

EXAFS and Mössbauer spectroscopic study of Fe-bearing tetrahedrites

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Abstract

EXAFS and Mössbauer data on synthetic silver-rich tetrahedrite, $(\text{Cu, Ag})_{10+x}\text{Fe}_{2-x}\text{Sb}_4\text{S}_{13}$, reveal the presence of Fe^{2+} and Fe^{3+} , the former occupying trigonal planar sites and the latter tetrahedral sites. There is also a clear relationship between increased silver substitution and an increase in Fe^{2+} . The amount of Fe^{3+} incorporated in the synthetic tetrahedrites is proportional to the excess of Cu^+ ($\text{Cu} + \text{Ag} > 10$ atoms) in the mineral, thus maintaining a charge balance. The iron in the natural tetrahedrites and the tennantite examined is mainly tetrahedrally co-ordinated Fe^{2+} .

KEYWORDS: EXAFS, Mössbauer, Fe-bearing, tetrahedrites.

Introduction

THE substitution of Fe and Ag into tetrahedrites has been the subject of various studies (Hall *et al.*, 1974; Charlat and Levy, 1974; Kalbskopf, 1972; Sugaki *et al.*, 1975; Patrick and Hall, 1983; Johnson and Burnham, 1985; Petersen and Miller, 1986; Charnock *et al.*, 1988). Of particular interest has been the site of substitution of the iron and silver and the oxidation state of the iron. In this investigation, the Mössbauer effect in ^{57}Fe was studied in order to determine the oxidation state, spin state and co-ordination of the iron in tetrahedrites. To complement the Mössbauer data, Fe *K*-edge EXAFS spectra were collected, providing further information on the co-ordination of the iron. Many of the samples examined were argentian, and the inter-relationship of iron and silver substitution was assessed.

The structure of tetrahedrite (general formula $(\text{Cu, Ag})_{10}(\text{Zn, Fe})_2(\text{Sb, As})_4\text{S}_{13}$) has been determined by Pauling and Neuman (1934), Wuensch (1964), and Wuensch *et al.* (1966). The formula is equivalent to $\frac{1}{2}$ a unit cell and the substituting elements are discussed in terms of atoms per $\frac{1}{2}$ unit cell. The basic elements of the structure relevant to this study are displayed in Fig. 1. The twelve metal atoms are distributed between two sites, a tetrahedral site (the Cu(IV) site) and a

trigonal planar site (the Cu(III) site) (Fig. 1). In natural tetrahedrites, Cu atoms occupy ten of these sites, Zn and/or Fe commonly occupying the remaining two sites. The inclusion of the Fe and Zn is important in controlling the stoichiometry of tetrahedrites. For instance, in an investigation of the Cu-Fe-Sb-S system, Tatsuka and Morimoto (1977) demonstrated that in tetrahedrites with <3.5 wt.% Fe (~ 1 atom) there is a wide compositional field, but if >1 atom Fe is present the field narrows dramatically and at 7.3 wt.% Fe the ideal formula of $\text{Cu}_{10}\text{Fe}_2$ is achieved.

Charlat and Levy (1974) noted that if Cu and Fe are the only elements in the Cu(III) and Cu(IV) sites, then the composition of the tetrahedrite can vary between that of the 'ideal' formula of $\text{Cu}_{10}\text{Fe}_2$ and $\text{Cu}_{11}\text{Fe}_1$. Hall *et al.* (1974) suggested that the charge balance can be maintained by the presence of Fe^{3+} , and suggested that a composition of $\text{Cu}_{11}^+\text{Fe}^{3+}$ would be more stable than $\text{Cu}_{10}^+\text{Fe}^{2+}$ because $\text{Fe}^{3+}(d^5)$ is more stable in tetrahedral (sp^3) sites than $\text{Fe}^{2+}(d^6)$. A previous Mössbauer study indicated both Fe^{2+} and Fe^{3+} to be present in tetrahedrite, the former occupying the tetrahedral sites (Cu(IV)) and the latter possibly in trigonal sites (Cu(III)) (Vaughan and Burns, 1972).

