Electronic Supplementary Information

Layered structure of the near-surface region of oxidized chalcopyrite (CuFeS₂): hard X-ray photoelectron spctroscopy, X-ray absorption spectroscopy and DFT+*U* studies

Yuri Mikhlin^{*},^a Vladimir Nasluzov,^a Alexander Romanchenko,^a Yevgeny Tomashevich,^a Alexey Shor^a and Roberto Félix^b

^a Institute of Chemistry and Chemical Technology of the Siberian Branch of the Russian Academy of sciences, Akademgorodok, 50/24, Krasnoyarsk, 660036, Russia

^b Renewable Energy, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Lise-Meitner-Campus, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

* corresponding author, e-mail: yumikh@icct.ru

Table S1. Characteristics of defects formed in bulk CuFeS₂ by removal of Fe atoms from a $Cu_{16}Fe_{16}S_{32}$ unit cell as calculated by DFT + *U* with *U* parameters for Fe 3d states of 1, 3 or 4 eV, which are marked by superscripts U1, U3, and U4. Low coordinated ions formed (e.g., $4S^{3c}$ means four S atoms coordinated with three neighbors each), coordination sphere of S species (bond lengths in pm), forbidden gap (E_g, eV), and magnetic moments of Fe ions (marked with superscript M, μ B) are given for each defect structure.

C_v^3 $E_g < 0.01$	^{U1} S ₂ [215; 2Fe ^{4c} (228)	$E_v^{3} E_g < 0.01$	$^{U1}S_2[223; 3Fe^{4c}(231) Cu^{4c}(232)]$
	$2Cu^{4c}(230)$]		^M 8×3.2 [↑] ; 7×3.2 [↓]
	^M 8×3.2 [↑] ; 8×3.3 [↓]		^{U3} S ₃ [214; Cu ^{4c} (231) 3Fe ^{4c} (236)]
	^{U3} S ₂ [212; 2Cu ^{4c} (228)		^M 8×3.5 [↑] ; 7×3.5 [↓]
4.2	$2Fe^{4c}(237)$]	V _{Cu} -Cu _{Fe}	^{U4} S ₃ [215; Cu ^{4c} (231) 3Fe ^{4c} (238)]
	$^{M}8\times3.5^{\uparrow}; 7\times3.6^{\downarrow}$	$Cu^{3c}Fe^{3c}$	^M 8×3.6 [↑] ; 7×3.6 [↓]
$V_{Fe} 2Cu^{3}$	U4 S ₂ [210; 2Cu ^{4c} (228)	$S_2 2S^{3c}$	
$S_2 2S^{3c}$	$2Fe^{4c}(241)$]		
	^M 8×3.6 [↑] ; 7×3.7 [↓]		
D_v^{3} ^{U1} $E_g = 0.07$	^{U1} S ₃ [210,217; Cu ^{3c} (222)	F_{vv}^{5} E _g < 0.03	^{U1} S ₂ [228; 2Fe ^{4c} (219)
$^{\rm U3}$ E _g =0.25	2Fe ^{4c} (226) 3Cu ^{4c} (232)		$2Cu^{4c}(232)$]
$^{\rm U4}{\rm E_g}=0.18$	$S^{3c}(278)]$		^M 8×3.1 [↑] ; 6x3.3 [↓]
.1 •	$^{M}8\times3.1^{\downarrow}$; 7×3.2 [↑]		^{U3} S ₂ [210; 2Cu ^{4c} (229)
	U3 S ₃ [2×212; Cu ^{3c} (222)		$2Fe^{4c}(238)$]
	$3Cu^{4c}(232) 2Fe^{4c}(233)$]		^M 8×3.5 [↑] ; 6×3.6 [↓]
	$^{M}8\times3.5^{\downarrow}; 7\times3.6^{\uparrow}$	$2V^{Fe} 2Cu^{3c}$	$^{\rm U4}$ S ₂ [210; 2Cu ^{4c} (229)
TTI	$^{\rm U4}S_3[2\times211; {\rm Cu}^{\rm 3c}(222)]$	$S_2 6S^{3c}$	2Fe ^{4c} (242)]
$V_{Fe} 2Cu^{3c} Fe^{3c}$	$3Cu^{4c}(232) 2Fe^{4c}(236)$]		^M 8×3.6 [↑] ; 6×3.7 [↓]
$\mathbf{S_3} \mathbf{S}^{3c}$	$^{M}8\times3.6^{\downarrow}; 7\times3.7^{\uparrow}$		



The C_v^{3} defect structure comprises, in addition to sulfide ions S^{3c} neighboring a V_{Fe} center, a disulfide group S_2 and low-coordinated Cu^{3c} ions. To obtain C_v^{3} from the B_v^{3} structure, two of four S^{3c} atoms surrounding the V_{Fe} approach each other in such a manner that two Cu-S bonds are broken to create Cu^{3c} centers and a S-S bond. The S_2 group is coordinated with two Cu^{4c} ions (bond distances of 228 - 230 pm) and two Fe^{4c} ions (228 - 241 pm); the S-S bond length is calculated to be of 210 - 215 pm (Table S1). The energy of this structure strongly depends on the U parameter applied, being generally higher than that of B_v^{3} and especially of A_v^{3} (Fig. S1). If both S-Cu and S-Fe bonds are cleaved to form a S_2 group, an equilibrium (optimized) structure containing S_2 group, Fe^{3c} , Cu^{3c} and two S^{3c} atoms is lesser stable than B_v^{3} (by 0.46 eV with U4 corrections). It was not possible to obtain any equilibrium structure with S_2 group and two Fe^{3c} centers without additional changes in the location of Fe and Cu cations. When positions of Cu^{3c} and a neighboring Fe^{4c} atom were exchanged in the C_v^{3} structure, the optimized structure with two Fe^{3c} centers and no Cu^{3c} centers became by about 1 eV less stable than the C_v^{3} .

