

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

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The coupled chemistry of In and Au in sphalerites studied by X-ray absorption spectroscopy of synthetic crystals

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Abstract:	<p>Processing of Zn ore accounts for >95% of production of In - a "critical" metal which is widely used in the high-tech electronics. The main source of In is sphalerite (Zn, Fe)S which also can host industrial concentrations of Au. Here we use X-ray absorption spectroscopy to investigate the coupled chemistry of In and Au in synthetic sphalerite crystals - analogues of natural minerals. The concentrations of In and Au were found to correlate with each other and reached 0.5 wt% in crystals synthesized at 850 °C. Both metals are homogeneously distributed within the sphalerite matrix. However, their positions within the mineral are different. In accord with X-ray absorption near edge structure (XANES) spectroscopy the formal oxidation state of these elements is +3 (In) and +1 (Au). Analysis of extended X-ray absorption fine structure (EXAFS) spectra revealed that In replaces Zn in the structure of sphalerite. The In-ligand distance increases by 0.12 Å and 0.09-0.10 Å for the 1st and 2nd coordination spheres, respectively, in comparison with pure ZnS. The In-S distance in the 3rd coordination sphere is close to the one of pure sphalerite. The In K-edge and Au L3-edge XANES and EXAFS spectra suggest that there is no In-Au clustering. Gold in sphalerite is</p>				

coordinated with 2.5 ± 0.3 S atoms at Au-S distance of 2.35 ± 0.01 Å in the 1st coordination sphere, whereas distant coordination spheres have disordered nature. Our data suggest that at least two different forms of Au are present in sphalerite. At high Au concentrations (0.03-0.5 wt%) the nanosized Au₂S clusters predominate, probably with small admixture of the Au solid solution characterized by higher Au-S distance. Alike Au, the other 1st group metals (Me) Cu and Ag, which often are present in high (tenths ppm to wt%) concentrations in sphalerite, can form nanosized Me-S clusters with only traces (ppm level) of metal in the solid solution state.

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1 **The coupled chemistry of In and Au in sphalerites studied by X-ray absorption**
2 **spectroscopy of synthetic crystals**

3

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41

42

43

44 **Abstract**

45 Processing of Zn ore accounts for >95% of production of In – a “critical” metal which is widely
46 used in the high-tech electronics. The main source of In is sphalerite (Zn, Fe)S which also can
47 host industrial concentrations of Au. Here we use X-ray absorption spectroscopy to investigate
48 the coupled chemistry of In and Au in synthetic sphalerite crystals - analogues of natural
49 minerals. The concentrations of In and Au were found to correlate with each other and reached
50 0.5 wt% in crystals synthesized at 850 °C. Both metals are homogeneously distributed within the
51 sphalerite matrix. However, their positions within the mineral are different. In accord with X-ray
52 absorption near edge structure (XANES) spectroscopy the formal oxidation state of these
53 elements is +3 (In) and +1 (Au). Analysis of extended X-ray absorption fine structure (EXAFS)
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57 pure sphalerite. The In K-edge and Au L₃-edge XANES and EXAFS spectra suggest that there is
58 no In-Au clustering. Gold in sphalerite is coordinated with 2.5±0.3 S atoms at Au-S distance of
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60 nature. Our data suggest that at least two different forms of Au are present in sphalerite. At high
61 Au concentrations (0.03-0.5 wt%) the nanosized Au₂S clusters predominate, probably with small
62 admixture of the Au solid solution characterized by higher Au-S distance. Alike Au, the other 1st
63 group metals (Me) Cu and Ag, which often are present in high (tenths ppm to wt%)
64 concentrations in sphalerite, can form nanosized Me-S clusters with only traces (ppm level) of
65 metal in the solid solution state.

66

67 **Keywords:** Indium; gold; trace elements; sphalerite; synthetic minerals; HERFD-XAS; EXAFS

68 **Introduction**

69 Indium is a critical metal which is of high demand in high-tech industries. It is used
70 worldwide for the production of flat-panel displays and touchscreens, in the manufacturing of
71 photovoltaic cells, fiber-optics, and has some other important industrial applications (Mercer
72 2015). The global primary production of In increased almost twofold during 2001-2011, and
73 totaled 759 t in 2015 and 655 t in 2016 (Tolchin 2017). The concentration of In in natural
74 environments is low and, therefore, In minerals are rare. Instead, it is concentrated in the
75 principal sulfide ore-forming minerals among which sphalerite (Zn, Fe)S is the most important
76 (Schwartz-Schampera 2015). The In content in sphalerite usually falls within 0.1-100 ppm range,
77 but can reach several wt% in minerals formed at high temperatures (400 - 725 °C) in volcanic
78 fumaroles (Chaplygin et al. 2007). Often the concentration of In is directly correlated with
79 concentration of Cu which implies the formation of solid solution by the coupled substitution
80 mechanism $2\text{Zn}^{2+} \leftrightarrow \text{Cu}^+ + \text{In}^{3+}$ (Chaplygin et al. 2007; Cook et al. 2009).

81 Indium is recovered as a byproduct of mining and refinement of Zn ore. The most
82 significant sources of In are sulfide Zn- and Zn-Cu ores of volcanogenic base metal-sulfide
83 (VMS) deposits (Mercer 2015; Schwartz-Schampera 2015). Many of these deposits and their
84 modern analogues – ores of submarine hydrothermal fields, are Au-rich (Bortnikov et al. 2003;
85 Melekestseva et al. 2017). Some VMS deposits belong to world-class gold mines with more than
86 100 t Au (e.g., Mercier-Langevin et al. 2011; Vikentyev et al. 2004, 2015). Determination of Au
87 concentration in submarine polymetallic sulfide ore from the Valu Fa Ridge (the Lau basin,
88 south-west Pacific) showed that the Au-bearing assemblages are dominated by Fe-poor
89 sphalerite (Herzig et al. 1993). Gold is present in sphalerites of VMS deposits of the Urals in
90 concentrations from n to $n \cdot 10$ ppm (Vikentyev 2015). Particles of Au were often observed on the
91 grains of In-bearing sphalerite and wurtzite crystals deposited in the fumarolic system of
92 Kudriavy volcano (Iturup Island, Russia, Chaplygin et al. 2007). Thus, both In and Au are
93 closely associated in natural environments and can be extracted as byproduct commodities from
94 sphalerite-bearing sulfide ores.

95 Investigation of spectroscopic properties of pure and doped ZnS, as well as the chemical
96 speciation of the impurities (dopants), is mostly driven by useful technical applications of these
97 materials (see, for example, Inorganic phosphors: composition, preparation, and optical
98 properties 2004). Recently, doped semiconductor nanocrystals (quantum dots) have drawn
99 significant attention due to their unique electronic and optical properties (Norris et al. 2008).
100 Apple and Williams (1959) and Koelmans (1960) synthesized and studied ZnS phosphors
101 activated with In and first-group metals (Ag, Cu). It was suggested that the formation of In-

102 bearing hexagonal ZnS (wurtzite) takes place by the charge compensation mechanism which
103 corresponds to the replacement of 3 Zn²⁺ ions by 2 In³⁺ ions and the formation of one Zn
104 vacancy (Koelmans 1960). Incorporation of In resulted in substantial increase of the ZnS lattice
105 constants which confirmed the solid solution formation. However, slow cooling from the
106 synthesis temperature or reheating to $t > 600$ °C killed fluorescence of the material. The lattice
107 spacings of these samples were found to be equal to those of pure ZnS. Association of charged
108 In³⁺ ion and negatively charged Zn²⁺ vacancy was suggested to be responsible for the emission
109 drop and the lattice constants decrease. Therefore, the suggested charge compensation scheme
110 seems to be pertinent only when In-bearing ZnS is rapidly quenched from the formation
111 (synthesis) temperature, whereas slow cooling or reheating (metamorphism) of natural ores can
112 result in redistribution of charges. Note that the coupled In-Cu substitution is not the necessary
113 condition for the formation of In-bearing sphalerites because both Cu- and In-bearing ZnS
114 materials were synthesized separately for technical applications.

