

Supporting Information for

**DFT+U and Low-Temperature XPS Studies of Fe-Depleted Chalcopyrite ( $\text{CuFeS}_2$ ) Surfaces:  
A Focus on Polysulfide Species**

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**Table S1.** Formation scheme and selected characteristics of the defects formed via deletion of single Fe atom of  $\text{Cu}_{16}\text{Fe}_{16}\text{S}_{32}$  unit cell of the slabs modeling  $\text{CuFeS}_2$  (012) and (110) surfaces (see Fig. 2): formation energy  $E^f$  (eV), 2S+1 spin state m, low coordinated metal ions formed instead of four-coordinated metal ions (+M<sup>LC</sup>), S-S bond lengths r<sup>S-S</sup> (pm), number of metal atoms in the first coordination sphere of the S<sub>3</sub> groups N<sup>M</sup> and the interatomic distances r<sup>S-M</sup> (pm).

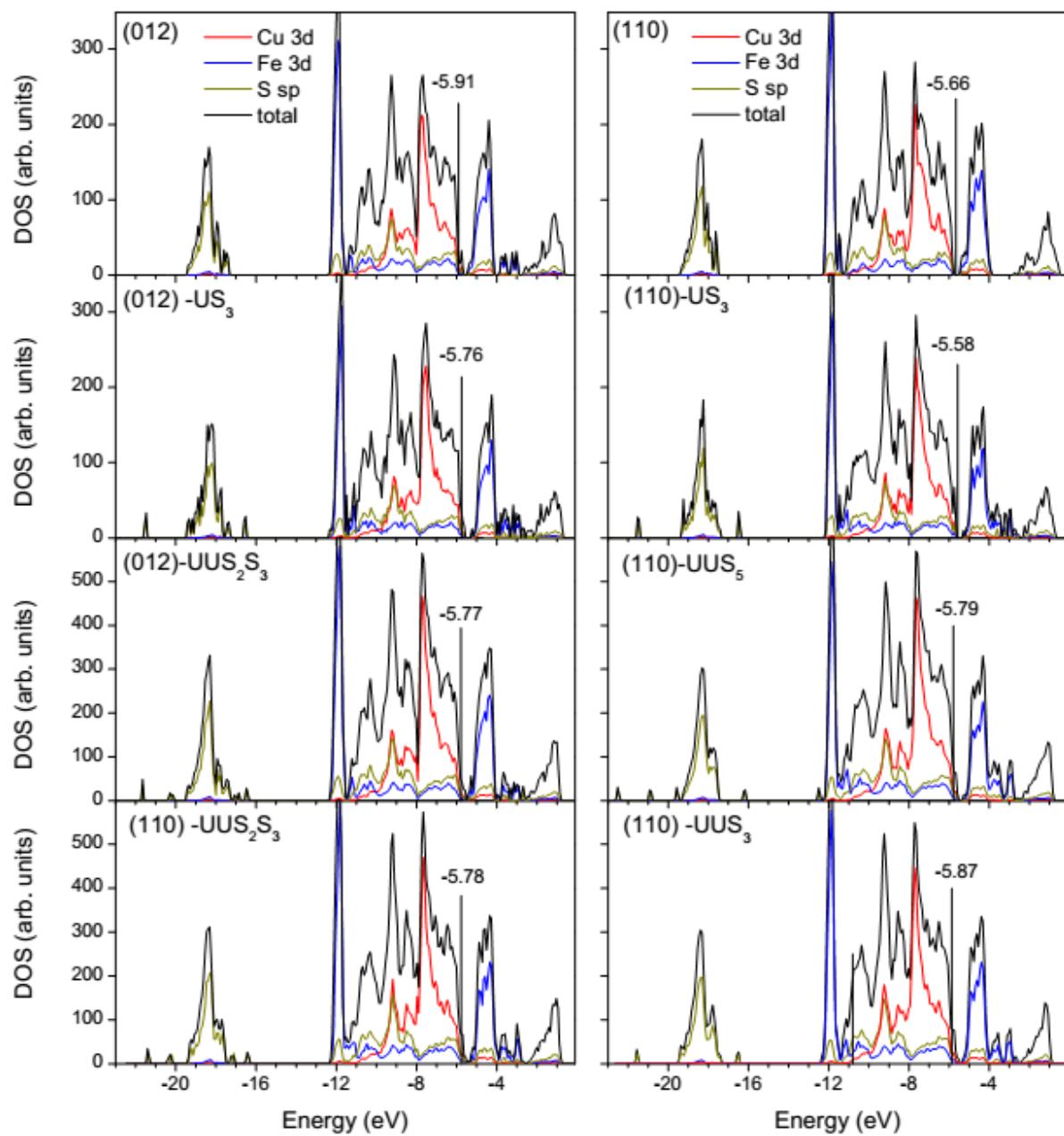
Defect	Formation scheme	m	+M <sup>LC</sup>	S <sub>3</sub> [r <sup>S-S</sup> ; N <sup>M</sup> (r <sup>S-M</sup> )]
