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The Crystal Structure of Cu_2CdGeS_4 and Other Quaternary Normal Tetrahedral Structure Compounds

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Single crystal diffraction methods have been used to solve the crystal structure of Cu_2CdGeS_4: space group $Pmn2_1$ (C^7_{2v}); $a=7{\cdot}692$, $b=6{\cdot}555$, $c=6{\cdot}299$ Å. 4 Cu in 4(*b*): 0·252, 0·324, 0; 2 Cd in 2(*a*): 0, 0·848, 0·995; 2 Ge in 2(*a*): 0, 0·179, 0·490; 4 S in 4(*b*): 0·226, 0·344, 0·359; 2 S in 2(*a*): 0, 0·199, 0·838; 2 S in 2(*a*): 0, 0·851, 0·394. The Cu_2CdGeS_4 structure is a superstructure of wurtzite with $a\sim 2a_W$, $b\sim a_W\sqrt{3}$ and $c\sim c_W$. It presents the wurtzite analog to the stannite structure.

Five other compounds of general composition 1_2246_4 also show superstructures either of wurtzite or of sphalerite, while the twenty investigated 12_236_4 compounds have no ordered cation arrangement producing simple wurtzite or zincblende diffraction patterns.

The problems in the determination of quaternary zincblende or wurtzite related superstructures in general are discussed.

Introduction

The tetrahedral structures have recently been thoroughly reviewed and systematized (Parthé, 1963, 1964). One subdivision of these structures is the group of normal tetrahedral structures where every atom has four nearest neighbor atoms located approximately at the corners of a surrounding tetrahedron. There are two basic normal tetrahedral structures for elements; one is the normal cubic diamond structure, the other the structure of hexagonal diamond called also lonsdaleite (Bundy & Kasper, 1967; Frondel & Marvin, 1967). The binary, ternary or quaternary normal tetrahedral structure compounds have structures which are closely related to either cubic or hexagonal diamond. The structure types for these compounds are shown in Fig. 1. Binary equiatomic compounds select either the sphalerite (=zincblende) type related to cubic diamond or the wurtzite type related to lonsdaleite or a stacking variation of these. The ternary compounds have zincblende or wurtzite supercells with an ordered cation arrangement on the former Zn sites. The zincblende related types are the chalcopyrite ($CuFe^{III}S_2$) type and the famatinite (Cu_3SbS_4) type. A wurtzite analog to chalcopyrite was first found in β-$NaFeO_2$ by Bertaut & Blum (1954) and Bertaut, Delapalme & Bassi (1964). The structure of $BeSiN_2$ (Eckerlin, 1967) is essentially isotypic to β-$NaFeO_2$ except that $BeSiN_2$ has axial ratios much closer to the ones expected from the structural relationship to wurtzite. The enargite (Cu_3AsS_4) type is the wurtzite analog to the famatinite type. An ordered structure type for quaternary normal tetrahedral structure compounds is the stannite ($Cu_2Fe^{II}SnS_4$) type which is a superstructure type based on zincblende. When we started our research program no wurtzite

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related ordered quaternary structure type was known and we found it of interest to investigate if such a structure type could occur.

It has been shown that a correlation exists between the structural features of a tetrahedral structure and the number of valence electrons of all the participating atoms (Parthé, 1964, 1967). In particular there are two electronic conditions which have to be fulfilled with normal tetrahedral structures having zincblende and wurtzite related structures:

(*a*) The average valence electron concentration has to be four.

(*b*) The total number of valence electrons per anion must be eight.

Simple considerations based on these two rules permit us to conclude that for quaternary normal tetrahedral structure compounds of general composition A_2BCD_4 with an ordered arrangement of three different cations on the Zn sites of wurtzite or zincblende, only four particular compositions are possible. Using large numerals to indicate the valence electron contribution of the different elements and small numerical subscripts as conventional chemical composition parameters the four compositions are:

$$12_236_4,\ 1_2246_4,\ 134_25_4,\ 23_245_4\ .$$

The quaternary normal tetrahedral structure compounds have never been studied systematically. As early as 1934 the stannite structure was solved by Brockway (1934). But, except for isolated studies on a few single compounds, the first lists of new 1_2246_4 compounds were published only recently by Hahn & Schulze (1965) and Nitsche, Sargent & Wild (1967). Literature data for compounds with composition 12_236_4, 134_25_4 and 23_245_4 are very scarce or even nonexistent. We report here on experimental studies we have made on 12_236_4 and 1_2246_4 compounds.

Experimental

We synthesized six compounds of general composition 1_2246_4:

Cu_2CdGeS_4, $Cu_2CdGeSe_4$, $Ag_2ZnGeSe_4$, Ag_2CdGeS_4, Ag_2CdSnS_4, $Ag_2CdSnSe_4$

and twenty compounds of general composition 12_236_4:

$CuZn_2AlSe_4$, $CuZn_2AlTe_4$, $CuZn_2GaSe_4$, $CuZn_2GaTe_4$, $CuZn_2InS_4$, $CuZn_2InSe_4$, $CuZn_2InTe_4$, $CuCd_2AlSe_4$, $CuCd_2InS_4$, $CuCd_2InSe_4$, $CuCd_2InTe_4$, $AgZn_2AlS_4$, $AgZn_2InS_4$, $AgZn_2InTe_4$, $AgCd_2AlS_4$, $AgCd_2GaSe_4$. $AgCd_2GaTe_4$, $AgCd_2InS_4$, $AgCd_2InSe_4$, $AgCd_2InTe_4$.

All samples used for X-ray powder photographs were prepared by direct reaction of the chemical elements. Stoichiometric mixtures of the elements were sealed in evacuated quartz capsules and then very slowly heated to temperatures of 600° to 800°C. Color changes indicated that in most cases a reaction occurred

