Supplemental material of "Local versus global electronic properties of chalcopyrite alloys: X-ray absorption spectroscopy and ab initio calculations"

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Validation of the supercells used for the electronic structure calculations of alloys

In Table 1 we report the experimental bond lenghts of $CuIn_xGa_{1-x}S_2$ (CIGS) alloys extracted from extended X-ray absorption fine structure (EXAFS) data at 17 K. The calculated bond lengths of alloys with similar compositions are given in Table 2. The alloy is modeled using special quasirandom supercells of 40 atoms and the geometrical relaxation is performed within density functional theory using different approximations for the exchange-correlation potential, i.e. Perdew–Burke–Ernzerhof (PBE), PBE+U, with $U = 6$ eV on Cu d states, and the screened hybrid Heyd–Scuseria–Ernzerhof (HSE). More details on the simulations and all relevant references can be found in the Letter. We can see that HSE calculations are in excellent agreement with experimental data for all the considered compositions. On the other hand, PBE systematically overestimate Ga-S and In-S bond lengths, while Cu-S bond lengths are quite close to HSE and experiments. PBE+U gives bond lengths of intermediate quality in comparison with PBE and HSE.

Table 1: Experimental bond lengths (Å) of CIGS alloys extracted from EXAFS data at 17 K. The uncertainty of the values is approximately ± 0.003Å. See also S. Eckner et al., Appl. Phys. Lett. 103, 081905, 2013.

Sample	Cu/III	In/III	d_{Cu-S}	d_{Ga-S}	d_{In-S}
A	0.99	1.00	2.325	-	2.463
B	0.99	1.00	2.325	-	2.463
C	0.93	0.80	2.324	2.299	2.458
D	0.90	0.75	2.325	2.298	2.461
E	1.05	0.64	2.323	2.297	2.456
F	1.07	0.43	2.320	2.294	2.451
G	0.97	0.40	2.320	2.293	2.452
H	1.10	0.30	2.318	2.292	2.446
I	0.99	0.29	2.318	2.291	2.449
K	1.07	0.22	2.318	2.291	2.442
L	0.99	0	2.312	2.286	-

Table 2: Calculated averaged bond lengths (Å) of 40 atom CIGS supercells, obtained from density functional theory using different exchange correlation potentials, as described in the manuscript. The error related to the supercell size is estimated to be smaller than 0.002Å.

In/III	d_{Cu-S} PBE	d_{Cu-S} PBE+U	d_{Cu-S} HSE	d_{Ga-S} PBE	d_{Ga-S} PBE+U	d_{Ga-S} HSE	d_{In-S} PBE	d_{In-S} PBE+U	d_{In-S} HSE
1.00	2.33	2.33	2.34	-	-	-	2.52	2.50	2.48
0.70	2.33	2.33	2.34	2.34	2.33	2.31	2.51	2.50	2.47
0.50	2.32	2.33	2.34	2.34	2.33	2.30	2.50	2.49	2.46
0.30	2.32	2.33	2.33	2.33	2.32	2.29	2.49	2.48	2.46
0.00	2.31	2.32	2.32	2.32	2.31	2.29	-	-	-

Experimental and simulated absorption edges

The absorption edges of CIGS thin-films, with $x = 0$, 0.67 and 1, were measured by near edge X-ray absorption fine structure (NEXAFS). We show here the curves that were not included in the Letter. Each experimental spectrum is presented together with the corresponding calculated projected density of states (pDOS) above the conduction band edge. A Gaussian broadening of 0.3 eV is applied to all the calculated pDOS. More details are given in the Letter.