115 The atomic and electronic structures of synthetic sphalerites doped with Mn, Fe, Co, and
116 Ni were studied using X-ray absorption spectroscopy (XAS) in Ławniczak-Jabłońska et al.
117 (1994, 1995, 1996) and Iwanowski et al. (1996, 1997, 1998). The authors showed that these
118 impurities are incorporated into the cationic position of the sphalerite lattice, evaluated the Me-S
119 distances in the doped sulfide, and calculated tetrahedral covalent radii of the dopants. Patrick et
120 al. (1998) studied local atomic structure of sphalerites doped with Mn, Cu/In, and Cd. The
121 concentration of CuInS₂ in synthesized sphalerites was 8-20 at%. It was found that these metals
122 are incorporated into the sphalerite cationic sublattice, and the S tetrahedra around the dopant are
123 compressed for Cu and expanded for In and other dopants. Besides, the authors determined that
124 In/In and Cu/In clustering occurs at these high concentrations of dopants (note that much lower
125 admixture concentrations are pertinent for natural sphalerites).

126 The solid solution model for Cu was not, however, confirmed in more recent XAS
127 studies of doped materials with lower Cu content. The local atomic structure of ZnS phosphors
128 doped with Cu and Mn was studied by extended X-ray absorption fine structure (EXAFS)
129 spectroscopy in Warkentin et al. (2007). An important issue of this study is that Mn substitutes
130 for Zn in cubic ZnS lattice, whereas Cu is present in the ZnS matrix mainly in the form of
131 nanosized CuS clusters with only small fraction of Cu substituting for Zn. Based on the EXAFS
132 data analysis, the CuS nanocrystallites are suggested to be integrated into the ZnS matrix and “do
133 not have a completely random orientation, i.e. there is not an amorphous layer between the CuS-
134 like nanocrystallites and the host crystal” (Warkentin et al. 2007). The formation of CuS
135 nanosized precipitates in the ZnS matrix was confirmed by EXAFS study of Cu-doped ZnS
136 nanoclusters reported in Corrado et al. (2009). The XAS studies of trace elements (Ge, Cu, Mn)

137 in natural sphalerites are limited to the X-ray near edge structure (XANES) spectra because of
138 small grain size, their zonal character, and low concentration of the admixtures (Cook et al. 2015,
139 Bonnet et al. 2016, 2017).

140 Recently we found that the concentration of Au in sphalerite increases with increasing In
141 content (Tonkacheev et al. 2015). In the present study, in order to determine the speciation of In
142 and Au in sphalerite, we introduced these impurities into synthetic pure and Fe-bearing
143 sphalerites and studied the synthesized crystals by means of XAS. The use of synthetic crystals
144 with elevated concentrations of admixtures made possible to acquire not only XANES spectra,
145 but to obtain good quality EXAFS and, as a result, unambiguously determine the local atomic
146 environment of In and Au. An important advantage of the use of Au – the heaviest 1st group
147 stable atom, is that in the case of In-Au clustering the contribution of this atom to the In K-edge
148 EXAFS can be recognized by the spectra analysis in contrast to light atom of Cu, which can not
149 be discriminated from Zn or Fe. For Au the High energy resolution fluorescence detection mode
150 was employed (HERFD-XAS, Glatzel and Bergman 2005). The measurement of HERFD-
151 XANES spectra allowed observation of important spectral features not manifested in total
152 fluorescence yield (TFY) detection (Tagirov et al. 2016; Trigub et al. 2017). Our experimental
153 results demonstrate that in sphalerite In exists in the solid solution state, whereas Au, despite
154 homogeneous distribution and possibility of charge compensation substitution, mostly forms
155 nanosized Au₂S clusters with only small fraction of the Au solid solution.

156

157 **Experimental**

158 **Methods of synthesis**

159 The crystal growth experiments were performed as described in Chareev et al. (2017)
160 using i) gas transport method, and ii) salt flux technique (KCl/NaCl eutectic mixture, Chareev
161 2016, Chareev et al. 2016). In gas transport method NH₄Cl was used as a transport agent. The
162 initial phases (~ 0.5 g of ZnS – wurtzite, with 3-5 wt% FeS), and, if necessary, several
163 milligrams of MnS, CdS, ZnSe, and In₂S₃ were powdered and loaded into a silica glass
164 ampoule (8 mm ID, 11 mm OD, ~110 mm length) together with Au wire and either ~ 5 mg of
165 transport agent or salt flux which filled the rest of the ampoule volume. The loaded ampoules
166 were evacuated, sealed, and placed into a horizontal tube furnace which was then heated to
167 the synthesis temperature over a period of 2-3 hours, and then kept at this temperature during
168 20-30 days. The temperature gradient in the furnace was 50-100 °C, and the measured
169 temperature at the hot end of the ampoules was 850 °C. At the end of the experiment the
170 ampoules were quenched in cold water. Sphalerite crystals precipitated at the cold end.

171 Gold sulfide Au₂S_(cr) was synthesized by sulfidizing aqueous Au cyanide solution at

172 ambient temperature as described in Tagirov et al. (2006).

173

174 **Analytical methods**

175 Morphology of the synthesized minerals was checked using scanning electron
176 microscopy (SEM), phase composition was obtained by means of X-ray diffraction (XRD),
177 chemical composition was determined with electron probe micro-analysis (EPMA) and laser
178 ablation inductively coupled mass spectrometry (LA-ICP-MS). The JSM-5610LV microscope
179 equipped with INCA-450 energy dispersive spectrometer was used for SEM studies. EPMA
180 analyses were performed using JEOL JXA-8200 WD/ED combined electron probe
181 microanalyzer equipped with 5 wavelength dispersive X-ray spectrometers. For major elements
182 (Cu, Fe, S) the operating conditions were 20 kV accelerating voltage, 20 nA beam current, with a
183 counting time of 10 s. Zinc, Fe, and S were determined using K_{α} lines with LiF (for Zn, Fe) and
184 PETH (for S) crystals. Chalcopyrite $CuFeS_2$ (for Fe) and pure sphalerite ZnS (for Zn and S) were
185 used as the calibration reference materials. Indium was determined using L_{α} line and PETH
186 crystal with 20 kV accelerating voltage and 20 nA beam current, counting time of 10 s. The InSb
187 was used as a reference material. The concentration of Au was determined using LiF crystal
188 accounting for the background dip immediately adjacent to the Au L_{α} line from the short-
189 wavelength side (Self et al., 1990). Limit of detection (2σ) for Au was 0.01 wt% at 100 nA beam
190 current and counting time of 100 s.

191 Concentrations of ^{197}Au and ^{113}In isotopes in the synthesized sphalerite crystals, and the
192 distribution modes (homogeneous/inhomogeneous) of Au and In were checked using LA-ICP-
193 MS. The New Wave 213 laser coupled with the Thermo X Series2 quadrupole ICP-MS was
194 used. The laser frequency was 10 Hz with the power of 6-8 J/cm² and beam size of 40-60 μm .
195 The analysis was carried out during 30 s preceded by 20 s for the gas blank. The ablation was
196 performed in He + 6% H₂ (0.6 L/min) atmosphere. The gas carrying ablated material to the ICP-
197 mass spectrometer was mixed with Ar (0.8 L/min). Sulfide reference material MASS-1 (Wilson
198 et al. 2002) was used as an external calibration standard for both In and Au together with in-
199 house pyrrhotite $Fe_{0.9}S$ (18 ppm Au, synthesized using method from Wohlgemuth-Ueberwasser
200 et al. (2007) and calibrated at the Université Québec à Chicoutimi (UQAC) with respect to
201 concentration of Au against standard prepared by J.H.G. Laflamme). Isotopes ^{68}Zn or ^{33}S were
202 used as internal standards. Detection limit for Au (2σ) was 0.1 ppm. Scan speed of 5 $\mu m/s$ was
203 used for analyses along lines.

204

205 **X-ray absorption spectroscopy**

206 X-ray absorption experiments were performed at the European Synchrotron Radiation
207 Facility (ESRF) in Grenoble, France; and Kurchatov Synchrotron Radiation Source (KSRS) in
208 Moscow, Russia.