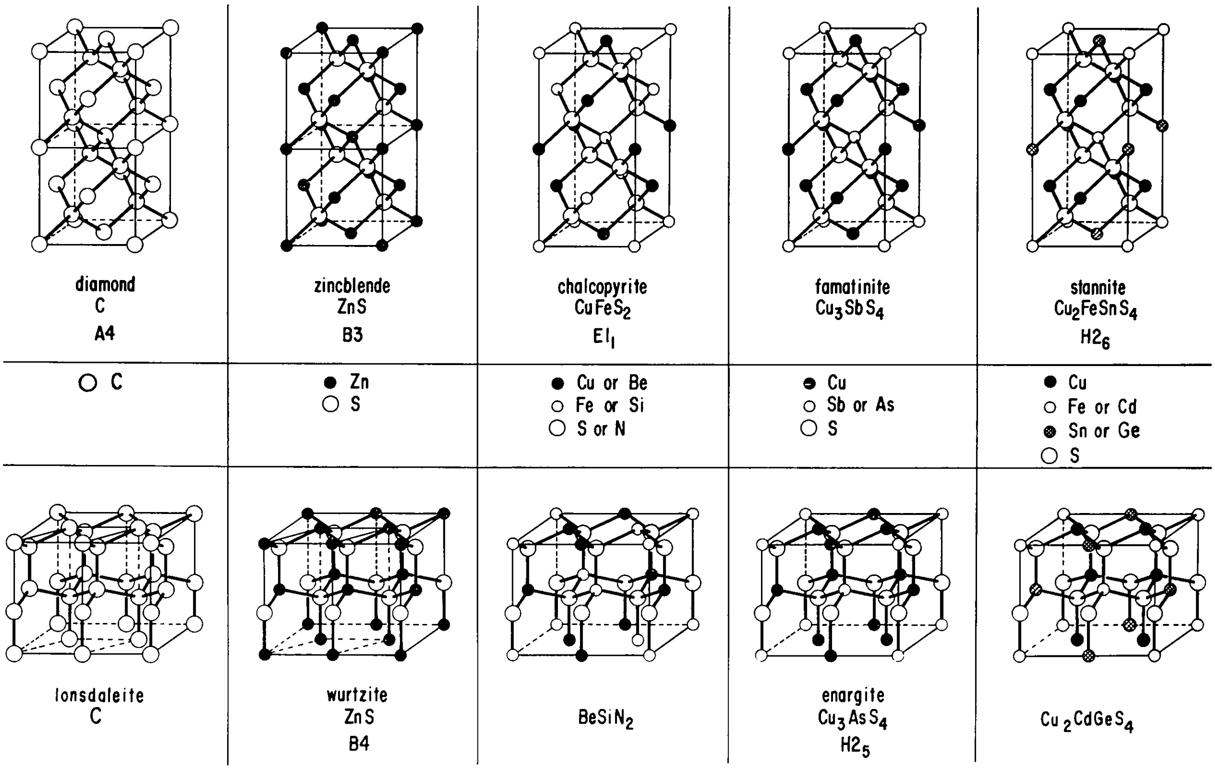

Fig. 1. Normal tetrahedral structure types geometrically related to diamond or lonsdaleite.

within one day. All samples were kept in the furnace for three days, then slowly cooled and the capsules broken. Homogenization is very difficult to obtain with those compounds which are primarily covalently bonded. It was then necessary to grind the resulting product, to mix it throughly and reanneal the specimen in evacuated quartz tubes for extended periods of three to four weeks. In individual cases it was even necessary to repeat the procedure a second time. There was no reaction with the quartz.

Single crystals of Cu_2CdGeS_4 were prepared from stoichiometric elemental mixtures by a vapor transport technique using iodine vapor as a transport medium ($\sim 7{\cdot}5$ mg.cm^{-3}). The procedure used was that described by Nitsche, Sargent & Wild (1967). The powder was placed at the hot end of a quartz tube and held at 1070 °C, while small Cu_2CdGeS_4 crystals formed at the cool end, which was kept at 760 °C.

Powder and single-crystal diffraction techniques were employed in this study, using Cu $K\alpha$ (λCu $K\alpha_1$ $= 1{\cdot}5405$ Å) and Cr $K\alpha$(λ Cr$K\alpha_1 = 2{\cdot}2896$ Å) radiation. A needle shaped Cu_2CdGeS_4 single crystal with a diameter of 0·002 cm and a length of 0·012 cm was rotated around the [001] direction.

The diffracted intensities were recorded photographically on a Nonius integrating Weissenberg camera with use of the multiple film technique and were visually estimated by comparison with a calibrated film strip. Precession photographs of the $h0l$ and the $0kl$ zones were used to cross-correlate the four different Weissenberg layers.

A total of 253 independent hkl reflections were examined and of these 200 were of measurable intensity. Data of Table 5.3.5B of *International Tables for X-ray crystallography* (1959) were used to calculate the absorption correction for a cylindrical specimen with $\mu R = 1{\cdot}03$. The (Lp)$^{-1}$ factor was obtained from values given in Tables 5.2.5F. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Structure determination of Cu_2CdGeS_4

Weissenberg and precession photographs of a Cu_2CdGeS_4 single crystal could be indexed with an orthorhombic unit cell. The lattice parameters refined with the least-squares program by Mueller, Heaton & Miller (1960) and Gvildys (1965) are:

$$a = 7{\cdot}692 \quad \pm 0{\cdot}002 \text{ Å}$$
$$b = 6{\cdot}555 \quad \pm 0{\cdot}002 \text{ Å}$$
$$c = 6{\cdot}299 \quad \pm 0{\cdot}002 \text{ Å},$$

in essential agreement with unit-cell values published by Nitsche, Sargent & Wild (1967). Assuming two formula units per unit cell the X-ray density can be calculated to be 4·60 g.cm^{-3}. All $h0l$ reflections with $h+l=2n+1$ are systematically absent leading to the possible space groups $Pmn2_1$ (C_{2v}^7) and $Pmnm$ (D_{2h}^{13}). From the intensities of the strong diffraction spots we could surmise that the structure of Cu_2CdGeS_4 might be a superstructure of wurtzite with $a \sim 2a_W$, $b \sim a_W\sqrt{3}$ and $c \sim c_W$. Thus we investigated the different ways of ordering the Cu, Cd and Ge atoms on the Zn sites of wurtzite. If one assumes that the overlapping of sp^3 hybridized orbitals is the predominant bonding mechanism in these compounds, one must allow for an electron transfer between the atoms so that each atom obtains the four electrons necessary for a sp^3 hybrid. For energetic reasons we should then expect to find in nature those ordered atomic arrangements which require only a minimum shift of the electrons. This implies that there are no electron transfers farther than one interatomic spacing. Applied to quaternary tetrahedral structures this simple rule which corresponds to Pauling's electrostatic valence rule (Pauling, 1960), suggests that one should find ordered arrangements where every anion is always surrounded by the four cations in the same ratio as given by the overall composition. In the particular case of Cu_2CdGeS_4 the rule says that every S should be bonded to two Cu, one Cd and one Ge atom. With the orthorhombic unit cell given above, one can prove on those assumptions that the two ordered atom arrangements shown on the top of Fig. 2 are the only ones which are compatible with the given rule. The drawings present projections along the c axis where, for simplicity in representation, the sulfur atoms (located $\frac{3}{8}$ of c above every atom) have been omitted. The model on the left corresponds to an orthorhombic wurtzite superstructure with space group $Pmn2_1(C_{2v}^7)$. The symmetry of the other model is actually monoclinic Pc, but with the chosen pseudo-orthorhombic unit cell it must be described with Pn. The ideal point positions for the two models are given in Table 1.