<b>I-U(012,S<sub>3</sub>)</b>	US <sup>U</sup>	3	Cu <sup>3c</sup>	<b>S<sub>3</sub>[208,212;3Cu(221-232),2Fe(236,240)]</b>
<b>2-U(110,S<sub>3</sub>)</b>	US <sup>U</sup>	1	Cu <sup>3c</sup>	<b>S<sub>3</sub>[208,210;3Cu(214-237),2Fe(2x239)]</b>
<b>3-U(110,Cu<sup>I</sup>S<sub>3</sub>)</b>	UCu <sup>I</sup> S <sup>Cu</sup>	3	Fe <sup>3c</sup>	<b>S<sub>3</sub>[209,210;3Cu(213-241),2Fe(238,243)]</b>
<b>4-U(012,Cu<sup>I</sup>S<sub>3</sub>)</b>	UCu <sup>I</sup> S <sup>Cu</sup>	1	Fe <sup>3c</sup>	<b>S<sub>3</sub>[210,214;2Cu(226,231),3Fe(234-240)]</b>
<b>5 U(110,S<sub>2</sub>)</b>	US <sup>I</sup>	3		<b>S<sub>2</sub>[216;3Cu(222-233),2Fe(240,246)]</b>
<b>6-U(110,Cu<sup>Fe</sup>)</b>	UCu <sup>U</sup>	3		—
<b>7-U(012,Cu<sup>Fe</sup>)</b>	UCu <sup>U</sup>	3		—
<b>8-U(110)</b>	U	3		—
<b>9-U(012)</b>	U	3		—
<b>10-U(012,S<sub>2</sub>)</b>	US <sup>I</sup>	3		<b>S<sub>2</sub>[214;2Cu(222,231),2Fe(240,243)]</b>

