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KESTERITE, $Cu_2(Zn,Fe)SnS_4$, AND STANNITE, $Cu_2(Fe,Zn)SnS_4$, STRUCTURALLY SIMILAR BUT DISTINCT MINERALS*

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ABSTRACT

The crystal structure of kesterite from Oruro, Bolivia has been determined by single-crystal X-ray diffraction methods and refined to an R value of 0.044 (all data). The mineral is tetragonal, a 5.427(1), c 10.871(5)Å, $Z=2$, space group $I\bar{4}$ and composition $Cu_{1.98}(Zn_{0.73}Fe_{0.29}Cd_{0.01})Sn_{0.99}S_{4.00}$. The crystal structure of the coexisting mineral stannite has been refined to an R value of 0.025 (all data). Stannite is tetragonal, a 5.449(2), c 10.757(3)Å, $Z=2$, space group $I\bar{4}2m$ and composition $Cu_{1.99}(Fe_{0.81}Zn_{0.18}Cd_{0.02})Sn_{1.00}S_{4.00}$. The kesterite structure is characterized by a cell that is pseudocubic ($2a \simeq c$). The Cu atoms are in the separate positions $2a$ (0,0,0) and $2c$ (0,½,¼). The (Zn,Fe), Sn and S atoms are in positions $2d$ (½,0,¼), $2b$ (½,½,0) and and $8g$ (.7560(2), .7566(2), .8722(2)), respectively. In the stannite structure the Cu, (Fe,Zn), Sn and S atoms are in positions $4d$ (0,½,¼), $2a$ (0,0,0), $2b$ (½,½,½) and $8i$ (.7551(1), .7551(1), .8702(1)), respectively. The structural differences due to the positioning of the Cu atoms account for the distinct unit cells and optical properties of these two minerals.

SOMMAIRE

La structure cristalline de la kesterite a été déterminée sur un cristal d'Oruro (Bolivie) de composition $Cu_{1.98}(Zn_{0.73}Fe_{0.29}Cd_{0.01})Sn_{0.99}S_{4.00}$; elle a été affinée jusqu'à un résidu de 0.044 (en utilisant toutes les réflexions). Tétragonale, avec a 5.427(1), c 10.871(5)Å, $Z=2$, elle possède la symétrie $I\bar{4}$. On a aussi affiné, jusqu'au résidu $R=0.025$ (sur données complètes), la structure d'une stannite co-existante de composition $Cu_{1.99}(Fe_{0.81}Zn_{0.18}Cd_{0.02})Sn_{1.00}S_{4.00}$, tétragonale avec a 5.449(2), c 10.757(3)Å, $Z=2$, de groupe spatial $I\bar{4}2m$. Une maille quadruple de la kesterite est pseudo-cubique ($2a \simeq c$). Les atomes Cu occupent deux positions distinctes $2a$ (0,0,0) et $2c$ (0,½,¼); les autres atomes se placent comme suit: (Zn, Fe) en $2d$ (½,0,¼), Sn en $2b$ (½,½,0) et S en $8g$ (0.7560(2), 0.7566(2), 0.8722(2)). Dans la structure de la stannite, les atomes se situent différemment: Cu en $4d$ (0,½,¼), (Fe,Zn) en $2a$ (0,0,0), Sn en $2b$ (½,½,½) et S en $8i$ (0.7551(1), 0.7551(1), 0.8702(1)). Les différences structurales qui résultent de l'emplacement des atomes de cuivre expliquent pourquoi ces deux minéraux ont des mailles et des propriétés optiques distinctes.

(Traduit par la Rédaction)

INTRODUCTION

The minerals stannite and kesterite are recognized as separate species because of their different Fe to Zn compositional ratios, and their distinct optical and physical properties. These minerals occur at a large number of localities, often as two-phase intergrowths. The compositional and crystal data for a number of these minerals from different localities are being compiled by Kissin & Owens (in prep.). The results of their study tend to discount the possibility that kesterite and stannite are members of pseudobinary solid solution series, as was originally suspected from the wide compositional range of Fe and Zn, because their cell dimensions are largely independent of Fe/Zn variation.

