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generation and application”, Novosibirsk

Near-surface regions of chalcopyrite ($CuFeS_2$) studied using XPS, HAXPES, XANES and DFT

Yuri Mikhlin, Alexander Romanchenko, Yevgeny Tomashevich, Vladimir Nasluzov, Valentin Shurupov, Sergey Vorobyev

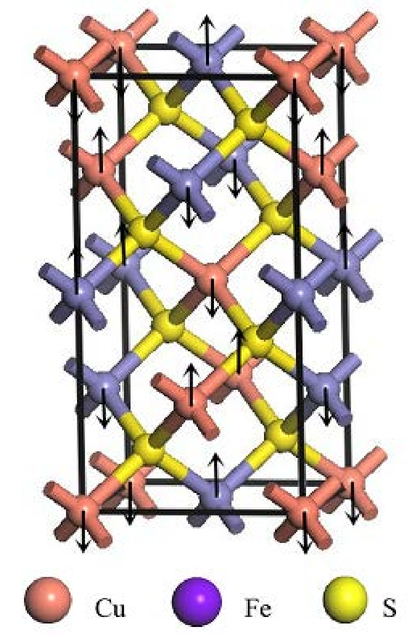
Institute of Chemistry and Chemical Technology of SB RAS of the Siberian Branch of the Russian Academy of sciences, Krasnoyarsk, Russia

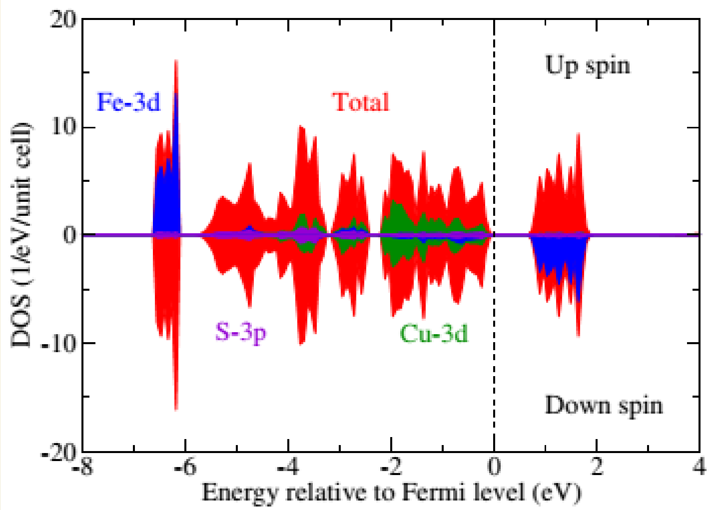
E-mail: yumikh@icct.ru

Chalcopyrites

$A^{I}B^{III}X^{VI}_2$ semiconductors – optoelectronics and solar cells, spintronics, etc.

$Cu^{+}\ Fe^{3+}\ S^{2-}_2$ - the main mineral of copper, magnetic and thermoelectric material





Fukushima et al. 2014

Sphalerite-type crystal structure

FeS_4 and CuS_4 tetrahedra

Fe(III) d^5 - antiferromagnetic ordering

magnetic moment of 3.6 μ_B per Fe atom

Cu (I) $d^{10}\ s^1$

Semiconductor with E_g = 0.5 eV

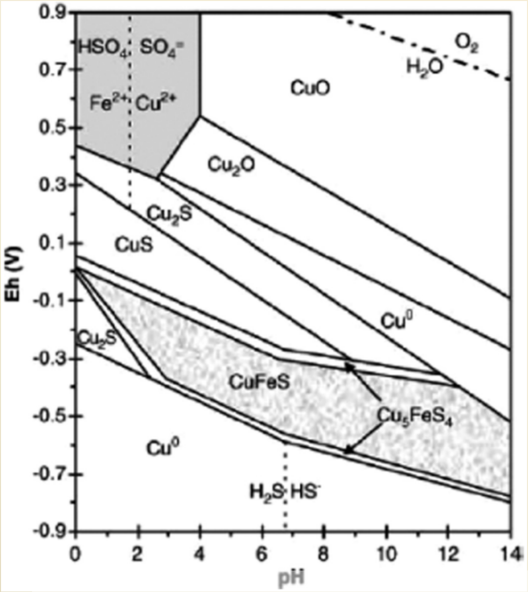
Mott-Hubbard Fe 3d band gap

Low carrier mobility

Electron – ferrion interaction

Chalcopyrite oxidation and dissolution

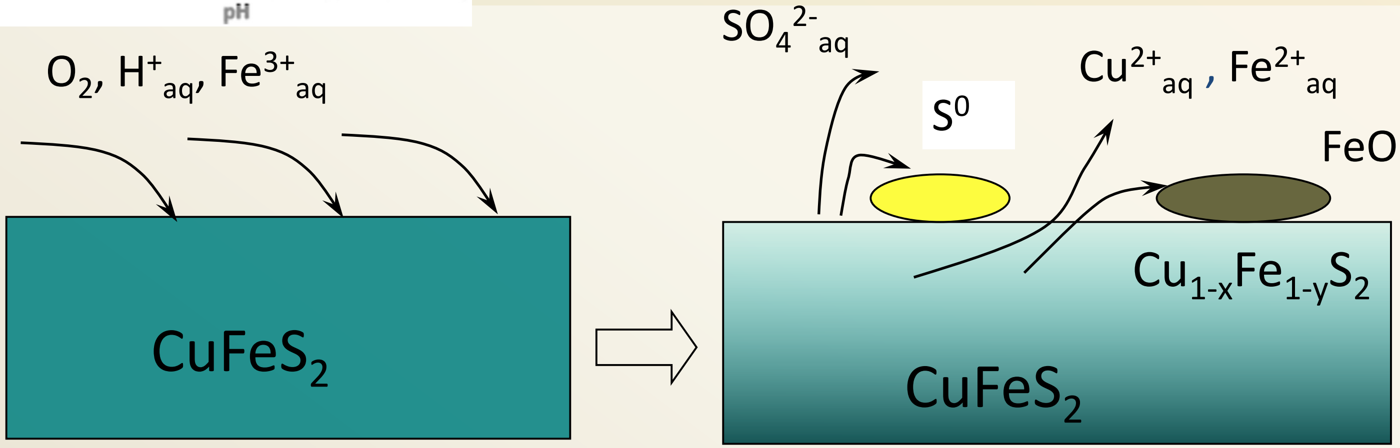
Thermodynamics



Principle oxidation reaction:

$$CuFeS_2 + Ox \rightarrow Cu^{2+} + Fe^{3+} + 2S^0 + Red$$

geochemistry, mineral processing and hydrometallurgy, materials science



O_2, H^+_{aq}, Fe^{3+}_{aq}

$CuFeS_2$

$SO_4{}^{2-}{}_{aq}$

S^0

Cu^{2+}_{aq} , Fe^{2+}_{aq}

$FeO(OH)_n$

$Cu_{1-x}Fe_{1-y}S_2$

$CuFeS_2$

Main findings from previous studies on reaction kinetics and surface structure

- Oxidation and dissolution are effectively impeded (*passivation*)
- The dissolution proceeds via the electrochemical mechanism, probably, with slow anodic half-reaction

