

Structure refinement of Cu_8GeS_6 using X-ray diffraction data from a multiple-twinned crystal

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Abstract

The structure of the orthorhombic room-temperature phase of Cu_8GeS_6 (copper germanium sulfide), $M_r = 773.27$, has been refined on the basis of X-ray diffraction data from a 12-fold twinned crystal applying a six-dimensional twin refinement technique. For 1804 unique reflections measured using Mo $K\alpha$ radiation, R_F was 0.083 with 77 structure parameters and 12 scale factors. The symmetry operations, the unit cell and other crystal data are $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + x, y, z; y, x, z; \frac{1}{4} - x, \frac{3}{4} - y, \frac{1}{2} + z; \frac{3}{4} - y, \frac{1}{4} - x, \frac{1}{2} + z; a = b = 9.9073$ (3) Å, $c = 9.8703$ (4) Å, $\alpha = \beta = 90^\circ$, $\gamma = 90.642$ (4) $^\circ$; $V = 968.7$ (1) Å 3 , $Z = 4$, $D_x = 5.358$ Mg m $^{-3}$, $\mu = 21.70$ mm $^{-1}$. The standard setting of the space group and the reduced unit cell are $Pmn2_1$; $a = 7.0445$ (3), $b = 6.9661$ (3), $c = 9.8699$ (5) Å; $Z = 2$.

1. Introduction

Three compounds have been known to exist in the Cu–Ge–S system. Cu_8GeS_6 belongs to the argyrodite family (Hahn *et al.*, 1965; Kuhs *et al.*, 1979), with a phase transition at ~ 330 K (Khanfer *et al.*, 1974; Wang & Viaene, 1974; Goetz, 1988). The high-temperature phase (phase I) of Cu_8GeS_6 is cubic with space group $F4\bar{3}m$, and the room-temperature phase (phase II) is orthorhombic with space group $Pmn2_1$ (Goetz, 1988; Ishii *et al.*, 1999). Cu_2GeS_3 was reported as a monoclinic phase (Khanfer *et al.*, 1973) and the crystal structure was analyzed by single-crystal X-ray diffraction techniques (De Chalbaud *et al.*, 1997). Cu_4GeS_4 was reported and predicted to be an orthorhombic phase (Wang, 1976). Recently, the crystal structure of Cu_4GeS_4 was described based on the monoclinic space group $P2_1/c$ (Chen *et al.*, 1999).

In the present paper the results of the structure refinement of the room-temperature phase (II) of Cu_8GeS_6 using the X-ray diffraction data from a multiple-twinned crystal are described.

2. Experimental

The specimen was obtained as a by-product of an experiment attempting to prepare the Cu_4GeS_4 phase. The preparation processes have been described in detail

previously (Chen *et al.*, 1999). After heating in an evacuated silica tube at 1103 K for 1 month and cooling, a small amount of triangular plate-like crystals were observed as the minor product, while the principal product was the gray prismatic crystals of Cu_4GeS_4 . Electron microprobe analysis of the plate-like crystal by Jeol JXA-8600 MX gives an approximate atomic ratio Cu:Ge:S of 8.4:1.0:5.8, in good agreement with that deduced from the structural refinement. The precession photographs indicated that the reciprocal lattice of these crystals mimicked trigonal symmetry.

Experimental details are summarized in Table 1. The inner residual factor, $R_{\text{int}}(F) = 0.051$, based on the assumed Laue group $\bar{3}m1$, and the qualities of the Weissenberg photographs show that it is difficult to accept the trigonal symmetry. As the powder X-ray diffraction pattern of the specimen with a chemical composition Cu_8GeS_6 shows orthorhombic symmetry character with space group $Pmn2_1$ (Goetz, 1988; Ishii *et al.*, 1999), the X-ray diffraction data collected by the four-circle diffractometer are considered to be from a multiple-twinned crystal.

