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# The structure of reconstructed chalcopyrite surfaces

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## ABSTRACT

Chalcopyrite (CuFeS<sub>2</sub>) surfaces are of major interest for copper exploitation in aqueous solution, called leaching. Since leaching is a surface process knowledge of the surface structure, bonding pattern and oxidation states is important for improving the efficiency. At present such information is not available from experimental studies. Therefore a detailed computational study of chalcopyrite surfaces is performed. The structures of low-index stoichiometric chalcopyrite surfaces {*hkl*} *h*, *k*,  $l \in \{0, 1, 2\}$  have been studied with density functional theory (DFT) and global optimization strategies. We have applied ab initio molecular dynamics (MD) in combination with simulated annealing (SA) in order to explore possible reconstructions via a minima hopping (MH) algorithm. In almost all cases reconstruction involving substantial rearrangement has occurred accompanied by reduction of the surface energy. The analysis of the change in the coordination sphere and migration during reconstruction reveals that S-S dimers are formed on the surface. Further it was observed that metal atoms near the surface move toward the bulk forming metal alloys passivated by sulfur. The obtained surface energies of reconstructed surfaces are in the range of 0.53–0.95 J/m<sup>2</sup>.

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### 1. Introduction

Chalcopyrite is an ore, which is widely used for copper production [1]. Extraction processes like metallurgic melting or electrolytic refining are extremely energy consuming and produce masses of noxious substances [1]. Alternatively, copper can be extracted using the hydrometallurgical path. The leaching process of copper ores has been therefore studied to refine and improve the extraction rate. An overview is given in the review articles [2-4] and the references therein. Experimentally chalcopyrite ores were characterized using X-ray photo electron spectroscopy (XPS) [5-8] or scanning photo electron microscopy (SPEM) [9,10] measurements. From XPS measurements  $S^{2-},\,S^{2-}_{2}$  and  $S_n^{2-}$  sulfur species are suggested to exist on the surfaces of chalcopyrite micro-crystals. Numerous theoretical investigations have been performed for structural [11-17] properties of chalcopyrite surfaces. However, previous simulations were restricted to small model systems or were not "complete" in terms of possible surface planes. None of the previous investigations considered surface reconstruction. The surface structures were optimized starting from usual bulk terminated structures. Considering a higher degree of structural flexibility by employing surface super-cell models, global optimization strategies and "completeness" in terms of possible surface indices, this work will allow to predict sulfur-sulfur bond formation and to quantitatively order reconproximately predict the natural shape of chalcopyrite micro-crystals. This article is structured as follows. First computational methods for bulk and surface calculations, as well as the global optimization procedure used in this work are described. In the results section structural properties, neighbour analysis and energetic properties are discussed. For structural properties atom migration, as well as sulfur-sulfur and metal-metal bond formation are investigated, showing that  $S_2$  species are formed during both, optimization and reconstruction, but to a different degree. In the section energetic properties, the stability order of the surfaces is given and the changes of surface energies upon global optimization are discussed.

structed chalcopyrite surfaces by their surface energy and hence to ap-

## 2. Computational methods

## 2.1. Bulk and surface calculations

As a starting point, the bulk structure of the chalcopyrite was calculated using DFT methods as implemented in the GPAW [18,19] package and compared to experimental results. Various standard DFT functionals, namely AM05 [20,21], PBE [22,23], PBEsol [24], and revPBE [25] were evaluated in terms of their accuracy of the calculated lattice parameters (see Table 1). A converged local basis set of TZP [26] quality was used for bulk and surface calculations. The density of the Monkhorst–Pack grid was converged independently for every surface

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#### Table 1

Functional dependent chalcopyrite lattice *a*, *c* and position parameters *u* in Å compared with neutron diffraction data from reference [27].

Functional	AM05	PBE	PBE-Sol	revPBE	Exp.
а	5.04	5.12	5.04	5.33	5.29
с	9.98	10.11	9.96	10.52	10.47
и	0.225	0.224	0.225	0.222	0.247

system. An energy convergence of  $10^{-5}$  eV/atom was achieved with these settings. Since no weakly bound molecules were absorbed and to avoid over-binding in the bulk, a dispersion correction was omitted. The experimental structure [27] has been determined at 4.2 K from neutron diffraction which allows comparison with theory. The space group of chalcopyrite is I42d. The measured lattice parameters are a=5.29 Å, c = 10.47 Å and the parameter u = 0.247 for sulfur at Wyckoff position 8d = (u, 1/4, 1/8). The best agreement with the experimental lattice parameters was obtained with the revPBE functional, a = 5.33 Å and c =10.52 Å, corresponding to relative deviations of less than 1%. The *u* parameter is underestimated compared to experimental data and almost the same with all tested functionals. Therefore revPBE was chosen for subsequent surface studies.