In order to confirm that kesterite was indeed structurally distinct from a coexisting stannite, crystals were selected for X-ray structure analysis from the specimens analyzed by Kissin & Owens (in prep.). The structure of stannite was determined by Brockway (1934), who assumed a stoichiometric composition Cu_2FeSnS_4, but the structure is redetermined here in order to provide a suitable comparison with that of kesterite.

EXPERIMENTAL

Kesterite

An irregular crystal fragment of kesterite of approximate dimensions 0.25×0.10×0.06mm was extracted from specimen 2R(2) (Kissin & Owens, in prep.), from Oruro, Bolivia. Gandolfi powder photographs of the fragment show that it is a single phase, and that it contains none of

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TABLE 1. CRYSTAL DATA

	Kesterite	Stannite
Source:	Oruro, Bolivia gr. 2R(2), (Kissin & Owens, in prep.)	Oruro, Bolivia gr. 2R(3), (Kissin & Owens, in prep.)
Composition: (microprobe analysis)	$Cu_{1.98}(Zn_{0.73}Fe_{0.29}Cd_{0.01})Sn_{0.99}S_{4.00}$	$Cu_{1.99}(Fe_{0.81}Zn_{0.18}Cd_{0.02})Sn_{1.00}S_{4.00}$
Cell dimensions:	a = 5.427(1), c = 10.871(5)Å	a = 5.449(2), c = 10.757(4)Å
Systematic absences:	$h+k+l = 2n+1$	$h+k+l = 2n+1$
Space group:	$I\bar{4}$ (#82), Z = 2	$I\bar{4}2m$ (#121), Z = 2
Absorption:	$\mu(\mathrm{Mo}K\alpha) = 151.3\mathrm{cm}^{-1}$	$\mu(\mathrm{Mo}K\alpha) = 147.5\mathrm{cm}^{-1}$
Data:	(1/8 of Ewald sphere) 1288 measured 3 times 1119 with $I>\sigma(I)$	(1/16 of Ewald sphere) 692 measured 3 times 684 with $I>\sigma(I)$

the stannite with which it coexists. Precession photographs show the crystal to be single, untwinned, and to have a diffraction pattern with systematically absent reflections when $h+k+l= 2n+1$. The absences and the general intensity equivalences of the pattern suggest the Laue group $4/mmm$. In turn, this limits the space group to $I\bar{4}2m$ because of the assumed sphalerite-like arrangement of sulfur and metal atoms, which usually occurs in this type of structure. Because of the close correspondence of hkl and khl intensities, this seemed from initial examination to be the only choice (Hall *et al.* 1975). Later, however, the refinement of a kesterite structural model based on this space group raised serious doubts about its applicability and suggested that the correct space-group is $I\bar{4}$. This will be discussed further below. In this section only the last data collection involving the Laue group $4/m$ and space group $I\bar{4}$ will be described.

The kesterite crystal was oriented on a Picker 4-circle automatic diffractometer by the best least-squares fit of the diffractometer angles for 40 reflections, assuming a triclinic cell. The best fit was obtained for the cell dimensions shown in Table 1. The errors shown represent 3σ as derived from the least-squares matrix.

The intensities of the hkl, $\bar{h}\bar{k}l$ and $\bar{h}k\bar{l}$ octants of data were measured to a 2θ limit of 115°, using graphite-monochromatized Mo$K\alpha$ radiation. Measurements were made in the $\theta/2\theta$ mode at a 2θ scan rate of two degrees per minute and with a scan width adjusted for dispersion (2.40 to 3.48°). Background counts were measured for 30 seconds on each side of the scan, and the intensities of three linearly independent reflections were recorded every 50 measurements to monitor the crystal alignment and instrument stability.