3. Refinement

3.1. Axis transformation and preliminary structure refinement

The observed reflections [$I > 2\sigma(I)$] seem to be caused by a twinned rhombohedral crystal (hexagonal setting: $a_h = b_h = 13.956 = 2^{1/2} \times 9.87$, $c_h = 17.048 = 3^{1/2} \times 9.84$ Å; rhombohedral setting: $a_r \simeq 9.9$ Å and $\alpha \simeq 90^\circ$), since they are of two groups, the major one of 1556 reflections satisfying the reflection condition $-h_h + k_h + l_h = 3n$ and the minor one consisting of 248 reflections fulfilling the condition $-(-h_h + k_h) + l_h = 3n$. The rhombohedral unit cell corresponds to the cubic cell ($a \simeq 9.9$ Å) of the basic structure of the argyrodite family to which our Cu_8GeS_6 belongs.

The observed reflections are therefore re-indexed based on the pseudocubic unit cell ($a = b = c \simeq 9.9$ Å, $\alpha = \beta = \gamma \simeq 90^\circ$) of the rhombohedral setting. The indexes of the major-group reflections are thereby converted to $h = (-h_h - 2k_h + l_h)/3$, $k = (2h_h + k_h + l_h)/3$ and $l = (-h_h + k_h + l_h)/3$ based on the lattice relations $\mathbf{a}_h = \mathbf{b} - \mathbf{c}$, $\mathbf{b}_h = \mathbf{c} - \mathbf{a}$, $\mathbf{c}_h = \mathbf{a} + \mathbf{b} + \mathbf{c}$. The minor group reflections are re-

Table 1. *Experimental details*

Crystal data	
Chemical formula	Cu_8GeS_6
Chemical formula weight	773.27
Cell setting	Orthorhombic
Space group	$Pmn2_1$
a (Å)	9.9073 (3)
b (Å)	9.9073
c (Å)	9.8703 (4)
V (Å ³)	968.7 (1)
Z	4
D_x (Mg m ⁻³)	5.358
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.70930
No. of reflections for cell parameters	25
θ range (°)	15–22.5
μ (mm ⁻¹)	21.70
Temperature (K)	293
Crystal form	Plate-like
Crystal size (mm)	0.18 × 0.12 × 0.08
Crystal color	Gray
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Data collection method	ω -2 θ scans
Absorption correction	Gaussian
T_{\min}	0.10
T_{\max}	0.23
No. of measured reflections	9341
No. of independent reflections	9341
No. of observed reflections	1805
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.054
θ_{\max} (°)	34.76
Range of h, k, l	0 → h_h → 19 0 → k_h → 19 -27 → l_h → 27
No. of standard reflections	3
Frequency of standard reflections	Every 200 reflections
Intensity decay (%)	None
Refinement	
Refinement on	F
R	0.087
wR	0.094
No. of reflections used in refinement	1805
No. of parameters used	89
Weighting scheme	$w = 1$
$(\Delta/\sigma)_{\max}$	0.001
Extinction method	None
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Tables 2.2B and 2.3.1)
Computer programs	
Structure refinement	<i>FMLSM</i> (Kato, 1998)

$$\dagger h = (-h_h - 2k_h + l_h)/3; \quad k = (2h_h + k_h + l_h)/3; \quad l = (-h_h + k_h + l_h)/3.$$

indexed as $h' = (h_h + 2k_h + l_h)/3$, $k' = (-2h_h - k_h + l_h)/3$ and $l' = (h_h - k_h + l_h)/3$ based on the relations $\mathbf{a}_h = \mathbf{c}' - \mathbf{b}'$, $\mathbf{b}_h = \mathbf{a}' - \mathbf{c}'$, $\mathbf{c}_h = \mathbf{a}' + \mathbf{b}' + \mathbf{c}'$.

