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Renierite crystal structure refined from Rietveld analysis of powder neutron-diffraction data

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ABSTRACT

The crystal structure of renierite (space group P$\bar{4}$2c, a = 10.6226(5) Å, c = 10.5506(8) Å) has been refined by the Rietveld method using powder neutron-diffraction data (R = 0.083, R_w = 0.093, R_{Bragg} = 0.039). Renierite has a sphalerite-derivative structure with an additional tetrahedral metal site containing Fe. This Fe site is similar to the V site in sulvanite and the 2a site in talnakite, having six next-nearest neighbor Fe and Cu atoms at only 2.65–2.81 Å. The closely spaced metals around this site (in particular the Fe atoms) are displaced away from each other relative to sphalerite-like positions, and S atoms are displaced toward shielding positions between the Fe atoms. As was predicted by previously obtained Mössbauer spectroscopic data, there are three Fe sites that have two, three, and four next-nearest-neighbor Fe atoms, with the site having three such next-nearest neighbors being twice as abundant as the other two sites. The previously observed coupled substitution of As(V) + Cu(I) for Ge(IV) + Zn(II) is accommodated by Ge and Zn being next-nearest neighbors.

INTRODUCTION

Renierite, $Cu_{10}(Zn_{1-x}Cu_x)(Ge_{2-x}As_x)Fe_4S_{16}$ ($0 \leq x \leq 1$), occurs in small amounts in many Cu-Pb-Zn sulfide deposits throughout the world (Bernstein, 1986). It is locally abundant at Kipushi, Zaire, and Tsumeb, Namibia. Powder X-ray–diffraction and single-crystal electron-diffraction data indicate that it has a tetragonal sphalerite-derivative structure with $a \approx c$ (Lévy and Prouvost, 1957; Viaene and Moreau, 1968; Bernstein, 1986). The absence of suitably large single crystals has prevented crystal-structure determination by single-crystal X-ray–diffraction methods. In addition, it is unlikely that the different metal sites could be confidently distinguished using X-ray diffraction because of the similar X-ray scattering factors of Cu, Zn, Ge, and As.

Electron diffraction on powdered renierite from Tsumeb showed most grains to conform to space group P$\bar{4}$2c, the only systemic absences being of the type *hhl, l* odd (Bernstein, 1986) gave the composition $Cu_{10}(Zn_{0.8}Cu_{0.2})$- the same composition based on semiquantitative energy-dispersive X-ray analysis), however, produced reflections forbidden for this space group (such as 111, 333, etc.), and the space group was therefore determined to be P$\bar{4}$2m (Bernstein, 1986). As was discussed in the 1986 paper, double-diffraction effects were excluded as a possible cause of these reflections.

In this study, a Rietveld structure refinement of renierite was performed using powder neutron-diffraction data. The neutron scattering lengths for all the elements in renierite are sufficiently different that, in principle, all the site occupancies can be uniquely determined.

EXPERIMENTAL MATERIALS AND METHODS

The sample investigated was a piece of massive renierite weighing about 25 g from the Prince Leopold mine, Kipushi, Zaire. Examination of a polished thin section by optical microscopy and by a scanning electron microscope equipped for energy-dispersive X-ray elemental analysis detected about 10% of quartz, about 2% of dolomite, and less than 0.1% of chalcocite. The renierite itself occurs as polysynthetically twinned anhedral grains generally 5–50 μm across. Electron-microprobe analysis (Bernstein, 1986) gave the composition $Cu_{10}(Zn_{0.8}Cu_{0.2})$-$(Ge_{1.8}As_{0.2})Fe_4S_{16}$.

The sample was ground by hand using an agate mortar and pestle, and a fraction containing particles less than 30 μm across was obtained using sieves. The resulting powder was then run through a Frantz magnetic separator three times (as renierite is weakly ferrimagnetic) to remove materials other than renierite. Powder X-ray diffraction and neutron diffraction showed, however, that the re-

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sulting sample still contained several percent of quartz and about 1% of dolomite.

The neutron-diffraction data[1] were collected at the University of Missouri Research Reactor facility (MURR) using the 2xD diffractometer. For this experiment, the beam from the reactor was monochromatized by Bragg diffraction from a Cu (220) crystal, giving a mean wavelength of 1.2869(2) Å (calibrated using Si powder). The powdered sample was held at about 295 K in a 6-mm-diameter, 75-mm-long welded tube of 0.05 mm thick V foil. Data were also collected at 8 and 50 K. A linear position-sensitive detector (PSD) enabled 25° 2θ of data to be collected simultaneously.