For some of the surfaces it was not possible to construct bulkterminated slab models that are at the same time stoichiometric and symmetric. To minimize the dipole moment along the surface normal vector for the non-symmetric surfaces (001), (010), (011) and (112) defective surface models were constructed in the following way: a translationally equivalent layer of sulfur atoms was added to the lower part of the slab and afterwards sulfur atoms were removed symmetrically on both sides of the slab until the correct stoichiometry was obtained, resulting in considerable reduction of the surface dipole moment. This strategy leads to a stable SCF-procedure and in addition a more stable surface model was created according to Taskers work on surface stability [28]. Figs. (S1-S4) for the strategy described above can be found in the supplementary material in Section 1. To compensate for the small surface dipole moment, a dipole correction [29] has been applied, in order to avoid artificial charge transfer between the upper and lower side of the slab. A vacuum of 15 Å ensures that interaction between the lower and the upper part of the model is negligible. For all surfaces, the convergence of the surface energy has been tested with respect to the number of atomic layers. Errors in the surface energies are smaller than  $0.02 \, \text{J/m}^2$ .

## 2.2. Global optimization

Reconstruction of surfaces involves considerable atom movement and can induce the formation of surface defects or facets. These rearrangements are usually connected with large activation barriers and require global optimization techniques such as molecular dynamics (MD) in combination with simulated annealing (SA) [30-32]. In the following we distinguish between relaxed structures obtained with standard gradient-based optimization techniques from bulk-terminated starting structures and reconstructed structures obtained by global optimization. For global optimization of the surfaces the minima hopping [33] (MH) algorithm, as implemented in the atomic simulation environment [34] (ASE) program package, was used. Within this global optimizer a series of NVE-ensemble molecular dynamic simulations combined with local optimization steps were performed. The method dynamically adjusts the MD temperature (similar to SA) and the so-called energy acceptance parameter, trying to find new minimum structures in a systematic way. For the optimization, a limited memory version of the Broyden-Fletcher-Goldfarb-Shanno (LBFGS) [35] algorithm was used. Starting at an MD temperature of 1000 K, the time step was set to 2 fs for the MH runs. It will be shown in the results section that this kind of global optimizer is a reasonable choice, because the bulk section of the slab model is only affected marginally at the selected MD temperatures.

Reconstruction as well as relaxation has been studied for  $2 \times 2$  surface super cells (SSC), ranging from 96 to 352 atoms per surface model. In order to reduce computational effort, the MH steps were limited to 50, that is 50 molecular dynamics simulations and 50 optimizations per surface were performed by the MH algorithm.

## 2.3. Wulff construction

Crystal shapes are created with the VESTA [36] program package. It allows to build crystal shapes giving the distances of surface planes from the crystals origin. Since according to Wullf's theorem [37] the distances are directly proportional to surface free energies, the surface energies were inserted instead of distances.

## 3. Results and discussion

In the following the structural and energetic properties of the selected chalcopyrite (001), (010), (011), (012), (110), (111), (112), (120), (121), (122) and (221) surfaces will be discussed. This set is complete within *h*, *k*,  $l \in \{0, 1, 2\}$  since all other planes are symmetry equivalent. Surfaces with *h*, *k*, *l* larger than two were not considered since they have never been mentioned in any paper in the literature known to us. For structural properties, we focus first on the statistical analysis of the structures, summarized for all the surfaces in Figs. 1–4 and then local structures formed during relaxation. The reconstruction will be discussed exemplarily (see Figs. 5 and 6). For energetic properties, the surface energies and changes upon reconstruction will be discussed and connected to structural changes. Eventually we will represent the shape of a particle based on reconstructed surface energies by a Wulff construction.

### 3.1. Structural properties

In general, by relaxing the surface geometries it was found that there is already a substantial reorganization of the surface atoms.

In Fig. 1 the displacement density along the surface normal vector in z-direction is plotted. The reference geometry is the bulk-terminated surface structure obtained from the revPBE bulk structure. The absolute displacement, shown in Fig. 1, of an atom at position  $\vec{r}$  is given by  $|\vec{r}_z - \vec{r}_{z,\text{bulk}}|$ . Positive numbers denote a displacement in direction to the vacuum region, while negative numbers denote a displacement toward the bulk. The graph is summing up all surfaces under investigation. Relaxing the system an overall small shift of the displacement density to negative displacements can be seen from Fig. 1 which corresponds to a compression of the surface. This is a common effect arising from the reduced coordination of surface atoms and the tendency to shorten the bond distances to inner atoms of the bulk. The graphs for relaxation and reconstruction show similarities. The broad maxima for Fe (red) at -1.4 Å and Cu (green) at -0.8 Å show that metal atoms are migrating into the bulk as reported in Ref. [12] for (001), (100), (111), (112), (101), and (110) chalcopyrite surfaces. In general this effect is more pronounced for iron atoms than for copper atoms. Sulfur atoms (blue) are less mobile than metal atoms during relaxation and reconstruction. In the case of reconstruction the vertical displacement densities are broadened and also positive displacements in direction to the vacuum occur more frequently. Comparing the upper and lower graph of Fig. 1 it can be observed that copper mobility is increased during reconstruction.

In Figs. 2 and 3 the neighbor analysis of all surfaces for relaxed and reconstructed surfaces are shown, respectively. In the bulk, the mean nearest neighbor (NN) distance is 2.3 Å. For increasing coordination numbers (CNs) the mean distance to the central atom will increase too. Hence, to generate Figs. 2 and 3 the first neighbor distances from the bulk were increased by 10%. Atoms within this distance to the central atom are considered as NN. In general the neighbor analysis shows, that the favoured CNs for sulfur and metal atoms are four as in chalcopyrite bulk, respectively, for both relaxation and reconstruction. In

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