Table 1. *Idealized point positions for two possible wurtzite superstructure models for* Cu_2CdGeS_4 ($a=2a_W$, $b=\sqrt{3}\, a_W$, $c=c_W$)

$Pmn2_1$ (C_{2v}^7)			
	x	y	z
4 Cu in 4(b)	$\frac{1}{4}$	$\frac{1}{3}$	0
2 Cd in 2(a)		$\frac{5}{6}$	0
2 Ge in 2(a)		$\frac{1}{6}$	$\frac{1}{2}$
4 S(1) in 4(b)	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{3}{8}$
2 S(2) in 2(a)		$\frac{5}{6}$	$\frac{3}{8}$
2 S(3) in 2(a)		$\frac{1}{6}$	$\frac{7}{8}$

Pn $xyz, x+\frac{1}{2}\,\bar{y}\,z+\frac{1}{2}$			
	x	y	z
2 Cu (1) with	$\frac{1}{4}$	$\frac{1}{3}$	0
2 Cu (2) with	$\frac{1}{2}$	$\frac{5}{6}$	0
2 Cd with	0	$\frac{5}{6}$	0
2 Ge with	$\frac{3}{4}$	$\frac{1}{3}$	0
2 S(1) with	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{3}{8}$
2 S(2) with	$\frac{1}{2}$	$\frac{5}{6}$	$\frac{3}{8}$
2 S(3) with	0	$\frac{5}{6}$	$\frac{3}{8}$
2 S(4) with	$\frac{3}{4}$	$\frac{1}{3}$	$\frac{3}{8}$

A study of the Weissenberg photographs clearly indicates that $|F(hkl)| = |F(h\bar{k}l)| = |F(\bar{h}kl)| = |F(hk\bar{l})|$ and one might think it would be appropriate to exclude the low symmetry Pn proposal from further consideration. With the pseudo-orthorhombic setting we have chosen for the monoclinic Pn model, the space group (considering only those conventional ones given in *International Tables*) is triclinic $P1$ where we generally expect $|F(hkl)| \neq |F(\bar{h}kl)| \neq |F(h\bar{k}l)| \neq |F(hk\bar{l})|$. The n

glide perpendicular to the b axis leads to a change of the inequalities to $|F(hkl)| = |F(h\bar{k}l)| \neq |F(\bar{h}kl)| = |F(hk\bar{l})|$. Thus, it would seem that, at least in principle it must always be possible to distinguish between both models by a simple inspection of symmetry equivalent reflections. This, however, is not the case if there are certain relations between the x and/or the z parameters of all the atoms in the Pn model. It is easy to verify that if the parameters $x_i, x_j \ldots, z_i, z_j \ldots$ of the participating atoms are all correlated according to

$$\tan 2\pi h x_i = \tan 2\pi h x_j \text{ and/or } \tan 2\pi l z_i = \tan 2\pi j z_j{}^*$$

then $F^2(hkl) = F^2(h\bar{k}l) = F^2(\bar{h}kl) = F^2(hk\bar{l})$. The model Pn corresponds to this case. It seems to be one of the rare and perhaps discomforting incidents where the diffraction symmetry does not coincide with the symmetry inherent in the structure. In our example it means that one can not distinguish between the orthorhombic $Pmn2_1$ and the pseudo-orthorhombic Pn model simply by inspection of symmetry related reflections. However, the two structure models are not homometric and therefore a consideration of the individual $|F(hkl)|$ values should in principle allow a distinction to be made between them.

For the particular case of Cu_2CdGeS_4 we have the additional complication that the Ge atoms have an atomic scattering factor which is only 10% larger than

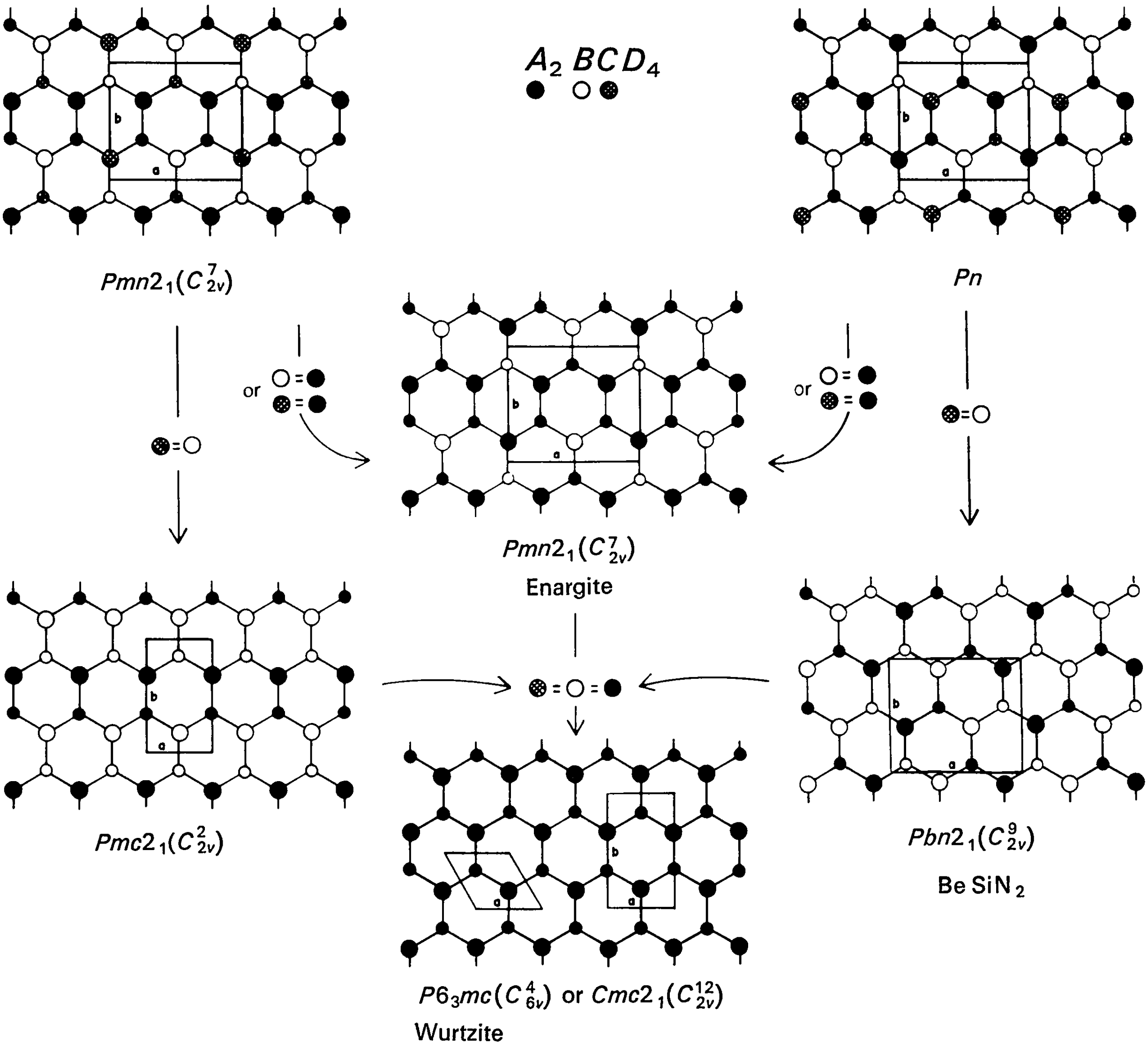

Fig. 2. Two wurtzite superstructure proposals for Cu_2CdGeS_4 and related compounds together with their apparent structures when the differences in the atomic scattering factors between certain participating atoms are very small. (Projections along the c axes; small circles at height 0, big circles at height $\frac{1}{2}$; sulfur atoms are not shown.)