The renierite diffraction pattern was then corrected for the presence of the several percent of quartz and about 1% of dolomite not removed by magnetic separation. The quartz contamination was corrected by obtaining a neutron-diffraction pattern of quartz under the same experimental conditions used for the renierite, then scaling the pattern to fit the major quartz peaks observed in the renierite pattern and subtracting out the quartz contribution. This correction was slightly complicated by overlap between the quartz and renierite peaks. For dolomite, which contributed much less to the renierite pattern, a synthetic diffraction pattern was generated using the known structure of the mineral; this pattern was then scaled and subtracted from the experimental data. Some errors were likely introduced by these correction procedures, but their magnitudes should be small because of the low concentrations of the contaminants.

Derivation of model structure

Several constraints were used in formulating a model structure. It was first assumed that the renierite structure consists of tetrahedrally coordinated metals and sulfurs in a sphalerite-like arrangement, plus one metal at an interstitial tetrahedral site (Bernstein, 1986). The next constraint was that local valence balance be maintained as closely as possible. Several additional constraints were derived from ^{57}Fe Mössbauer spectroscopic data (Bernstein, 1986). These data indicate Fe(III) in three distinct, magnetically ordered sites, with one site approximately twice as abundant as the other two. The three Fe sites were proposed to be antiferromagnetically coupled to 4, 3, and 2 next-nearest-neighbor Fe(III) cations.

Model structures with space-group symmetry $P\bar{4}2m$ could not be derived that would meet the above constraints without having several mixed-occupancy sites. A structure having space-group symmetry $P\bar{4}2c$ was then derived, based in part on the isometric structure of colusite (Orlandi et al., 1981; S. Merlino, unpublished data). This model structure meets all of the above constraints and has no mixed-occupancy sites (except for the known solid solution). It was used as the starting point for the successful structure refinement.

Rietveld crystal-structure refinement

The Rietveld refinement program used in this study was a version created at MURR in 1986 (W. Yelon, personal communication, 1989), which uses the Voigt function for profile fitting. This Voigt parameter allows the peak profile to vary through a convolution of Gaussian (instrumental contribution) and Lorentzian (mainly particle-size contribution) profiles. Use of this function has been found to improve the curve-fitting significantly by allowing instrumental contributions and particle-size contributions to vary independently of each other (David and Matthewman, 1985). The background was visually fit using 11 linear segments.

During refinement, the positions of the metal atoms converged rapidly. The S positions converged more slowly with larger standard deviations because of the relatively low scattering length of S and the large number of positional variables. The quality of the data did not permit complete refinement of the isotropic temperature factors (*B*). The temperature factors were first allowed to vary independently for each of the nine metal sites, with one variable for the four S sites, while the other refined variables were held constant. In the final overall refinement, one temperature-factor variable was used for the metals, and one was used for the sulfurs on the temperature factors already obtained. The scale factor, zero-point, cell dimensions, Gaussian peak-profile variables (*u, v, w*), the Voigt parameter, the "overall temperature factor" (actually an absorption and scale correction), asymmetry factor, and preferred-orientation (on 110, a possible cleavage in renierite) factor (11 variables) were refined together immediately before the final refinement. The final refinement varied the 20 positional variables, the nine occupancy variables for the metals, and the two isotropic-temperature-factor variables referred to above (31 variables). Refinement of all 42 variables together produced no change. Repeated refinements that varied different subsets of the 31 variables from different initial values led to very similar results. In addition, refinements were attempted with Cu1 and Cu2 replaced by Cu in a general position initially at ¼, ¼, ¼ or ¼, ¼, ⅛ and by Cu atoms initially at special positions 0, 0, ¼ and 0, ½, ¼; these all diverged rapidly.

RESULTS

The refined parameters for the renierite structure are given in Table 1, and the fitted neutron-diffraction pattern is shown in Figure 1. A schematic representation of the renierite structure is shown in Figure 2. The somewhat low metal occupancies (except for Zn and Cu4) may be due to a small amount of Zn (which has the lowest scattering length of the metals present) occurring at some of the other metal sites.