  $2.5\ O_2 + 10H^+ + 5e \rightarrow 5H_2O$ cathodic

  $CuFeS_2 \rightarrow Cu^{2+} + Fe^{3+} + 2S^0 + 5e^-$ anodic
- Reaction rate is controlled by solid-state diffusion of cations towards the interface ***or***

  Reaction rate is controlled by electron transport
- Surface reaction products akin to elemental S, iron hydroxides, and so on, are not responsible for passivation
- Metal-deficient layers play a crucial role

What is known about the metal-deficient layers

- Strongly non-stoichiometric composition found by XPS

(pioneered by Buckley et. al., 1982)

- Contain disulfide and polysulfide anions
- Extended to the depth down to dozens of nanometers (XANES, AES profiling)

Some researchers (Klauber et al.) deny the above and suggest the formation of chemically adsorbed elemental sulfur

The aim of the current study

To understand characteristics and role of reacted, non-stoichiometric chalcopyrite surfaces

- To study the near-surface layers in depth using non-destructive HAXPES and XAS techniques
- To calculate Fe-vacation structures using DFT + *U*
- To correlate the spectroscopic and DFT data with surface conductivity and reactivity

Some experimental details

Material:

Plates (1 x 4 x 5 mm) of natural polycrystalline chalcopyrite $CuFeS_2$ (Primorski ore deposit)

Chemical treatment:

Polished in air, cleaned with wet filter paper
etched in acidic 0.5 M Fe^{3+} solutions
electrochemically polarized in 0.5 M HCl

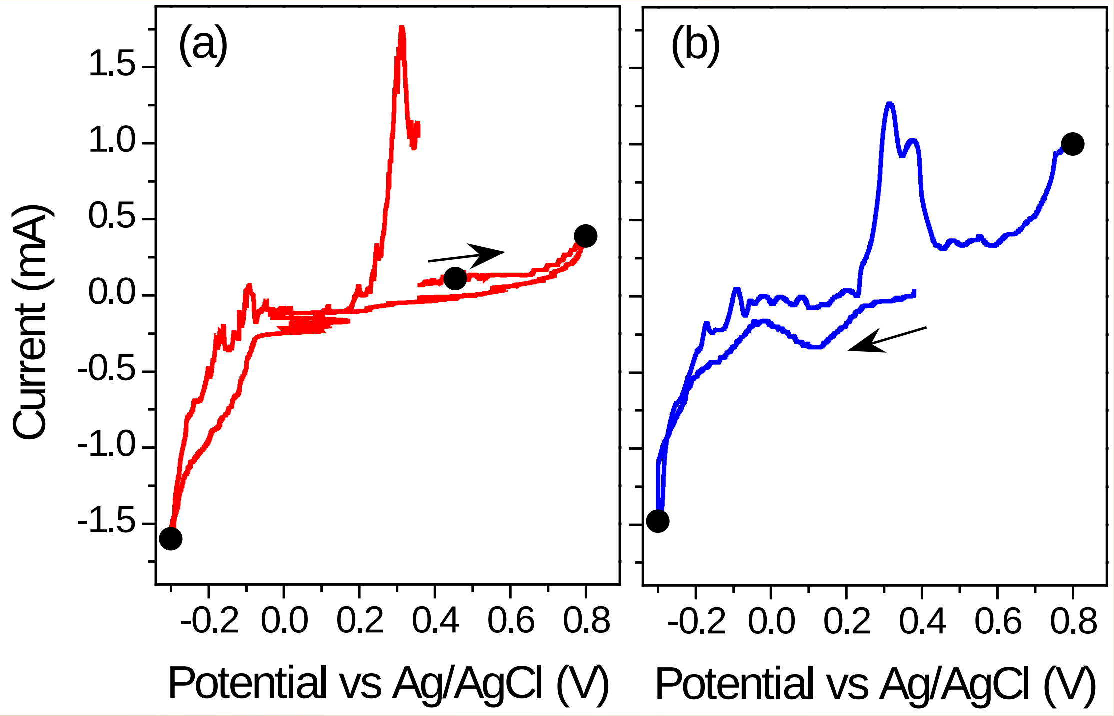
Spectroscopic techniques and facilities used:

SPECS spectrometer, Institute of Chemistry @ Chemical Technology SB RAS (Krasnoyarsk) - conventional XPS

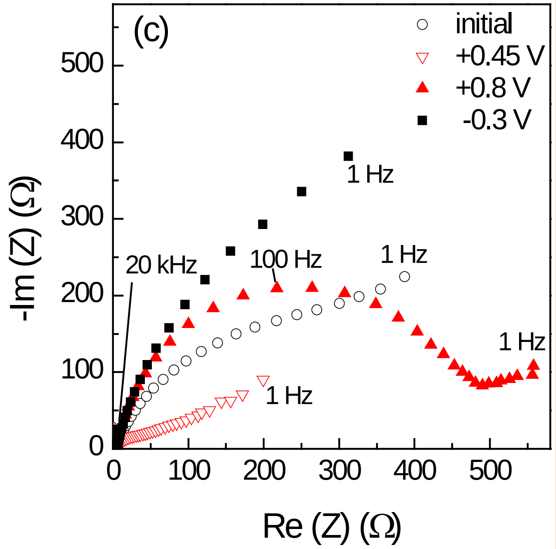
Russian-German Laboratory at BESSY II:
Soft X-ray absorption spectroscopy (Cu L-, Fe L-, S L-edge TEY XANES)

HIKE endstation at BESSY II:
HAXPES (2 keV – 9 keV) and Fe K-edge and S K-edge TEY and PFY XANES

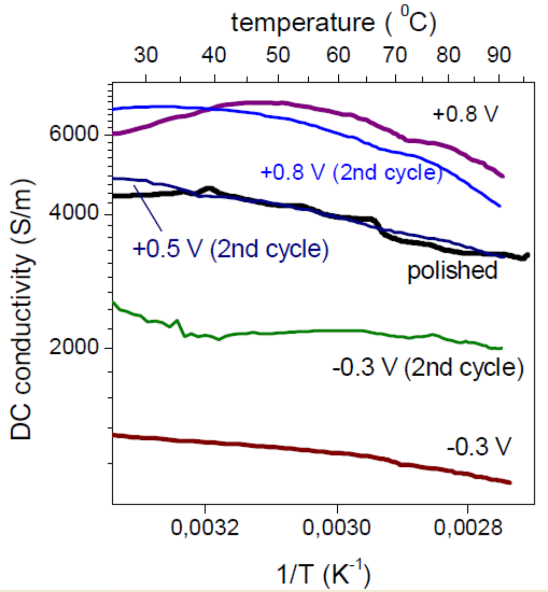
Cyclic voltammetry of chalcopyrite in 1 M HCl