209 The Au L₃-edge spectra were collected at the high-brilliance X-ray absorption/X-ray
210 emission spectroscopy undulator beamline ID26 (Gauthier et al. 1998) of the ESRF. The storage-
211 ring operating conditions were 6.0 GeV and the ring current was varied between 150 and 200
212 mA. The incident energy was selected using the <111> reflection from a double Si crystal
213 monochromator. Rejection of higher harmonics was achieved by three Pd mirrors positioned at
214 an angle of 2.5 mrad relative to the incident beam. The incident X-ray beam had a flux of
215 approximately $2 \cdot 10^{13}$ photons s⁻¹ on sample position. The spectra were measured in high energy
216 resolution fluorescence detection (HERFD) mode using an X-ray emission spectrometer (Glatzel
217 and Bergman 2005; Kvashnina and Scheinost 2016). The sample, analyzer crystal and photon
218 detector (silicon drift diode) were arranged in a vertical Rowland geometry. The Au L₃-edge
219 HERFD-XAS spectra were obtained by recording the intensity of the Au L_{α1} emission line (9713
220 eV) as a function of the incident energy. The emission energy was selected using the <555>
221 reflection of four spherically bent Ge crystal analyzers (1 m curvature radius) aligned at 78°
222 Bragg angle. A combined (incident convoluted with emitted) energy resolution of 1.5 eV was
223 determined as the full width at half maximum of the elastic peak. The intensity was normalized
224 to the incident flux.

225 The In K-edge spectra were recorded at the Rossendorf Beamline BM20 of the ESRF.
226 The storage-ring operating conditions were 6.0 GeV and 80-100 mA. The photon energy was
227 scanned from 27700 to 28570 eV using the Si(111) monochromator coupled to Rh-coated
228 mirrors for the collimation and reduction of higher harmonics. Energy calibration was performed
229 using the K-edge excitation energy of In metal foil (27940 eV). The spectra for reference
230 substances were collected in transmission mode while for sphalerite samples the spectra were
231 recorded in total fluorescence yield (TFY) mode using 13-element high-throughput Ge-detector.
232 The total energy resolution (incident energy and core – hole lifetime broadening) has been
233 evaluated as 8.8 eV. The detected intensity was normalized to the incident photon flux.

234 The Zn and Fe K-edge spectra were measured at the Structural Materials Science station
235 (Chernyshov et al. 2009) of the KSRS. The storage-ring operating conditions were 2.3 GeV and
236 80-100 mA. A Si(111) monochromator was used and the energy calibration was performed using
237 the K-edge absorption energy of Zn and Fe foils. The X-ray absorption spectra of Zn were
238 registered in transmission mode and the spectra of Fe in fluorescence mode using an avalanche
239 photodiode (FMB OXFORD).

240

241 EXAFS spectra fitting

242 The EXAFS ($\chi_{exp}(k)$) data were analyzed using IFEFFIT package (Ravel and Newville
243 2005). Following standard procedures for pre-edge subtraction and spline background removal, the
244 structural parameters - interatomic distances (R_i), coordination numbers (N_i), and Debye–Waller
245 factors (σ_i^2) - were determined via the non-linear fit of theoretical spectra to the experimental ones
246 with the equation

$$247 \quad \chi(k) = S_0^2 \sum_{i=1}^n \frac{N_i F_i(k)}{R_i^2 k} e^{\frac{-2R_i}{\lambda(k)}} e^{-2\sigma_i^2 k^2} \sin(2kR_i + \varphi_i(k)) \quad . \quad (1)$$

248 Theoretical spectra were simulated using photoelectron mean free path $\lambda(k)$, amplitude $F_i(k)$, and
249 phase shift $\varphi_i(k)$ parameters calculated *ab initio* using the program FEFF6 (Zabinsky et al. 1995).

250 In addition, the Au L₃-edge spectra were fit with the aid of Reverse Monte Carlo (RMC)
251 method. The advantage of this method in comparison with the ARTEMIS program (a part of
252 IFEFFIT software package) is that it allows one to perform accurate analysis of EXAFS data
253 from distant coordination spheres, taking into account both multiple-scattering and disorder
254 (thermal and static) effects (e.g., Rossberg and Scheinost 2005; Timoshenko et al. 2012, 2017).
255 In this case the atomic structure of a material is generated through random displacements of
256 atoms in order to minimize the difference between experimental and theoretically calculated
257 EXAFS spectra. EXAFS spectrum of every random atomic configuration was calculated using
258 *ab initio* real-space multiple-scattering code FEFF8.5L (Ankudinov et al. 1998). To fit the
259 experimental spectra the least square minimization of difference between calculated and
260 experimental $\chi(k) \cdot k^2$ values was performed. These data allow calculation of the radial density
261 $\rho(R)$ of surrounding atoms which is related to coordination numbers N via expression

$$262 \quad N(R) = \int_0^R 4\pi r^2 \rho(R) dr \quad . \quad (2)$$

263

264 Results and discussion

265 Concentration and distribution of In and Au

266 As a result of the synthesis experiments aggregates of crystals with grain size $n \cdot 0.1 - 1$
267 mm were obtained (an example of the synthesis product is shown in Fig. 1). The XRD pattern of
268 synthesized samples corresponded to pure sphalerite phase PDF#5-566. Chemical composition
269 of crystals is listed in Table 1. High-temperature sphalerites synthesized at 850 °C incorporated
270 extremely high (up to 0.5 wt%) concentrations of both In and Au. Both In and Au were found to
271 be dispersed in the state “invisible” by optical and electron microscopies. The concentrations of
272 these admixtures in the synthesized crystals are close to each other and directly correlated.

273 Homogeneous In and Au distribution patterns are confirmed by small scatter of measured
274 concentrations (see uncertainties of measured concentrations given in Table 1) and smooth
275 character of LA-ICP-MS time-resolved spectra (Fig. 2).

276

277 **XANES spectroscopy**

278 The In K-edge XANES and Au L₃-edge HERFD-XANES spectra of sphalerite samples
279 are compared to the reference substances in Fig. 3, and energy positions of the edge jump (e.j.)
280 and the first intense feature known as white line (WL) are listed in Table 2.

281

282 *In K-edge*

283 For all In-bearing sphalerites the e.j. and WL positions of In K-edge spectra are identical
284 independently of the concentration of In, Fe, and Au. This means that the concentration of Fe,
285 Au, and In itself, has negligible effect on the chemical state (local atomic environment and the
286 valence state) of In. At the same time, the e.j. and WL positions are different from those of the
287 In₂O₃ and In₂S₃: they are shifted by 0.7-1 eV to lower energies in comparison with In₂O₃, and, on
288 the contrary, by ~1 eV to higher energies compared to In₂S₃ (Table 2). Accordingly, the chemical
289 state of indium in sphalerite is different from oxide and sulfide.

290 We may interpret the observed e.j. energy position in the sphalerites by saying that the
291 oxidation state of In is intermediate between In₂O₃ and In₂S₃; however, the formal oxidation state
292 of In in sphalerite is +3. The higher energy of the e.j. position in In-bearing sphalerite in
293 comparison with In₂S₃ can be ascribed to stronger In-S interaction in the state of the solid
294 solution, which results in a more effective negative charge transfer from In to S. The latter would
295 result in a shorter In-S distance in In-bearing sphalerite compared to In₂S₃. Additional reason in
296 favor of the compression of the 1st coordination sphere is that the minima of the XANES spectra,
297 which separates WL and the 2nd spectral feature, is located at much higher energy of ~27980 eV
298 for In-bearing sphalerite than for In₂S₃ (~27972 eV).

299

300 *Au L₃-edge*

301 The Au L₃-edge HERFD-XANES spectra of sphalerites differ from the spectra of Au and
302 Au₂S. The e.j. and WL positions are shifted to higher energies compared to the Au₂S spectra.
303 Position of the second spectral feature also exhibits large positive shift by ~3 eV. The low WL
304 intensity in comparison with Au³⁺ state (e.g., Tagirov et al. 2016) suggests that the formal
305 oxidation state of Au is +1. The shape of the WL feature of sphalerite spectra, unlike Au₂S, is
306 highly asymmetric which can be explained by the presence of several different geometries of the
307 local atomic environment of Au. At the same time, the shape and positions of the spectral

308 features are identical for In-rich and In-free sphalerites, which suggests the absence of In/Au
309 clustering. This important conclusion will be checked via EXAFS spectra analysis.

