Probing the local atomic structure of In and Cu in sphalerite by XAS spectroscopy enhanced by reverse Monte-Carlo algorithm

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Table S1. Interatomic distances in sphalerite with and without dopants determined by DFT calculations. Literature data on the interatomic distances of unrelaxed pure sphalerite structure are given at the bottom of the table. Data for the systems ZnS+In was obtained in the present study, all other data are adopted from [1,2]. The method of the calculations is described in [1].

Bond		Coordination shels							
		Me-S		Me-Zn		Me1-Me2		Me-S	
		N	R,Å	N	R,Å	N	R,Å	N	R,Å
ZnS+In Me=In		4	2.50	12	3.93	-	-	12	4.53
ZnS+Cu Me=Cu		4	2.33	12	3.81	-	-	12	4.51
ZnS+Ag Me=Ag		4	2.50	12	3.86	-	-	12	4.51
ZnS+Cu+In (In and Au atoms are located in neighboring cites)	Me1=In	4	2.46, 2.50, 2.50, 2.51	12	3.85-3.97	1	3.87	12	4.50-4.54
	Me2=Cu	4	2.31, 2.32, 2.32, 2.34	12	3.82-3.92			12	4.45-4.55
ZnS+Cu+In (In and Au atoms are located far from each other)	Me1=In	4	2.49	12	3.93	1	12.78	12	4.53
	Me2=Cu	4	2.33	12	3.81			12	4.51
ZnS+2In, (2 In atoms are placed far from each other), Me=In		4	2.51	12	3.93	-	-	12	4.53
ZnS+2In, (2 In atoms are placed in the nearest positions), Me=In		4	2.50 - 2.54	12	3.89 - 4.01	1	4.01	12	4.46 - 4.61
ZnS+2In+□, (In atoms are placed far from each other), Me=In		4	2.50-2.51	12	3.90 - 3.93	-	-	12	4.50 - 4.54
ZnS+2In+□, (In atoms and Zn vacancy are placed in the nearest positions), Me=In		4	2.46-2.51	11	3.86 - 3.97	1	3.86	12	4.44 - 4.60
ZnS		4	2.36	12	3.86	-	-	12	4.51
ZnS, literature XRD data [3]		4	2.34	12	3.83	-	-	12	4.49