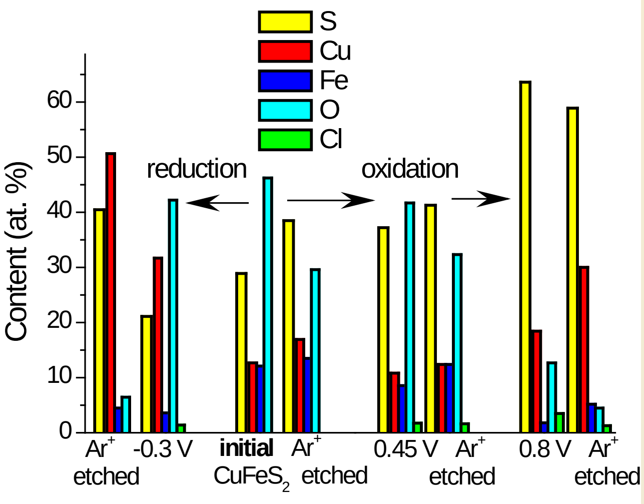
Electrochemical impedance

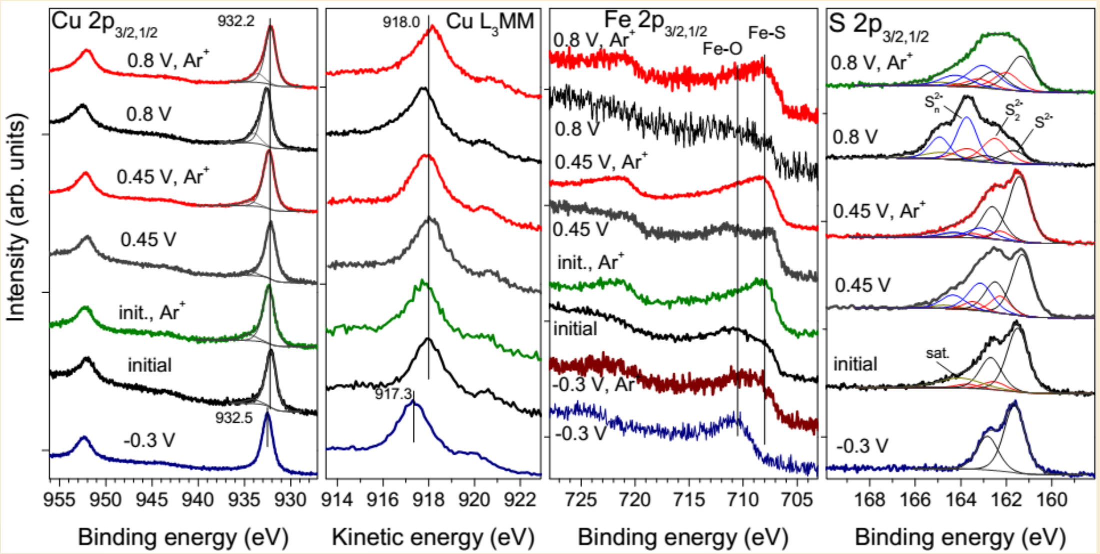


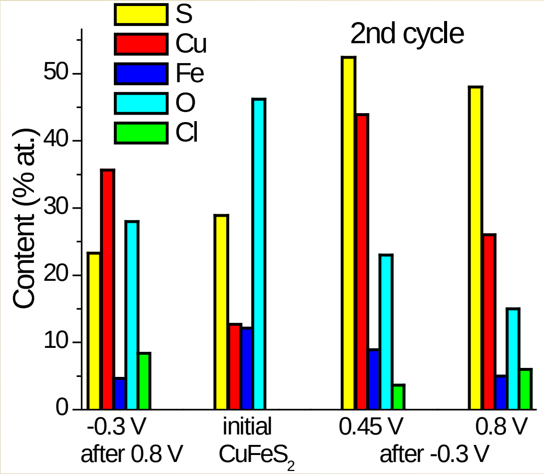
DC conductivity of dry surfaces of the reacted chalcopyrite (4-spring-loaded probes)