The three octants of data were merged after the application of generalized Gaussian absorption corrections (Gabe & O'Byrne 1970) into an asymmetric data set containing the mean net intensity $\overline{I}_{net}$ and the r.m.s. deviation $\sigma(I)$. Negative net intensities were set to zero. Of the 1288 independent reflections, 1119 had mean intensities greater than $\sigma(I)$ and an overall agreement factor $\Sigma\Delta\overline{I}/\Sigma\overline{I}$ of 0.054. This agreement factor is significantly higher than that achieved subsequently for stannite (0.021), and reflects the difficulty in describing the very irregular shape and smaller size of the fragment in terms of plane faces for the purpose of applying absorption corrections. Structure factors were derived by application of Lorentz and polarization factors with $\sigma(F)$ set at $\frac{1}{2}\sigma(I)\,(I.Lp)^{-\frac{1}{2}}$.

Stannite

A fragment of stannite 0.29×0.17×0.06mm was extracted from an area designated as grain 2R(3) by Kissin & Owens (in prep.), adjacent to the kesterite grain 2R(2) used in the above analysis. Gandolfi and precession photographs show the fragment to be homogeneous and a single untwinned crystal. Diffraction intensities confirmed the space group as $I\bar{4}2m$ (Brockway 1934). The crystal was aligned on a Picker 4-circle diffractometer and its cell dimensions determined by a least-squares fit (Busing 1970) of the 2θ, χ and ω angles for 20 reflections in the range $67° < 2\theta < 72°$. The same procedure used for the kesterite data collection was adopted for the measurement of three separate segments (each 1/16 of the Ewald sphere) of stannite intensities. The segments collected were *hkl*, *khl* and $k\bar{h}\bar{l}$ with $h \geqq k$, and they were merged into an asymmetric data set of 692 reflections. Of these, 684 had mean net intensities above σ(I), and an overall agreement factor $\Sigma\Delta\bar{I}/\Sigma\bar{I}$ of 0.021.

TABLE 2. STRUCTURAL MODELS

Proposed Models with Refined Average Temperature Factors and Agreement Values

	Kesterite						Stannite		
$I\bar{4}$ position		Model 1		Model 2		$I\bar{4}2m$ position			
		Atom	B(Å^2)	Atom	B(Å^2)			Atom	B(Å^2)
2*a*	(0,0,0)	Zn,Fe	1.42	Cu	1.44	2*a*	(0,0,0)	Fe,Zn	0.93
2*b*	(½,½,0)	Sn	0.66	Sn	0.65	2*b*	(½,½,0)	Sn	0.78
2*c*	(0,½,¼)	Cu	1.55	Cu	1.29	4*d*	(0,½,¼)	Cu	1.55
2*d*	(½,0,¼)	Cu	0.99	Zn,Fe	1.17	8*i*	(x,x,z)	S	0.93
8*g*	(x,y,z)	S	0.85	S	0.85				
R	(all data)		0.045		0.044	*R*	(all data)		0.025
R_w	(all data)		0.027		0.025	R_w	(all data)		0.017
R	(I > σ(I))		0.036		0.035				
R_w	(I > σ(I))		0.026		0.025				

STRUCTURE SOLUTION AND REFINEMENT

Kesterite

The consistently stoichiometric proportions of Cu, (Zn,Fe), Sn and S in kesterite for the range of specimens and locations studied by Kissin & Owens (in prep.) suggest that these atoms fully occupy specific sites in the structure. As discussed in the experimental section, the initial space-group choice of $I\bar{4}2m$ for kesterite necessitated the placement of the Cu atoms in the 4*d* (0,½,¼) position, and Sn and (Zn,Fe) at either 2*a* (0,0,0) or 2*b* (½,½,0). Least-squares refinement converged rapidly with this model but provided thermal parameters for the Cu and (Zn, Fe) which were inconsistent with those of stannite and other comparable sphalerite-like structures (Hall 1975; Szymański 1976, 1978; Kudoh & Takéuchi 1976).