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* This means $x_i = x_j$ or $x_j + \frac{1}{2}$ and/or $z_i = z_j + \frac{1}{2}$ if there are no restrictions on h or l. If $h = 2n$ only (as for example the case with the S atoms) then also $x_i = x_j \pm \frac{1}{4}$.

the one for Cu. In the middle part of Fig. 2 we can see that, in the case of identical atomic scattering factors for atoms on the Cu and Ge sites, both the $Pmn2_1$ and the Pn model will give the same diffraction pattern of enargite. Thus it would not be possible to decide between the two models if the atoms had identical scattering factors, while in our case the intensity differences would be small but still measurable.

In view of these considerations we decided to refine both structure models and to base our final conclusions not only on the R value but also on the interatomic distances obtained from the final parameters. Both structure proposals were refined on an IBM 7040 computer by the use of a full-matrix least-squares program written by Gantzel, Sparks & Trueblood (1961) and modified by Okaya. The function minimized was $\Sigma w\,(|F_{\rm obs}|-|F_{\rm calc}|)^2$. The amplitudes of reflections too weak to be observed were given zero weight for the refinement, while the weighting factor of all the other reflections was given unity. We assumed the following isotropic temperature factors: $B_{\rm Cu}=1{\cdot}5\times10^{-16}\ {\rm cm}^2$, $B_{\rm Cd}=1{\cdot}0\times10^{-16}\ {\rm cm}^2$, $B_{\rm Ge}=0{\cdot}5\times10^{-16}\ {\rm cm}^2$ and $B_{\rm S}=1{\cdot}0\times10^{-16}\ {\rm cm}^2$.

The residual value $R(=\Sigma\,||F_{\rm calc}|-|F_{\rm obs}||/\Sigma\,|F_{\rm obs}|)$ for the $Pmn2_1$ model using the idealized parameters given on the left hand side of Table 1 was found to be 0·25 before refinement. After 7 cycles all parameter shifts were less than 10^{-4} of the estimated standard deviations computed from the inverse matrix. The final parameters as given on the left hand side of Table 2 lead to a final R value of 0·10. Although the structure has 14 adjustable parameters only 13 of them are actually independent. Since there is no center of symmetry one of the six z parameters can be fixed in order to define the orgin of the unit cell. This was done with the z parameter of the Cu atom positions.

For the Pn model an R value of 0·29 was obtained before refinement by use of the idealized parameters given on the right hand part of Table 1. After 5 cycles an R value of 0·15 was obtained with atomic parameters as given in the right hand part of Table 2.

Although the residual value of 0·10 for the orthorhombic proposal is better than the value of 0·15 for the monoclinic one, the existence of the structure having the Pn symmetry cannot definitely be eliminated for that reason alone. The only conclusive way to decide

Table 2. *The refined parameters for the two structure proposals of* Cu_2CdGeS_4 *together with their standard deviations*

$Pmn2_1(C_{2v}^7)$

	x	y	z
4 Cu in 4(*b*)	0·252 (0·001)	0·324 (0·001)	0·0
2 Cd in 2(*a*)	0	0·848 (0·001)	0·995 (0·004)
2 Ge in 2(*a*)	0	0·179 (0·001)	0·490 (0·004)
4 S(1) in 4(*b*)	0·226 (0·002)	0·344 (0·002)	0·359 (0·004)
2 S(2) in 2(*a*)	0	0·199 (0·004)	0·838 (0·004)
2 S(3) in 2(*a*)	0	0·851 (0·004)	0·394 (0·004)

Pn

2(*a*): $x\,y\,z,\ x+\frac{1}{2}\,\bar{y}\,z+\frac{1}{2}$

	x	y	z
2 Cu(1) in 2(*a*)	0·250	0·366 (0·002)	0·0
2 Cu(2) in 2(*a*)	0·489 (0·002)	0·827 (0·003)	0·019 (0·005)
2 Cd in 2(*a*)	0·989 (0·002)	0·830 (0·002)	0·010 (0·004)
2 Ge in 2(*a*)	0·745 (0·002)	0·320 (0·002)	0·996 (0·004)
2 S(1) in 2(*a*)	0·222 (0·004)	0·339 (0·004)	0·359 (0·008)
2 S(2) in 2(*a*)	0·504 (0·004)	0·851 (0·004)	0·368 (0·007)
2 S(3) in 2(*a*)	0·000 (0·004)	0·844 (0·004)	0·387 (0·007)
2 S(4) in 2(*a*)	0·742 (0·004)	0·312 (0·004)	0·371 (0·007)

Table 3. *The interatomic distances (in Å) for the two refined structure models of* Cu_2CdGeS_4 *together with the distances expected from the tetrahedral radii, after Pauling & Huggins* (1934)

$Pmn2_1(C_{2v}^7)$		Arithmetic mean	Expected distances
Cu–1 S(1)	2·28 ± 0·02	2·33	2·38
–1 S(1′)	2·36 ± 0·02		
–1 S(2)	2·34 ± 0·02		
–1 S(3)	2·33 ± 0·02		
Cd–2 S(1)	2·60 ± 0·02	2·55	2·52
–1 S(2)	2·51 ± 0·03		
–1 S(3)	2·51 ± 0·04		
Ge–2 S(1)	2·21 ± 0·02	2·21	2·26
–1 S(2)	2·20 ± 0·04		
–1 S(3)	2·23 ± 0·03		

Pn	
Cu(1)–S(1)	2·28 ± 0·05
–S(2)	2·20 ± 0·04
–S(3)	2·19 ± 0·07
–S(4)	2·41 ± 0·03
Cu(2)–S(1)	2·33 ± 0·08
–S(2)	2·20 ± 0·05
–S(3)	2·38 ± 0·04
–S(4)	2·46 ± 0·04
Cd–S(1)	2·50 ± 0·04
–S(2)	2·46 ± 0·03
–S(3)	2·38 ± 0·05
–S(4)	2·46 ± 0·07
Ge–S(1)	2·32 ± 0·03
–S(2)	2·39 ± 0·07
–S(3)	2·30 ± 0·05
–S(4)	2·36 ± 0·05

between the two models is offered by a comparison of the interatomic distances which should show characteristic values in tetrahedral structures. The Cu–S, Cd–S and Ge–S distances calculated from the refined structure data for both models are compared with the expected distances in Table 3. From this table it becomes obvious that the distances in the *Pmn*2₁ model show a smaller spread and agree far better with the expected values than the distances in the *Pn* model. Thus we can finally conclude that the preferred structure of Cu_2CdGeS_4 is orthorhombic with space group *Pmn*2₁ and point positions as given on the left hand side of Table 2. A perspective drawing of one unit cell of Cu_2CdGeS_4 is shown in the lower right corner of Fig. 1.