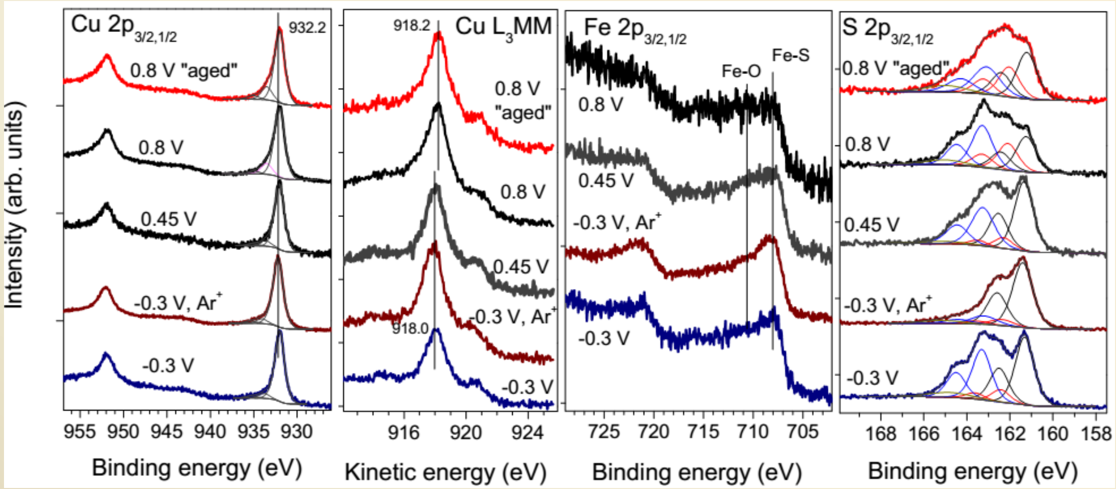


X-ray photoelectron spectra of electrochemically reacted chalcopyrite









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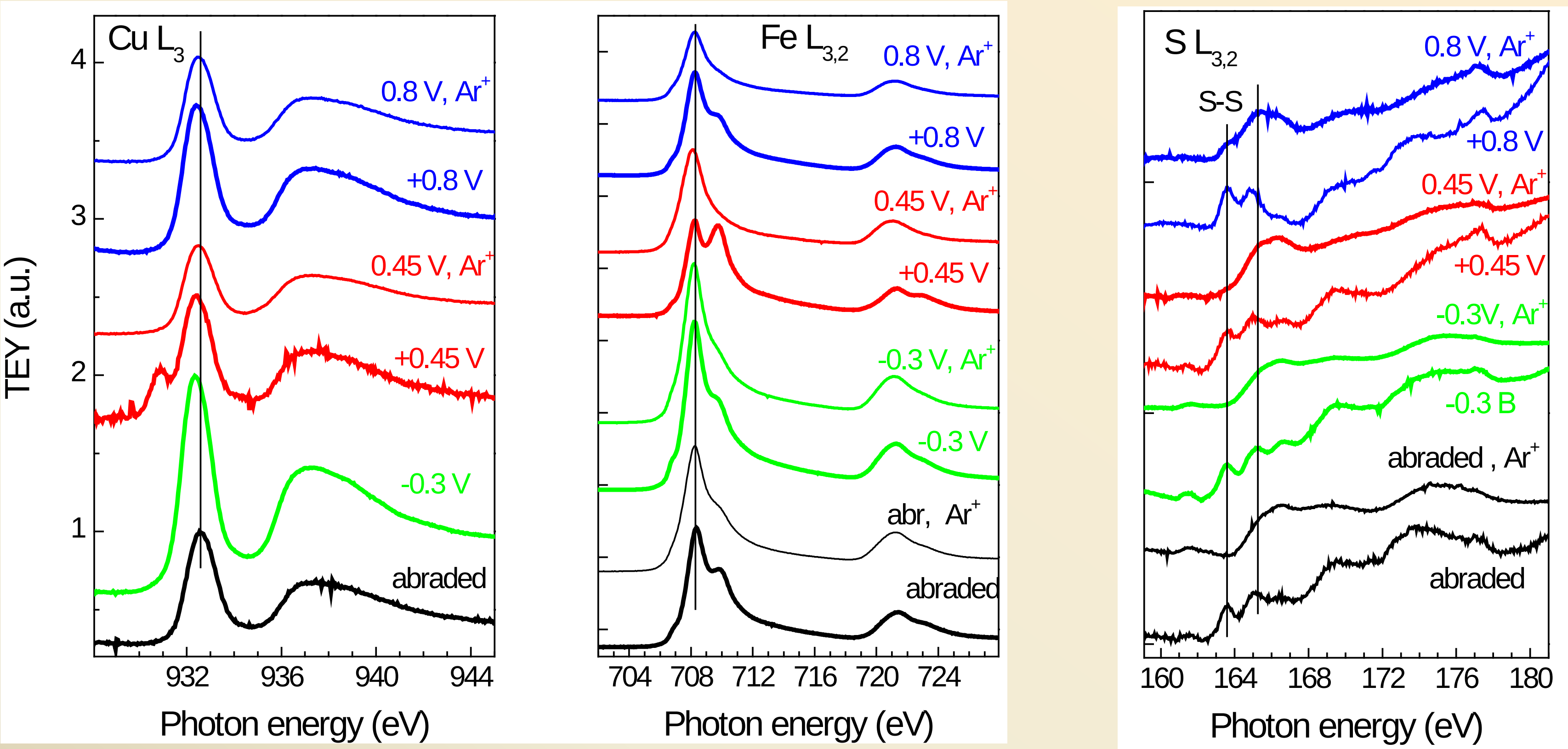
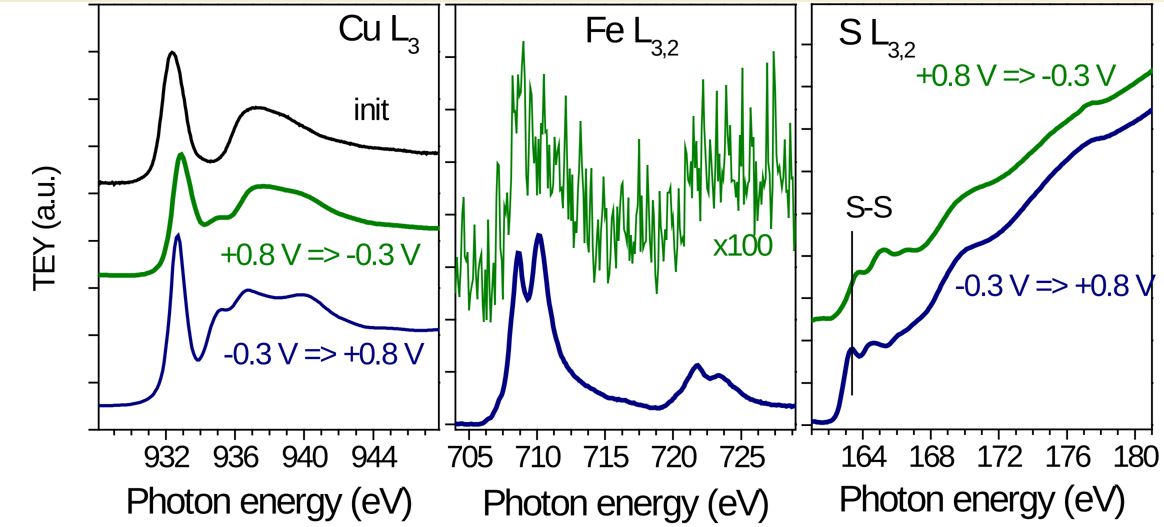
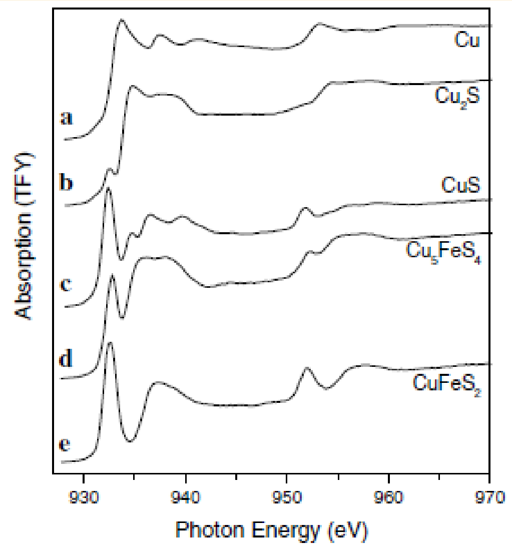
Fe- и Cu $L_{3,2}$ –edge TEY XANES of reacted chalcopyrite



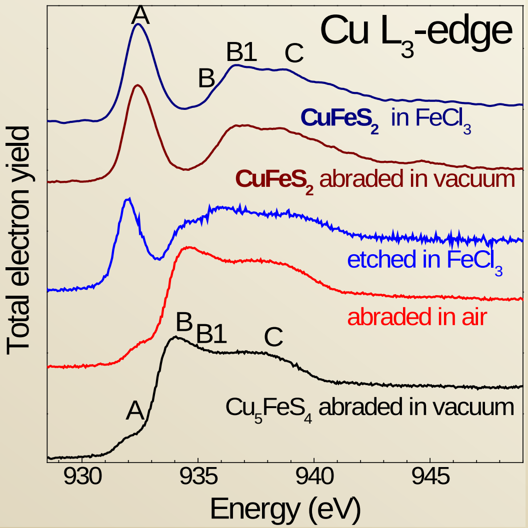
Cu L-edge TEY XANES remains almost the same, similar to Cu 2p and Cu L_3MM, and in contrast to Fe L- and S L-edge spectra, despite tremendous compositional changes

2^{nd} cycle of chalcopyrite polarization





Oxidation of chalcopyrite and bornite Cu_5FeS_4

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Geochimica et Cosmochimica Acta 70 (2006) 2210–2228

Geochimica

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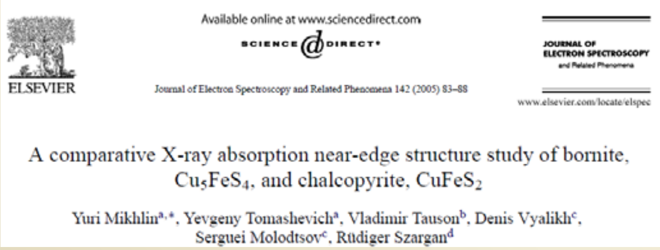
The oxidation states of copper and iron in mineral sulfides, and the oxides formed on initial exposure of chalcopyrite and bornite to air

