

THE CRYSTAL STRUCTURE OF ČERNÝITE, $\text{Cu}_2\text{CdSnS}_4$, A CADMIUM ANALOGUE OF STANNITE*

J. T. SZYMAŃSKI

Mineral Sciences Laboratories, CANMET, Department of Energy, Mines and Resources,
555 Booth Street, Ottawa, Ontario K1A 0G1

ABSTRACT

The crystal structure of cernyite, $\text{Cu}_2(\text{Cd}_{0.37}\text{Zn}_{0.33}\text{Fe}_{0.26}\text{Mn}_{0.005})\text{SnS}_4$, has been determined and refined to an R value of 0.072 (all 767 data) and 0.034 (475 observed data only). The mineral is tetragonal, a 5.487(2), c 10.848(3) Å, space group $I\bar{4}2m$, and structurally very close to stannite ($\text{Cu}_2(\text{Fe,Zn})\text{SnS}_4$). Černýite has been shown to differ mineralogically from stannite and kesterite: all three minerals co-exist; černýite is evidently immiscible with these two minerals.

SOMMAIRE

On a déterminé et affiné la structure cristalline de la černýite, $\text{Cu}_2(\text{Cd}_{0.37}\text{Zn}_{0.33}\text{Fe}_{0.26}\text{Mn}_{0.005})\text{SnS}_4$. Le résidu R pour l'ensemble des 767 réflexions est de 0.072; pour les 475 réflexions observées, il descend à 0.034. Tétraogonale, avec a 5.487(2), c 10.848(3) Å, la structure, dans le groupe $I\bar{4}2m$, est très proche de celle de la stannite, $\text{Cu}_2(\text{Fe,Zn})\text{SnS}_4$. La cernyite est minéralogiquement distincte de la stannite ainsi que de la kesterite. Ces trois espèces co-existent, la černýite est donc immiscible aux deux autres.

(Traduit par la Rédaction)

INTRODUCTION

Černýite, ideally $\text{Cu}_2\text{CdSnS}_4$, has been discovered at the Tanco mine, Bernic Lake, Manitoba and the Hugo mine, Keystone, Pennington Co., South Dakota. A detailed description of cernýite and the reasons for considering it as a new mineral have been given by Kissin *et al.* (1978). It occurs as intergrowths in stannite and kesterite, and is apparently immiscible with these.

No suitable single crystals could be obtained from the Tanco mine, but the Hugo mine yielded a small untwinned single-crystal fragment which was used to investigate the structure of cernýite, even though its composition is further removed from the cadmium end-member than the Tanco specimen. The syn-

thetic cadmium end-member has been prepared by Nitsche *et al.* (1967) using iodine-transport methods. The cell dimensions of the synthetic crystals were refined from the powder pattern by Schäfer & Nitsche (1974): a 5.585(5), c 10.834(10) Å.

The investigation was undertaken as part of a study of quaternary tin-bearing sulfides, and to determine the structural relationship among cernyite, stannite and kesterite (Hall *et al.* 1978).

EXPERIMENTAL

The results of electron microprobe analysis are reported in Kissin *et al.* (1978), and are quoted in Table 1. The Hugo mine single-crystal fragment (0.12×0.07×0.02mm) was extracted from a polished section and mounted on a glass fibre for preliminary photographic study. Gandolfi photographs were taken to provide a powder pattern, and precession photographs were used to identify the crystal symmetry and probable space group. The crystal was mounted on a four-circle automatic X-ray diffractometer in a general orientation. The cell dimensions were determined from a least-squares refinement of the 2θ , χ and ω angles (Busing 1970) for 42 reflections in the range $53^\circ > 2\theta > 64^\circ$, using a triclinic cell. As the crystal fragment was small, it was not considered necessary to correct the 2θ values of these reflections for absorption. The difference between the a and b cell edges was less than 1σ , and the maximum deviation from orthogonality was less than 1 of arc. The errors quoted in Table 1 represent 3σ as derived from the least squares matrix.

Absorption corrections were calculated using a Gaussian integration procedure and selected equivalent reflections in Laue symmetry $4/mmm$ were measured to determine whether the symmetry was only approximately $4/mmm$ but really $4/m$, as was the case with kesterite. The higher symmetry was confirmed and the space group was identified as $I\bar{4}2m$. Five equivalent segments of data were collected (hkl , $\bar{h}\bar{k}l$, $\bar{h}k\bar{l}$,

*Minerals Research Program, Processing Contribution No. 56

TABLE 1. CRYSTAL DATA FOR ČERNÝITE, $\text{Cu}_2\text{CdSnS}_4$.