Limited silver substitution for copper in natural tetrahedrites is common and, in most cases, the

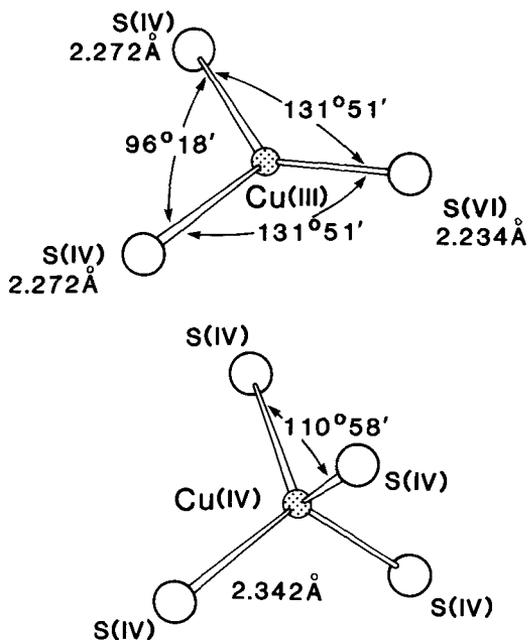


Fig. 1. Coordination polyhedra in tetrahedrite showing the Cu(III) and Cu(IV) sites (after Wuensch, 1964).

silver content is <4 atoms. In silver-rich ores, higher Ag-contents are found and, in exceptional circumstances (particularly in tetrahedrites formed by replacement or exsolution) end-members such as $\text{Ag}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}$ and $\text{Ag}_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13}$ have been recorded (Imai and Lee, 1980; C. J. Stanley, pers. comm.). Microprobe analyses of a large number of natural argentian tetrahedrites have revealed a positive correlation between high iron and high silver content, suggesting a 'sympathetic' substitution of these two elements (Patrick and Hall, 1983; Johnson *et al.*, 1986).

The structural refinements of Kalbskopf (1972), Johnson and Burnham (1985), and Petersen and Miller (1986) on natural argentian tetrahedrites have demonstrated that silver preferentially occupies the Cu(III) site. The structural refinement of a tetrahedrite with a composition of $\text{Cu}_{5.84}\text{Ag}_{4.22}\text{Fe}_{1.59}\text{Zn}_{0.43}\text{Sb}_{4.0}\text{S}_{13}$ suggested all the Fe to be in the trigonal site in contrast to silver-free tetrahedrite where there was no evidence of a single site occupancy (Petersen and Miller, 1986). Tetrahedrite is cubic ($I\bar{4}3m$) and the cell-size normally increases with increasing Ag content. Riley (1974), however, noticed that in natural iron tetrahedrites with $\text{Ag} > 4$ atoms the cell size was anomalously low or 'collapsed', possibly due to the substitution of some silver into the tetrahedral

site. This phenomenon does not occur in synthetic tetrahedrites (Patrick and Hall, 1983). EXAFS of a natural tetrahedrite with 5.8 atoms of silver suggests that the collapse of the cell-size involves interaction of antimony atoms and the Cu(III)- S_3 polyhedra (Charnock *et al.*, 1988). The same study confirmed the location of silver in the Cu(III) sites.

Experimental methods and samples

Samples. The chemical compositions of the samples used in this study are shown in Table 1. The synthetic samples (1-5) chosen for analysis display variable concentrations of iron and silver, enabling changes in the behaviour of Fe with increasing Ag substitution to be monitored. Natural tetrahedrites were supplied by the British Museum (Natural History). Samples 6-8 are tetrahedrites with variable Fe and Ag content but that also contain some Zn and have a formula $\approx (\text{Cu}, \text{Ag})_{10}(\text{Fe}, \text{Zn})_2$. Sample 9 is a natural tetrahedrite with 5.7 atoms Ag and displays the cell size 'collapse' discussed above. Sample 10 is a tennantite with an excess of Cu. Sample purity was determined by optical examination and X-ray diffraction analysis and impurities revealed were below levels that would be a significant contribution to the spectra.

