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The Crystal Structure of the 'Normal Tetrahedral' Compound Cu_2CdSiS_4*

G. CHAPUIS AND A. NIGGLI

Federal Institute of Technology, Department of Crystallography and Petrography, 8006 *Zürich, Switzerland*

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The structure of Cu_2CdSiS_4 is a superstructure of the wurtzite type. Crystallizing in the space group $Pmn2_1$ with the lattice parameters $a=7{\cdot}60$ ($\simeq 2a_{\text{wurtzite}}$), $b=6{\cdot}48$ ($\simeq \sqrt{3}a_{\text{wurtzite}}$) and $c=6{\cdot}25$ Å ($\simeq c_{\text{wurtzite}}$), the unit cell contains 2 formula units Cu_2CdSiS_4 (calculated density $D_x=4{\cdot}26$). The structure was postulated by geometrical considerations and by taking into account systematic and pseudo-selection rules; it was confirmed by Fourier syntheses. Half the tetrahedral voids of the hexagonal close sulphur packing are regularly occupied by two Cu, one Cd and one Si atom, while the coordination of the electropositive elements by sulphur is also tetrahedral. This structure is a 'normal tetrahedral' one, [after Parthé, E., *Crystal Chemistry of Tetrahedral Structures*, New York, Gordon & Breach (1964)], and represents a limiting member of the series wurtzite–Cu_2CdSiS_4, just as Cu_2FeSnS_4 does in the series sphalerite–stannite with cubic close sulphur packing.

Introduction

In a short communication (Chapuis & Niggli, 1968) the idealized structure of the new compound Cu_2CdSiS_4 has been described. Simultaneously and independently, Parthé, Yvon & Deitch (1969) solved the structure of an isomorphous compound Cu_2CdGeS_4. This structure type belongs to the 'tetrahedral structures' (Parthé, 1964) and may be described as a superstructure of the wurtzite type. Cu_2CdSiS_4 and Cu_2CdGeS_4 are the first tetrahedral quaternary compounds known with a hexagonal close-packing of sulphur atoms; the mineral stannite (Cu_2FeSnS_4) has a corresponding tetrahedral structure with a cubic close-packing of sulphur atoms.

Experimental

Crystal data

Cu_2CdSiS_4, formula weight: 395·8
Habit: prismatic c
$a=7{\cdot}598$ (8), $b=6{\cdot}486$ (6), $c=6{\cdot}258$ (11) Å
$V=1978{\cdot}5$ (1·4) Å^3
$Z=2$, $D_x=4{\cdot}27$ g.cm^{-3}
$\lambda_{\text{Mo }K\alpha}=0{\cdot}71069$ Å
Selection rule for $h0l$: $h+l=2n$
Approximate pseudo-extinctions:
$(h=2n)$ $\frac{1}{2}h+k=2n$, $(h=2n,\ k=3n)$ $\frac{1}{2}h+\frac{1}{3}k+l=2n$
Space group $Pmn2_1$
$\mu_{\text{Mo}}=117$ cm^{-1}
Crystal size of the specimen cut: 0·1 × 0·1 × 0·1 mm.

The compound Cu_2CdSiS_4 has been synthesized by Nitsche, Sargent & Wild (1967) by transport reactions with iodine in the gas phase and a temperature gradient of 800 to 750°C. The crystal has been measured on a Picker automatic diffractometer (FACS 1). With an Ni filter (0·05 mm) in the diffracted beam and a maximal 2θ-value of 65°, 2440 reflexions hkl have been measured with a scintillation counter by the θ–2θ scan method (scanning length: $2\theta=1{\cdot}2°$, this value being corrected for the separation of the $K\alpha_1$ and $K\alpha_2$ lines). For each reflexion, the background has been measured on both sides of the peak. After correction of the Lorentz and polarization factors (no absorption correction), 642 independent reflexions have been obtained with the calculated weights $w=1/\sigma^2(F)=(2F/\sigma_c)^2$ where σ_c = standard deviation of the observation (Poisson).

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* This work is a part of the Ph.D. thesis of G. C.