In Table 4 are compared the observed F values with the $|F|$ values calculated for the final structure proposal. In Table 5 are listed observed and calculated intensities for a Debye–Scherrer powder photograph. The latter were calculated by use of a computer program written by Jeitschko & Parthé (1966). All strong lines correspond to the wurtzite structure as expected. It is perhaps worthwhile to mention that the superstructure line intensities are extremely sensitive to small shifts of the atoms from their ideal positions. This distortion effect can be so large that a simple comparison with the intensities for the idealized structure models does not permit the determination of the type of atomic ordering. To demonstrate this point, we have listed, in the last two columns of Table 5, the Debye–Scherrer intensities for the *Pmn*2₁ and the *Pn* model using the idealized parameters of Table 1. As expected, we note measurable intensity differences in the superstructure lines, particularly in the small θ region, while the substructure line intensities are the same. The experimentally observed superstructure line intensities given on the left, however, show no relation to any of the intensities for the idealized structures. Thus, without refinement it is impossible to state which structure model we actually have.*

It should be mentioned that in the meantime the *Pn* structure has been found with Na_2ZnSiO_4. The first report on the structure of Na_2ZnSiO_4 was given by Ilyukhin, Nikitin & Belov (1967) who described a distorted structure with fivefold coordination for Na. However, Joubert-Bettan, Lachenal, Bertaut & Parthé (1969) found that the diffraction data can be assigned to a much less distorted structure where all atoms have tetrahedral coordination and which corresponds to the *Pn* model discussed above. According to the last cited reference the Na_2ZnSiO_4 structure occurs also with Na_2ZnGeO_4 and Na_2MgGeO_4.

Structures of other quaternary compounds

For a proper discussion of the results obtained for the structures of the other quaternary compounds it is necessary to investigate how the diffraction patterns are changed if some of the participating atoms have nearly equal atomic scattering factors. This information will help in the interpretation of the observed diffraction patterns.

We have seen above that there are two wurtzite related quaternary superstructure types: the orthorhombic Cu_2CdGeS_4 and the monoclinic Na_2ZnSiO_4 type. In Fig. 2 are shown the apparent structures which will be observed if some of the atoms in the compound A_2BCD_4 have the same scattering factor. If $B=A$ or $C=A$, both the *Pmn*2₁ and the *Pn* structure will give the diffraction pattern of enargite. If $B=C$, the *Pn*

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* *Note added in proof:–* Chapuis & Niggli (1968) have just published the structure of Cu_2CdSiS_4, which is isotypic to Cu_2CdGeS_4 (space group *Pmn*2₁).

Table 4. *Calculated and observed structure factors for* Cu_2CdGeS_4

Reading from left to right, the columns contain the values of h, $|F_{obs}|$ and $|F_{calc}|$.

h00		
2	49	43
4	220	248
6	42	43
8	118	129
h10		
0	21	24
1	16	9
2	172	160
3	31	26
4	25	23
5	<19	4
6	90	87
7	19	21
8	16	22
9	<14	8
h20		
0	150	162
1	39	48
2	16	13
3	25	23
4	121	113
5	41	43
6	19	15
7	<17	5
8	55	62
h30		
0	35	31
1	37	45
2	236	241
3	38	44
4	35	34
5	25	29
6	142	150
7	23	31
8	30	35
9	19	17
h40		
0	103	105
1	<16	5
2	19	23
3	<18	14
4	76	82
5	<22	2
6	<22	22
7	<19	16
8	43	46
h50		
0	<19	<1
1	39	40
2	88	83
3	45	49
4	<19	3
5	19	20
6	56	58
7	38	40
h60		
0	144	139
1	50	56
2	19	16
3	40	46
4	111	115
5	44	50
6	19	20
h70		
0	<19	14
1	<18	16
2	54	53
3	<16	11
4	<14	15
h80		
0	42	41
1	34	35
2	<11	4
h01		
1	23	16
3	45	38
5	16	13
7	31	32
9	16	14
h11		
0	31	29
1	21	20
2	172	150
3	16	12
4	33	23
5	21	22
6	102	93
7	<21	10
8	21	16
9	16	15
h21		
0	150	143
1	<11	10
2	50	42
3	16	13
4	121	110
5	<19	8
6	34	27
7	<21	12
8	55	66
9	<12	8
h31		
0	31	30
1	21	21
2	<20	9
3	13	10
4	23	22
5	25	29
6	34	27
7	<20	15
8	57	66
9	17	21
h41		
0	119	111
1	27	26
2	19	13
3	23	28
4	79	90
5	21	20
6	<22	11
7	<20	23
8	41	57
h51		
0	51	44
1	<20	18
2	70	79
3	<21	19
4	33	36
5	<20	14
6	42	58
7	<15	15
h61		
0	<19	12
1	<19	6
2	23	30
3	19	12
4	<17	9
5	<15	13
6	19	20
h71		
0	<17	8
1	19	25
2	50	60
3	20	23
4	<13	8
5	17	24
h81		
0	35	40
1	16	21
2	34	32
h02		
2	49	43
4	175	169
6	40	35
8	90	96
h12		
0	27	32
1	36	34
2	116	102
3	28	23
4	27	26
5	34	32
6	69	63
7	<18	16
8	19	19
h22		
0	104	100
1	36	40
2	9	11
3	39	40
4	85	76
5	30	31
6	<18	11
7	25	30
8	38	45
9	19	20
h32		
0	42	38
1	25	28
2	164	165
3	25	27
4	34	34
5	9	20
6	104	109
7	13	19
8	25	28
9	16	12
h42		
0	82	75
1	<16	7
2	38	42
3	13	17
4	59	61
5	<18	5
6	25	30
7	19	18
8	33	38
h52		
0	<18	16
1	30	33
2	64	58
3	34	33
4	<18	12
5	23	28
6	38	41
7	21	27
h62		
0	114	101
1	34	36
2	34	27
3	28	32
4	90	85
5	25	32
6	27	23
h72		
0	39	39
1	<15	9
2	39	40
3	<13	9
4	30	33
h82		
0	30	32
1	20	23
h03		
1	28	27
3	<12	9
5	35	30
7	<15	8
9	20	21
h13		
0	27	26
1	19	18
2	218	196
3	30	25
4	35	27
5	<15	6
6	137	125
7	23	20
8	28	28
h23		
0	198	191
1	13	17
2	31	27
3	16	18
4	166	149
5	<15	12
6	30	28
7	<16	15
8	80	85
h33		
0	<14	6
1	9	15
2	9	8
3	28	26
4	<16	5
5	<16	5
6	<16	6
7	27	24
8	<10	4
h43		
0	164	148
1	40	44
2	19	17
3	33	31
4	136	121
5	39	42
6	25	19
h53		
0	13	18
1	31	33
2	92	113
3	30	30
4	16	19
5	22	28
6	85	79
h63		
0	9	11
1	19	15
2	<14	6
3	<14	5
4	9	9
5	25	19
h73		
0	9	9
1	40	39
2	64	77
3	45	44

Table 5. *Powder intensity calculation for* Cu_2CdGeS_4 (λCr $K\alpha_1 = 2·2896$ Å)