Composition (microprobe analysis):	
$\text{Cu}_{1.99}(\text{Cd}_{0.37}\text{Zn}_{0.33}\text{Fe}_{0.29}\text{Mn}_{<0.01})_{1.01}\text{Sn}_{1.00}\text{S}_{4.00}$	
Source: Hugo mine, Keystone, Pennington County, South Dakota, U.S.A.	
Cell Dimensions: $a=5.487(2)$, $c=10.848(3)\text{Å}$ at 20°C , using $\lambda(\text{MoK}\alpha_1) = 0.70926\text{Å}$.	
Systematic Absences: $h + k + l = 2n + 1$	
Space Group: $I\bar{4}2m$ (#121).	
Density: $D_{\text{calc}} = 4.62\text{g.cm}^{-3}$; $Z = 2$. (Density not measured)	
Absorption: $\mu(\text{MoK}\alpha) = 145.8\text{cm}^{-1}$	
Data: 767 measured 5 times, 475 with $I > \sigma(I)$.	

$h\bar{k}l$ and $\bar{k}hl$, for $h > k$, 2θ limit of 120°) using a θ - 2θ scan mode with graphite-monochromatized $\text{MoK}\alpha$ radiation. The 2θ scan width was 2.3° plus the a_1 - a_2 dispersion. The scan rate was 2° per minute, and the background counts were measured on either side of the peak for approximately the same time as was used for the scan. Three reference reflections were measured every 50 measurements in order to monitor crystal alignment and instrument stability. No significant variation was noted during the data collection.

After application of absorption corrections using a Gaussian integration procedure (Gabe & O'Byrne 1970), the five data sets were merged into a single set. Standard deviations were calculated from counting statistics and from the relative agreement of the five measurements. The final data set contained 767 reflections, of which 475 were considered as observed on the criterion that $I > \sigma(I)$. The agreement factor ($\Sigma\Delta I / \Sigma I$) between the data sets was 0.040; this residual value can be attributed mainly to the difficulty in describing, for absorption corrections, the very small and irregular fragment in terms of plane faces. Structure factors were derived by application of the Lorentz and

polarization factors, with $\sigma(F)$ set to $\frac{1}{2}\sigma(I)$ ($I.L.p$)^{1/2}.

STRUCTURE SOLUTION AND REFINEMENT

Examination of the cell dimensions for this specimen of černýite show that $2a > c$ in about the same proportion as is true for stannite, rather than $2a \approx c$ as is true for kesterite (Kissin *et al.* 1978, Figs. 2, 3; Kissin & Owens, in prep.). Though the dimensions are significantly larger than those of stannite or kesterite, they do suggest a stannite-like structure rather than a kesterite-like structure. Examination of strong, absorption-corrected intensities in the eight equivalent segments in Laue symmetry $4/mmm$ did show individual variations, but not a systematic variation between the two sets of four-fold equivalences of Laue symmetry $4/m$. The individual variations were attributed to inaccuracies in describing the crystal shape in the calculation of absorption corrections. This confirmed the higher Laue symmetry and led to the unique choice of space group as $I\bar{4}2m$.

The structure was solved and refined in this space group. As with stannite (Hall *et al.* 1978), copper was assigned to position $4d$ ($0, \frac{1}{2}, \frac{1}{4}$), tin to $2b$ ($\frac{1}{2}, \frac{1}{2}, 0$), sulfur to $8i$ (x, x, z with $x \approx \frac{3}{4}$, $z \approx \frac{7}{8}$) and a composite (Cd, Zn, Fe, Mn) atom to position $2a$ ($0, 0, 0$). In all analyses of stannite-type minerals (stannite, kesterite (Kissin & Owens, in prep.), černýite (Kissin *et al.* 1978), mawsonite (Szymański 1976), stannoidite (Kudoh & Takéuchi 1976), and references quoted therein in each case), it has been found that Cu, Sn and S are in stoichiometric proportions within the limits of accuracy of the analyses. Minor substitutions do occur (Ag for Cu, Sb for Sn and Se for S), but this does not detract from the argument that in each case, each one of these atomic types fully occupies a given site or sites within the structure, without substituting in the sites occupied by atoms of the (Zn, Fe, Cd, Mn) type. Therefore, no attempt was made to refine the structure using a full disorder of the metal types between the various sites.