310

311 **EXAFS spectra fitting**

312 Results of EXAFS spectra fitting obtained using IFEFFIT software package (ARTEMIS
313 program) for Zn, Fe, In K-edges, and for Au L₃-edge are collected in Table 3 and compared with
314 the experimental spectra in Fig. 4a (In K-edge) and 4b (Au L₃-edge). The results of Au L₃-edge
315 RMC fits are shown in Fig. 5.

316

317 *Fe, Zn K-edges*

318 The local atomic structures around Zn and Fe (coordination numbers and interatomic
319 distances) are identical within the uncertainty of the experimental data, and correspond to pure
320 sphalerite (Zn, Fe)S (top of Table 3). Admixtures of In and Au have no effect on the interatomic
321 distances between Zn/Fe and surrounding atoms.

322

323 *In K-edge*

324 For In-bearing sphalerites, the best fit of the experimental spectra is achieved when Au
325 substitutes Zn in the sphalerite lattice. In the structure of sphalerite a cation is tetrahedrally
326 coordinated by S atoms; the 2nd coordination sphere consists of 12 Zn atoms, and the 3rd
327 coordination sphere contains 12 S atoms. Preliminary fits of the experimental spectra were
328 performed with calculation of the coordination numbers of atoms in the 2nd and 3rd coordination
329 spheres. The calculated values of *N* fell within the range of 10-19, but the uncertainty of the
330 values was quite large. Therefore, during the final fits these values were fixed in accord with the
331 sphalerite structure parameters (*N* = 12).

332 Data of Table 3 indicate that the In-S distance increased by 0.12 Å with respect to the
333 crystal structure of pure sphalerite in the 1st coordination sphere, by 0.09-0.1 Å for Zn atoms in
334 the 2nd sphere, whereas the In-S distance for the 3^d coordination sphere is close to that of pure
335 ZnS or even slightly decreased (by 0.01 – 0.03 Å which is, however, within the uncertainty of
336 the calculated values). Thus, our data demonstrate that the distortion of the sphalerite crystal
337 structure, caused by the replacement of Zn with In, decreases for distant coordination spheres
338 and disappears at *R* > 4.6 Å. The admixture of Fe in sphalerite (up to 10 wt%) does not change
339 the structural parameters of In. This conclusion is in line with the fact that In K-edge XANES
340 spectra are similar for pure and Fe-bearing sphalerites.

341 Despite high Au concentrations, we did not observe a contribution of this heavy atom to
342 In K-edge EXAFS spectra up to the 3rd coordination sphere. Therefore, the In-Au clustering is

343 not necessary for the formation of In solid solution in sphalerite. Generalizing these results to all
344 the 1st group metals one can say that the charge compensation coupled substitution scheme $2Zn^{2+}$
345 $= (Cu, Ag, Au)^{1+} + In^{3+}$ (e.g., Chaplygin et al. 2007; Cook et al. 2009) takes place without
346 formation of the roquesite $CuInS_2$ or laforetite $AgInS_2$ components in solid solution. This means
347 that In and the 1st group metals are statistically (randomly) distributed within the sphalerite
348 matrix.

349

350 *Au L₃-edge*

351 In sphalerite the nearest neighbors around Au are S atoms with $N_S \sim 2.5$. The Au-S
352 distance of 2.35 Å is higher than in Au_2S where Au is linearly coordinated with S atoms ($N = 2$,
353 $R_{Au-S} = 2.30$ Å, Table 3 and Fig. 4b). In contrast to In, for which the structural parameters can be
354 obtained up to 3rd coordination sphere composed by 12 S atoms, the absence of a distinct
355 maxima of the FT for Au L₃-edge EXAFS spectra at $R > 2.5$ Å (Fig. 4b) implies that the second
356 coordination sphere of Au is of disordered nature. The mentioned values of N and R , complex
357 lineshape of HERFD-XANES spectra with broad asymmetric WL (Fig. 3), as well as disordered
358 distant coordination spheres, can be interpreted as the presence of at least two different forms of
359 Au. This suggestion is confirmed by RMC EXAFS fitting where two peaks of radial density of S
360 at ~ 2.3 Å (main feature) and ~ 2.6 Å (weak feature) are present (Fig. 5a,b). Comparing these data
361 with results obtained for Cu-bearing sphalerites (Warkentin et al. 2007) and taking into account
362 similarity of Cu and Au chemical properties, we suggest that these forms can be Au_2S nanosized
363 clusters ($R_{Au-S} \sim 2.3-2.4$ Å) and a small admixture of the Au solid solution ($R_{Au-S} \sim 2.6$ Å). The
364 pronounced increase by ~ 0.25 Å of the Au-S distance for Au solid solution with respect to the
365 Zn-S distance in sphalerite can be explained by large difference in the ionic radii of these metals
366 (0.6 Å for Zn vs 1.37 Å for Au, Shannon 1976). Our data, however, do not allow to determine if
367 the Au_2S nanosized clusters were formed at the synthesis temperature, or they are a quench
368 product formed by the solid solution decomposition. Alike CuS in Cu-bearing sphalerite
369 (Warkentin et al. 2007), the Au_2S clusters can be integrated into the sphalerite host matrix in
370 accord with the crystallographic axes of the sphalerite structure and, by this way, the metastable
371 gold sulfide can be stabilized. An absence of a contribution from heavy In atom in the distant
372 coordination spheres of Au is an additional argument for the absence of the In-Au clustering. We
373 can speculate that at high temperature Au existed mostly in the solid solution state which
374 decomposed upon cooling with the formation of Au_2S nanosized clusters because i) the
375 concentration of Au in sphalerite is proportional to the In content (these elements can form
376 isomorphous solid solution via the charge compensation scheme), and, ii) Au_2S is a metastable
377 phase which decomposes at high temperature (Tagirov et al. 2006). However, the speciation of

378 Au in sphalerite at high temperature can be unambiguously determined only by means of in situ
379 spectroscopic experiment performed for sphalerite heated to the formation (synthesis)
380 temperature.

381

382 **Conclusions**

383 In the present work we synthesized crystals of In and Au-bearing sphalerite (Zn, Fe)S
384 with dopants concentration of 0.03–0.5 wt%. Results of EPMA and LA-ICP-MS chemical
385 analyses showed that both In and Au are homogeneously distributed within the sphalerite matrix.
386 X-ray absorption spectroscopy was applied in order to determine the chemical state (local atomic
387 environment and valence state) of In and Au in synthesized crystals. In accord with XANES
388 spectroscopy these elements are present in sphalerite in +3 (In) and +1 (Au) formal oxidation
389 states. At ambient temperature In is present in sphalerite in the solid solution state where it
390 substitutes for Zn. Analysis of EXAFS spectra shows that the bond length of In increases
391 (relatively to pure ZnS) from 2.34 to 2.46 Å in the 1st coordination sphere where In is
392 tetrahedrally coordinated with S, from 3.83 to 3.92 Å in the 2nd coordination sphere ($N_{Zn} = 12$),
393 and is close to the Me-S distance of the pure sphalerite for the 3^d coordination sphere ($N_S = 12$,
394 $R_{In-S} = 4.46-4.48$ Å). Gold, in contrast to In, is mainly present in the form identified as Au₂S
395 nanosized clusters with $R_{Au-S} = 2.35$ Å, with minor contribution of the second form with $R_{Au-S} \sim$
396 2.6 Å which is attributed to the Au solid solution. The second coordination sphere of Au is of
397 disordered nature. These data, together with information published in the literature for Cu-
398 bearing sphalerites, demonstrate that the admixture of the 1st group elements in sphalerite is not
399 necessarily incorporated in the solid solution state, but rather forms Me-S nanosized clusters
400 when the concentration of these elements exceeds ppm level. Hence, the homogeneous character
401 of a trace element distribution, which is often observed in natural sulfide minerals, is not
402 necessarily accounted for by the solid solution formation. Additional experiments with in situ
403 registration of XAS spectra are necessary in order to determine whether the Me¹⁺-S nanosized
404 clusters were formed at the synthesis temperature, or they represent the decomposition product
405 of the In-Me¹⁺-S solid solution which was formed via the charge compensation mechanism by
406 substitution for Zn in the sphalerite structure.