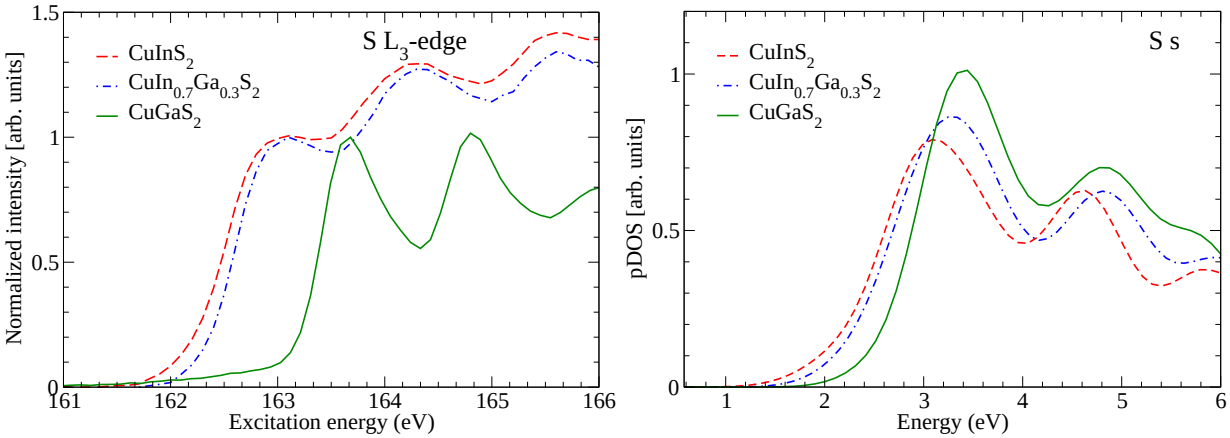

Figure 1: (Color online) Left panel: measured absorption L_3-edges of S in $CuInS_2$ (red dashed line), $CuIn_{0.67}Ga_{0.33}S_2$ (blue dot-dashed line) and $CuGaS_2$ (green solid line). Right panel: calculated pDOS of s states on S atoms for the conduction bands of $CuInS_2$ (red dashed line), $CuIn_{0.7}Ga_{0.3}S_2$ (blue dot-dashed line) and $CuGaS_2$ (green solid line). A gaussian broadening of 0.3 eV is applied to all the calculated pDOS.

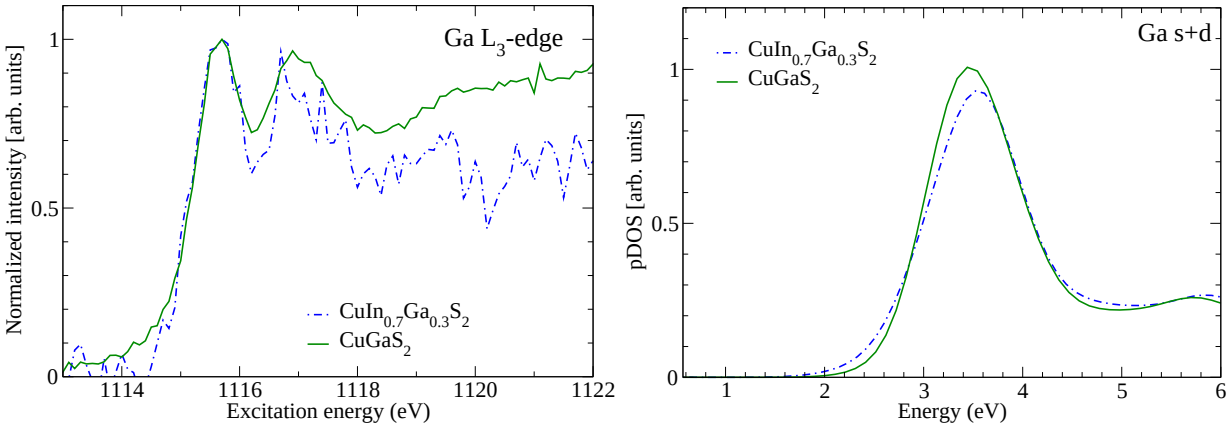

Figure 2: (Color online) Left panel: measured absorption L_3-edges of Ga in $CuIn_{0.67}Ga_{0.33}S_2$ (blue dot-dashed line) and $CuGaS_2$ (green solid line). Right panel: calculated pDOS of s and d states on Ga atoms for the conduction bands of $CuIn_{0.7}Ga_{0.3}S_2$ (blue dot-dashed line) and $CuGaS_2$ (green solid line).