As renierite displays bulk magnetism and Mössbauer spectroscopic data indicate that the Fe atoms are mag-

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[1] A copy of the observed and calculated neutron-diffraction data may be ordered as Document AM-89-418 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

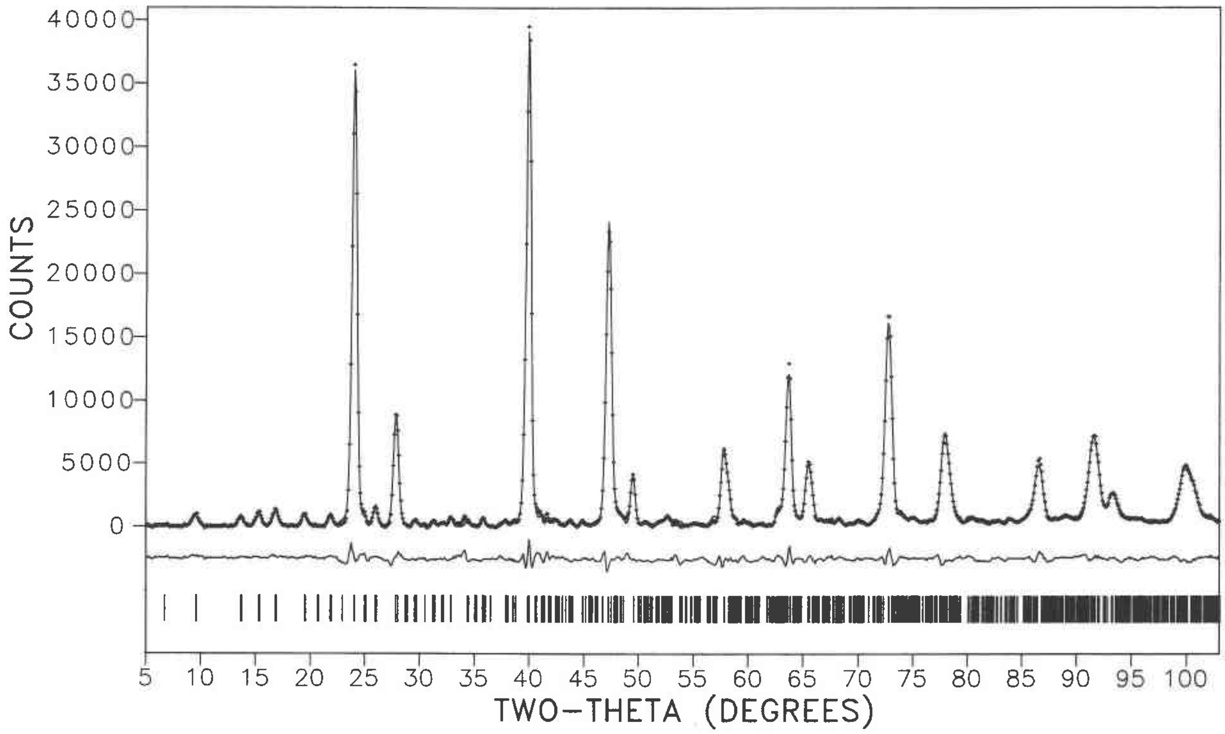

Fig. 1. Fitted powder neutron-diffraction pattern for renierite (background-subtracted observed data are indicated as crosses). The difference between the calculated pattern and the observed data is indicated in the lower curve, which is to the same scale as the rest.

netically ordered (Bernstein, 1986), effects of magnetic ordering were looked for in the neutron-diffraction data. Because of the good fit between the calculated and observed diffraction patterns without magnetic scattering effects being taken into account (Figure 1), the data were deemed insufficient to detect or constrain any magnetic-ordering parameters. In addition, the diffraction patterns obtained at 8 and 50 K were essentially identical to the pattern obtained at 295 K, indicating no enhanced spin ordering upon cooling.

DISCUSSION AND CONCLUSIONS

As proposed by Bernstein (1986), the renierite structure is a derivative of the sphalerite structure with an "extra" tetrahedral metal site, Fe2. The Fe2 site is octahedrally coordinated by Fe1, Cu1, and Cu3 at only 2.65–2.81 Å (Fig. 3), indicating probable metal-metal interactions. This site is similar to the V site in sulvanite (Trojer, 1966) and colusite (Orlandi et al., 1981), the 1*a* site in mooihoekite (Hall and Rowland, 1973), and the 2*a* site in talnakite (Hall and Gabe, 1972). The entire structure is similar to the isometric structure of talnakite, $Cu_9Fe_8S_{16}$, which has the same metal : sulfur ratio and similar cell dimensions ($a = 10.293$ Å), with all the metals in positions equivalent to those in renierite.