407

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Figure captions

Figure 1. Optical microscope image of aggregate of sphalerite crystals (Sample 1661). Concentrations of admixtures: 1.9 wt% Fe, 0.22 wt% In, 0.25 wt% Au. FOV 0.3x0.4 mm. Photo by T. Pashko.

Fig. 2. Laser ablation-ICP-MS time-resolved spectra for line analysis across sphalerite grains. Compositions of samples are given in Table 1.

Fig. 3. *Left:* In K-edge XANES spectra of In-Au-bearing sphalerites and model substances (In_2O_3 and In_2S_3). *Right:* Au L_3 -edge HERFD-XANES spectra for Au \pm In-bearing sphalerites and model substances (Au and Au_2S). Vertical dashed lines indicate positions of the most intense spectral features of sphalerite samples.

Fig. 4. In K-edge (a) and Au L_3 -edge (b) EXAFS spectra of In-Au-bearing sphalerites, the Au L_3 -edge spectra of $\text{Au}_2\text{S}_{(\text{cr})}$ is shown for comparison. *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, MS – multiple-scattering contributions. Fit results are listed in Table 3.

Fig. 5. Results of RMC fitting, Au L_3 -edge EXAFS spectra for In-Au-bearing sphalerites: sample 1450 (a) and sample 1661 (b). *Left:* k^2 -weighted background-subtracted EXAFS spectra (points – experimental spectra, red lines – results of RMC fitting); *middle:* Fourier transform of the k^2 -weighted EXAFS spectra (not corrected for phase shift); *right:* radial density distribution (blue lines) and coordination numbers (red lines) of Au. Coordination number during the fits was fixed as 2 in assumption that Au_2S predominates. Asymmetric shape of the radial density curve with the second weak maxima at $R \sim 2.6 \text{ \AA}$ indicates presence of two different forms of Au.

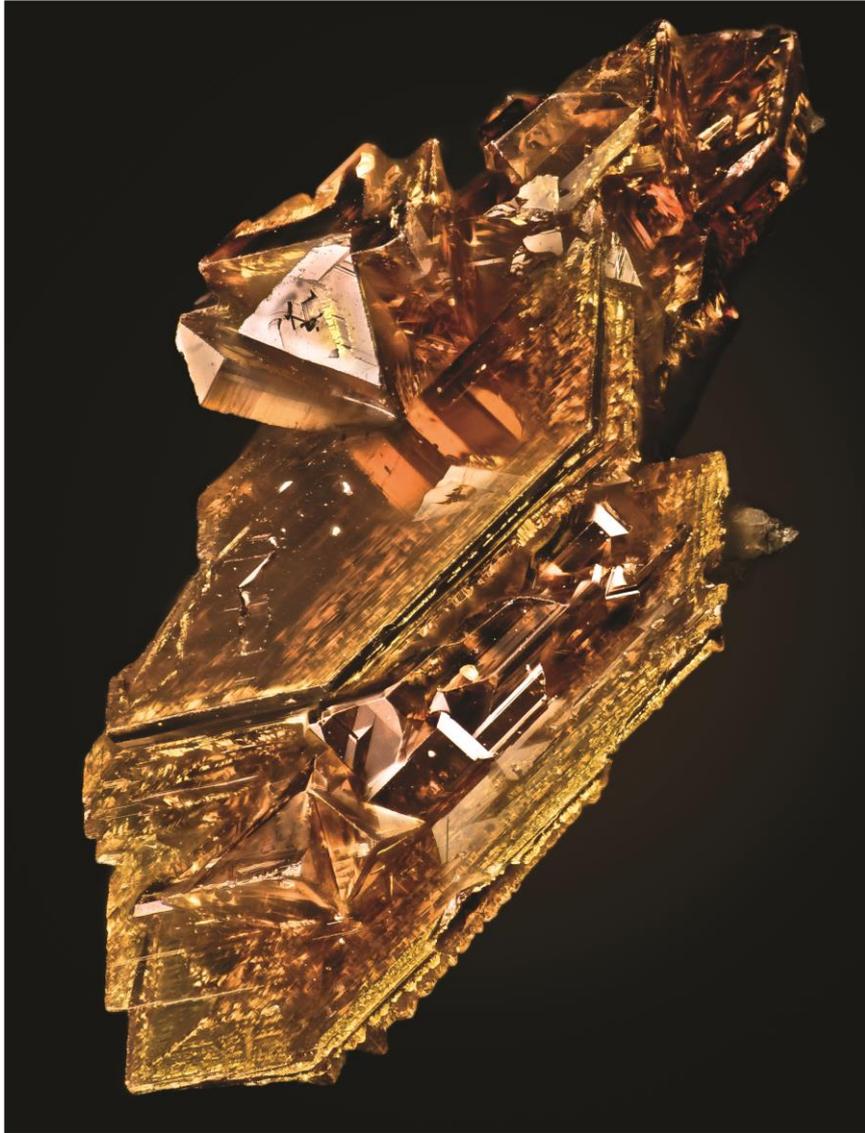


Fig. 1.

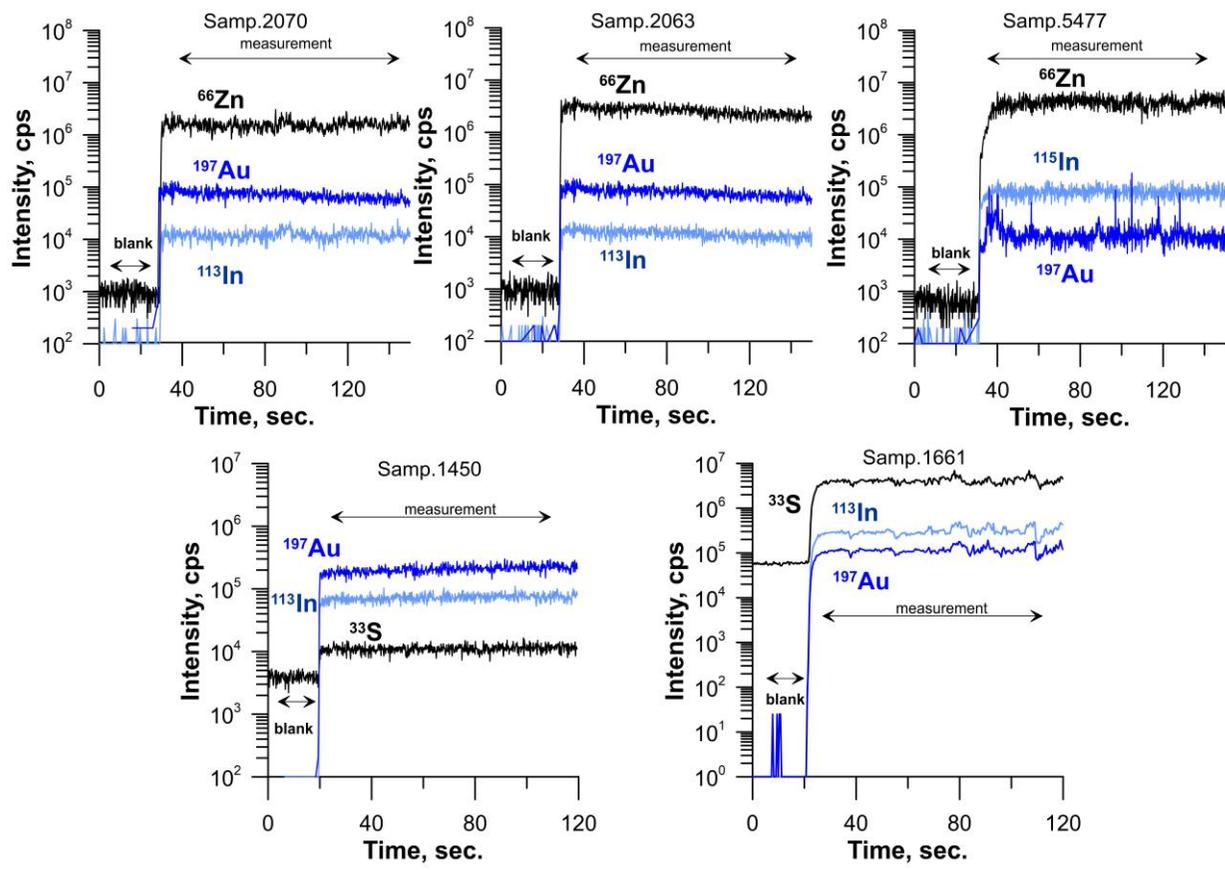


Fig. 2.