Synthesis was undertaken in sealed evacuated silica tubes at 400°C using high-purity ($>99.99\%$) elements as starting materials. One gram charges were run for 7 days, then quenched and ground before running for a further 7 days. Tetrahedrite compositions (Table 1) were calculated from electron probe microanalyses performed on a Cameca Camebax electron probe using wavelength spectrometry at 20 kV and using CuSbS_2 , AgBiS_2 , FeS_2 , ZnS , FeAsS as standards.

Mössbauer spectra (^{57}Fe) were obtained from powdered samples at room temperature and liquid nitrogen temperature ($\sim 77\text{ K}$). The equipment used consisted of the Harwell Spectrometer drive and counter systems coupled to an Ino-tech 5200 Multichannel Analyser utilizing 512 channels for data collection. The γ -ray source was ^{57}Co in a palladium matrix and the spectrometer was calibrated using iron foil (all isomer shifts are quoted relative to iron). Computer fitting of spectral data was undertaken using the program written by A. J. Stone (see Bancroft *et al.*, 1967).

EXAFS. The data were recorded at room temperature on station 7.1 at the Daresbury Synchrotron Radiation Source, using samples ground up and diluted with boron-nitride, and packed into aluminium sample holders with Sellotape windows. Data analysis utilized a single scattering

Table 1. Compositions of tetrahedrite-tennantites used in this study. Analyses given as unit formulae, assuming $\text{Cu}+\text{Ag}+\text{Fe}+\text{Zn} = 12$. († denotes synthetic samples)

Sample	Ref. No.	Cu	Ag	Fe	Zn	Sb	As	S	$a(\text{\AA})$
25B†	1	11.04	0.00	0.96	-	3.99	-	12.77	10.34
17A†	2	10.32	0.72	0.96	-	4.11	-	13.00	10.37
17B†	3	8.86	2.05	1.09	-	4.04	-	12.81	10.44
11B†	4	7.26	3.21	1.55	-	4.22	-	12.64	10.51
11D†	5	4.10	5.94	1.96	-	4.22	-	12.22	10.72
BM 1929, 64	6	9.85	0.06	1.63	0.46	3.99	0.18	12.89	10.38
BM 40456	7	8.96	1.09	0.30	1.65	3.69	0.43	12.66	10.44
BM 57605	8	7.53	2.45	1.13	0.89	3.93	0.21	12.68	10.52
BM 88668	9	4.52	5.51	1.68	0.29	4.10	0.05	12.50	10.50
BM 15480	10	10.88	0.00	1.12	0.00	0.00	3.91	12.89	10.21