Siew Wei Goh [a], Alan N. Buckley [a,*], Robert N. Lamb [a],
Richard A. Rosenberg [b], Damian Moran [c]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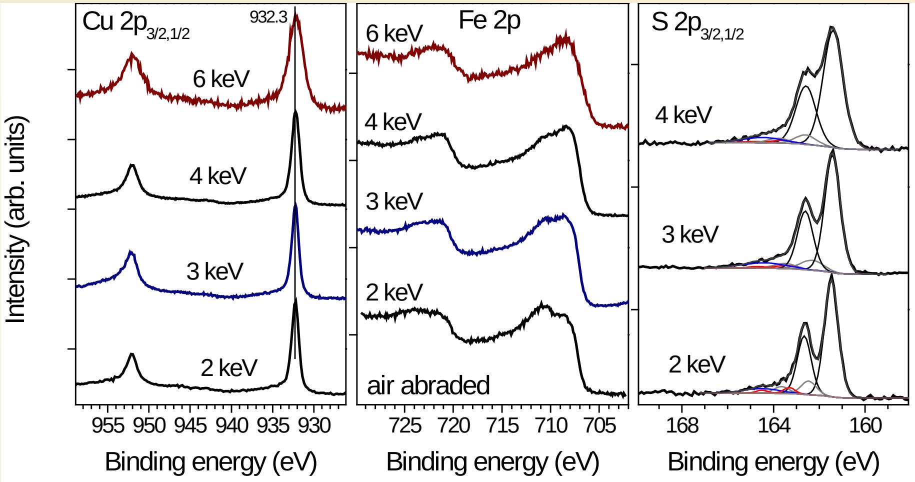
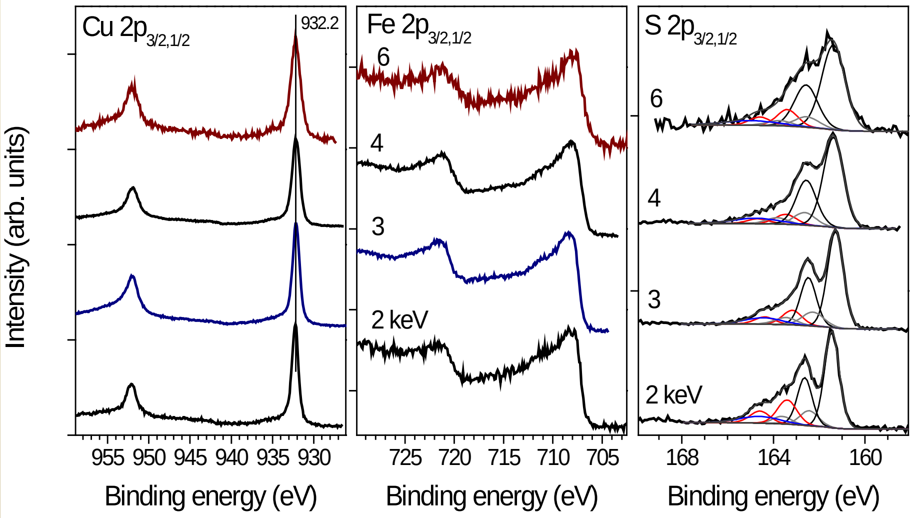
A comparative X-ray absorption near-edge structure study of bornite, Cu_5FeS_4, and chalcopyrite, $CuFeS_2$

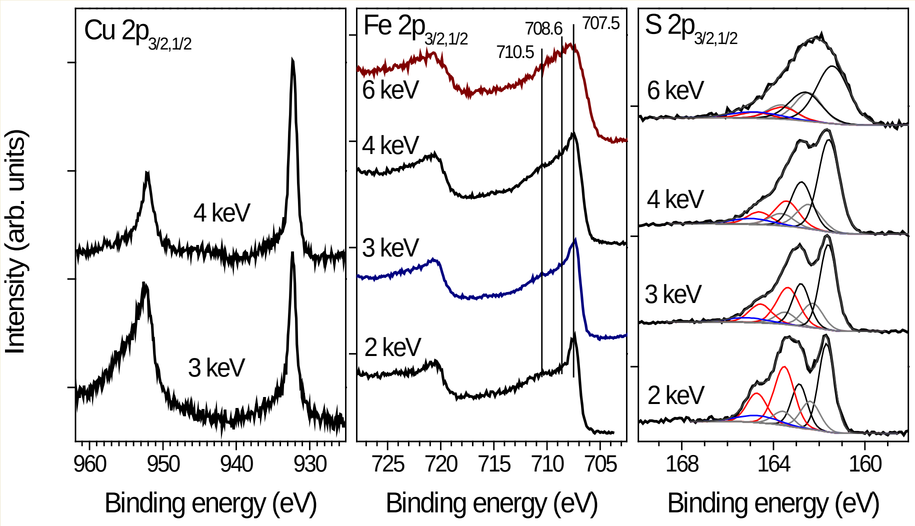
Yuri Mikhlin [a,*], Yevgeny Tomashevich [a], Vladimir Tauson [b], Denis Vyalikh [c],
Serguei Molodtsov [c], Rüdiger Szargan [d]