**Table S2.** Formation scheme and selected characteristics of the defects formed on deletion of two Fe atoms of top metal layers of CuFeS<sub>2</sub>(012) surface (see Fig. 3): 2S+1 spin state (m), low coordinated metal ions formed instead of four-coordinated metal ions (+M<sup>LC</sup>), S-S bond lengths (r<sup>S-S</sup>, pm), number of metal atoms in first coordination sphere of the S<sub>n</sub> groups (N<sup>M</sup>) and distances to these atoms (r<sup>S-M</sup>, pm).

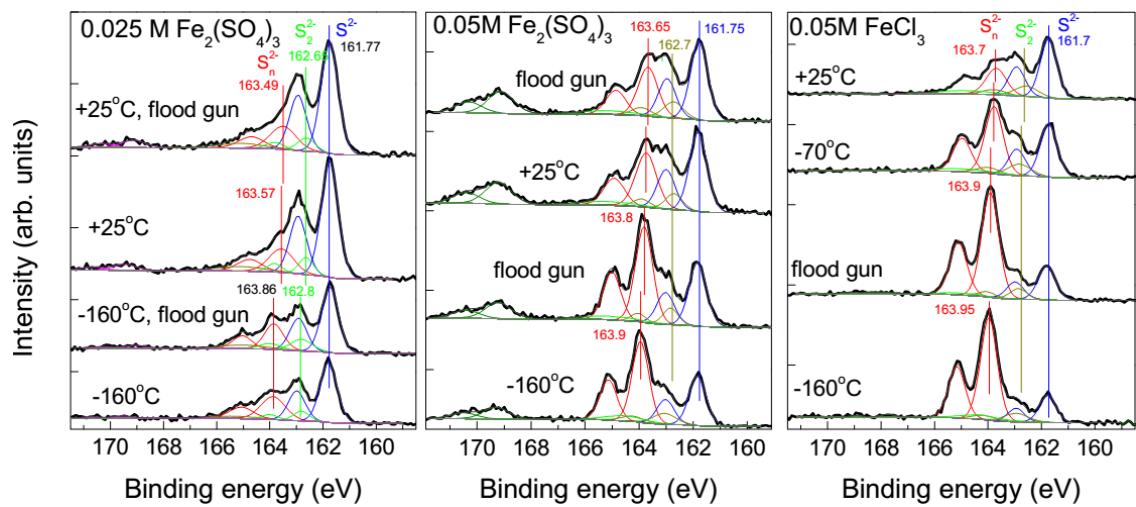
Defect	Formation scheme	m	+M <sup>LC</sup>	S <sub>n</sub> [r <sup>S-S</sup> ; N <sup>M</sup> (r <sup>S-M</sup> )]
<b>13-UU(2a,S<sub>2</sub>S<sub>3</sub>)</b>	US <sup>I</sup> ,US <sup>U</sup>	1	Cu <sup>3c</sup>	<i>S<sub>2</sub>[215;2Cu(224,230),2Fe(2x237)] S<sub>3</sub>[202,220;3Cu(229-237),1Fe(241)]</i>
<b>15-UU(1a,S<sub>2</sub>S<sub>3</sub>)</b>	US <sup>I</sup> ,US <sup>U</sup>	1	Cu <sup>3c</sup>	<i>S<sub>2</sub>[220;3Cu(226-232),2Fe(238,244)] S<sub>3</sub>[203,213;4Cu(227-234),1Fe(242)]</i>
<b>17-</b>	UCu <sup>I</sup> S <sup>I</sup> ,US <sup>U</sup>	1	—	<i>S<sub>2</sub>[216;3Cu(224-242),2Fe(241,245)] S<sub>3</sub>[209,212;5Cu(225-253),1Fe(238)]</i>
<b>19-UU(2a,S<sub>5</sub>)</b>	US <sup>U</sup> ,US <sup>U</sup>	1	2Cu <sup>3c</sup> Fe <sup>3</sup>	<i>S<sub>5</sub>[2x205,2x214;4Cu(230-237),2Fe(236,239)]</i>
<b>21-UU(1a,Cu<sup>I</sup>2S<sub>3</sub>)</b>	US <sup>U</sup> ,UCu <sup>I</sup> S <sup>Cu</sup>	1	Cu <sup>3c</sup> Fe <sup>3c</sup>	<i>S<sub>3</sub>[206,213;4Cu(226-233),Fe(240)] S<sub>3</sub>[2x215;3Cu(222-234),3Fe(235-239)]</i>
<b>23-UU(1a,Cu<sup>I</sup>S<sub>3</sub>)</b>	US <sup>U</sup> ,UCu <sup>U</sup>	1	Cu <sup>3c</sup>	<i>S<sub>3</sub>[204,215;4Cu(221-231),1Fe(237)]</i>
<b>25-UU(2a,Cu<sup>I</sup>S<sub>5</sub>)</b>	UCu <sup>I</sup> US <sup>U</sup>	1	Cu <sup>3c</sup> 2Fe <sup>3</sup>	<i>S<sub>5</sub>[2x206,2x216;3Cu(230-235),3Fe(237-244)]</i>
<b>26-UU(2a,Cu<sup>I</sup>S<sub>5</sub>)</b>	US <sup>U</sup> ,UCu <sup>I</sup> S <sup>Cu</sup>	1	Cu <sup>3c</sup> Fe <sup>3c</sup>	<i>S<sub>5</sub>[198,211,216,224;3Cu(228-235),3Fe(238-255)]</i>