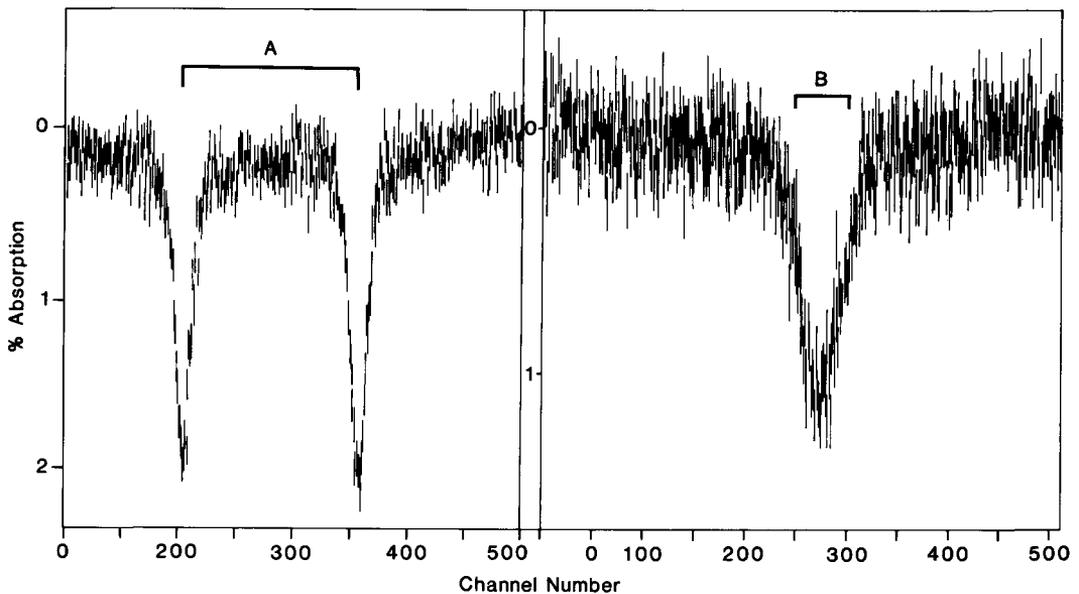


Fig. 2. Mössbauer spectra of synthetic tetrahedrite displaying the two extremes of the spectra recorded. The spectrum from sample 5 (left) is dominated by sub-spectrum A (tetrahedral Fe^{2+}) and sample 1 (right) by sub-spectrum B (trigonal Fe^{3+}).

spherical wave method for calculating EXAFS (Lee and Pendry, 1975), with phase shifts derived from *ab initio* calculations, using the Daresbury program EXCURVE (Gurman *et al.*, 1984).

Mössbauer spectra

Mössbauer spectra of iron-bearing tetrahedrites show considerable variation with compo-

sition. At one extreme are found spectra comprised of a single quadrupole doublet (sub-spectrum A in Table 2 and Fig. 2) with a relatively large isomer shift ($\sim 0.64 \text{ mm sec}^{-1}$) and quadrupole splitting (2.76 mm sec^{-1}). Comparison of these Mössbauer parameters with those obtained for iron in other, well characterized, sulphides (see, for example, Vaughan and Craig, 1978), sug-

TABLE 2. Mössbauer parameters for iron (± silver) tetrahedrites†.

Ref. No.	Tetrahedrite Composition	% Fe ³⁺	Subspectrum A		Subspectrum B	
			δ	Δ	δ	Δ
1	Cu _{11.04} Ag ₀ Fe _{0.96}	100	-	-	0.32	0.29
2	Cu _{10.32} Ag _{0.72} Fe _{0.96}	100	-	-	0.45	0.32
3	Cu _{8.86} Ag _{2.05} Fe _{1.09}	~40	0.58	2.28	0.37	0.33
4	Cu _{7.26} Ag _{3.21} Fe _{1.55}	-30	0.59	2.54	0.34	0.43
5	Cu _{4.10} Ag _{5.94} Fe _{1.96}	0	0.64	2.76	-	-
8	Cu _{7.53} Ag _{2.45} Fe _{1.13} Zn _{0.89}	0	0.60	3.12	-	-
9	Cu _{4.52} Ag _{5.51} Fe _{1.68} Zn _{0.29}	-13	0.56	3.13	0.21	0.41
10	Cu _{10.88} Ag _{0.00} Fe _{1.12} As _{3.9}	0?	0.52	2.62	-	-

† Values for isomer shift (δ) and quadrupole splitting (Δ) are given in mm sec⁻¹, the former relative to iron foil as a standard.

gests that this arises from high-spin Fe²⁺ in the tetrahedral sites of the tetrahedrite structure. This spectrum was derived from synthetic sample 11D (sample 5 in Tables 1–3) which contains ≈6 atoms silver. In contrast, in sample 25B (No. 1 in Tables 1–3) which contains no silver, the spectrum is dominated by another doublet (subspectrum B in Table 2 and Fig. 2) with a much smaller isomer shift (0.36 mm sec⁻¹) and quadrupole splitting (0.37 mm sec⁻¹). Again, comparison with the Mössbauer parameters obtained for iron in other well studied sulphide systems suggests that subspectrum B arises from high-spin Fe³⁺. The isomer shift and quadrupole splitting values are, in this case, rather larger than expected for tetrahedrally co-ordinated Fe³⁺ suggesting some possible occupancy of the trigonal sites.