Hard X-ray photoemission spectra



Abraded in ambient air

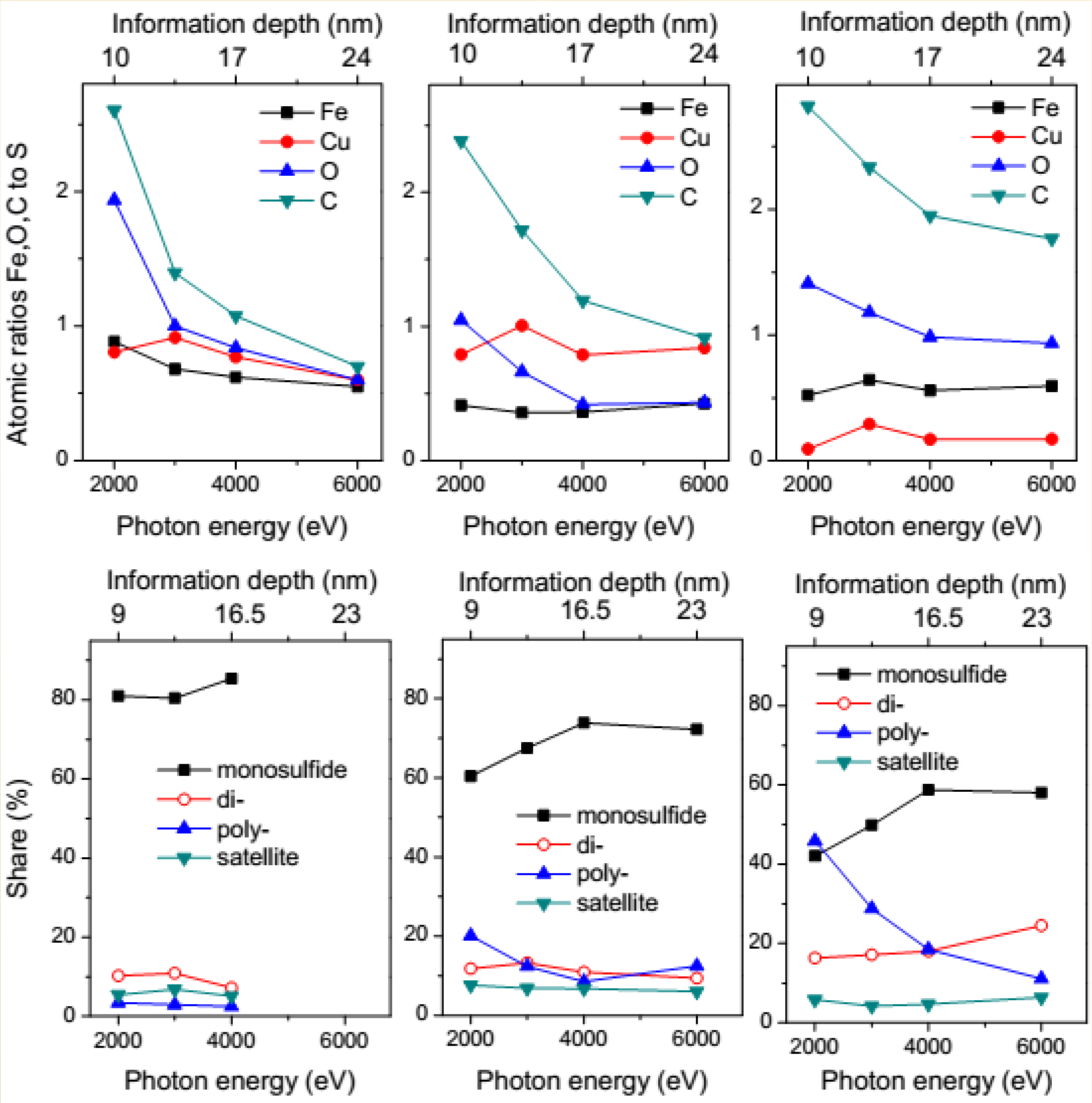




Reacted in 0.25 M $Fe_2(SO_4)_3$ + H_2SO_4

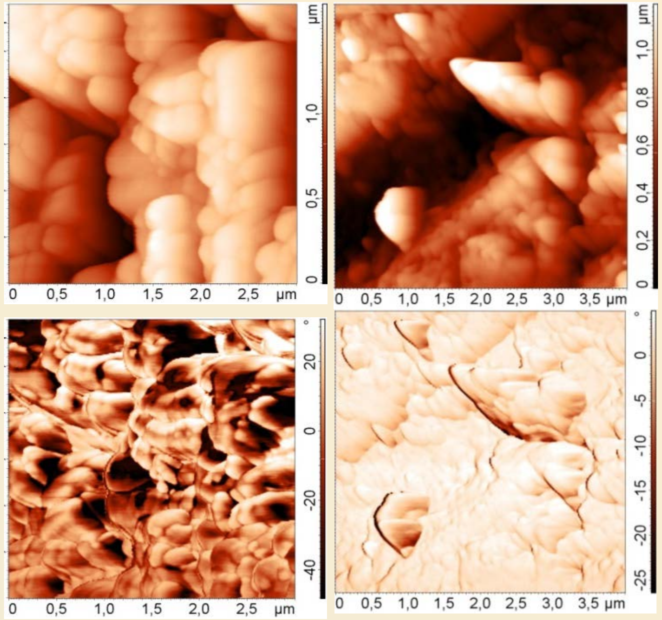
Reacted in 0.5 M $FeCl_3$ + HCl

Summary of HAXPES results



Air-abraded 0.25 M $Fe_2(SO_4)_3$ 0.5 M $FeCl_3$

AFM images
(height and phase contrast)

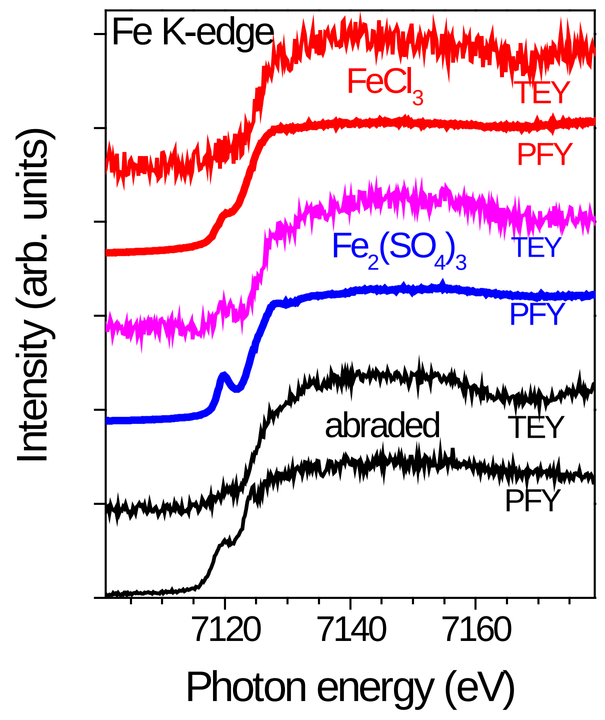


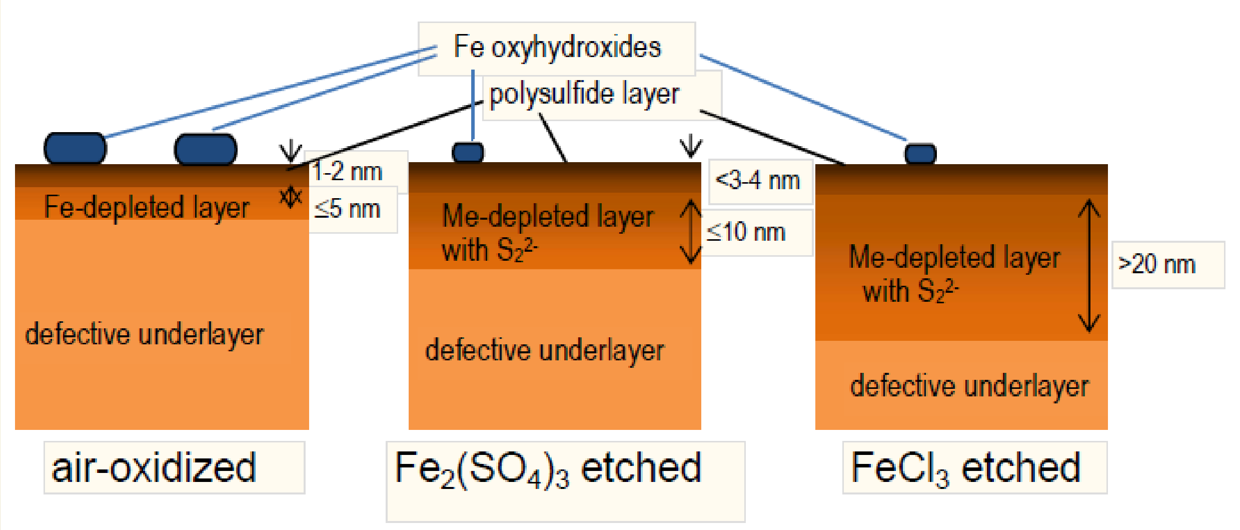
0.5 M $FeCl_3$
+ 1 M HCl

0.25 M $Fe_2(SO_4)_3$
+ 0.5 M H_2SO_4

50^0C, 30 min

Fe K-XANES in TEY and PFY modes and layered structure of near-surface region of chalcopyrite