The unacceptability of the thermal parameters was enhanced by the fact that the structural similarity of the $I\bar{4}2m$ model with that of stannite was totally unexplainable: kesterite and stannite are found coexisting adjacently with no indication of miscibility; there appears to be a compositional discontinuity in the Fe/Zn ratio between them, and this is reflected in a discontinuity in the cell parameters (Kissin & Owens, in prep.). These factors are strongly indicative of a structural break between stannite and kesterite, and the $I\bar{4}2m$ assignment cannot explain such a break. This reasoning suggests that the correct space group may in fact be $I\bar{4}$, as this would permit a reordering of the metal atoms. The data were subsequently recollected assuming the lower symmetry Laue group 4/*m* and several small but significant differences between *hkl* and *khl* intensities were observed. Structural models were refined for the permutations of metal types in the possible positions of $I\bar{4}$. The two with best agreement are shown in Table 2. It should be pointed out that the composite (Zn, Fe,Cd) *f* curve, generated from the atomic scattering curves in the proportion indicated by the microprobe analysis, differs from the copper *f* curve by a maximum of 0.32*e* and has a mean difference of 0.11*e* over the whole range used. Hence, differentiating the Cu atoms from the composite (Zn,Fe,Cd) atom is not easy, and interchanging these two atomic types in a given position affects the *R* value very slightly. Of the two models given in Table 2, model 1 is equivalent to space group $I\bar{4}2m$, but with positions 2*c* and 2*d* independent, whereas model 2 is only possible in space group $I\bar{4}$. The final *R* values for both structures are similar, but favor model 2. Significantly, however, the thermal parameters for the second model are consistent between the two Cu positions, and are in the same proportion as those observed in other sphalerite-like structures (Hall 1975). For a final comparison, the $I\bar{4}$ intensity data were averaged between the *hkl* and *khl* reflections, and model 1 was refined in space group $I\bar{4}2m$. The *R* values were higher than in space group $I\bar{4}$ (R=0.046, R_w=0.028), and the thermal parameters for (Zn, Fe), Sn, Cu and S were 1.46, 0.66, 1.24 and 0.86Å^2, respectively. These values are in poor agreement with those in similar structures.

Refinement with the full-matrix least-squares program CRYLSQ (Stewart *et al.* 1972) employed weights derived during the data-merge process. The scattering-factor curves used were those of Cromer & Mann (1968). The anomalous dispersion coefficients of Cromer & Liberman (1970) were used in the structure factor and least-squares calculations to define the enantiomorphic configuration of the structure, with respect to the arbitrary choice of right-handed axes selected at the time of data collection. Analysis of the structure factor agreement in the later stages of refinement indicated the need for an extinction parameter *g* (Larson 1970) in the least squares. The parameter *g* refined to 1.36×

TABLE 3. ATOMIC PARAMETERS

The anisotropic temperature factors are expressed in the form:
$T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + 2U_{12}a^*b^*hk + \ldots)]$, and the values quoted are x 10^4.

Kesterite

$I\bar{4}$ position	Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
2*a*	Cu	0	0	0	184(1)	184(1)	192(2)	0	0	0
2*b*	Sn	½	½	0	85(1)	85(1)	77(1)	0	0	0
2*c*	Cu	0	½	¼	171(8)	171(8)	148(11)	0	0	0
2*d*	Zn,Fe	½	0	¼	146(8)	146(8)	153(11)	0	0	0
8*g*	S	.7560(2)	.7566(2)	.8722(1)	108(2)	106(2)	107(2)	-4(2)	4(2)	5(2)

Stannite

$I\bar{4}2m$ position	Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
2*a*	Fe,Zn	0	0	0	105(2)	105(2)	139(2)	0	0	0
2*b*	Sn	½	½	0	95(2)	95(2)	107(2)	0	0	0
4*d*	Cu	0	½	¼	190(3)	190(3)	209(3)	0	0	0
8*i*	S	.7551(1)	.7551(1)	.8702(1)	118(2)	118(2)	117(2)	-4(2)	3(2)	3(2)