Solution of the structure

From the point of view of the method, it is interesting that all atomic positions in the unit cell have been found by geometrical considerations, taking into account systematically absent reflexions and approximate pseudo-selection rules (Niggli, 1959). The packing of the sulphur atoms can be found by juxtaposition of two orthohexagonal cells of wurtzite as confirmed by the relations between the cell parameters:

$$a \simeq 2a_{\text{wurtzite}},$$
$$b \simeq \sqrt{3}a_{\text{wurtzite}},$$
$$c \simeq c_{\text{wurtzite}}.$$

Among the three possible space groups given by the systematic absences: $Pmn2_1$ (standard orientation), $P2_1nm$ (same group with a different orientation), and $Pmnm$ (standard symbol $Pmmn$), $Pmn2_1$ is the only one which is compatible with the structure. Indeed, $P2_1mn$ can be eliminated by steric considerations, and $Pmnm$ would not allow any tetrahedral void to have a multiplicity less than 4. The only way to place the glide planes in the unit cell perpendicular to the b axis and the mirror planes is shown in Fig. 1. Placing the two Cd and Si atoms on the special positions with a multiplicity of 2 and the Cu in the general position, the structure given in Fig. 1 results. This model has also been confirmed by the approximate pseudo-selection rules. If the first rule $\frac{1}{2}h+k=2n$ ($h=2n$) were absolutely fulfilled, one of the subcells with $a'=a/2$ and with Cu atoms on the edges would be base-centred. The presence of Cd in one centre and of Si in the other one reduces this selection rule to an approximate one. The second approximate selection rule $\frac{1}{2}h+\frac{1}{3}k+l=2n$ ($h=2n$, $k=3n$) gives information about the space distribution of the atoms. The centres of the new subcells are on the top of tetrahedra with a basis limited by the atoms determined by the precedent rule (2 Cu and 1 Cd or 1 Si atoms).

Table 1. *Fractional atomic coordinates*

	Multiplicity	x	y	z
S(1)	2	0	0·3648 (8)	0·4691 (12)
S(2)	2	0	0·7044 (9)	0·0449 (12)
S(3)	4	0·2755 (6)	0·1617 (7)	0 (def.)
Cu	4	0·2748 (3)	0·1761 (3)	0·3645 (4)
Cd	2	0	0·3479 (2)	0·8718 (7)
Si	2	0	0·6808 (7)	0·3809 (16)

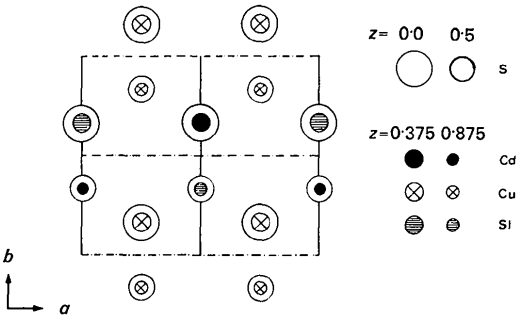


Fig. 1. Projection of the structure of Cu_2CdSiS_4 along **c**.

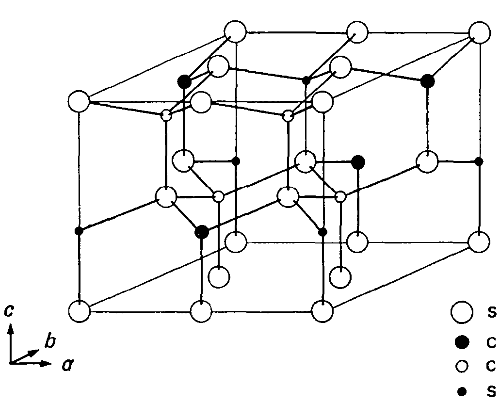


Fig. 2. Three-dimensional view of the structure. For convenience the origin has been put on an S atom.

Structure refinement and results

The model has been refined by a full-matrix least-squares program written by Cromer, Roof & Larson (1965). The effect of anomalous dispersion $\Delta f=\Delta f'+i\Delta f''$ has been corrected with the values given by Cromer (1965). After three least-squares cycles an isotropic extinction correction has been applied. Tables 1 and 2 give the final positional parameters calculated as

$$T(h,k,l)=\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$$

Table 2. *Thermal parameters*

$\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$ *for* Cu, Cd *and* Si *atoms, and* $\exp[-B\sin^2\theta/\lambda^2]$ *for* S *atoms*

	$B_{11}(B)$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0·0046 (4)	0·0083 (4)	0·0082 (5)	−0·0008 (6)	−0·0011 (9)	0·0000 (9)
Cd	0·0038 (4)	0·0065 (3)	0·0073 (4)	0	0	−0·0009 (9)
Si	0·0008 (4)	0·0026 (10)	0·0040 (13)	0	0	−0·0004 (5)
S(1)	0·61 (9)					
S(2)	0·72 (9)					
S(3)	0·63 (6)					

for the electropositive elements. The final value of

$$R=\frac{\sum w^{1/2}||F_o|-|F_c||}{\sum w^{1/2}|F_o|}$$

after 6 cycles was equal to 0·033 with an extinction parameter given by Larson (1967), $g=4{\cdot}31(7).10^{-5}$.