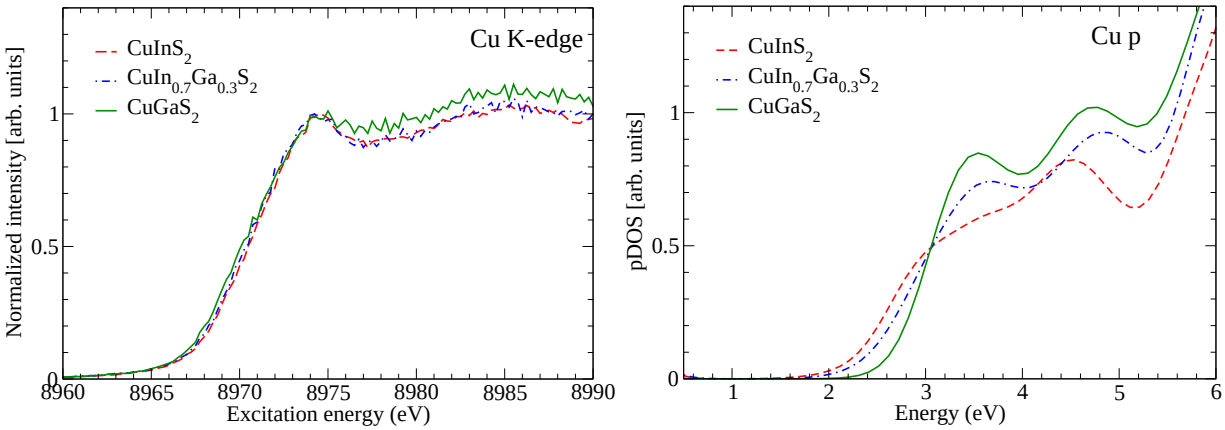

Figure 3: (Color online) Left panel: measured absorption K-edges of Cu in $CuInS_2$ (red dashed line), $CuIn_{0.67}Ga_{0.33}S_2$ (blue dot-dashed line) and $CuGaS_2$ (green solid line). Right panel: Calculated pDOS of p states on Cu atoms for the conduction bands of $CuInS_2$ (red dashed line), $CuIn_{0.7}Ga_{0.3}S_2$ (blue dot-dashed line) and $CuGaS_2$ (green solid line).

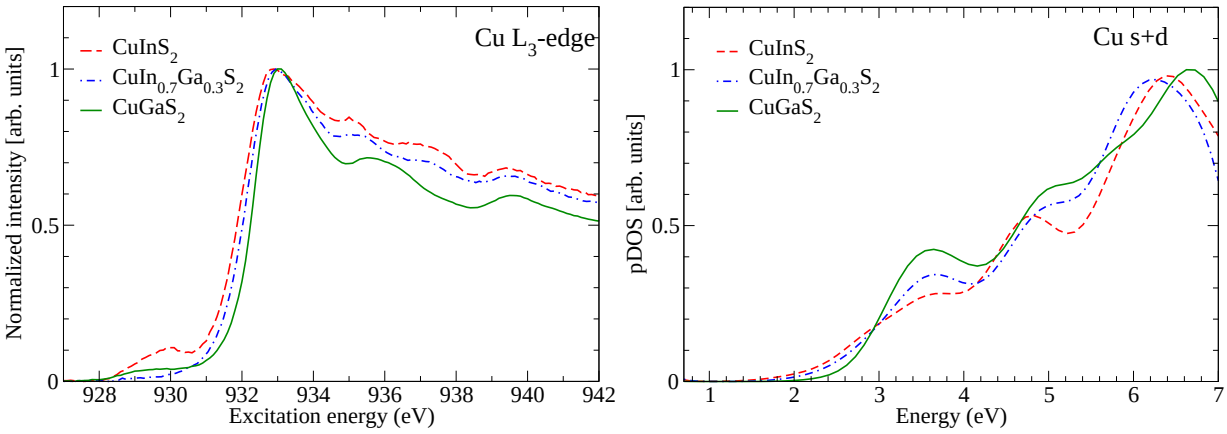

Figure 4: (Color online) Left panel: measured absorption L_3-edges of Cu in $CuInS_2$ (red dashed line), $CuIn_{0.67}Ga_{0.33}S_2$ (blue dot-dashed line) and $CuGaS_2$ (green solid line). Right panel: calculated pDOS of s and d states on Cu atoms for the conduction bands of $CuInS_2$ (red dashed line), $CuIn_{0.7}Ga_{0.3}S_2$ (blue dot-dashed line) and $CuGaS_2$ (green solid line).