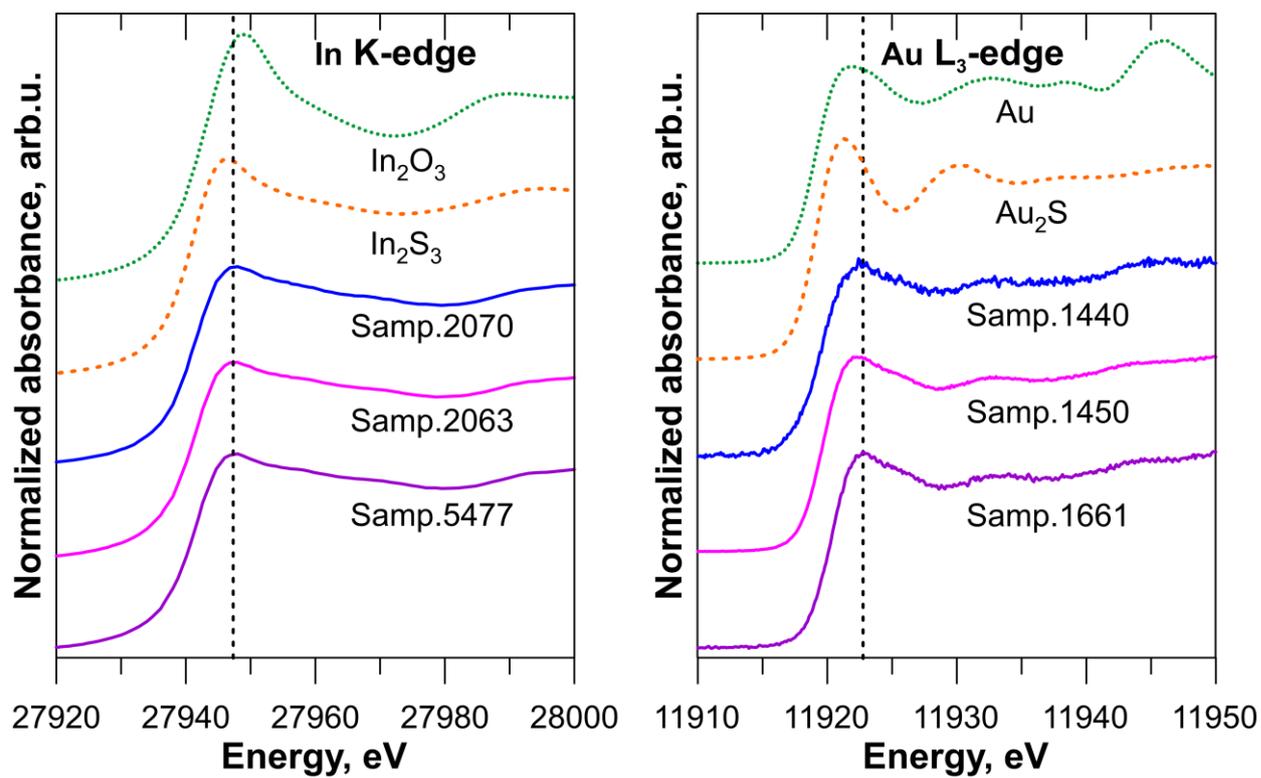


Fig. 3.

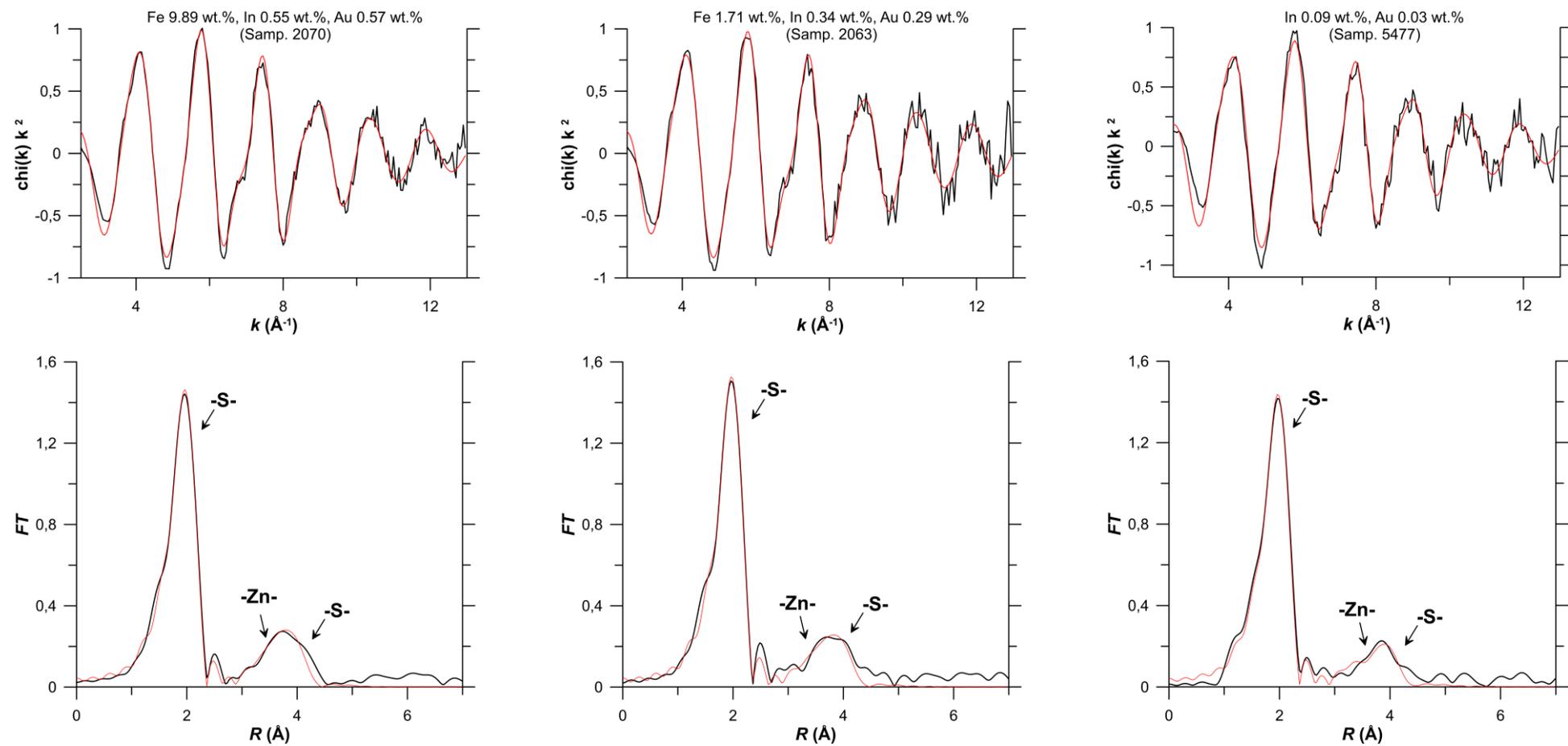


Fig. 4a.