The E_v^{3} structure involves a Cu_{Fe} - V_{Cu} defect configuration, low coordinated ions Fe^{3c}, Cu^{3c}, S^{3c}, and a S₂ group near the V_{Cu}, with the calculated S-S bond lengths of 214 - 223 pm, which are by 2 nm - 8 pm longer that for S₂ near the V_{Fe} in the C_v^{3} -defect, and indicate weaker bonding. The coordination sphere of the S₂ group is filled with Cu^{4c} center at a distance of 231 - 232 pm from the nearest S atoms, and with three Fe^{4c} centers at the distance of 231 - 237 pm. Formation of a S₂ group near both V_{Fe} and V_{Cu} results also in the appearance of Cu^{3c} ions. Both Cu^{3c} ion and Fe^{3c} ion, instead of two Cu^{3c} ions in the C_v^{3} defect, arise in the E_v^{3} -defect, which is calculated to be 0.3 - 0.4 eV less stable. The difference in stability and longer S-S bonding may be rationalized by divergence of the Madelung potential, which is less negative at the V_{Cu} position than at V_{Fe}, making oxidation of S anions to S₂ species less favorable.

The \mathbf{D}_v^{3} structure that incorporates trisulfide anion S₃ along with V_{Fe} and Cu^{3c}, Fe^{3c} and S^{3c} ions can be rearranged from a \mathbf{B}_v^{3} -defect when one of S^{3c} atoms fills the V_{Fe} position. The bonds of this S atom to surrounding cations are broken to expose one Fe^{3c} and two Cu^{3c} centers. The relocated S atom is engaged in two bonds of 210 - 217 pm long with two of three neighboring S^{3c} atoms (Table S1). Coordination sphere of the S₃ moiety contains Cu^{3c} at a distance of 222 pm, three Cu^{4c} and two Fe^{4c} ions at distances of 226 - 236 pm. The \mathbf{D}_v^{3} structure with S₃ group is calculated to be less stable than the \mathbf{C}_v^{3} (with S₂ group) by 0.24 eV and 0.04 eV with U1 and U3 corrections, respectively, and to become more stable with U4 corrections (Fig. S1). The equilibrium structures of a defect structure containing Cu_{Fe}-V_{Cu} defect pairs and S₃ group (not

presented in Tables and Figures) were also determined, which are found with U4 and U3 corrections to be 0.2 - 0.6 eV less stable than the related E_v^3 structure with a S₂ group and a Cu_{Fe}-V_{Cu} pair.

Therefore, the C_v^{3} and D_v^{3} defect structures incorporating S₂ and S₃ groups neighboring a V_{Fe} are less stable than the B_v^{3} defect by 0.75 eV and 1.0 eV, respectively, in calculations with U1 corrections. Upon increasing the U parameter, the formation energy of the defects with S₂ and S₃ species relative to that of B_v^{3} decreases, for example, to 0.31 and 0.35 eV, respectively, for U3-corrections, and the energies are within 0.12 eV with U4-corrections, suggesting considerably higher relative stability. The configurations with Cu_{Fe}-V_{Cu} pairs and a S₂ group, and a V_{Cu} and a S₃ group are calculated to be the least stable.

The $\mathbf{F_{vv}}^5$ structure is obtained from $\mathbf{C_v}^3$ with one V_{Fe} by removal of a Fe atom neighboring a S₂ group to form eight Fe centers with spin up electron density and six Fe atoms with spin down density. The minimal S-S distance in the $\mathbf{F_{vv}}^5$ becomes as long as 228 pm in calculations with U1 corrections (i. e., by 13 pm longer than in the $\mathbf{C_v}^3$) and is equal to 210 pm (similar to that in $\mathbf{C_v}^3$) with U3 and U4 corrections; coordination of the S₂ moiety is analogous (Table S1). The formation of a second V_{Fe} center by going from $\mathbf{C_v}^3$ to $\mathbf{F_{vv}}^5$ is only 0.02 - 0.05 eV less endothermic than that of the first V_{Fe} (in $\mathbf{B_v}^3$), and so the $\mathbf{F_{vv}}^5$ structure is 0.2 - 0.9 eV less stable than $\mathbf{D_{vv}}^5$.

The $\mathbf{E_{vv}}^{1}$ structure formed from the $\mathbf{E_v}^{3}$ configuration with a Cu_{Fe}-V_{Cu} defect pair by slightly exothermically adding a second Cu_{Fe}-V_{Cu} pair comprises Fe^{3c} and S^{3c} ions, and a S₂ group with the S-S bond distance of 212 pm close to one of two V_{Cu} centers. The coordination sphere of this S₂ group is the same as in the $\mathbf{E_v}^{3}$ defect, however, the $\mathbf{E_{vv}}^{1}$ arrangement does not have Cu^{3c} ions (Table S1). Formation of a S₂ group in the vicinity of V_{Cu} site by going from an $\mathbf{A_{vv}}^{1}$ to an $\mathbf{E_{vv}}^{1}$ arrangement is found to be more than 1.2 eV endothermic and very unfavorable.



Fig. S1. Formation energies (eV) of bulk defects in $CuFeS_2$ produced by removal of one, two and three Fe ions from $Cu_{16}Fe_{16}S_{32}$ translation cell calculated for arbitrary reaction (2) using DFT+*U* with U = 1 eV, 3 or 4 eV (red, blue and black bars, respectively).