Some clues to understanding the oxidized layers from DFT + U

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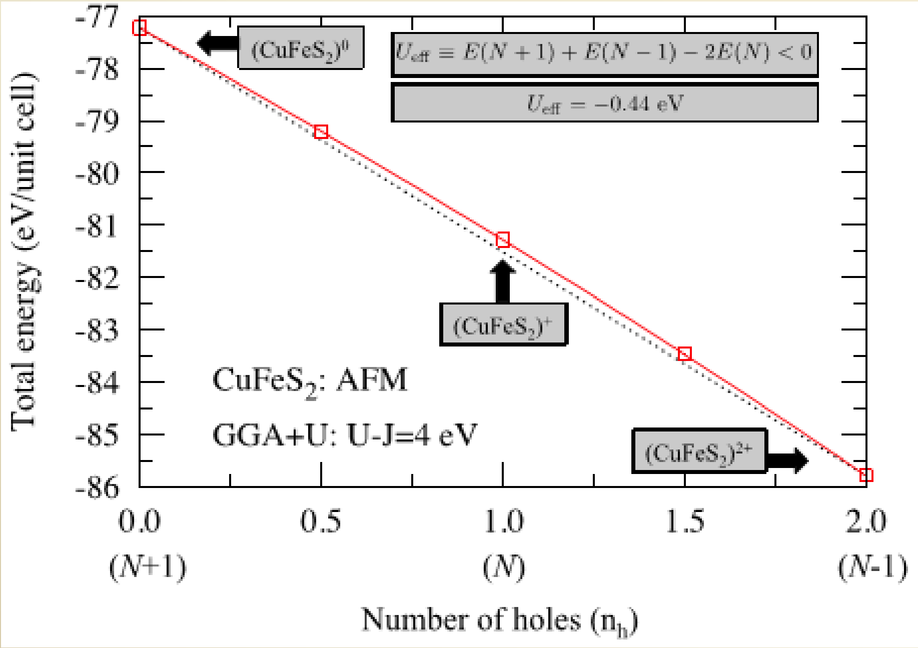
Journal of Physics: Condensed Matter

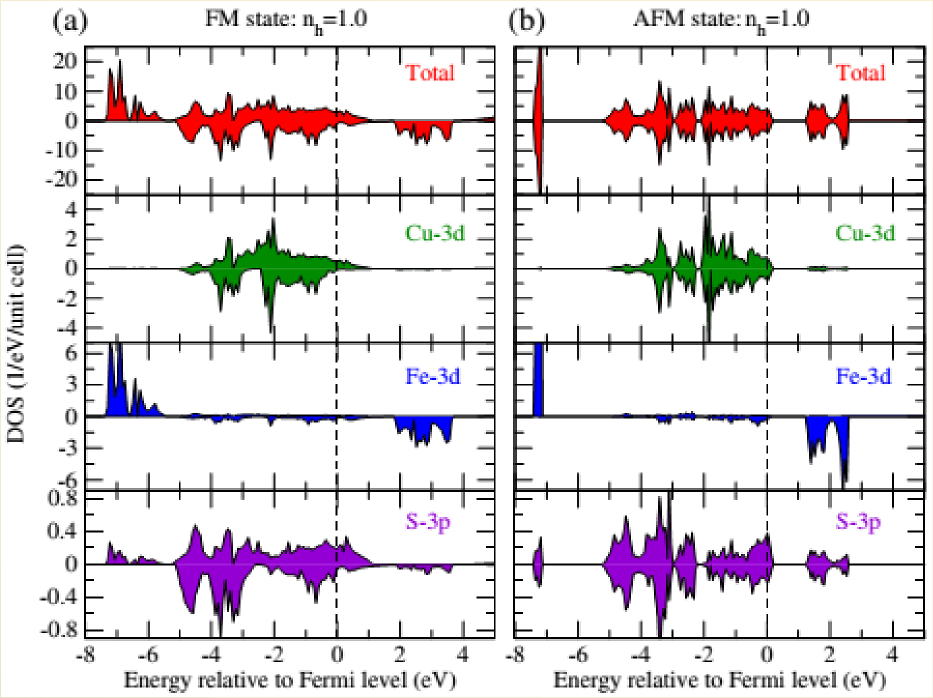
J. Phys.: Condens. Matter **26** (2014) 355502 (8pp)

doi:10.1088/0953-8984/26/35/355502

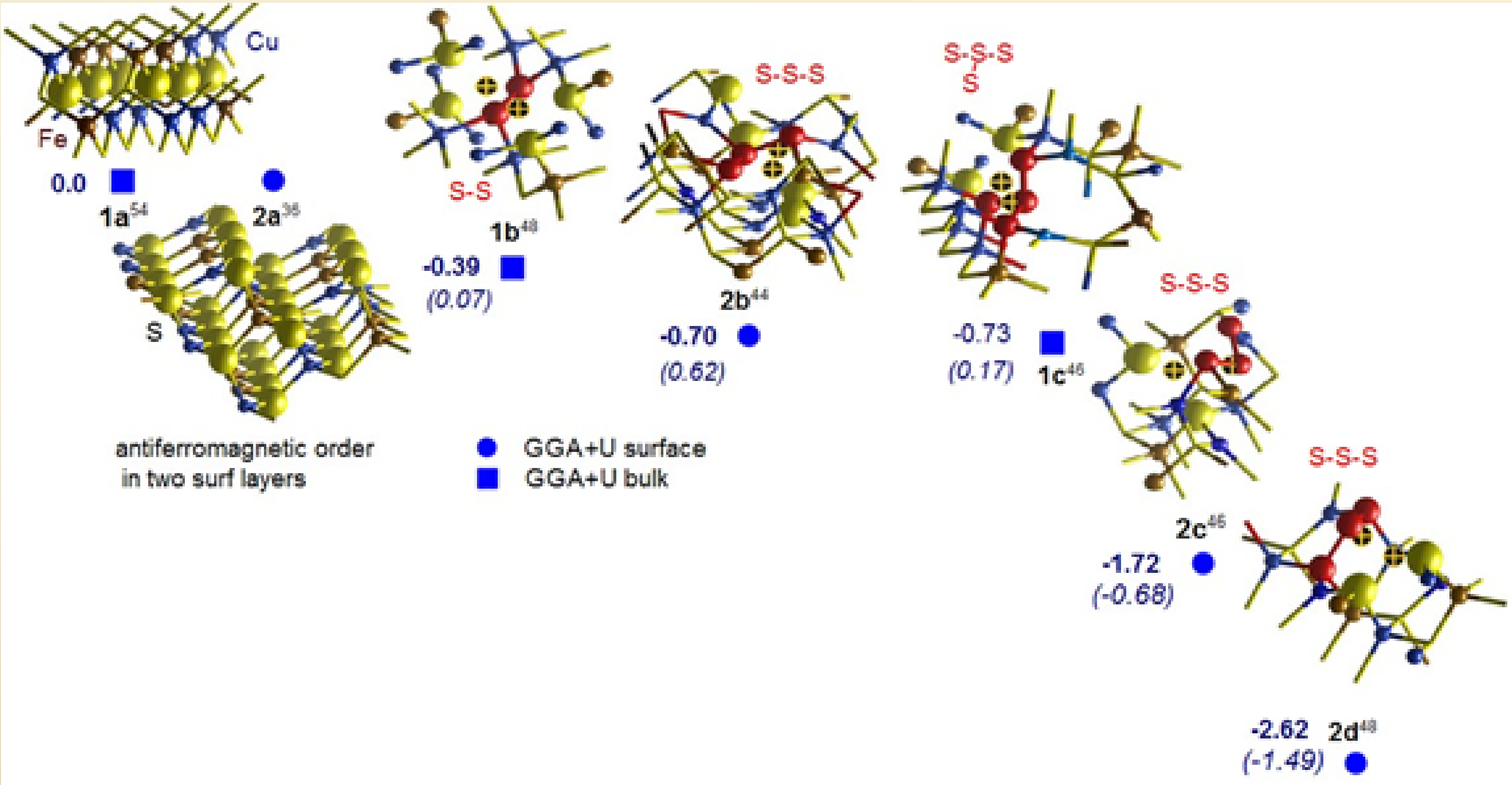
Computational materials design of negative effective *U* system in hole-doped chalcopyrite $CuFeS_2$