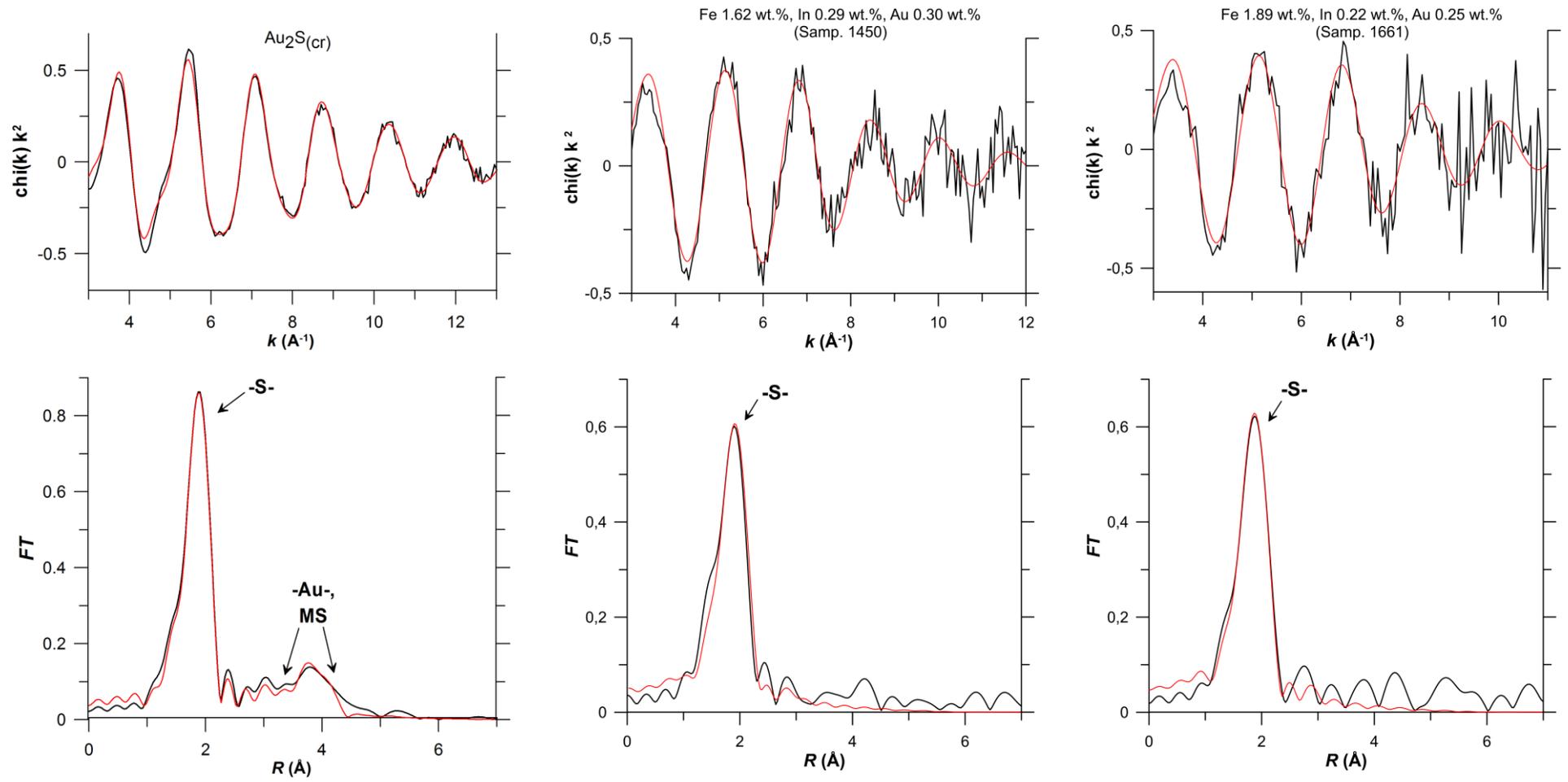


Fig. 4b.

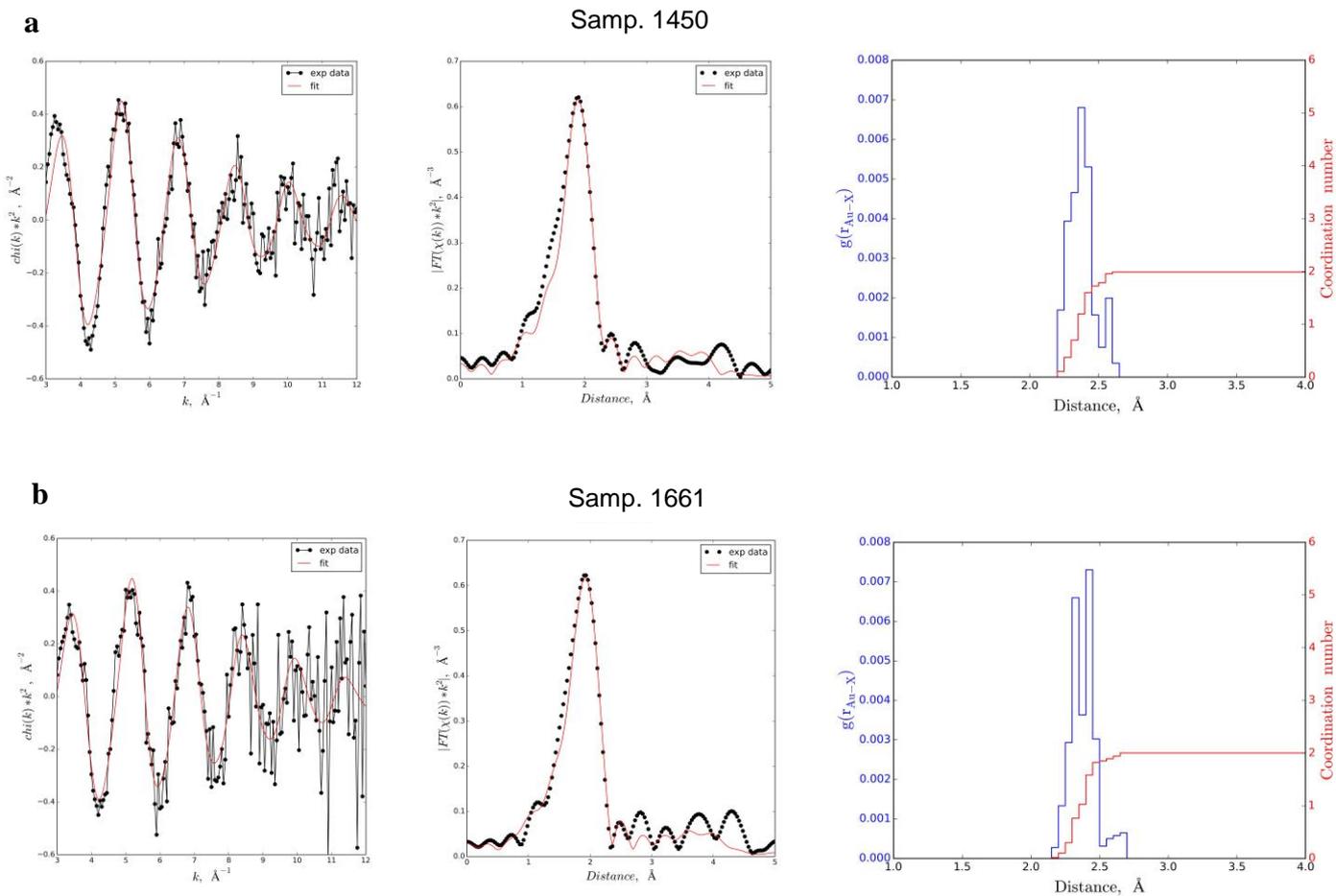


Fig. 5.

Table 1. Compositions of synthetic sphalerites used in XAS experiments. Concentrations are given in wt% ($\pm 2\sigma$).