As was predicted from the Mössbauer data, there are three Fe sites, with Fe1 having three, Fe2 having two, and Fe3 having four next-nearest-neighbor Fe atoms. Also as predicted, Fe1 is twice as abundant as Fe2 or Fe3.

The observed metal–sulfur distances are generally comparable to those in other tetrahedral sulfides (Table 2). Some of the distances near the Fe2 site, however, are

TABLE 1. Refined parameters for renierite

Site	Occupancy	*x*/*a*	*y*/*b*	*z*/*c*	*B* (Å²)
Cu(1)	0.82(4)	0.2484(19)	0.0	0.25	1.6(1)
Cu(2)	0.90(5)	0.2336(19)	0.5	0.25	1.8(1)
Cu(3)	0.96(3)	0.0	0.5	0.0015(15)	1.3(1)
Cu(4)	1.04(2)	0.2544(15)	0.2585(16)	0.5107(8)	1.4(1)
Zn	1.12(4)	0.0	0.0	0.0	2.4(1)
Ge	0.81(5)	0.0	0.2498(12)	0.25	0.6(1)
Fe(1)	0.90(4)	0.5	0.2646(12)	0.25	0.9(1)
Fe(2)	0.84(3)	0.5	0.0	0.25	0.9(1)
Fe(3)	0.92(4)	0.5	0.5	0.0	0.3(1)
S(1)	1.0	0.3938(25)	0.1390(39)	0.1240(32)	1.0(1)
S(2)	1.0	0.1232(36)	0.3699(39)	0.1186(30)	1.0(1)
S(3)	1.0	0.3797(34)	0.3766(38)	0.3736(43)	1.0(1)
S(4)	1.0	0.1225(36)	0.1398(31)	0.3852(30)	1.0(1)

Note: Scattering factors used (Sears, 1986) (10^{-12} cm): Cu, 0.7718; Fe, 0.954; Zn, 0.609 (contains 0.8 Zn and 0.2 Cu); Ge, 0.803 (contains 0.9 Ge and 0.1 As); S, 0.2847. Other refined parameters: $a = 10.6226(5)$ Å, $c = 10.5506(8)$ Å; zero-point: $-0.2525(25)°\ 2\theta$; asymmetry parameter: 0.00001(1); preferred orientation parameter (on 110): $-0.01(14)$ (no preferred orientation); overall temperature factor: $-0.563(20)$; Gaussian parameters: $u = 11361\ (677)$, $v = -8896(660)$, $w = 3411(144)$; Voigt parameter: 256(49); scale factor: 0.462(5). $R = 0.083$; $R_w = 0.093$; $R_{Bragg} = 0.039$.