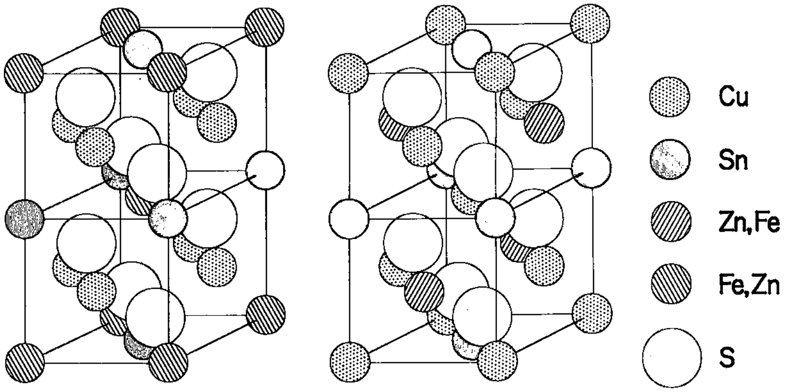
10^{-4}. The final atomic parameters are listed in Table 3.

Stannite

The atomic parameters of stannite were refined by full-matrix least-squares, starting with the model determined by Brockway (1934). Steps in the refinement process were identical to those employed for kesterite and resulted in final R values for all data of $R = 0.025$ and $R_w=0.016$. The refined atomic parameters are listed in Table 3. Final g was 2.72×10^{-4}. The observed $(10\times F_o)$ and calculated $(10\times F_c)$ structure factors for stannite and kesterite are given in Tables 4a and 4b, which are available at nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

DESCRIPTION OF THE STRUCTURES

These analyses show that kesterite and stannite are structurally distinct minerals. The principal structural difference is that in stannite, the (Fe,Zn) atoms share the $z=0$ and $z=½$ metal layers with Sn, whereas in kesterite these layers are occupied by Cu and Sn atoms (Fig. 1). This metal interchange means that the metal layers at $z=¼$ and $z=¾$, which in stannite are oc-



(a) STANNITE ($I\bar{4}2m$) (b) KESTERITE ($I\bar{4}$)

FIG. 1. Diagrammatic representation of the kesterite and stannite structures, emphasizing the difference in metal ordering. The radius of the spheres is arbitrary.

TABLE 4. METAL ORDERING IN ONE SHEET OF THE PSEUDO-CUBIC (111) PLANES IN CHALCOPYRITE, STANNITE AND KESTERITE.

z	chalcopyrite	stannite	kesterite
0	Cu Fe Cu Fe	Fe Sn Fe Sn	Cu Sn Cu Sn
1/4	Fe Cu Fe Cu	Cu Cu Cu Cu	Zn Cu Zn Cu
1/2	Cu Fe Cu Fe	Fe Sn Fe Sn	Cu Sn Cu Sn
3/4	Fe Cu Fe Cu	Cu Cu Cu Cu	Cu Zn Cu Zn
1	Cu Fe Cu Fe	Fe Sn Fe Sn	Cu Sn Cu Sn

cupied only by Cu sites, are shared both by Cu and (Zn,Fe) atoms in kesterite. An alternative way of illustrating the metal ordering in these structures, and in chalcopyrite, is obtained by considering the arrangement of metal atoms in one sheet of the (111) plane of the pseudocubic substructure. This is shown in Table 4.

This metal re-ordering is a profound structural change, and would certainly account for the significant miscibility gap observed by Kissin & Owens (in prep.), and the consistently different unit cells for the two minerals. The energy considerations for this structural change are not clear, though it appears that the similarity of the effective radii of Zn and Fe accounts for the almost identical cell volumes of the two species.

