacancies, in agreement with DFT calculations [5]. The present results are now explained in detail below.

Pyrite (100) surface structure in dry ambient conditions

The pyrite (100) surface in dry ambient conditions has a bulk terminated surface structure with small relaxations in the topmost atom layers. The surface is not reconstructed, which was also confirmed by H- and K-scans for every part of the experiment.

The surface cell is equal to the cubic bulk unit cell ($a = 5.417\text{\AA}$), with layers consisting of 2 Fe and 4 S atoms, paired as dimers. We tested the refinement of site occupation factors (sof) and positions of single and paired S atoms, respectively. Both models yielded two types of surface terminations, which differ in the amount of vacancies present in the first atom layer. Type 1 has a S vacancy in the topmost layer, originating from the breaking of an S-S bond. This surface model is in agreement with the defect pyrite surface model from DFT-calculations published by Stirling et al. [5]. The other type of surface defect structure, type 2, consist of a weakly occupied surface layer with sofs of Fe and S in the range of 0.2 – 0.3, whereas the following layers are completely occupied. The four surface models have a χ^2 of 7.1 - 8.6 so far, so it is necessary to further refine the surface model, e.g. by a combination of both surface defect types in a larger surface cell. The fit of the data is shown for two CTRs in fig. 1. The atom relaxations are very small, but for type 2 larger compared to type 1. Here especially the shift in z-direction (perpendicular to the surface) is larger than that in the surface plane.

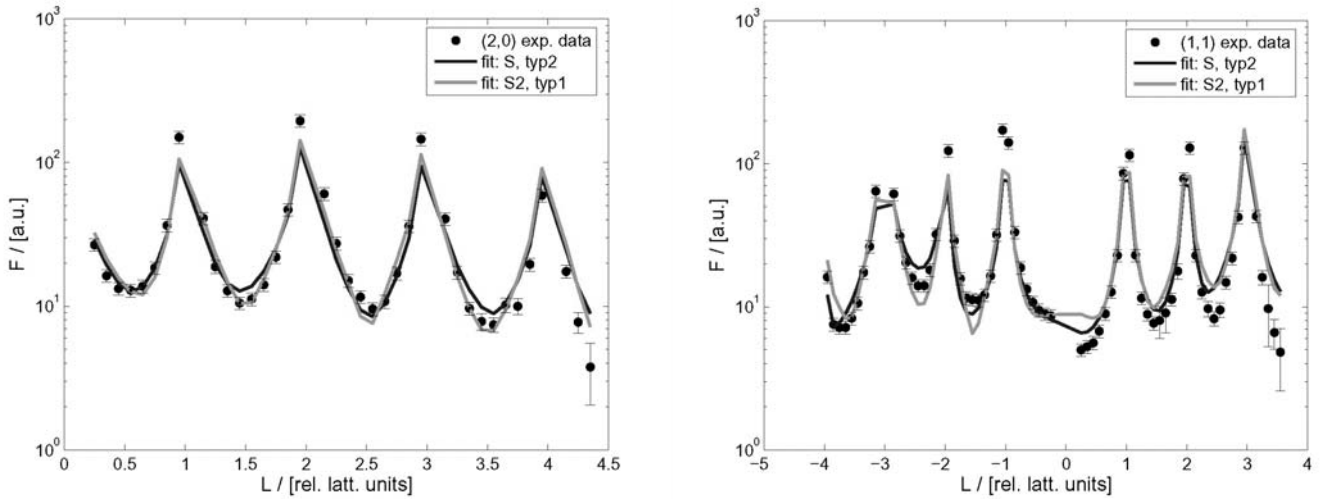


Fig. 1: Fit of the (2,0) and (1,1) CTR of with the pyrite surface in dry ambient conditions with single and dimer S atoms (S and S2), yielding two types of surface defects (type1 and type 2, see text).

Pyrite-water-interface structure

The hydrated pyrite (100) surface shows a defect surface termination similar to the surface in dry ambient conditions. The first model refined was a surface cell analogue to the bulk model used for the dry surface without water or O atoms representing water molecules. Here we also used single and paired S atoms, reaching a χ^2 of about 8 and about 13, respectively, so that for the following models single S atoms were used. The refinement without water went down to a χ^2 of 5.3. The topmost layer is weakly occupied with an Fe vacancy ($\text{sof} = 0.5$) and S sofs between 0.2 and 0.4. The next layer is similar to the type 1 model of the dry ambient surface with a S vacancy, breaking a S-S bond ($\text{sof} = 0.5$) and an sof of 0.8 for Fe. With increasing depth the layers are completely occupied. The relaxations of the atoms in the topmost layers are very small, but the shift in z-direction is larger than that in the surface plane.