The Mössbauer parameters for the synthetic tetrahedrites ranging in composition from silver-free to those with approximately six atoms per formula unit of silver, and with iron content increasing from 0.96 to 1.96 atoms per formula unit, are presented in Table 2. The samples (numbers 1 and 2) with 0.96 atoms of iron and little or no silver exhibited only the doublet assigned to Fe³⁺ (subspectrum B) in the Mössbauer spectrum. The synthetic tetrahedrites with intermediate silver compositions (numbers 3 and 4) exhibit spectra with both quadrupole doublets (sub-spectra A and B) Sample 5, which contains 5.94 atoms of silver, only displayed sub-spectrum A. Thus, with increasing iron and silver contents (and hence decreasing copper), a systematic increase in Fe²⁺/Fe³⁺ ratio is observed until only Fe²⁺ is present. Certain general trends are also

discernible in the isomer shift and quadrupole splitting parameters, with a general increase in isomer shift and quadrupole splitting of the A subspectrum, and increase in quadrupole splitting of the B subspectrum. The increase in isomer shift in the Fe³⁺ spectra (subspectrum B) suggests distortion of the Cu(III) site due to silver substitution and is probably a function of increased Fe–Ag interaction.

Mössbauer spectra of three natural samples are presented in Table 2. The tetrahedrite containing 2.45 atoms Ag (sample 8) displayed only subspectrum A, inferring the iron to present as Fe²⁺. In contrast the spectrum derived from the high silver tetrahedrite (Sample 9), which has the ‘collapsed cell’, suggests the presence of ≈13% Fe³⁺. The spectrum of the tennantite (sample 10) was of slightly inferior quality although it clearly showed that most, if not all, the iron is Fe²⁺. From its composition of Cu_{10.88}Fe_{1.12} a majority of Fe³⁺ might have been predicted in this sample to maintain the charge balance. These data suggest that the controls on the oxidation state of iron in natural tetrahedrites is more complex than the synthetic samples.

It is important to note that delocalization of electrons means the assignment of formal oxidation states to the cations in many sulphide structures represents an oversimplification (viz. Amthauer and Bente, 1983). However, it is clear from the above data, in which two doublets are discernible, that two distinct types of iron occur in the tetrahedrite structure and these have Mössbauer parameters that approximate to those assigned to Fe³⁺ and Fe²⁺ ions in other sulphides.

TABLE 3. Parameter values for the best fit simulations of the Fe EXAFS spectra

Ref. No.	Composition	$R/\text{\AA}$ (Fe-S) ^a	N ^b	$\sigma/\text{\AA}^2$ ^c
1	$\text{Cu}_{1.04}\text{Ag}_{0.00}\text{Fe}_{0.96}$	2.268	3.0	0.002
2	$\text{Cu}_{1.032}\text{Ag}_{0.72}\text{Fe}_{0.98}$	2.275	3.2	0.002
3	$\text{Cu}_{0.86}\text{Ag}_{2.05}\text{Fe}_{1.09}$	2.283	3.3	0.006
4	$\text{Cu}_{7.26}\text{Ag}_{3.21}\text{Fe}_{1.55}$	2.290	3.7	0.012
5	$\text{Cu}_{4.10}\text{Ag}_{5.94}\text{Fe}_{1.96}$	2.307	3.9	0.016
6	$\text{Cu}_{9.85}\text{Ag}_{0.06}\text{Fe}_{1.69}\text{Zn}_{0.46}$	2.300	3.8	0.016
7	$\text{Cu}_{8.96}\text{Ag}_{1.09}\text{Fe}_{0.30}\text{Zn}_{1.65}$	2.300	3.7	0.011
8	$\text{Cu}_{7.53}\text{Ag}_{2.45}\text{Fe}_{1.13}\text{Zn}_{0.89}$	2.313	3.8	0.010
9	$\text{Cu}_{4.52}\text{Ag}_{5.51}\text{Fe}_{1.66}\text{Zn}_{0.29}$	2.301	3.7	0.011
10	$\text{Cu}_{10.86}\text{Ag}_{0.00}\text{Fe}_{1.12}$	2.307	4.0	0.012