**Table S3.** Formation scheme and selected characteristics of the defects formed upon deletion of two Fe atoms of the top CuFeS<sub>2</sub>(110) surface layers: 2S+1 spin state (m), low coordinated metal ions formed instead of four-coordinated metal ions (+M<sup>LC</sup>), S-S bond lengths (r<sup>S-S</sup>, pm), number of metal atoms in first coordination sphere of the S<sub>n</sub> groups (N<sup>M</sup>) and distances to these atoms (r<sup>S-M</sup>, pm).

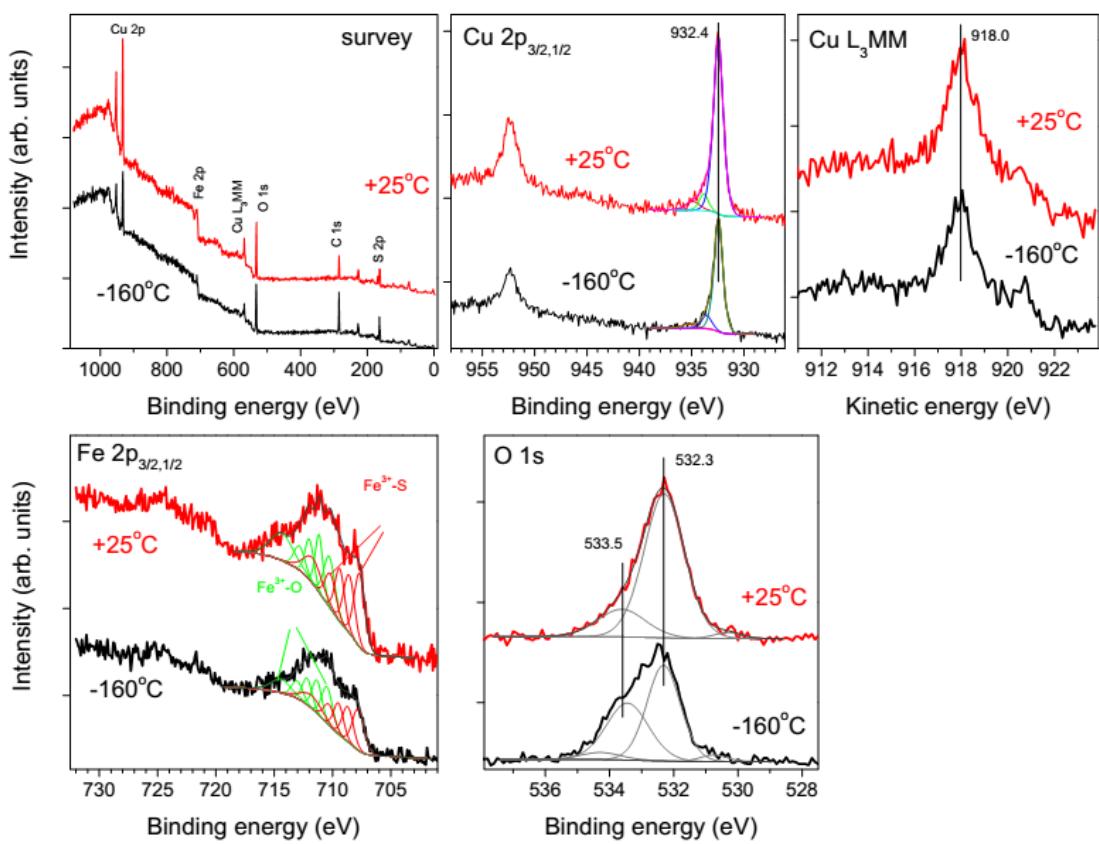
Defect	Formation scheme	m	+M <sup>LC</sup>	S <sub>n</sub> [r <sup>S-S</sup> ; N <sup>M</sup> (r <sup>S-M</sup> )]
<b>I1-UU(2a,Cu<sup>Fe</sup>S<sub>3</sub>)</b>	UCu <sup>U</sup> ,US <sup>U</sup>	1	Cu <sup>3c</sup>	S <sub>3</sub> [207,209;3Cu(224-232),2Fe(237,242)]
<b>I2-</b>	UCu <sup>U</sup> S <sup>Cu</sup> ,US <sup>U</sup>	3	Cu <sup>3c</sup>	S <sub>2</sub> [218;2Cu(226,236),3Fe(237-259)] S <sub>3</sub> [208,211;3Cu(225-
<b>I4-UU(2a,Cu<sup>I</sup>S<sub>5</sub>)</b>	UCu <sup>I</sup> S <sup>Cu</sup> ,US <sup>U</sup>	1	2Cu <sup>3c</sup> Fe <sup>3</sup>	S <sub>5</sub> [204,208,2x216;3Cu(230-240),3Fe(235-239)]