To obtain the water layer structure 2 O atoms were positioned above the topmost Fe atoms, according to [6,7]. The refinement of the model with different start heights, i.e. Fe-O distances, ranging between 1 - 5 \AA , resulted in three different z-positions of the O atoms in about 2.8 \AA , 5.0 \AA and 6.7 \AA height above the topmost Fe position. This is in general agreement with the results of the molecular dynamics simulation of a water film on pyrite by Philpott et al., where three ordered water layers were found in about 2.0 \AA , 3.3 \AA and 5.1 \AA above the topmost Fe layer [7]. In difference to the model without O atoms, the refinement of the sofs resulted in a very weakly occupied topmost surface layer with sofs of 0.1 for Fe and 0.2 - 0.3 for S. Additionally here an O position was found at about 3 \AA above the 2nd pyrite layer.

The refinement of the atom positions in the surface plane yielded different x- and y-coordinates for O and S atoms, depending on the initial parameters, especially the initial height of the O atoms, so that here no general prediction of the lateral in-plane structure was possible.

The quality of the fits are not yet sufficient with χ^2 values of 5.6–7, so that here more structure refinement runs will be necessary.

The next structure model used consists of 4 O atoms positioned in two different initial heights above the topmost Fe layer according to [7]. Here the refinements of models with different initial parameters (esp. O heights) yielded results similar to the model with 2 O atoms. Again three water positions above the topmost surface Fe layer were found, in about 1.9 Å, 2.8 Å and 5.4 Å height above the z-position of the topmost Fe atoms (fig. 2). This is in very good agreement with the water layer structure found by Philpott et al. [7]. But here also the topmost layer is only about half occupied for Fe and S, so that we found another O position in 3 Å distance above the 2nd Fe layer of the pyrite surface. The determination of the O site occupation of every water layer and the specific lateral positions will be the task for the following refinement runs, because the χ^2 values of 5.2–6.5 are not yet sufficient (fig. 3).

However, merging the present results we found for the pyrite surface in dry ambient conditions and the pyrite-water interface a surface structure with a high defect density, showing both Fe and S vacancies. The hydration layer consists of four layers of water molecules, with the first water layer penetrating into the topmost pyrite layer, due to the surface defect structure.

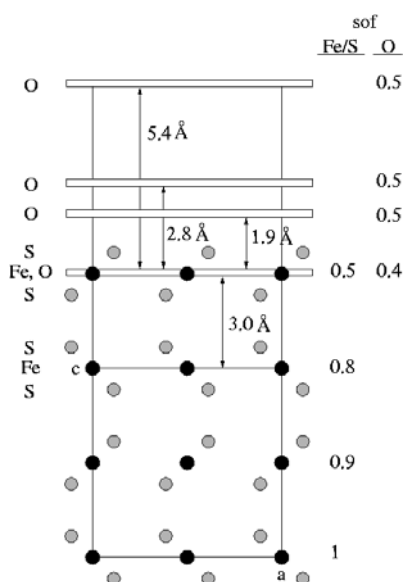
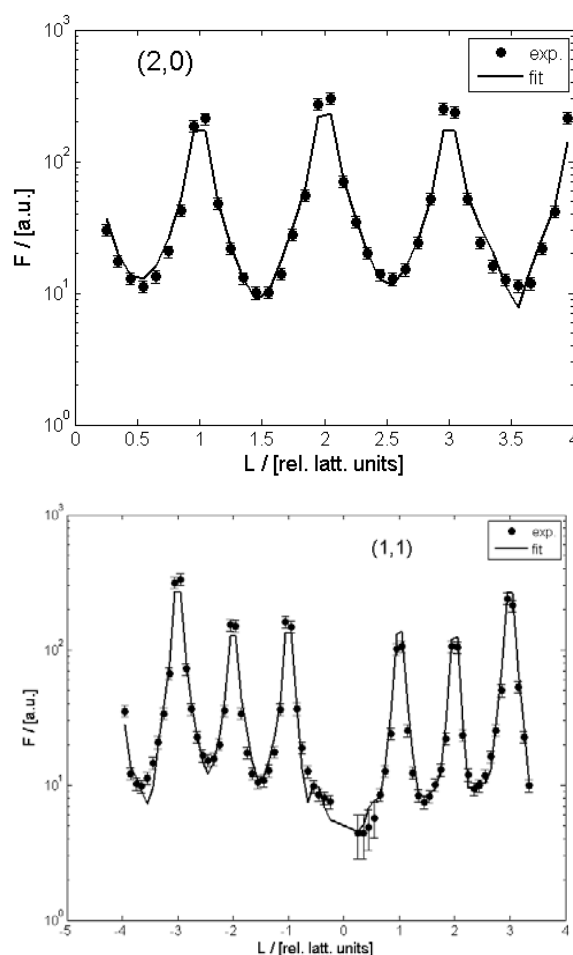


Fig. 2: Present model of the pyrite water interface with 4 water (O) layers above the surface, layer heights agreeing with DFT simulation results [7].

Right: Fig. 3: Fit of the (2,0) and (1,1) CTR of the hydrated pyrite surface with the model shown in Fig. 2.



References:

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