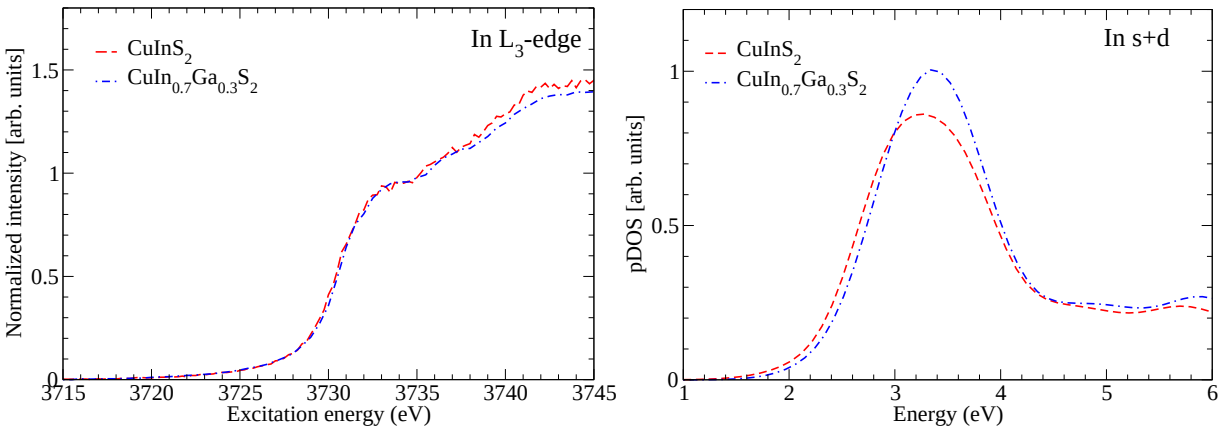

Figure 5: (Color online) Left panel: measured absorption L_3-edges of In in $CuInS_2$ (red dashed line) and $CuIn_{0.67}Ga_{0.33}S_2$ (blue dot-dashed line). Right panel: calculated pDOS of s and d states on In atoms for the conduction bands of $CuInS_2$ (red dashed line) and $CuIn_{0.7}Ga_{0.3}S_2$ (blue dot-dashed line).

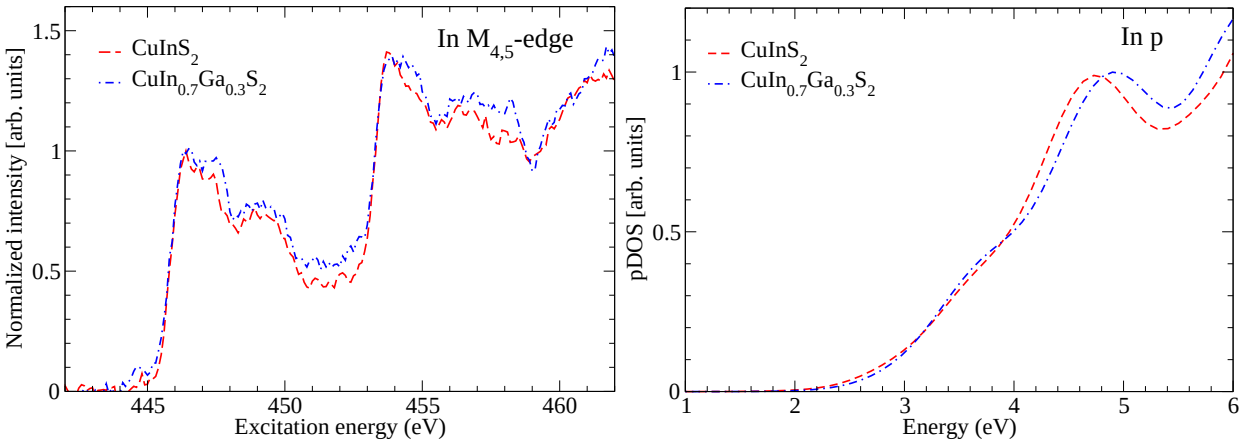

Figure 6: (Color online) Left panel: measured absorption $M_{4,5}$-edges of In in $CuInS_2$ (red dashed line) and $CuIn_{0.67}Ga_{0.33}S_2$ (blue dot-dashed line). Right panel: calculated pDOS of p states on In atoms for the conduction bands of $CuInS_2$ (red dashed line) and $CuIn_{0.7}Ga_{0.3}S_2$ (blue dot-dashed line).