					Intensity calculated for an ideal undistorted structure (parameters from Table 1)	
Pmn2_1 *hkl*	$10^3 . \sin^2 \theta_{cal}$	$10^3 . \sin^2 \theta_{obs}$	I_{cal}	I_{obs}	*Pmn*2_1	*Pn**
010	30·5	30·5	28	*vw*	26·7	14·8
110	52·7	—	7	—	49·1	67·9
101	55·2	54·9	18	*vvw*	59·4	80·7
011	63·5	63·1	40	*w*	65·2	38·1
111	85·7	85·5	37	*vw*	17·7	23·9
200	88·6	88·4	31	*vw*	27·3	16·4
210	119·1	119·2	720	*vs*	864·1	864·1
020	122·0	121·5	379	*s*	396·4	396·4
002	132·1	132·0	680	*vs*	827·5	827·5
120	144·2	144·0	47	*vw*	12·7	16·7
211	152·1	151·4	1000	*vvs*	1000·0	1000·0
021	155·0	155·2	446	*vs*	477·9	477·9
012	162·6	162·8	15	*vw*	5·7	3·5
121	177·2	—	3	—	6·3	8·4
112	184·8	184·0	30	*w*	17·4	23·0
220	210·6	—	2	—	4·0	2·4
202	220·7	220·4	17	*vw*	14·7	8·8
310	229·9	—	8	—	6·2	8·3
301	232·4	233·0	17	*vvw*	8·0	10·7
221	243·6	244·0	38	*w*	18·9	11·2
212	251·2	251·5	237	*s*	303·8	303·8
022	254·1	254·5	120	*ms*	151·3	151·3
311	262·9	—	3	—	3·3	4·5
030	274·5	276·1	4	*w*$_{diff}$	5·3	3·1
122	276·3		26		9·0	12·3
130	296·7	296·6	16	*vw*	<0·1	<0·1
031	307·5	306·2	10	*vw*	<0·1	<0·1
103	319·4	—	6	—	4·9	6·7
320	321·4	—	4	—	3·6	4·9
013	327·8	324·4	6	*vw*	6·2	3·5
131	329·7		6		9·2	12·8
222	342·7	—	2	—	4·0	2·2
113	349·4	—	5	—	2·1	2·9
400	354·4	354·7	239	*s*	294·3	294·3
321			2		2·1	2·9
312	362·0	—	6	—	6·0	8·5
230	363·1	363·9	442	*vs*	564·5	564·5
410	384·9	—	3	—	1·7	0·9
231	396·1	—	<1	—	<0·1	<0·1
032	406·6	—	7	—	6·4	3·4
213	416·4	416·6	522	*vs*	619·4	619·4
411	417·9		6		9·2	4·9
023	419·3	418·3	244	*s*	301·7	301·7
132	428·8	—	8	—	<0·1	<0·1
123	441·4	—	3	—	1·6	2·3
322	453·5	—	15	—	4·4	6·5
330	473·9	—	10	—	<0·1	<0·1
420	476·4	475·6	79	*ms*	99·0	99·0
402	486·5	486·0	166	*s*	231·5	231·5
040	488·0		30		46·1	46·1
232	495·2	494·8	311	*vs*	453·1	453·1
303	496·6	—	<1	—	2·7	4·0
331	506.9	—	1	—	5.3	7.9
223	507·9	508·7	9	*s*	7·8	3·9
421	509·4		144		174·4	174·4
140	510·2	—	<1	—	2·0	3·0
412	517·0	—	6	—	2·6	1·3
041	521·1	520·9	72	*w*	86·9	86·9
313	527·1	—	6	—	1·3	1·9
004	528·5	527·9	33	*vw*	36·0	36·0
141	543·2	—	8	—	1·2	1·8
014	559·0	—	4	—	1·3	0·6
033	571·8	—	<1	—	<0·1	<0·1
240	576·6	—	2	—	1·2	0·6
114	581·1	—	3	—	3·6	5·6
510	584·3	—	<1	—	1·8	2·8

Table 5 (*cont.*)

*Pmn*2$_1$ *hkl*	$10^3 . \sin^2 \theta_{cal}$	$10^3 . \sin^2 \theta_{obs}$	I_{cal}	I_{obs}	*Pmn*2$_1$	*Pn**
501	586·8	—	1	—	2·4	3·7
133	593·9	—	2	—	4·8	7·4
332	606·0	—	7	—	<0·1	<0·1
422	608·5	609·1	68	*w*	99·7	99·7
241	609·7	—	1	—	1·6	3·6
204	617·1	—	8	—	5·0	2·4
511	617·3	—	5	—	1·2	1·8
323	618·6	—	3	—	1·2	1·9
042	620·1	619·3	29	*vw*	47·5	47·5
430	628·9	—	6	—	5·1	2·4
142	642·3	—	<1	—	3·7	5·7
214	647·6	649·0	27	*vw*	32·8	32·8
024	650·5		16		16·7	16·7
233	660·4	—	<1	—	<0·1	<0·1
431	662·0	—	7	—	<0·1	<0·1
124	672·6	—	2	—	3·6	5·8
520	675·8	—	10	—	1·8	2·9
413	682·2	—	10	—	8·0	3·7
340	687·4	—	1	—	1·9	3·0
242	708·7	708·0	20	*vvw*	2·7	1·2
521	708·8	—	1	—	1·3	2·0
512	716·4	—	10	—	3·8	6·1
341	720·4	—	11	—	1·2	2·0
224	739·1	—	<1	—	3·0	1·3
314	758·3	—	<1	—	4·1	6·6
432	761·0	—	14	—	12·2	5·5
050	762·5	—	<1	—	0·8	0·4
333	771·1	—	9	—	5·6	9·0
423	773·7	774·5	323	*vs*	484·5	484·5
150	784·7	—	10	—	2·1	3·5
043	785·3	785·4	169	*s*	251·1	251·1
051	795·6	—	15	—	4·9	2·2
600	797·4	—	7	—	3·3	1·5
034	803·0	—	11	—	6·8	3·0
143	807·4	808·1	28	*vvw*	1·5	2·4
522	807·9		12		4·5	7·4
151	817·7	—	7	—	1·6	2·6
342	819·5	—	3	—	4·8	7·8
134	825·2	—	4	—	<0·1	<0·1
610	827·9	828·0	63	*w*	103·4	103·4
530	828·3	—	6	—	<0·1	<0·1
440	842·4	841·2	56	*w*	106·4	106·4
105	847·9	—	9	—	3·5	5·7
324	849·9	—	12	—	5·2	8·5
503	851·0	851·1	8	*w*	3·5	5·7
250	851·1		72		115·9	115·9
015	856·3	—	6	—	6·1	2·7
611	860·9	860·9	172	*ms*	218·3	218·3
531	861·3	—	13	—	7·2	11·9
243	873·9	—	7	—	13·3	5·8
441	875·5	875·1	169	*ms*	231·6	231·6
115	878·4	—	9	—	1·9	3·2
513	881·5	—	<1	—	2·0	3·2
404	882·9	882·2	84	*w*	98·0	98·0
251	884·2	884·1	137	*ms*	235·0	235·0
234	891·6	890·8	157	*ms*	204·8	204·8
052	894·7	—	4	—	2·5	1·1
414	913·4	—	13	—	5·4	2·3
152	916·8	—	23	—	7·1	11·8
620	919·4	—	4	—	2·9	1·2
433	926·2	—	<1	—	<0·1	<0·1
602	929·5	—	16	—	12·1	5·2
215	944·9	944·7	534	*vs*	999·3	999·3
025	947·8	947·9	275	*s*	505·9	505·9

