Supplementary Material to

Substitution mechanisms in In, Au, and Cu-bearing sphalerites studied by X-ray absorption spectroscopy of synthetic and natural minerals

O.N. Filimonova, A.L. Trigub, D.E. Tonkacheev, M.S. Nickolsky, K.O. Kvashnina,

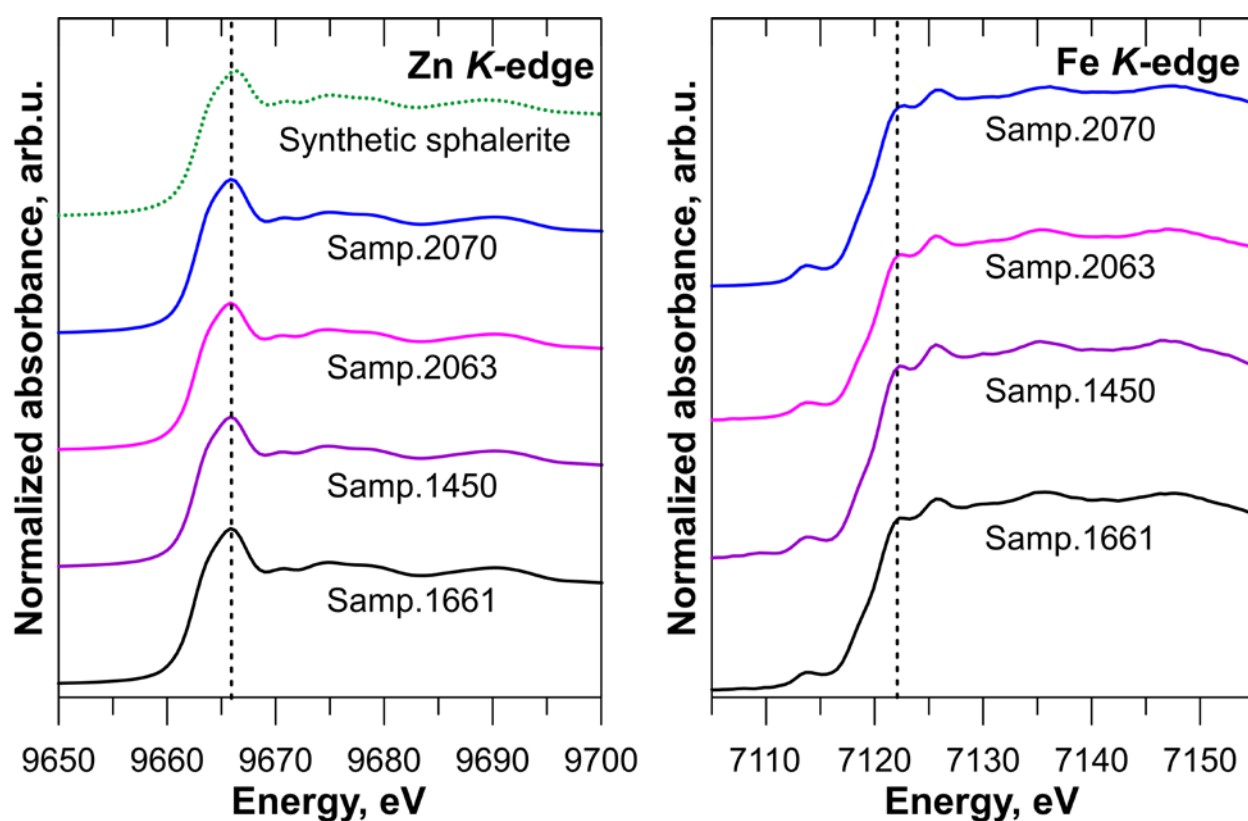D.A. Chareev, I.V. Chaplygin, E.V. Kovalchuk, S. Lafuerza, and B.R. Tagirov