TABLE 2. ATOMIC PARAMETERS

The anisotropic temperature factors are expressed in the form:

$$T = \exp[-2\pi^2(U_{11}a^2h^2 + 2U_{12}a^*b^*hk + \dots)], \text{ and the values quoted are } \times 10^4.$$

Position	Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	\bar{B}
2a	Cd, Zn, Fe	0	0	0	159(3)	159(3)	167(4)	0	0	0	1.28
2b	Sn	$\frac{1}{2}$	$\frac{1}{2}$	0	119(2)	119(2)	85(2)	0	0	0	0.85
4d	Cu	0	$\frac{1}{2}$	$\frac{1}{4}$	216(3)	216(3)	191(4)	0	0	0	1.64
8i	S	.7500(3)	.7500(3)	.8648(2)	157(4)	157(4)	126(5)	17(5)	22(4)	22(4)	1.16

TABLE 3. BOND DISTANCES AND ANGLES WITH STANDARD DEVIATIONS.

a) Bond distances (Å)	c) Non-bonded tetrahedra (Å)
Sn — S 2.408(2)	1. Around Sn
Mcd* — S 2.408(2)	S ¹ ...S ³ 3.880(2)
Cu — S 2.327(2)	S ¹ ...S ⁵ 3.959(2)
b) Bond angles (°)	2. Around Mcd
S ¹ — Sn — S ³ 107.32(6)	S ² ...S ³ 3.880(2)
S ¹ — Sn — S ⁴ 110.56(6)	S ² ...S ⁶ 3.959(2)
S ² — Mcd — S ³ 107.32(6)	3. Around Cu
S ² — Mcd — S ⁶ 110.56(6)	S ⁴ ...S ⁶ 3.880(2)
S ⁴ — Cu — S ⁶ 112.98(6)	S ⁶ ...S ⁷ 3.759(2)
S ⁶ — Cu — S ⁷ 107.75(6)	4. Around S ⁴
Sn — S ⁴ — Mcd ⁸ 107.32(7)	Sn...Mcd ⁸ 3.880(1)
Sn — S ⁴ — Cu ⁹ 109.10(7)	Cu...Cu ⁹ 3.880(1)
Cu — S ⁴ — Cu ⁹ 112.98(7)	Sn...Cu 3.858(1)
Cu — S ⁴ — Mcd ⁸ 109.10(7)	Cu...Mcd ⁸ 3.858(1)

*) Mcd denotes the composite Cd/Zn/Fe atom type.

Superscripts used above, and in the diagram, refer to the following equivalent positions:

- | | |
|-----------------------|--|
| 1: $x, y, -1+z$ | 7: $\frac{1}{2}-x, \frac{1}{2}-y, z$ |
| 2: $-1+x, -1+y, -1+z$ | 8: $x, 1+y, z$ |
| 3: $-x, -y, -1+z$ | 9: $y, 1+x, z$ |
| 4: $1-x, y, 1-z$ | 10: $-\frac{1}{2}x, -\frac{1}{2}y, -\frac{1}{2}+z$ |
| 5: $x, 1-y, 1-z$ | 11: $1-x, -1+y, 1-z$ |
| 6: $-1+x, 1-y, 1-z$ | |

The refinement converged to $R=0.072$, $R_w=0.056$ (all 767 data) and $R=0.034$, $R_w=0.030$ (475 observed data only). The scattering curves were taken from Cromer & Mann (1968) for the neutral atomic species, and the anomalous dispersion corrections from Cromer & Liberman (1970). As with the structure refinements of stannite and kesterite (Hall *et al.* 1978) and mawsonite (Szymański 1976) better agreement was found in using neutral atomic species than ionized species. The anomalous scattering components provided a check on the chirality of the model relative to the optional choice of a_1 , a_2 axes at data-collection time. In the last stages of refinement, an isotropic extinction parameter (Larson 1970) was included, and this refined to $1.67(4) \times 10^{-5}$. No significant features were observed in the final difference synthesis. The atomic parameters in Table 2 pertain to the refinement treating all data as "observed". The refined parameters based on the observed data only differ by less than 1σ .