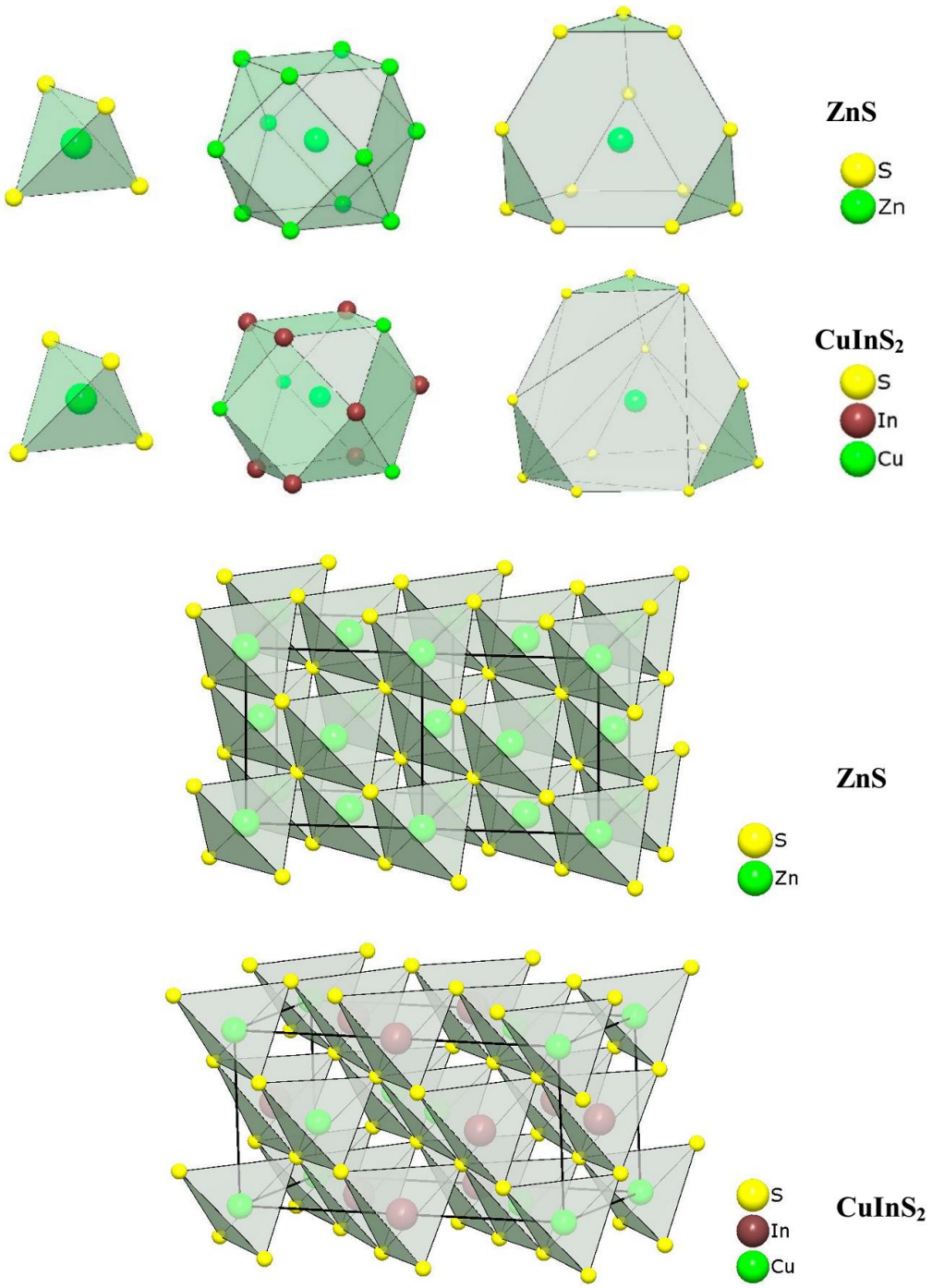

Figure S1. ***Top:*** Coordination polyhedra of the cations in the structures of sphalerite ZnS [3] and roquesite $CuInS_2$ [4] (Adopted from Trofimov et al.[2]). ***Bottom:*** Crystal structures of sphalerite (doubled cell is shown to make comparison with $CuInS_2$ easier) and roquesite [4].