The bond lengths and angles are shown in Figures 2 and 3, and indicate that whereas the close-packing of the S atoms is the dominant structural mechanism accounting for the spha-

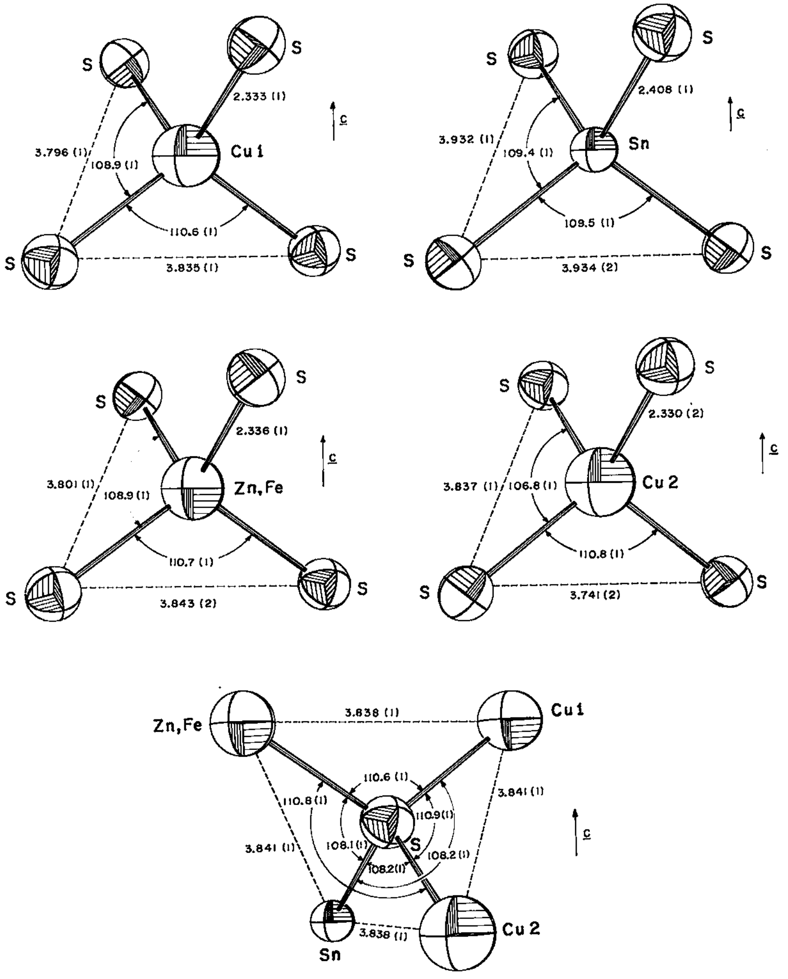


FIG. 2. The atomic coordination of each atom site in kesterite showing interatomic distances in Ångstroms and angles in degrees. The estimated standard deviations are given in parentheses. The atoms are shown as thermal ellipsoids, plotted at the 99% probability limit (Johnson 1965).