<b>I6-UU(2a,2S<sub>3</sub>)</b>	US <sup>U</sup> ,US <sup>U</sup>	5	Fe <sup>3c</sup>	S <sub>3</sub> [208,217;4Cu(222-234),1Fe(232)] S <sub>3</sub> [205,211;4Cu(224-231),1Fe(233)]
<b>I8-UU(1a,Cu<sup>Fe</sup>2S<sub>2</sub>)</b>	US <sup>U</sup> ,UCu <sup>U</sup> S <sup>Cu</sup>	3	—	S <sub>2</sub> [214;2Cu(238,249),4Fe(238-261)] S <sub>2</sub> [209;3Cu(233,249),2Fe(246,253)]
<b>20-UU(2a,Cu<sup>I</sup>S<sub>2</sub>S<sub>3</sub>)</b>	US <sup>U</sup> ,UCu <sup>I</sup> S <sup>Cu</sup>	3	2Cu <sup>3c</sup>	S <sub>2</sub> [208;3Cu(228-231),Fe(234)] S <sub>3</sub> [201,215;1Cu(231),3Fe(233-245)]
<b>22-UU(2a,S<sub>2</sub>S<sub>3</sub>)</b>	US <sup>U</sup> ,US <sup>U</sup>	3	Fe <sup>3c</sup>	S <sub>2</sub> [215;3Cu(224-236),2Fe(236,244)] S <sub>3</sub> [202,210;4Cu(226-234),1Fe(239)]
<b>24-UD(1a,Cu<sup>Fe</sup>S<sub>4</sub>)</b>	US <sup>U</sup> ,DCu <sup>D</sup> S <sup>I</sup>	1	2Cu <sup>3c</sup>	S <sub>4</sub> [201,207,220;2Cu(229,235),2Fe(235,239)]