T Fukushima[1], H Katayama-Yoshida[1], H Uede[1], Y Takawashi[1], A Nakanishi[1] and K Sato[2]



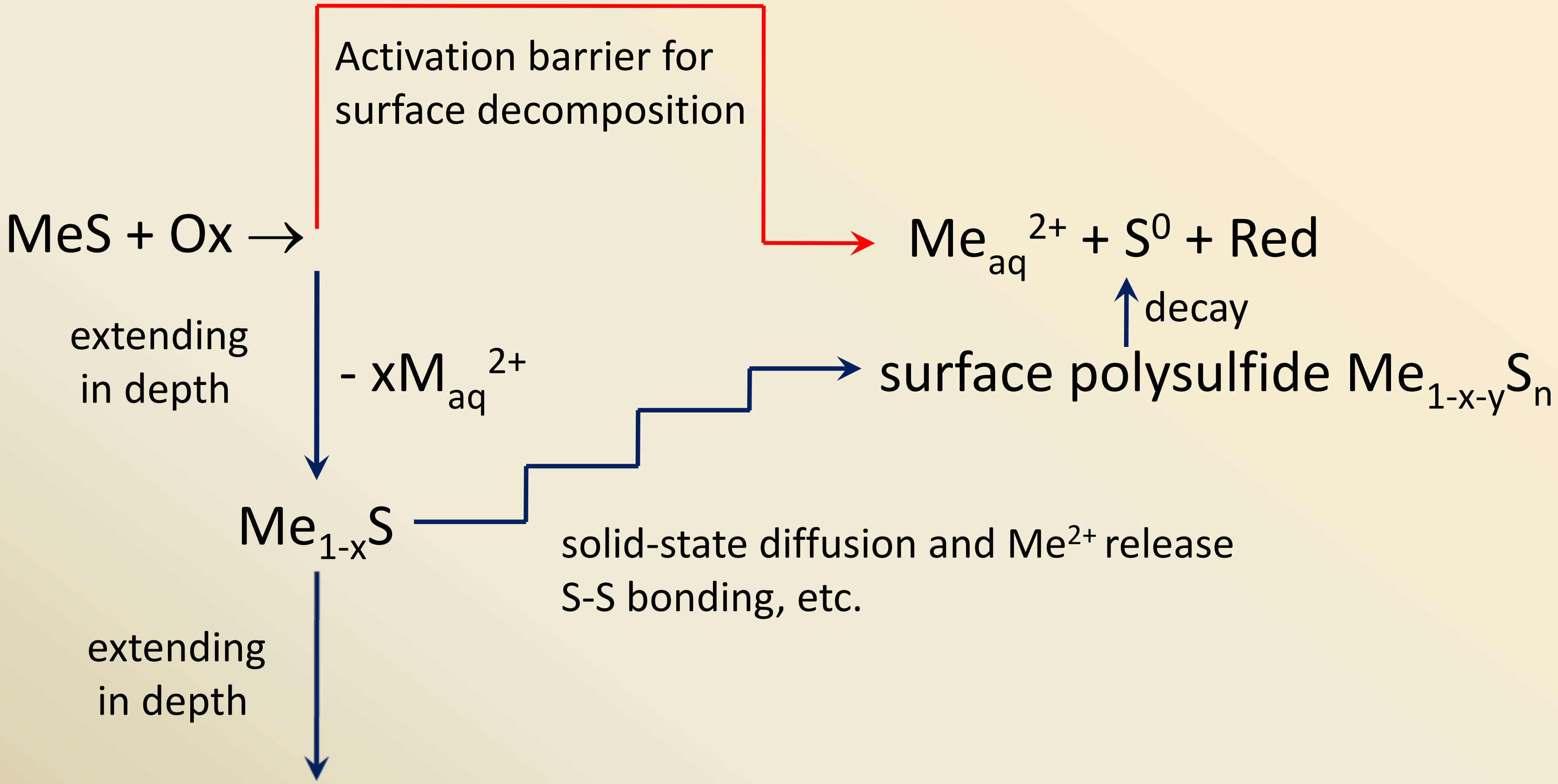


DFT + *U* calculations of Fe-deficient chalcopyrite under oxidative conditions



- Vacation structures are stable under oxidation conditions
- Polysulfide species are stabilized and can exist in surface layers
- CuS_4 tetrahedra are stable, Cu coordination number decreases only in surface polysulfide structures
- Insulator-metal transition occurs in Fe-depleted structures
- Antiferromagnetic to paramagnetic transition

On the mechanism of “*passivity*” of chalcopyrite and other metal chalcogenides



MeS + Ox →

Activation barrier for
surface decomposition

$Me_{aq}^{2+} + S^0 + Red$

decay

surface polysulfide $Me_{1-x-y}S_n$

extending
in depth

$- xM_{aq}^{2+}$

$Me_{1-x}S$

solid-state diffusion and Me^{2+} release
S-S bonding, etc.

extending
in depth

Conclusions

- XPS, HAXPES, XANES studies revealed that the preferential release of cations from chalcopyrite lattice results in the formation of near-surface region with

(i) a thin, no more than 1-4 nm in depth, outer layer containing polysulfide species,

(ii) a layer exhibiting less pronounced stoichiometry deviations and low, if any, concentrations of polysulfide, the composition and dimensions of which depend on the chemical treatment,

(iii) an extended almost stoichiometric underlayer yielding modified FE K-TEY XANES spectra, probably, due to a higher content of defects

- DFT + U calculations show a high stability of Fe-deficient structures, particularly CuS_4 units
- The undersurface exhibits an increased (metallic) conductivity
- Low reactivity of chalcopyrite is due to stability of the metal-depleted structures; no special “passivation” exists

Acknowledgements

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- We thank HZB for the allocation of synchrotron radiation beamtime for XANES and HAXPES measurements
- Special thanks to Dr. R. Félix Duarte and personnel of BESSY II for their assistance

Thank you for your patience