Figure S1. *Left*: Zn K-edge XANES spectra of In-Au-bearing sphalerites and pure synthetic sphalerite ZnS. *Right*: Fe K-edge XANES spectra In-Au-bearing sphalerites. Vertical dashed lines indicate positions of the white line.
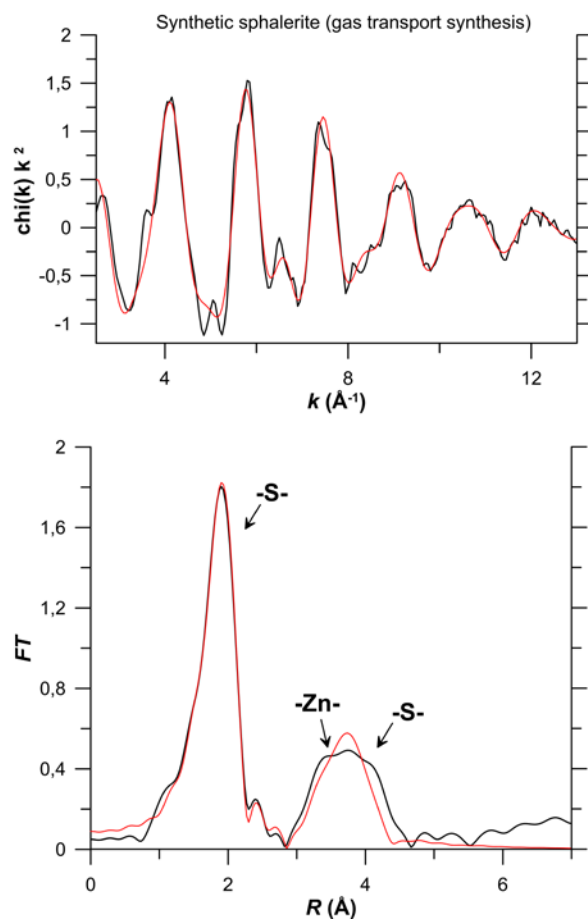
Figure S2. Zn K-edge EXAFS spectra of pure synthetic sphalerite, and In-Au-bearing sphalerites. *Top*: k^2-weighted background-subtracted EXAFS spectra, *Bottom*: Fourier transforms (FT) of the k^2-weighted EXAFS spectra (not corrected for phase shift). Black lines – experiment, red lines – fit results. Scattering atoms are indicated near FT peaks. Fit results are listed in Table 3.
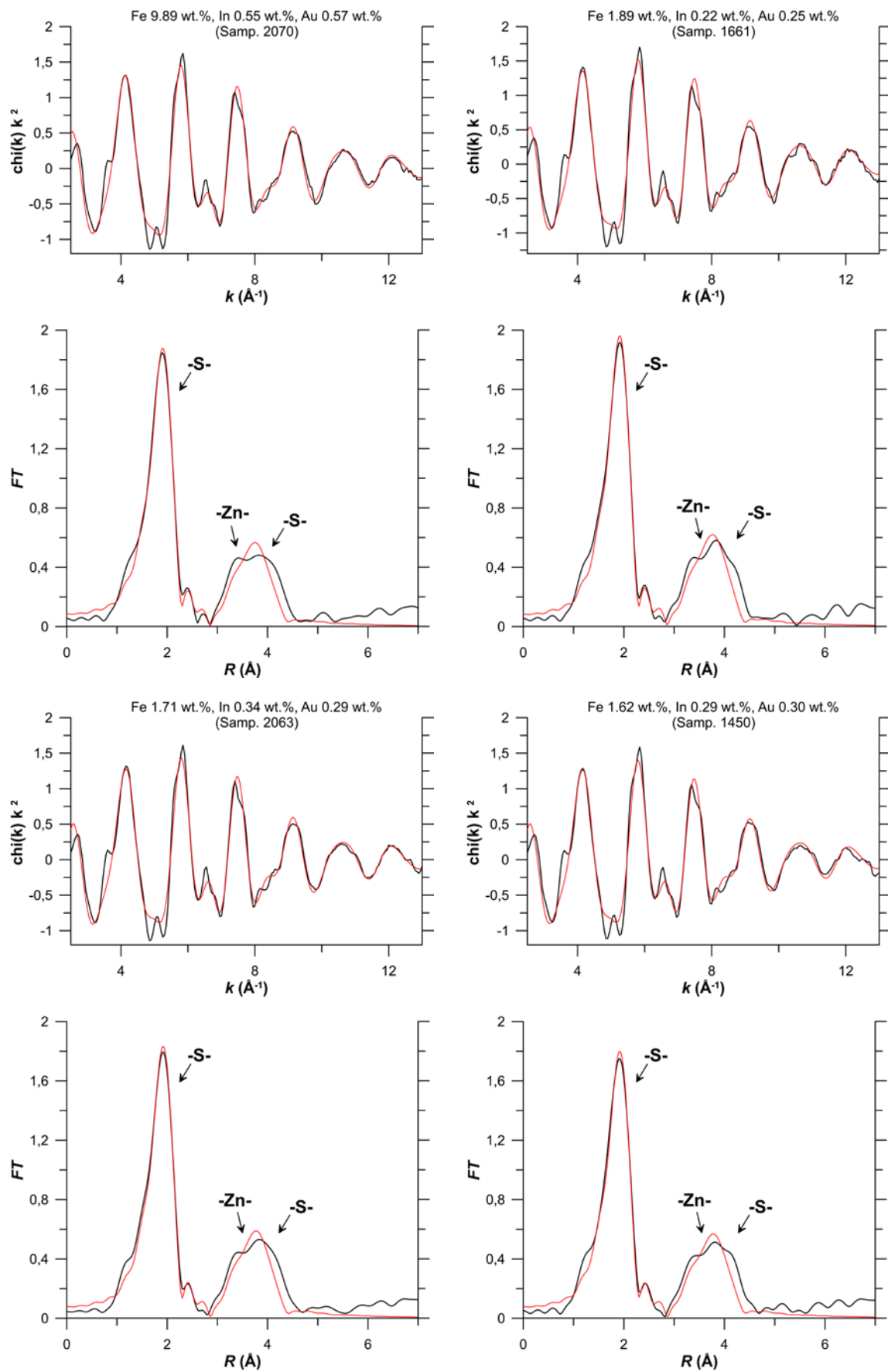
Fe 9.89 wt.%, In 0.55 wt.%, Au 0.57 wt.%
(Samp. 2070)