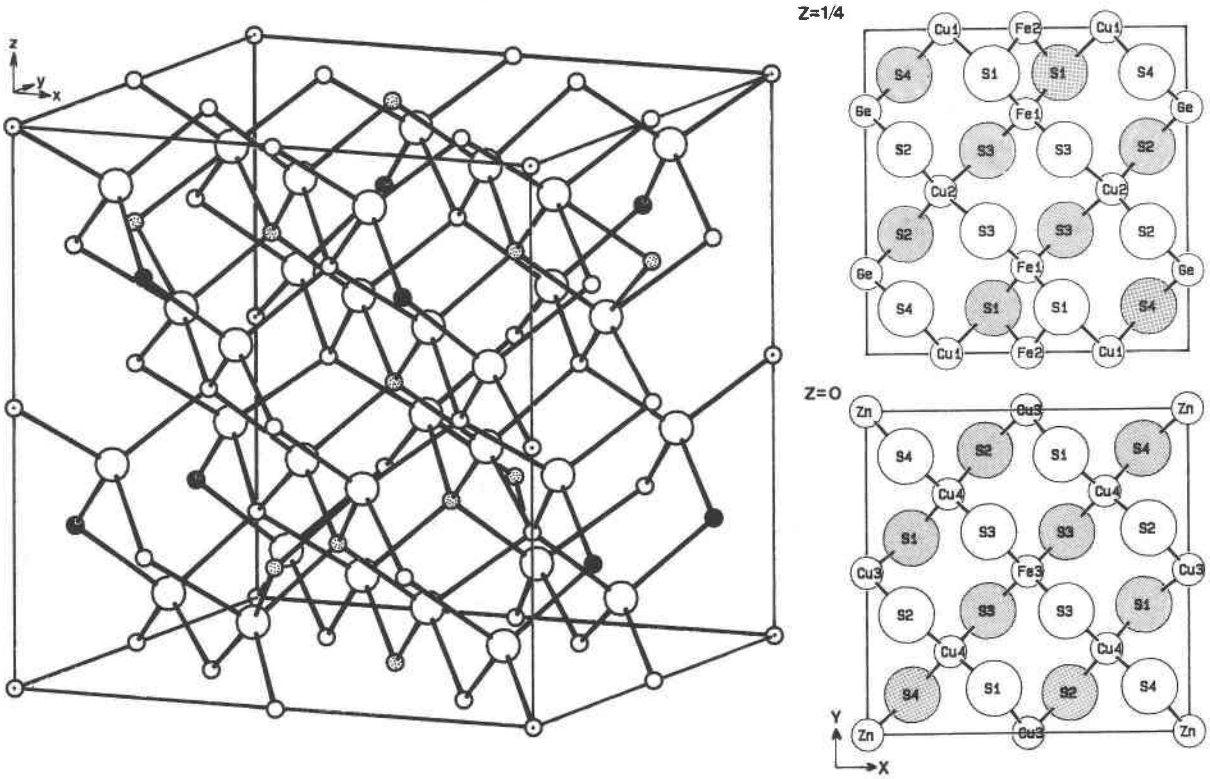

Fig. 2. Schematic representations of the renierite crystal structure. In the diagram on the left, large open circles are S, small open circles are Cu, small open circles with a central dot are Zn, small stippled circles are Fe, and small closed circles are Ge. The diagrams on the right represent projections of parts of the structure on (001) taken near $z = 0$ and $z = 1/4$. The unshaded S atoms are at about $z + 1/8$, and the shaded ones are at about $z - 1/8$ (note that the unshaded sulfurs in the lower diagram represent the identical atoms as the shaded sulfurs in the upper diagram).

significantly different (see Fig. 2). The metals surrounding Fe2 (Cu1, Cu3, Fe1) are all displaced away from Fe2 relative to sphalerite-like positions, with Fe1 showing the greatest displacement (because of its higher positive charge). Cu2 is displaced away from the two nearby displaced Fe1 atoms. S1 (which has five nearest-neighbor metals) is displaced toward a shielding position lying between the closely spaced Fe1 and Fe2 atoms, and the other S positions also compensate. The S1–S1 distance that represents the tetrahedral edge shared by Fe1 and Fe2 is only 3.49 Å, compared to S1–S1 edge distances of 3.97 Å and 3.72 Å between Fe2 and Cu1 and between Fe2 and Cu3. The small S1–S1 distance reflects the great shortening of the shared tetrahedral edge needed to counteract the repulsive force between the two highly charged Fe(III) atoms.

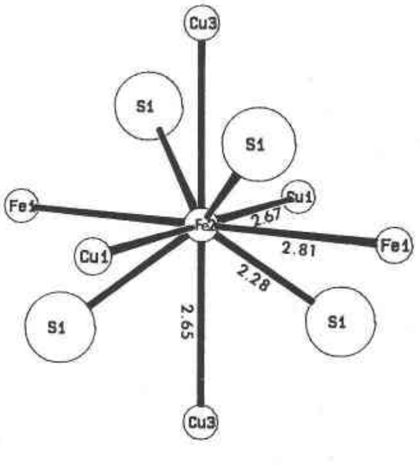

Fig. 3. Coordination of S and metal atoms around Fe2. Distances are in angstroms.

The results of these displacements are seen mainly in the large Cu–S distances for Cu1 and for Cu2–S3 and the somewhat short Fe1–S distances. The average Cu1–S distance (2.49(1) Å) is considerably larger than that reported in other tetrahedral sulfides (2.30–2.38 Å). The somewhat low refined occupancies for Cu1 and Fe2 could represent, in part, vacancies that arise from these sites not being as energetically favorable for occupancy as the other metal sites. A slight deficiency of metals is consistent with the p-type electrical conductivity found for renierite (Bernstein, 1986). In addition, a small amount of the coupled substitution As(V) + □(0) for Ge(IV) + Cu(I) may occur.