a, bond length; b coordination number; c Debye-Waller factor

EXAFS spectra

The Fe EXAFS K edge spectra are presented in Table 3. All of the iron spectra exhibit similar features, and for each sample a good theoretical fit to the data was obtained using a single shell of sulphur back-scatterers: this is illustrated for sample 1 (25B) in Fig. 3. In some spectra the data quality was sufficiently high to reveal the presence of further shells of back-scattering atoms beyond the first co-ordination sphere, but analyses of these did not contribute any useful information to aid interpretation of the data, and so only the first shell data are discussed here. Table 3 lists the best fit parameters for all the samples. The errors quoted for N are usually ± 1 . However, this value is an error in the absolute value and the observed changes in relative values are still significant. This quoted error is also often unrealistically high for first shell co-ordination. Co-ordination numbers derived from EXAFS spectra of metal-sulphur clusters using calculated phase shifts are typically low by 20% (Abrahams, 1986). For instance, values of N derived from EXAFS spectra of CuFeS_2 are 3.7 and 3.5 for Cu and Fe, respectively. Therefore, in this study calibrated phase shifts were employed, using CuFeS_2 (assuming $N = 4$) as the model compound. Values of R are accurate to $\pm 0.015\text{\AA}$ and, where single site occupancy of iron is indicated, they represent true bond lengths.

As the observed EXAFS is an average of the contributions from Fe in both the Cu(III) and Cu(IV) sites, the changes in the apparent bond length ($R/\text{\AA}$) and co-ordination number (N)

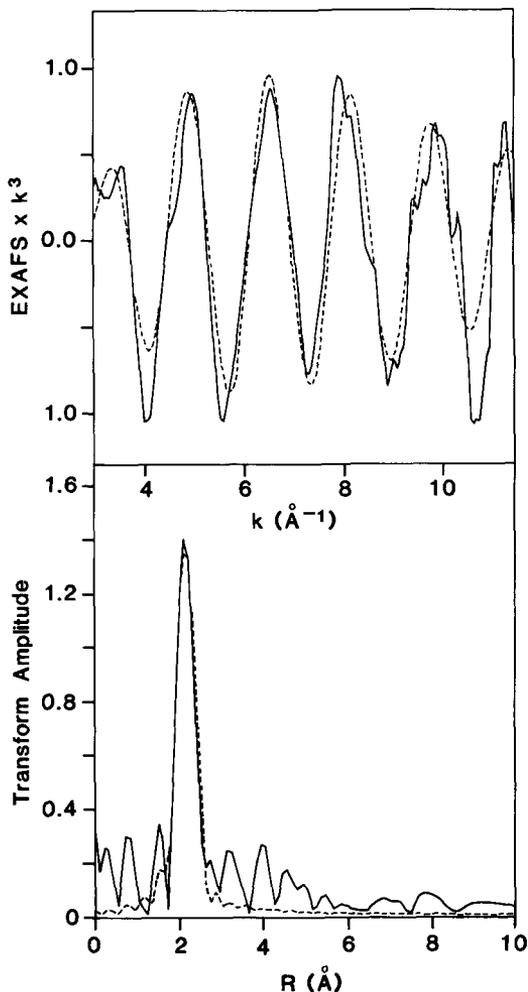


Fig. 3. The k^3 -weighted Fe EXAFS spectrum (solid line, top) and Fourier transform (solid line, bottom) of sample 5. The broken lines represent the best-fit theoretical simulations.

reflect changes in the ratio of iron atoms in these two environments.

In the synthetic samples it is clear that the Fe-S bond length and Fe co-ordination number increases from 3.0 to 3.9 with increasing silver content. These data imply that in silver-free tetrahedrites with compositions $\approx \text{Cu}_{11}\text{Fe}_1$, the iron occupies the trigonal site, and as silver replaces copper the proportion of tetrahedrally co-ordinated iron increases. In contrast, the natural tetrahedrites have relatively large Fe-S bond lengths and co-ordination numbers between 3.7 and 3.8, suggesting that iron mainly occupies Cu(IV) sites

irrespective of silver content. EXAFS data for tennantite (sample 10) also suggest that the iron is in tetrahedral co-ordination.