The calculations were carried out using the X-RAY system of programs (Stewart *et al.* 1972). The bond lengths and angles are given in Table 3 and are shown in Figure 1. Observed ($10 \times F_o$) and calculated ($10 \times F_c$) structure

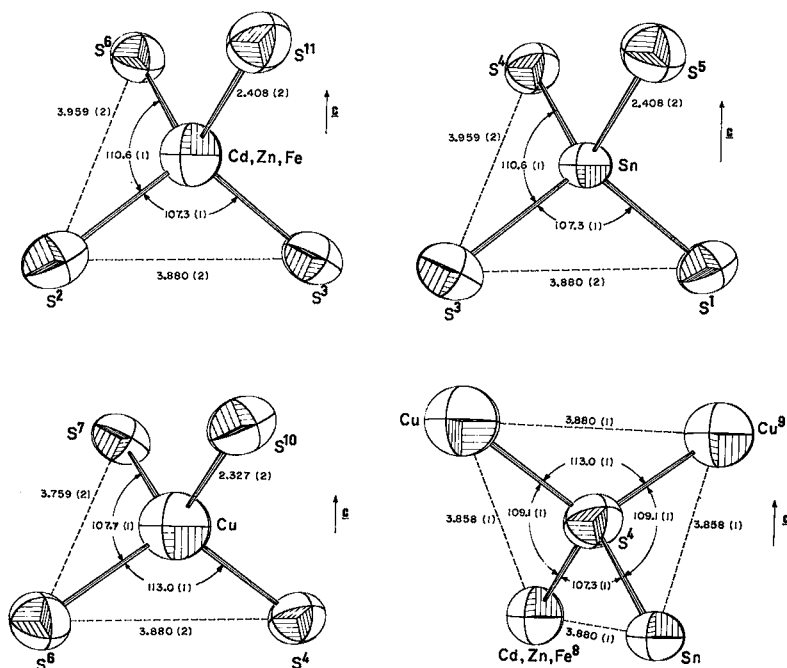


FIG. 1. The atomic coordination of each atom site in čerňite, showing interatomic distances in Ångstroms and angles in degrees. The estimated standard deviations are given in parentheses. The atoms shown as thermal ellipsoids are plotted at the 99% probability limit (Johnson 1965). The superscript designations are listed in Table 3.

factors are given in Table 4, available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

DISCUSSION

The mineralogical reasons for considering černýite as a separate species, rather than as a cadmium end-member of the stannite family, have been discussed by Kissin *et al.* (1978). Stannite, kesterite and černýite are mutually immiscible and all three have been found coexisting in adjacent grains. Within the stannite-kesterite family, a [Zn(+minor Cd)] atomic fraction greater than 0.5 results in a kesterite-type structure (Kissin & Owens, in prep.). In černýite, the sum of the atomic fractions of zinc and cadmium is 0.708. Many of the kesterite specimens examined by Kissin & Owens are close to this value for (Zn+Cd) though in these, the zinc atomic fraction greatly exceeds that of cadmium. However, the presence of sufficient cadmium in černýite stabilizes a stannite-type structure, even though according to Kissin & Owens (in prep.), a kesterite-type structure would have been expected.

The cell dimensions of the Tanco specimen, much richer in cadmium (refined from Gandolfi powder diagrams: Kissin *et al.* 1978) and of the synthetic cadmium end-member (refined from Guinier powder data: Schäfer & Nitsche 1967) both follow the stannite pattern ($2a > c$) rather than the kesterite pattern ($2a \approx c$). It can be safely assumed that both of these have a stannite-like structure. Hence, the specimen investigated is representative of the pure cadmium end-member, even though relatively far from it compositionally.

The bond lengths and angles follow the pattern expected in this type of mineral. The Sn-S bond length of 2.408(2)Å compares with 2.408(2)Å for stannite, 2.411(1)Å for kesterite and 2.409(1)Å for mawsonite (Szymański 1976). The (Cd,Zn,Fe)-S distance of 2.408(2)Å is longer than the (Fe,Zn)-S distance in stannite (2.248(2)Å), the (Zn,Fe)-S distance in kesterite (2.336(3)Å) and the Fe-S distances in mawsonite (2.262(1), 2.269(1)Å), though this is not unexpected in view of the larger size of the average (Cd,Zn,Fe) atom.

