

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application**:

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

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The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

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Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
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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.



Experiment title:
Investigation of the surface structure of glycine at the pyrite-water interface

Experiment number:
SI-1585

Beamline: ID03	Date of experiment: from: 28 November 2007 to: 04 December 2007	Date of report: 29.02.2008
Shifts: 18	Local contact(s): Dr. Didier WERMEILLE	<i>Received at ESRF:</i>

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Report:

Here we report about the investigation of the interaction of glycine molecules with the pyrite (100) surface in aqueous solution using grazing incidence X-ray diffraction methods.

The experiment was carried out in ambient conditions at room temperature and normal pressure in three steps: The first part was the measurement of the pyrite surface in dry atmosphere, followed by the coverage with a water film to obtain information about the hydrated surface structure. The third part was the coverage of the surface with aqueous glycine solution.

For each part of the experiment the specular reflectivity and three data sets 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.

The specular reflectivity of the surface shows different intensity variations related to the different experiment parts (Fig. 1 (left)). With water or glycine film the background signal is enhanced, but also the reflectivity exhibits additional peaks. The features indicate a different vertical surface structure for the surface in contact with water or glycine, compared to the dry surface, respectively. This result is confirmed with the preliminary analysis of the measured L-scans, as shown e.g. for the (2,2) CTR in Fig. 1 (right).

For pyrite in dry conditions we obtained the integrated and corrected intensities, together with a preliminary fit, calculated from the bulk structure model. Fig. 2 shows the experimental and the calculated structure factors of the (1,2) and the (0,2) CTR. The general agreement of the fit with the experimental data indicates, that the surface structure of the pyrite (100) surface in dry ambient conditions resembles the bulk structure, but with relaxed surface layers. The surface is not reconstructed, which was also confirmed by H- and K-scans for every part of the experiment.

The further analysis of the data set for dry conditions is in progress. It will soon be followed by the integration and correction of the raw data of the hydrated surface and the glycine-pyrite-interface and the analysis of this two data sets.

Experimental details:

The experiment was carried out at the surface diffraction beamline ID03. The sample was a cube-shaped natural single crystal of pyrite with flat (100)-faces the size of about 5 x 5 mm. The crystal was mounted in air in an electrochemical cell attached to the diffractometer in vertical scattering geometry. In dry ambient conditions the specular reflectivity (Fig. 1 left), as well as L-scans and rocking scans of a set of non-specular CTR were measured (Fig. 1 right and Fig. 2). Then a drop of deionized water was applied to the surface. The cell was closed with mylar foil (thickness 6 μ m) and the water drop on the surface was reduced to a film by generating a small depression in the cell using a syringe. The measurement of the specular and nonspecular intensity was repeated. Additionally H- and K-scans were performed to obtain information about reconstruction/superstructure ordering on the surface. In the third part of the experiment the surface was dried with a N₂ gas stream, then the saturated glycine aqueous solution was applied. The cell was closed with mylar foil again and the drop was spread out to a film on the pyrite surface. A data set of specular and nonspecular CTR, as well as H- and K-scans were measured.

The measurements were performed in vertical scattering geometry. The incoming beam was vertically focused to about 0.2 mm and horizontally defined by slits to 0.8 mm at the sample position. The incidence angle between the horizontally mounted sample surface and the X-ray beam was selected to 0.5°. The scattered beam was defined by a pair of slits in front of the detector set to 2 mm x 2 mm along the surface normal (vertical) and surface plane (horizontal), respectively.

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. Two CTRs of the data set measured in dry conditions are shown in Fig. 2. The line marks the structure factors calculated from the bulk structure of pyrite (space group Pa $\bar{3}$, $a = 5.417 \text{ \AA}$, $Z = 4$). The general agreement of the experimental and calculated data indicates an unreconstructed, bulk-determined surface structure in dry ambient conditions. This result is consistent with the observations made in UHV-experiments on the clean (100) surface [1-4]. Further refinement of the surface model will give information about the relaxation of the surface atomic layers. At ambient conditions mineral surfaces are partially covered with water molecules, but an ordered hydration layer forms with increasing humidity, only [5,6]. Nevertheless we will also check the model for an ordered hydration layer on the surface.

According to the differences of the specular reflectivity and the L-scans of the dry conditions surface compared to the water-pyrite- and the glycine-pyrite-interface and according to molecular dynamics simulations [7,8], we expect to find for the solution-covered surface an ordered monolayer of adsorbed water molecules. Presumably adsorption sites for the water molecules are the surface Fe²⁺ ions. The model will be checked for a second ordered monolayer of water connected to the surface S-ions, also.

From the comparison of the L-scans of the hydrated pyrite surface and the glycine-pyrite-interface we assume that the adsorption of the glycine molecules competes with the adsorption of water molecules in the first adsorbate layer. The further analysis of the rocking scan intensities of the third experimental data set will yield information about the ordering and orientation of the glycine molecules on the pyrite surface. During the refinement of the interface model surface vacancies will have to be considered.