Fe 1.89 wt.%, In 0.22 wt.%, Au 0.25 wt.%
(Samp. 1661)

Fe 1.71 wt.%, In 0.34 wt.%, Au 0.29 wt.%
(Samp. 2063)

Fe 1.62 wt.%, In 0.29 wt.%, Au 0.30 wt.%
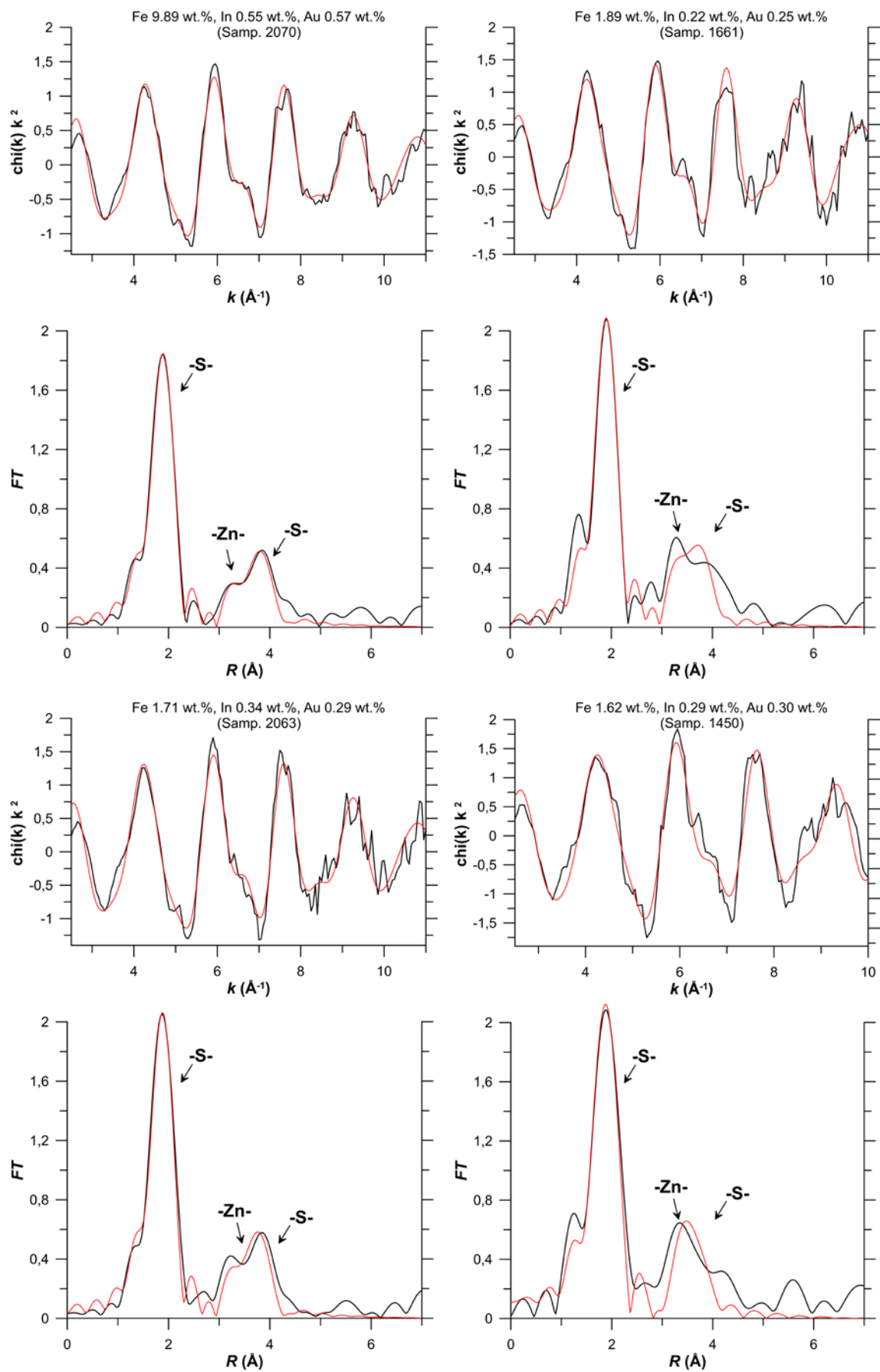(Samp. 1450)

Figure S2 - continued

Figure S3. Fe K-edge EXAFS spectra of In-Au-bearing sphalerites (see Fig. S2 for explanation).

Table S1. Calculated Bader partial atomic charges for pure and doped ZnS. Data for Au_2S from Trigub et al. (2017) are shown for comparison. For Au-In- and Cu-In-bearing sphalerites atomic charges given for Zn and S correspond to atoms which charges exhibit the most pronounced difference from the charges of the atoms in the pure sphalerite.

Au(Cu)	In	Zn	S
ZnS			
		+0.92	-0.92
InS			
+0.88			-0.88
In$_2$S$_3$			
+0.74			-0.89
+0.95			
Au in Au$_2$S[1]			
+0.21			-0.42
Au in ZnS (nearest atoms to Au)			
+0.17		+0.92	-0.84
In in ZnS (nearest atoms to In)			
	+1.24	+0.92	-0.91
In and Au in ZnS (In and Au atoms are located in neighboring cites)			
+0.16	+1.28	+0.92	-0.83
In and Au in ZnS (In and Au atoms are located far from each other)			
+0.17	+1.27	+0.92	-0.84
In and Cu in ZnS (In and Cu atoms are located in neighboring cites)			
+0.52	+1.27	+0.91	-0.88
In and Cu in ZnS (In and Cu atoms are located far from each other)			
+0.52	+1.28	+0.91	-0.90
[1] calculated for Au$_2$S structure relaxed with DFT method, optimized lattice constant $a = 5.35$ Å, Au-S distance $R = 2.32$ Å.			