The observed isotropic temperature values are com-

TABLE 2. Selected bond lengths (Å) and angles (°) for renierite

Cu1–S1 ×2	2.52(3)	S1–Cu1–S4 ×2	106.6(10)	Zn–S4 ×4	2.32(4)	S4–Zn–S4 ×4	105.9(10)
Cu1–S4 ×2	2.45(4)	S1–Cu1–S4 ×2	112.5(10)			S4–Zn–S4 ×2	116.9(10)
mean	2.49	S1–Cu1–S1	104.3(10)			mean	109.5
		S4–Cu1–S4	114.0(10)				
		mean	109.5	Ge–S2 ×2	2.29(4)	S2–Ge–S4 ×2	109.9(10)
				Ge–S4 ×2	2.26(4)	S2–Ge–S4 ×2	103.6(10)
Cu2–S2 ×2	2.28(4)	S2–Cu2–S3 ×2	109.3(10)	mean	2.27	S2–Ge–S2	112.4(10)
Cu2–S3 ×2	2.41(4)	S2–Cu2–S3 ×2	109.3(10)			S4–Ge–S4	117.6(11)
mean	2.35	S2–Cu2–S2	118.2(11)			mean	109.5
		S3–Cu2–S3	100.0(10)				
		mean	109.5	Fe1–S1 ×2	2.20(3)	S1–Fe1–S3 ×2	105.7(10)
				Fe1–S3 ×2	2.18(4)	S1–Fe1–S3 ×2	113.1(10)
Cu3–S1 ×2	2.28(3)	S1–Cu3–S2 ×2	112.8(10)	mean	2.19	S1–Fe1–S1	105.2(11)
Cu3–S2 ×2	2.27(4)	S1–Cu3–S2 ×2	104.1(10)			S3–Fe1–S3	113.8(11)
mean	2.28	S1–Cu3–S1	109.1(10)			mean	109.4
		S2–Cu3–S2	114.0(10)				
		mean	109.5	Fe2–S1 ×4	2.28(3)	S1–Fe2–S1 ×2	108.8(10)
						S1–Fe2–S1 ×2	99.5(10)
Cu4–S1	2.24(3)	S1–Cu4–S2	116.6(10)			S1–Fe2–S1 ×2	120.8(10)
Cu4–S2	2.21(4)	S3–Cu4–S4	106.6(10)			mean	109.7
Cu4–S3	2.33(4)	S1–Cu4–S3	107.4(10)				
Cu4–S4	2.30(4)	S1–Cu4–S4	109.0(10)	Fe3–S3 ×4	2.27(4)	S3–Fe3–S3 ×4	110.3(10)
mean	2.27	S2–Cu4–S3	110.7(10)			S3–Fe3–S3 ×2	107.9(10)
		S2–Cu4–S4	106.2(10)			mean	109.5
		mean	109.5				
			Metal–metal				
Cu1–Fe2 ×2	2.67(2)	S1–Fe2–Cu1 ×4	119.6(8)	S1–Cu3–Fe2 ×2	54.5(7)		
Cu3–Fe2 ×2	2.65(2)	S1–Fe2–Cu3 ×4	125.6(8)	S2–Cu3–Fe2 ×2	123.0(7)		
Fe1–Fe2 ×2	2.81(1)	S1–Fe2–Fe1 ×4	130.3(8)	S1–Fe1–Fe2 ×2	52.6(8)		
		S1–Cu1–Fe2 ×2	52.1(7)	S3–Fe1–Fe2 ×2	123.1(8)		
		S4–Cu1–Fe2 ×2	123.0(7)				

parable to those reported for other tetrahedral sulfides (e.g., 0.9 for Fe, 1.5 for Cu, and 1.0 Å^2 for S in chalcopyrite; Hall and Stewart, 1973). The observed value for Fe3 (0.3 Å^2) is somewhat small, however. As mentioned, the quality and nature of the data are such that low confidence must be given to the refined B values.

The refined structure clearly conforms to space group $P\bar{4}2c$, not $P\bar{4}2m$. A re-examination of the TEM electron-diffraction data used to derive space group $P\bar{4}2m$ shows that the critical reflections (*hhl, l* odd) are observed only in a small percentage of grains. It is concluded that these grains are of a compositionally very similar but structurally distinct phase, probably germanite (space group $P\bar{4}3n$ or $P\bar{4}3m$ on the basis of unpublished data) or a related phase. Germanite and other Ge-bearing sulfides are commonly mixed with renierite at Tsumeb, where that sample is from.

The refined structure accommodates well the observed coupled solid solution of As(V) + Cu(I) ⇌ Ge(IV) + Zn(II) found in the chemical data (Bernstein, 1986). The sites for Ge and Zn are next-nearest neighbors, so that local valence balance is maintained as As and Cu are substituted.

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