The coordination tetrahedra are similar to those in stannite, though the bond angles reflect the increase in size of the cell parameters and the larger size of the (Cd,Zn,Fe) atom in position 2a in comparison with stannite. Thus, the coordination tetrahedron around Sn is more

distorted than it is in stannite (110.6° and 107.3° as opposed to 109.6° and 109.2°). The sulfur tetrahedron angles around (Cd,Zn,Fe) (110.6° and 107.3°) are close to those around (Fe,Zn) in stannite (110.7° and 107.0°).

The thermal parameters are in good agreement with those in related structures. The absolute magnitudes of these are higher than in stannite, kesterite and mawsonite, but they still follow the established pattern that $\bar{B}(\text{Cu}) > \bar{B}[(\text{Zn,Fe}), (\text{Fe,Zn}), (\text{Cd,Zn,Fe})] > \bar{B}(\text{S}) > \bar{B}(\text{Sn})$.

ACKNOWLEDGEMENTS

The author is grateful to Dr. S. A. Kissin, formerly N.R.C. Post-doctoral fellow in this laboratory, for the crystal specimen and for much discussion on the mineralogy of the system, and to Mr. D. R. Owens for the microprobe analyses. The diagrams were prepared using a modified version of ORTEP 2 (Johnson 1965).

REFERENCES

- BUSING, W. R. (1970): Least-squares refinement of lattice and orientation parameters for use in automatic diffractometry. *In* Crystallographic Computing (F. R. Ahmed ed.), Munksgaard, Copenhagen.
- CROMER, D. T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* 53, 1891-1898.
- & MANN, J. B. (1968): X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Cryst.* A24, 321-325.
- GABE, E. J. & O'BYRNE, T. (1970): An absorption correction program for the PDP-8. *Amer. Cryst. Assoc. Summer Meet.* Abstr. A4.
- HALL, S. R., SZYMAŃSKI, J. T. & STEWART, J. M. (1978): Kesterite, $\text{Cu}_2(\text{Zn,Fe})\text{SnS}_4$, and stannite, $\text{Cu}_2(\text{Fe,Zn})\text{SnS}_4$, structurally similar but distinct minerals. *Can. Mineral.* 16, 131-137.
- JOHNSON, C. K. (1965): ORTEP: A FORTRAN thermal ellipsoid plot program for crystal structure illustrations. *Rep.* ORNL-3794, 2nd Rev. ORTEP-II addition 1971, *Oak Ridge Nat. Lab.*, Oak Ridge, Tennessee; modified for use in the X-RAY STEWART System by J. F. Guédon, S. Hall, P. Richard and S. Whitlow, 1974.
- KISSIN, S. A., OWENS, D. R. & ROBERTS, W. L. (1978): Černýite, a copper-cadmium-tin sulfide with the stannite structure. *Can. Mineral.* 16, 139-146.
- KUDOH, Y. & TAKÉUCHI, Y. (1976): The superstructure of stannoidite. *Z. Krist.* 144, 145-160.

- LARSON, A. C. (1970): The inclusion of secondary extinction in least-squares refinement of crystal structures. In *Crystallographic computing* (F. R. Ahmed, ed.), Munksgaard, Copenhagen.
- NITSCHKE, R., SARGENT, D. F. & WILD, P. (1967): Crystal growth of quaternary 1_2246_4 chalcogenides by iodine vapor transport. *J. Crystal Growth* 1, 52-53.
- SCHÄFER, W. & NITSCHKE, R. (1974): Tetrahedral quaternary chalcogenides of the type $Cu_2-II-IV-S_4(Se_4)$. *Mat. Res. Bull.* 9, 645-654.
- STEWART, J. M., KRUGER, G. J. AMMON, H. L., DICKINSON, C. H. & HALL, S. R. (1972): The X-RAY System of crystallographic programs. *Univ. Maryland Comp. Sci. Ctr. Tech. Rep. TR-192*.
- SZYMANSKI, J. T. (1976): The crystal structure of mawsonite, $Cu_8Fe_2SnS_8$. *Can. Mineral.* 14, 529-535.

Received February 1977; revised manuscript accepted January 1978.