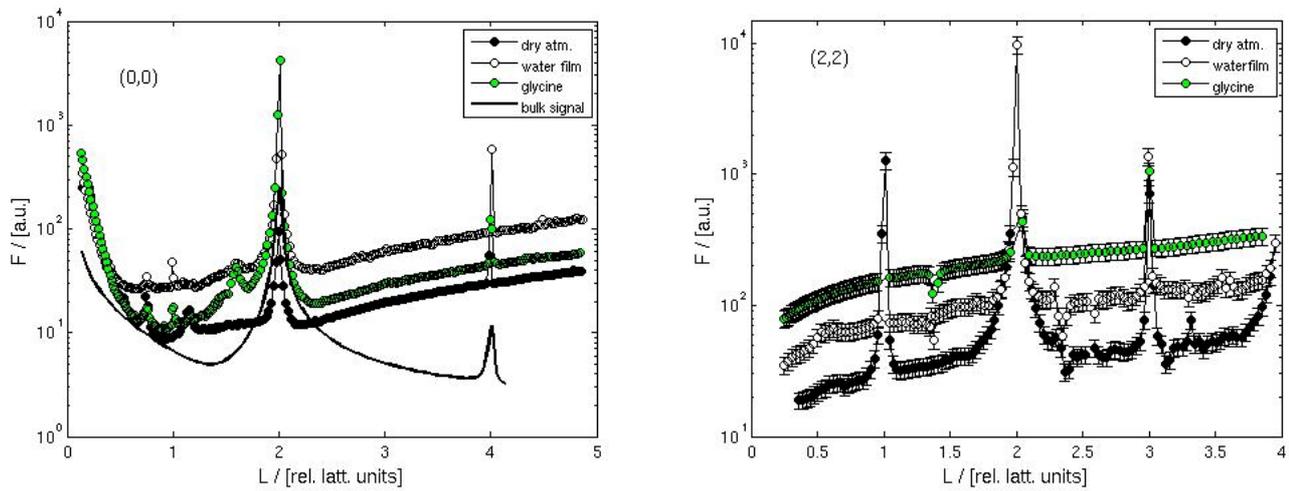


Fig. 1: (left) Specular reflectivity of the pyrite surface in dry ambient conditions (black circles), the hydrated surface (white circles) and the pyrite-glycine interface (green circles), respectively. The black line shows the specular reflectivity calculated from the pyrite bulk structure. (right) L-scans of the (2,2) CTR for the three parts of the experiment: dry conditions (black circles), completely hydrated surface (white circles) and with aqueous glycine solution (green circles).

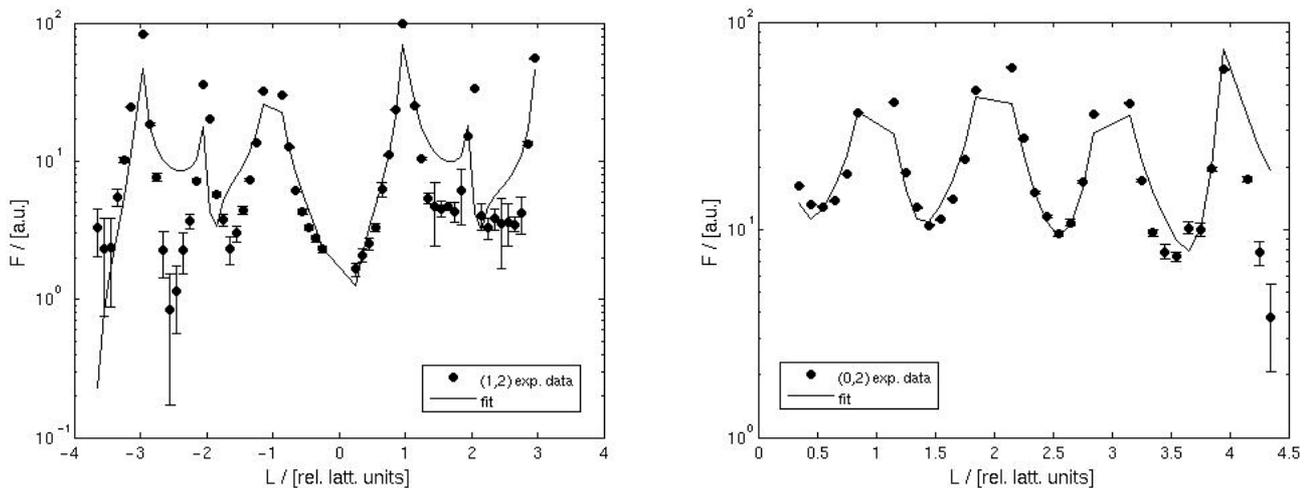


Fig. 2: Integrated rocking scan intensities of the (1,2) and (0,2) CTRs from the dataset measured with the pyrite surface in dry conditions. The fit (line) is calculated from the bulk structure model of pyrite.

References:

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