Table 5 (*cont.*)

$Pmn2_1$ *hkl*	$10^3 . \sin^2 \theta_{cal}$	$10^3 . \sin^2 \theta_{obs}$	I_{cal}	I_{obs}	$Pmn2_1$	Pn*
621	952·5	—	27	—	22·4	9·6
612	960·0	961·0	151	*ms*	260·8	260·8
532	960·4		13		<0·1	<0·1
350	961·9		43		5·4	9·0

* The true symmetry of this structure proposal is monoclinic *Pc*, but, with a pseudo-orthorhombic unit cell setting, the apparent symmetry is *Pn*. The conventional space group notation for this setting would be triclinic *P*1, but the *n* glide leads to relations between the $|F|$ values: $|F(hkl)| = |F(h\bar{k}l)| \neq |F(\bar{h}kl)| = |F(hk\bar{l})|$. If we consider the additional case that the structure is ideal and the x parameters of all atoms are 0, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$, then the relation $|F(hkl)| = |F(h\bar{k}l)| = |F(\bar{h}kl)| = |F(hk\bar{l})|$ holds and the intensities can be calculated as for a regular orthorhombic structure.

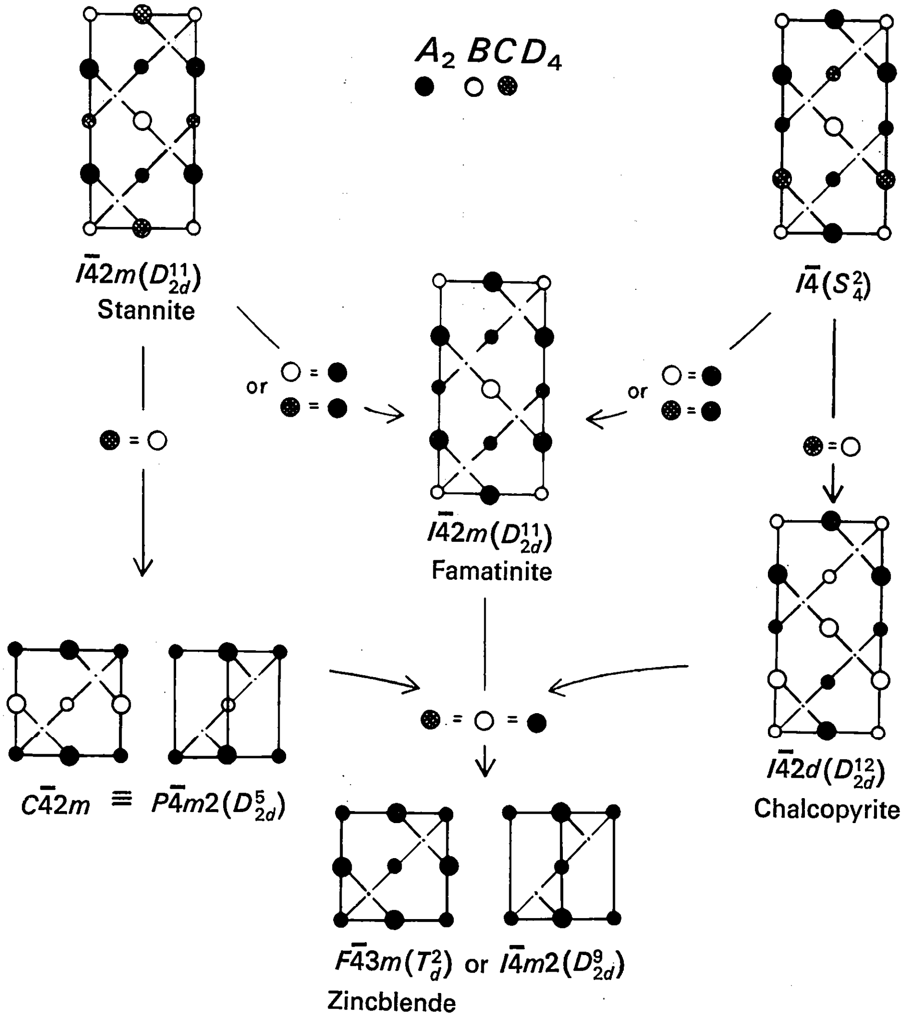

Fig. 3. Two quaternary zincblende superstructure proposals, together with their apparent structures when the differences in the atomic scattering factors between certain participating atoms are very small (Projections along the *b* axes; or for $P\bar{4}m2$ and $I\bar{4}m2$ along the [110] direction; small circles at height 0, big circles at height $\frac{1}{2}$; sulfur atoms are not shown).

structure appears like the $BeSiN_2$ structure with equal cell size, but the $Pmn2_1$ structure can now be described with a cell of half the original volume. If $A=B=C$ the patterns of both models are identical to that for wurtzite or, if the a/b ratio were not exactly $2/\sqrt{3}$, some lines will be split requiring in place of the hexagonal cell the corresponding orthohexagonal cell with apparent space group $Cmc2_1$.

The stannite structure type with space group $I\bar{4}2m$ is the only published zincblende related quaternary structure type. However, one can imagine a second tetragonal type with space group $I\bar{4}$, shown in the upper right hand part of Fig. 3, which satisfies equally well the above rule for atom ordering. In the lower part of Fig. 3 are drawn the apparent structures which will be observed if some atoms have the same scattering factor. With $B=A$ or $C=A$, both the $I\bar{4}2m$ and $I\bar{4}$ structures will show the diffraction pattern of famatinite. If $B=C$, the $I\bar{4}$ structure will appear like chalcopyrite having the same unit cell size, but, to index the diffraction pattern of the $I\bar{4}2m$ structure, one needs only a cell one fourth the size with $a=\frac{\sqrt{2}}{2}a_{\text{stannite}}$ and $c=\frac{1}{2}c_{\text{stannite}}$ and apparent space group $P\bar{4}m2$. If $A=B=C$, both models will give the cubic zincblende pattern or, if c/a was not exactly 2, the pattern can be indexed with a body centered tetragonal cell half as large as zincblende.