During the refinement, only S(1) and S(2) atoms showed significant changes relative to the ideal positions (0·3 Å). Tables 3 and 4 give the distances and bond angles characterizing the structure. The distances S–electropositive elements are all near the mean value, especially for Si–S distances.

Table 3. *Interatomic distances (in Å)*

The triplet given for one sulphur atom [S(3′)] shows its position in the adjacent cell.

Central atom	S(1)	S(2)	S(3)	S(3′)
Cu	2·339 (4)	2·326 (5)	2·292 (7)	2·365 (5) (0$\bar{1}$0)
Cd	2·522 (7)	2·528 (7)	2·547 (5)	2·547 (5) ($\bar{1}$01)
Si	2·132 (8)	2·136 (15)	2·135 (6)	2·135 (6) ($\bar{1}$00)

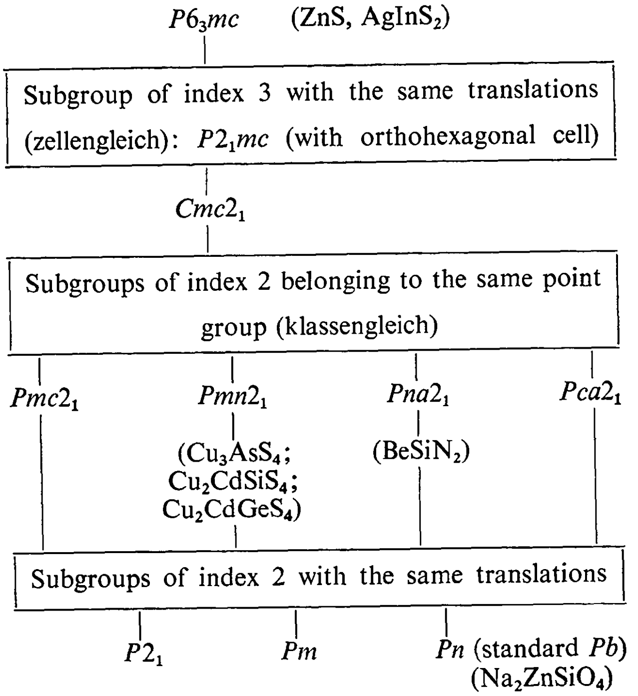
Table 4. *Bond angles*

The position of the S(3′) atoms in the adjacent cells is given in Table 3. *E.g.*, the neighbours S(3′), S(3) with centre Cu indicate the triangle S(3′)–Cu–S(3).

Neighbours		Centre Cu	Centre Cd	Centre Si
S(3′)	S(3)	109·1 (2)	110·6 (2)	106·0 (4)
S(3′)	S(1)	109·0 (2)	109·6 (1)	111·1 (3)
S(3′)	S(2)	101·9 (2)	107·9 (1)	109·3 (3)
S(3)	S(1)	112·0 (2)	109·6 (1)	111·1 (3)
S(3)	S(2)	113·2 (2)	107·8 (1)	109·3 (3)
S(2)	S(1)	111·1 (2)	111·3 (2)	110·1 (5)

Discussion

Cu_2CdSiS_4 is a 'normal tetrahedral' structure with the symbol 1_2246_4 (Parthé, 1964): every electropositive element is tetrahedrally surrounded by 4 S atoms and each S atom is surrounded by 2 Cu, 1 Cd and 1 Si atoms as shown in Fig. 2 (for convenience the origin has been put on an S atom). Parthé has given a synopsis of the crystal chemistry of tetrahedral structures (Parthé, 1964). It is interesting to consider these structures according to their group-subgroups relations. Considering all the known superstructures of wurtzite, the following representation shows that their corresponding space groups belong to the subgroups of $P6_3mc$ (wurtzite):



(Joubert-Bettan, Lachenal, Bertaut & Parthé, 1970).

For tetrahedral structures, the group-subgroups relations are adequate to connect the compounds by showing the elements of symmetry which are lost during the substitution of atoms in the different structures. These group-theoretical considerations give an alternative for the solution of the structure of Cu_2CdSiS_4: the possible space group *Pmnm* considered earlier is not a subgroup of $P6_3mc$ and may be eliminated. In analogy with the preceding scheme it is possible to show the same relations in the superstructure of zincblende ($F\bar{4}3m$).

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