Discussion

The information from the Mössbauer and EXAFS spectra of the synthetic tetrahedrites confirm the presence of Fe^{2+} and Fe^{3+} in tetrahedrites and show the former to be occupying tetrahedral sites and the latter trigonal planar sites. The amount of Fe^{3+} incorporated is proportional to the excess Cu^+ (>10 atoms) and the charge balance is maintained, such that, for example, sample 25B (number 1) displays a configuration of $\text{Cu}_1^+\text{Fe}_1^{3+}$, confirming the hypothesis of Hall *et al.* (1974). It is also clear from the synthetic samples that the increase in Fe^{2+} is a function of increasing silver. The silver atoms presumably occupy the Cu(III) sites favoured by Fe^{3+} , and thus 'displacing' the iron into Cu(IV), sites where Fe^{2+} is the preferred oxidation state.

This relationship between oxidation state and site occupancy is also generally true of the natural tetrahedrites and the tennantite examined in this study, the evidence suggesting that the iron is present mainly as tetrahedrally co-ordinated Fe^{2+} . The Mössbauer data from sample 9 (5.5 atoms Ag) reveal the presence of $\approx 13\%$ Fe^{3+} and the EXAFS spectra suggest the iron to be mainly in Cu(IV) sites. However, the EXAFS data ($N = 3.7$) do not exclude the possibility of the Fe^{3+} in this sample occupying the Cu(III) site. This may be an indirect indication that silver is present in both the Cu sites. Although the combined data from the tennantite show the iron to be tetrahedrally coordinated Fe^{2+} , the resulting apparent charge imbalance is unexplained. It may be a feature of tennantites, but further data are required to establish this.

The increase in Fe–S bond lengths with increasing silver content in the synthetic tetrahedrites reflects the change in iron to a lower oxidation state and its occupancy of a site with higher co-ordination number. The absolute bond lengths derived by EXAFS (Table 3) can be compared with data from the structural refinements (Weunsch, 1964; Johnson and Burnham, 1985; Petersen and Miller, 1986), although it is important to note that the former are an average of all Fe–S bond lengths, irrespective of site, and the latter are average inter-atomic distances, irrespective of the elements occupying the site. The Fe–S bond lengths (Table 3) determined from the EXAFS spectra in synthetic sample 1, in which the iron is all Fe^{3+} and is assumed to occupy Cu(III) sites, is within error identical to the value

of 2.259 Å derived for average Cu(III)–S distances in structural refinements of silver-free natural tetrahedrites. However, the comparative covalent radii of Cu^+ (0.635 Å) and Fe^{3+} (0.555 Å) in tetrahedral coordination (Shannon, 1981), and metal–sulphur bond lengths in mineral such as CuFeS_2 , suggest that the Fe^{3+} (III) bond lengths should be smaller than Cu^+ (III) bond lengths. In samples in which the iron is assumed to be mainly in the Fe^{2+} in Cu(IV) sites (sample number 5 and the natural tetrahedrite and tennantite samples), the average Fe^{2+} –S distance is 2.305 Å (Table 3) compared with Cu(IV)–S distances of 2.337 Å derived from structural refinements of silver-free tetrahedrites. As Cu^+ and Fe^{2+} covalent radii are similar (Shannon, 1981), these two values should also be similar. Thus, the EXAFS data for Fe–S display values intermediate between the Cu(III)–S and Cu(IV)–S distances derived from structural data. This implies that, although there is a clear relationship between oxidation state and site occupancy, it is an oversimplification to presume that iron of a particular valence exclusively occupies a single site in tetrahedrites.

The combination of data from EXAFS and Mössbauer spectroscopy has led to a better understanding of the behaviour of iron in tetrahedrites, confirming the presence of Fe^{3+} and Fe^{2+} in tetrahedrites and their preferred occupancy of the Cu(III) and Cu(IV) sites, respectively. While the behaviour of iron in synthetic tetrahedrites is relatively clear, further data from both EXAFS and Mössbauer spectra are still needed to provide a comprehensive understanding of Fe in natural samples.

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