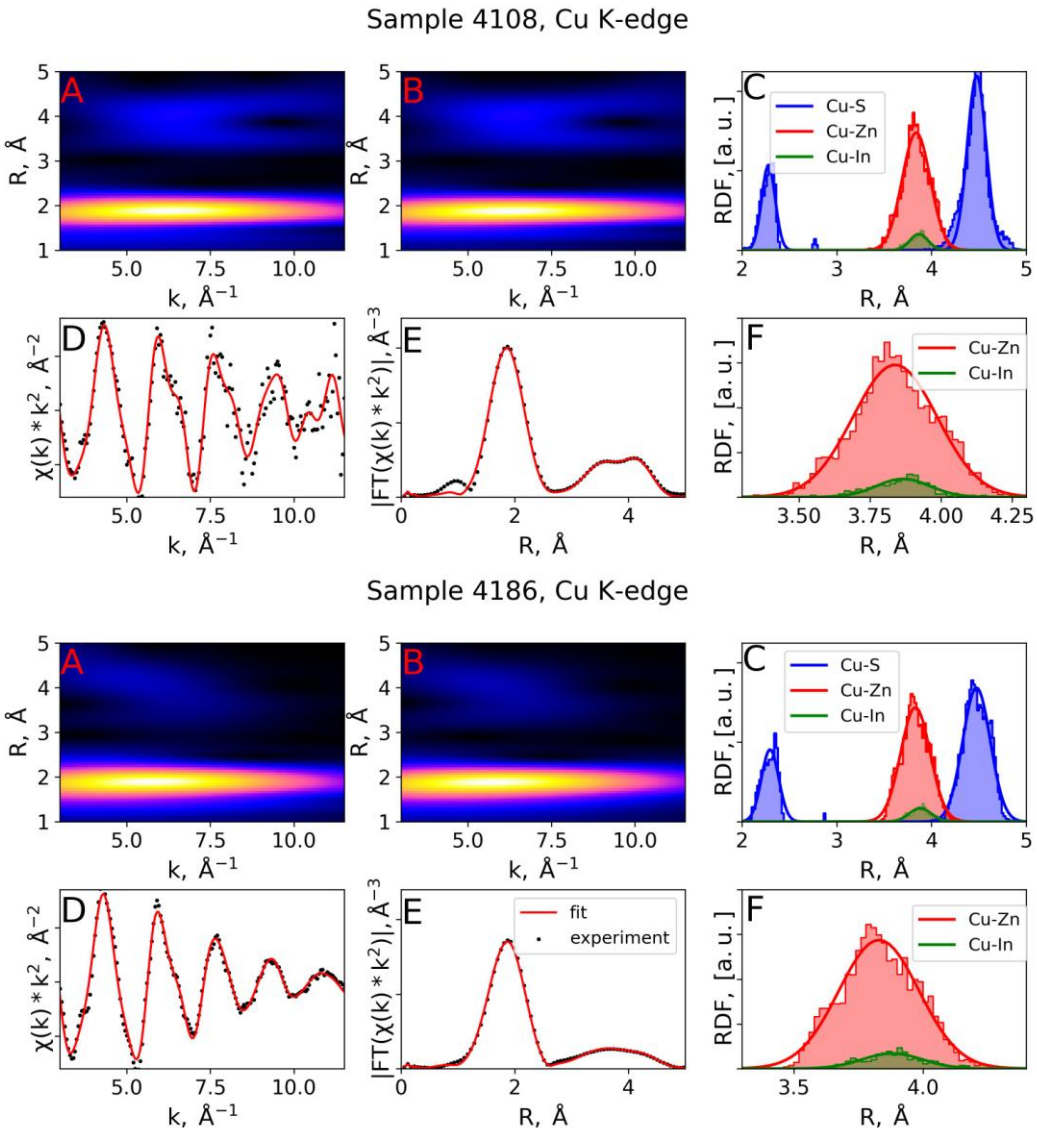

Figure S2. The RMC fit results of Cu *K*-edge EXAFS spectra of samples 4108 and 4186 (the 2nd coordination shell of Cu is described by Zn+In atoms). Panel A: experimental WT image; panel B: fitted WT image; panel C: calculated RDF for first three coordination shells around absorbing atom; panel D: experimental (black dotted line) and fitted (red solid line) EXAFS signal $\chi(k)*k^2$; panel E: Fourier transform magnitudes of experimental (black dotted line) and fitted (red solid line) $\chi(k)*k^2$ function; panel F: close view of Cu-Zn and Cu-In RDF. The RDFs fitted by Gaussians are shown by solid lines..

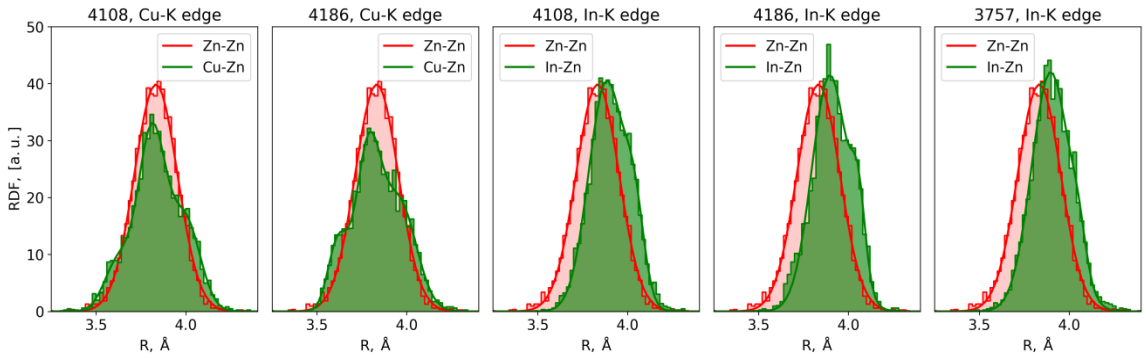

Figure S3. Comparison of Cu-Zn and In-Zn RDFs with Zn-Zn RDF derived from RMC EXAFS fits. The model assumes In atoms in the 2nd coordination shell of In and Cu.

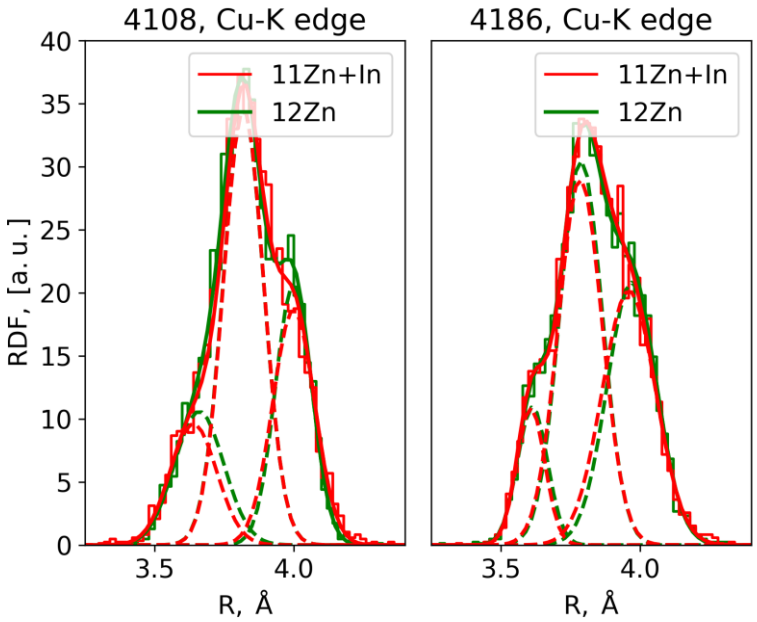

Figure S4. Comparison of Cu-Zn and Cu-(Zn+In) RDFs for Cu *K*-edge EXAFS fitting with and without In in the 2nd coordination shell of Cu. Note that the shapes of the curves representing the two models (11Zn+In and 12 Zn) are very close to each other which means that incorporation of In atom in the 2nd sphere of Cu is not necessary for the accurate approximation of the experimental data.

References

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