For the interpretation of the diffraction patterns of the quaternary compounds we must be aware that the observed lattice parameters and space groups are not necessarily the true ones. In Tables 6 and 7 are given the observed unit-cell parameters and apparent space groups together with the probable structure types. A study of Figs. 2 and 3 will permit one to arrive at the conclusions concerning the possible ordered structure types listed in the last column of Tables 6 and 7. We note that ordered superstructures are found only with 1_2246_4 compounds. This must be also the case for Ag_2CdSnS_4 and $Ag_2CdSnSe_4$ where the atomic scattering factors of the cations are all nearly the same. We do not observe here a hexagonal cell ($P6_3mc$) but an orthorhombic cell ($Cmc2_1$). The latter is not expected if all the cations are randomly arranged. Not one ordered structure is found with the twenty 12_236_4 com-

Table 6. *Lattice parameters, apparent space groups and possible structures of the* 1_2246_4 *compounds*

Compound	Type of diffraction pattern*	Apparent space group	Observed lattice parameters a (Å)	b (Å)	c (Å)	Possible structures
Cu_2CdGeS_4	W	$Pmn2_1$	7·692 ± 0·002	6·555 ± 0·002	6·299 ± 0·002	Cu_2CdGeS_4 type
$Cu_2CdGeSe_4$	S	$I\bar{4}2m$	5·657 ± 0·005		10·988 ± 0·01	Stannite or $I\bar{4}$ with c/a= 1·94
$Ag_2ZnGeSe_4$	S	$P\bar{4}m2$	4·269 ± 0·005		5·659 ± 0·005	Stannite type with c/a= 1·88
Ag_2CdGeS_4	W	$Pmn2_1$	8·044 ± 0·008	6·849 ± 0·005	6·593 ± 0·005	Cu_2CdGeS_4 or Pn type
Ag_2CdSnS_4	W	$Cmc2_1$	4·111 ± 0·005	7·038 ± 0·005	6·685 ± 0·005	Order exists but cannot be determined with X-rays
$Ag_2CdSnSe_4$	W	$Cmc2_1$	4·262 ± 0·005	7·314 ± 0·005	6·979 ± 0·005	Order exists but cannot be determined with X-rays

* W = wurtzite related structure; see Fig. 2
S = sphalerite related structure; see Fig. 3.

Table 7. *Lattice parameters and space groups of the investigated* 12_236_4 *compounds*

Compound	Type of diffraction pattern*	Space group	Observed lattice parameters a (Å)	c (Å)	Remarks
$CuZn_2AlSe_4$	S	$F\bar{4}3m$	5·624 ± 0·005		not ordered
$CuZn_2AlTe_4$	S	$F\bar{4}3m$	6·043 ± 0·005		not ordered
$CuZn_2GaSe_4$	S	$F\bar{4}3m$	5·653 ± 0·005		order cannot be determined
$CuZn_2GaTe_4$	S	$F\bar{4}3m$	6·057 ± 0·005		order cannot be determined
$CuZn_2InS_4$	S	$F\bar{4}3m$	5·475 ± 0·005		not ordered
$CuZn_2InSe_4$	S	$F\bar{4}3m$	5·733 ± 0·005		not ordered
$CuZn_2InTe_4$	S	$F\bar{4}3m$	6·153 ± 0·005		not ordered
$CuCd_2AlSe_4$	W	$P6_3mc$	4·106 ± 0·005	6·752 ± 0·005	not ordered
$CuCd_2InS_4$	W	$P6_3mc$	4·047 ± 0·005	6·617 ± 0·005	not ordered
$CuCd_2InSe_4$	S	$F\bar{4}3m$	5·934 ± 0·005		not ordered
$CuCd_2InTe_4$	S	$F\bar{4}3m$	6·335 ± 0·005		not ordered
$AgZn_2AlS_4$	W	$P6_3mc$	3·846 ± 0·005	6·313 ± 0·005	not ordered
$AgZn_2InS_4$	W	$P6_3mc$	3·944 ± 0·005	6·459 ± 0·005	not ordered
$AgZn_2InTe_4$	S	$F\bar{4}3m$	6·253 ± 0·005		not ordered
$AgCd_2AlS_4$	W	$P6_3mc$	4·134 ± 0·005	6·723 ± 0·005	not ordered
$AgCd_2GaSe_4$	W	$P6_3mc$	4·251 ± 0·005	6·956 ± 0·005	not ordered
$AgCd_2GaTe_4$	S	$F\bar{4}3m$	6·375 ± 0·005		not ordered
$AgCd_2InS_4$	W	$P6_3mc$	4·112 ± 0·005	6·709 ± 0·005	order cannot be determined
$AgCd_2InSe_4$	W	$P6_3mc$	4·277 ± 0·005	6·988 ± 0·005	order cannot be determined
$AgCd_2InTe_4$	S	$F\bar{4}3m$	6·438 ± 0·005		order cannot be determined

* W = wurtzite related structure; see Fig. 2.
S = sphalerite related structure; see Fig. 3.

pounds; however, in five cases ordering could not be determined even if it existed. We note that the patterns all have high symmetry ($F\bar{4}3m$ for zincblende and $P6_3mc$ for wurtzite related compounds). Ordering of the cations seems rather unlikely. The composition 1_22364_4 is located on the connecting line between 26 and 136_2. Examples are known where a complete series of solid solutions exists between 26 and 136_2. Goryunova (1965) lists for example CdTe–$AgInTe_2$ and CdTe–$CuInTe_2$ where the zincblende structure type is found over the entire concentration range. The compositions $CuCd_2InTe_4$ and $AgCd_2InTe_4$ given in Table 7 are, therefore, only selected points of a complete series of solid solutions. For the other compounds given in Table 7 no homogeneity range measurements have been made, and it must be left for further research to determine if these alloys really correspond to independent quaternary compounds or to the quaternary compositions in a solid solution range between a binary and a ternary normal tetrahedral structure compound.

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Eine neue Absorptionsfaktortafel für kugelförmige Proben

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A new table of spherical absorption factors is calculated for $0 \le \mu R \le 31{\cdot}5$ with an accuracy better than 10^{-3}. Errors up to 2% are detected in the absorption factor tables 5.3.6B of *International Tables for X-ray Crystallography*, Vol. II.

Überblick

Das Integral A_{Kug} zur Berechnung von Kugelabsorptionsfaktoren ist, wenn man von den Beugungswinkeln $\theta = 0°$ und $\theta = 90°$ absieht, nicht geschlossen darstellbar (Bond, 1957); es muss daher numerisch bestimmt werden.

Die ersten Berechnungen von A_{Kug}-Werten findet man bei Taylor (1944). Er setzte die Kugel nach Fig. 1 aus Kreisscheibchen abnehmenden Halbmessers r zusammen, wodurch sich das Kalkül auf eine eindimensionale Integration über die bereits bekannten Absorptionsfaktoren A_{Zyl} des Kreiszylinders (Claasen, 1930; Bradley, 1935) reduzieren lässt.

Unter Berücksichtigung der Volumennormierung findet man für eine Scheibchendicke Δz

$$A_{\text{Kug}} \simeq \Sigma\, r^2 \pi A_{\text{Zyl}}(\mu r) \Delta z / (4\pi R^3/3)\,, \qquad (1)$$

wobei, wie üblich, R für den Kugelradius und μ für den linearen Schwächungskoeffizienten gesetzt ist. Für