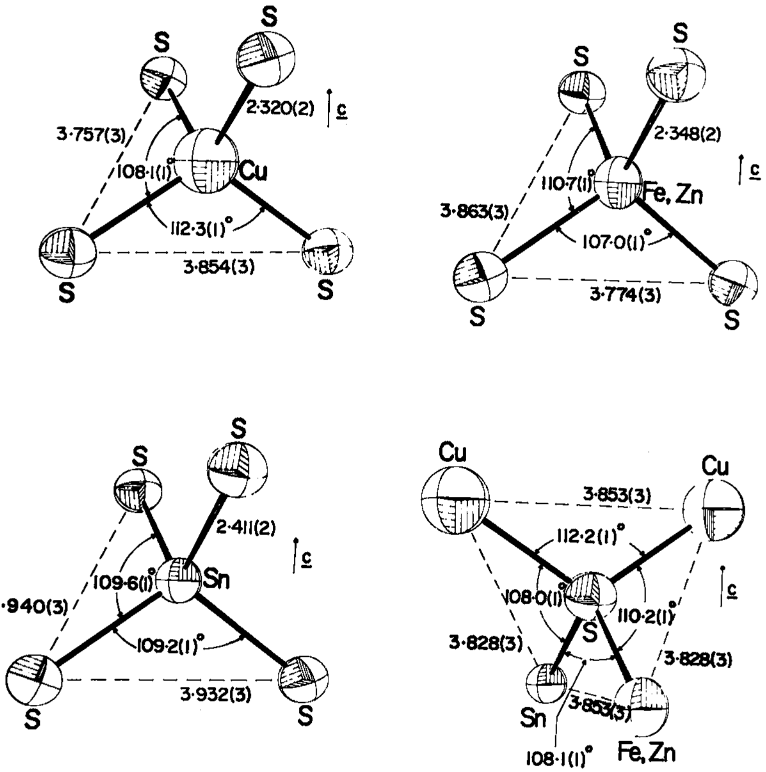


FIG. 3. The atomic coordination of each atom site in stannite showing interatomic distances in Ångstroms and angles in degrees. The estimated standard deviations are given in parentheses. The atoms are shown as thermal ellipsoids, plotted at the 99% probability limit (Johnson 1965).

lerite-like subcell, the larger radius of the Sn atom causes considerable movement from the "ideal" tetrahedral S sites in both structures. The "squashing" effect of the Sn atom results in angles Sn–S–Cu = 108.0(1°) and Sn–S–(Fe, Zn) = 108.1(1)° in stannite, and angles Sn–S–Cu(1) = 108.2(2)°, Sn–S–Cu(2) = 108.2(2)° and Sn–S–(Zn,Fe) = 108.1(2)° in kesterite. As expected, other coordination angles about the S atoms are expanded to Cu–S–Cu = 112.2(1)° and Cu–S–(Fe,Zn) = 110.2(1)° in stannite, and Cu(1)–S–Cu(2) = 110.9(2)°, Cu–Sn–(Zn,Fe) = 110.6(2)° and Cu(2)–S–(Zn,Fe) = 110.8(2)° in kesterite.

For these structures the Sn–S interatomic distances of 2.408(2) and 2.411(1)Å are the same within the standard deviation and agree well with the value of 2.409(1)Å in mawsonite, $Cu_6Fe_2SnS_8$ (Szymański 1976). The kesterite Cu–S distances of 2.330(2) and 2.332(2)Å agree closely, and are significantly larger than the 2.320(2)Å in stannite. These values are marginally larger than those observed in the chalcopyrite structures where values ranged from 2.30–2.33Å. Most significant of the metal–sulfur distances is (Fe,Zn)–S, 2.348(2)Å in stannite, much longer than that for $CuFeS_2$, 2.302(1)Å (Hall & Stewart 1973), and outside the Fe–S range of 2.26–2.30Å for chalcopyrite-type minerals (Hall 1975). This contrasts with the kesterite (Zn,Fe)–S distance of 2.336(3)Å, which is shorter than both the ZnS value of 2.342(1)Å and the (Fe,Zn)–S distance in stannite. The reason for this apparent reversal of radii is not clear, but it is no doubt related to the interchange of Cu and (Zn,Fe) positions between stannite and kesterite.

The thermal parameters for stannite and kesterite are consistent with those observed in mawsonite (Szymański 1976) and other chalcopyrite-type structures (Hall 1975). The mean isotropic *B* value of 0.78Å^2 for the Sn atom in stannite is marginally higher than the values of 0.65 and 0.68Å^2 in kesterite and mawsonite, as are the equivalent sulfur *B* values; this probably reflects overall differences in the diffraction data rather than increased thermal activity in stannite. Most important, however, the relative magnitudes of the (Fe,Zn) and the Cu thermal parameters in stannite are very close to those observed in the chalcopyrite-like structures and in cubanite (Szymanski 1974). Similarly, the Cu *B* values in kesterite are both larger than the (Zn,Fe) *B* value, though the expected average for the latter cannot be well established from comparable structures in the literature. The importance of the relative magnitudes of the thermal parameters in identifying metal sites in this type of structure has been demonstrated for chalcopyrite-like minerals (Hall 1975), and was one of the principal reasons why model 2 for kesterite (Table 2) was more acceptable than model 1.

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