Sample No	EPMA ³										LA-ICP-MS
	Zn	In	Fe	S	Au	Cd	Mn	Se	Total	Empirical formula	Au
2070 ¹	54.97 (1.59)	0.55 (0.01)	9.89 (0.03)	33.16 (0.28)	0.57 (0.01)	n/d	n/d	n/d	99.14 (1.74)	(Zn _{0.94} ,Fe _{0.05})S _{1.01}	0.560 (0.015)
2063 ¹	63.89 (1.00)	0.34 (0.02)	1.71 (0.07)	33.06 (0.57)	0.29 (0.03)	n/d	n/d	n/d	99.29 (1.69)	(Zn _{0.96} ,Fe _{0.03})S _{1.01}	0.310 (0.004)
5477 ¹	65.84 (1.26)	0.09 (0.02)	n/d	33.69 (0.69)	0.03 (0.02)	n/d	n/d	n/d	99.65 (1.99)	Zn _{0.98} S _{1.02}	0.035 (0.003)
1440 ²	64.74 (1.06)	n/d	1.49 (0.02)	33.81 (0.59)	n/d	n/d	n/d	n/d	100.04 (1.30)	(Zn _{0.95} ,Fe _{0.03})S	0.020 (0.003)
1450 ²	63.95 (0.51)	0.29 (0.02)	1.62 (0.13)	33.73 (0.32)	0.30 (0.05)	0.48 (0.11)	0.24 (0.05)	0.13 (0.07)	100.74 (0.59)	(Zn _{0.95} ,Fe _{0.03})S	0.29 (0.05)
1661 ¹	65.24 (0.31)	0.22 (0.03)	1.89 (0.06)	33.76 (0.53)	0.25 (0.05)	n/d	n/d	n/d	101.36 (0.55)	(Zn _{0.96} ,Fe _{0.03})S _{1.01}	0.21 (0.05)

¹ Salt flux synthesis method; ² gas transport synthesis method; ³ n/d = not determined.

Table 2. Positions of edge jump (e.j.) and the first intense feature (white line, WL) of In *K*-edge and Au L₃-edge spectra recorded for Au±In-bearing sphalerites and standards (±0.5 eV).

Sample, standard	Feature	Position, eV
In K-edge XANES		
In ₂ O ₃	e.j.	27942.7
	WL	27949.1
In ₂ S ₃	e.j.	27940.9
	WL	27946.9
Sample 2063 Fe 1.71 wt%, In 0.34 wt%, Au 0.31 wt%	e.j.	27942.0
	WL	27948.1
Sample 2070 Fe 9.89 wt%, In 0.55 wt%, Au 0.56 wt%	e.j.	27942.0
	WL	27948.1
Sample 5477 In 0.09 wt%, Au 0.035 wt%	e.j.	27941.5
	WL	27948.2
Au L₃-edge HERFD-XANES		
Au	e.j.	11919.3
		11922.0
Au ₂ S	e.j.	11919.3
		11921.3
Sample1440 Fe 1.49 wt%, Au 0.02 wt%	e.j.	11919.8
		11922.5
Sample1450 Fe 1.62 wt%, In 0.29 wt%, Au 0.29 wt%	e.j.	11919.8
	WL	11922.3
Sample1661 Fe 1.89 wt%, In 0.22 wt%, Au 0.21 wt%	e.j.	11920.3
	WL	11922.8

Table 3. Indium, gold, and iron local atomic structure in sphalerite determined by EXAFS fitting using IFEFFIT package (fit in k -space unless otherwise indicated, k^2 weighting). Numbers without uncertainties were fixed during the fit. Uncertainties are calculated by ARTEMIS program.

Scattering atoms	N	$r, \text{\AA}$	$\sigma^2, \text{\AA}^2$	E^0, eV	R-factor
Zn K-edge¹					
Synthetic sphalerite (gas transport synthesis), k -space: 2.5 – 13					
S	4	2.34±0.01	0.005±0.001	4.0±0.6	0.012
Zn	12	3.84±0.01	0.015±0.001		
S	12	4.46±0.02	0.018±0.003		
Sample 2070 (Fe 9.89 wt.%, In 0.55 wt.%, Au 0.57 wt%), k -space: 2.5 – 13					
S	4.00±0.44	2.34±0.01	0.005±0.001	4.5±1.0	0.045
Zn	12	3.84±0.02	0.015±0.002		
S	12	4.45±0.03	0.018±0.005		
Sample 2063 (Fe 1.71 wt.%, In 0.34 wt.%, Au 0.29 wt%), k -space: 2.5 – 13					
S	3.84±0.44	2.34±0.01	0.005±0.001	5.0±1.1	0.048
Zn	12	3.84±0.02	0.015±0.002		
S	12	4.45±0.03	0.017±0.005		
Sample 1450 (Fe 1.62 wt.%, In 0.29 wt.%, Au 0.30 wt%), k -space: 2.5 – 13					
S	3.82±0.45	2.34±0.01	0.005±0.001	5.1±1.1	0.051
Zn	12	3.84±0.02	0.015±0.002		
S	12	4.45±0.03	0.017±0.005		
Sample 1661 (Fe 1.89 wt.%, In 0.22 wt.%, Au 0.25 wt%), k -space: 2.5 – 13					
S	4.04±0.45	2.34±0.01	0.005±0.001	5.0±1.0	0.047
Zn	12	3.84±0.02	0.015±0.002		
S	12	4.45±0.03	0.016±0.005		
Fe K-edge²					
Sample 2070, k -space: 2.5 – 11					
S	3.68±0.54	2.34±0.01	0.003±0.002	2.7±1.3	0.051
Zn	12	3.84±0.02	0.016±0.003		
S	12	4.42±0.04	0.017±0.007		
Sample 2063, k -space: 2.5 – 11					
S	4.26±0.82	2.34±0.01	0.003±0.002	1.3±1.8	0.081
Zn	12	3.83±0.03	0.014±0.004		
S	12	4.40±0.05	0.015±0.008		
Sample 1450, k -space: 2.5 – 10					
S	4.84±1.45	2.34±0.02	0.003±0.003	2.6±3.3	0.097
Zn	12	3.81±0.04	0.012±0.004		
S	12	4.40±0.15	0.027±0.032		
Sample 1661, k -space: 2.5 – 11					
S	3.75±0.81	2.34±0.01	0.001±0.002	2.5±2.1	0.087
Zn	12	3.83±0.03	0.013±0.003		
S	12	4.43±0.08	0.022±0.015		
In K-edge³					
Sample 2063, k -space: 2.5 – 13					
S	4.22±0.46	2.46±0.01	0.004±0.001	5.5±1.2	0.049
Zn	12	3.92±0.03	0.018±0.004		
S	12	4.48±0.04	0.016±0.006		
Sample 2070, k -space: 2.5 – 13					
S	4.46±0.35	2.46±0.01	0.005±0.001	5.0±0.9	0.026
Zn	12	3.92±0.02	0.018±0.002		
S	12	4.48±0.03	0.015±0.004		
Sample 5477 (In 0.09 wt.%, Au 0.03 wt%), k -space: 2.5 – 13					
S	4.23±0.52	2.46±0.01	0.005±0.001	6.2±1.3	0.057
Zn	12	3.93±0.04	0.020±0.005		
S	12	4.46±0.05	0.017±0.008		

Table 3. – continued.

Au L₃-edge⁴					
Au ₂ S, synthetic, <i>k</i> -space: 3– 13					
S	2	2.30±0.005	0.0040±0.0003	5.1±0.7	0.017
Au	6	3.75±0.08	0.03±0.02		
Sample 1450, <i>k</i> -space: 3 – 12, fitting in R-space: 1.2-3.0.					
S	2.39±0.27	2.35±0.01	0.008±0.001	0.4±1.3	0.015
Sample 1661, <i>k</i> -space: 3 – 11, fitting in R-space: 1.2-3.0					
S	2.48±0.34	2.35±0.01	0.008±0.002	0.7±1.5	0.018
¹ $S_0^2 = 0.85$ ² $S_0^2 = 0.75$ ³ Sphalerite structure from Jamieson and Demarest (1980) was used as initial model for EXAFS fitting, $S_0^2 = 0.95$ was calculated from fitting of In ₂ S ₃ model spectra; ⁴ Au ₂ S structure (Ishikawa et al., 1995) was used as initial model for EXAFS fitting, the value of $S_0^2 = 0.84$ calculated from fitting of Au ₂ S model spectra was used for fitting of Au-In-sphalerite spectra.					