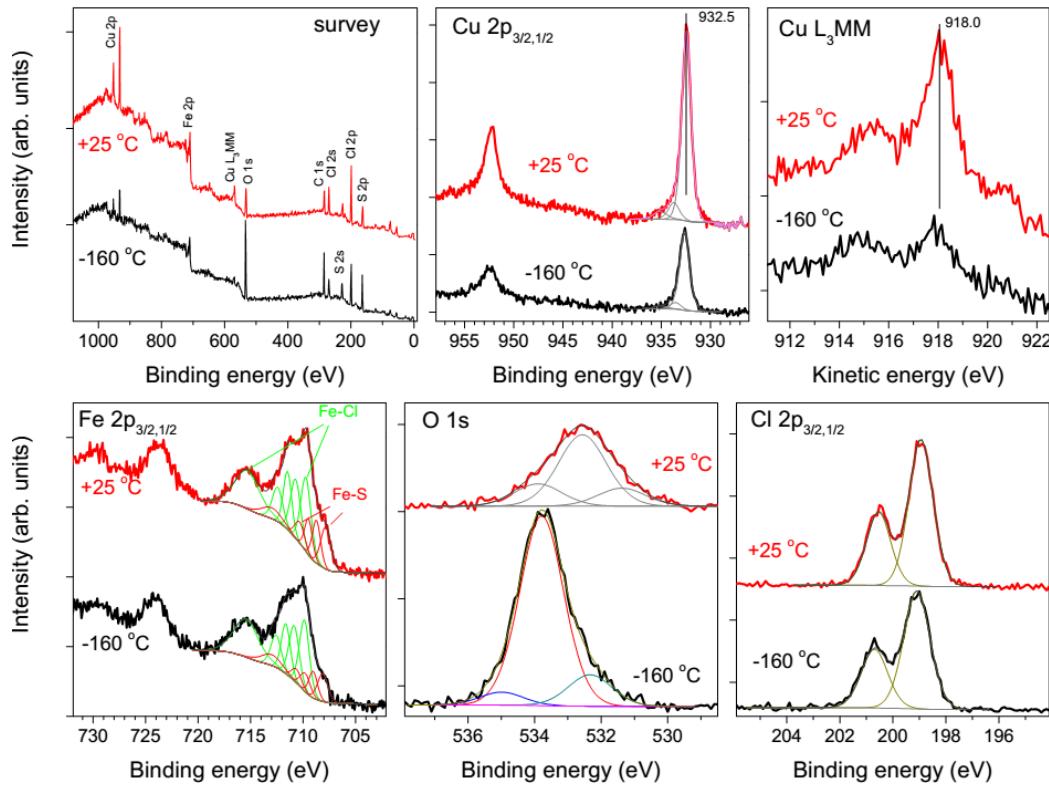
**Figure S1.** Total and partial densities of states for the stoichiometric unreconstructed CuFeS<sub>2</sub> (012) and (110) surfaces and a series of the Fe-deficit surfaces as calculated using DFT + *U*. Defect structure types are denoted in the plots; the energies of the Fermi level are marked.



**Figure S2.** X-ray photoelectron S 2p spectra of particulate chalcopyrite oxidized in 0.025 M  $\text{Fe}_2(\text{SO}_4)_3$  + 0.01 M  $\text{H}_2\text{SO}_4$  for 10 min, 0.05 M  $\text{Fe}_2(\text{SO}_4)_3$  + 0.01 M  $\text{H}_2\text{SO}_4$  for 30 min, and 0.05 M  $\text{FeCl}_3$  + 0.01 M HCl for 30 min at 50°C, centrifuged and fast-frozen, measured at -160 °C and then warmed up in the vacuum without and with employing slow electron flood gun (0.5 eV, 12 mkA).



**Figure S3.** X-ray photoelectron spectra of particulate chalcopyrite oxidized in 0.05 M  $\text{Fe}_2(\text{SO}_4)_3$  + 0.01 M  $\text{H}_2\text{SO}_4$  (30 min, 50 °C), centrifuged and fast-frozen, measured at -160 °C and then warmed up to +25 °C.



**Figure S4.** X-ray photoelectron spectra of chalcopyrite oxidized in 0.05 M  $\text{FeCl}_3$  + 0.01 M HCl (30 min, 50 °C), centrifuged and fast-frozen, measured at -160 °C and then warmed up to +25 °C.