The initial structural model is that obtained by the Rietveld analysis of the powder specimen of the room-

Table 2. *Relations (M^*) among reciprocal bases, σ , Z , T matrixes, t operation, symmetry and twin operations*

M^*	$\mathbf{a}^* = -\mathbf{a}^*/3 + 2\mathbf{b}^*/3 + 2\mathbf{c}^*/3$, $\mathbf{b}^* = 2\mathbf{a}^*/3 - \mathbf{b}^*/3 + 2\mathbf{c}^*/3$, $\mathbf{c}^* = 2\mathbf{a}^*/3 + 2\mathbf{b}^*/3 - \mathbf{c}^*/3$
σ matrix	$(-\frac{1}{3}\frac{2}{3}\frac{2}{3} \frac{2}{3} \frac{2}{3} - \frac{1}{3}\frac{2}{3} \frac{2}{3} \frac{2}{3} - \frac{1}{3})$
Z matrix	(100000 010000 001000)
T matrix	(000100 000010 000001 100000 010000 001000)
t	$\mathbf{t} = \{\mathbf{T} 0\}$
Symmetry operations	(i) x, y, z, u, v, w (ii) y, x, z, v, u, w (iii) $\frac{1}{4} - x, \frac{3}{4} - y, \frac{1}{2} + z, \frac{1}{4} - u, \frac{3}{4} - v, \frac{1}{2} + w$ (iv) $\frac{3}{4} - y, \frac{1}{4} - x, \frac{1}{2} + z, \frac{3}{4} - v, \frac{1}{4} - u, \frac{1}{2} + w$ (v) $\frac{1}{2} + x, \frac{1}{2} + y, z, \frac{1}{2} + u, \frac{1}{2} + v, w$ (vi) $\frac{1}{2} + y, \frac{1}{2} + x, z, \frac{1}{2} + v, \frac{1}{2} + u, w$ (vii) $\frac{3}{4} - x, \frac{1}{4} - y, \frac{1}{2} + z, \frac{3}{4} - u, \frac{1}{4} - v, \frac{1}{2} + w$ (viii) $\frac{1}{4} - y, \frac{3}{4} - x, \frac{1}{2} + z, \frac{1}{4} - v, \frac{3}{4} - u, \frac{1}{2} + w$
Domain 1	Symmetry operation 1–8
Domain 2	(Twin operation y, z, x, v, w, u) × (symmetry operation 1–8)
Domain 3	(Twin operation z, x, y, w, u, v) × (symmetry operation 1–8)
Domain 4	(Twin operation $x, -y, -z, u, -v, -w$) × (symmetry operation 1–8)
Domain 5	(Twin operation $-y, -z, x, -v, -w, u$) × (symmetry operation 1–8)
Domain 6	(Twin operation $-z, x, -y, -w, u, -v$) × (symmetry operation 1–8)
Domain 7	\mathbf{t} × (symmetry operation 1–8)
Domain 8	\mathbf{t} × (twin operation y, z, x, v, w, u) × (symmetry operation 1–8)
Domain 9	\mathbf{t} × (twin operation z, x, y, w, u, v) × (symmetry operation 1–8)
Domain 10	\mathbf{t} × (twin operation $x, -y, -z, u, -v, -w$) × (symmetry operation 1–8)
Domain 11	\mathbf{t} × (twin operation $-y, -z, x, -v, -w, u$) × (symmetry operation 1–8)
Domain 12	\mathbf{t} × (twin operation $-z, x, -y, -w, u, -v$) × (symmetry operation 1–8)

temperature phase of Cu_8GeS_6 with lattice constants $A = 7.0445$ (3), $B = 6.9661$ (3), $C = 9.8699$ (5) Å and a space group $Pmn2_1$ (Ishii *et al.*, 1999). To express the model based on the cell with $a = b = c \simeq 9.9$ Å and $\alpha = \beta = \gamma \simeq 90^\circ$, new basis $\mathbf{a} = \mathbf{A} + \mathbf{B}$, $\mathbf{b} = \mathbf{B} - \mathbf{A}$, $\mathbf{c} = \mathbf{C}$ are selected. The lattice constants of the pseudocubic cell are $a = b = 9.9073$ (3), $c = 9.8703$ (4) Å, $\alpha = \beta = 90^\circ$, $\gamma = 90.642$ (4)°, and a centering translation $(\frac{1}{2}, \frac{1}{2}, 0)_+$ is generated. Atomic parameters x, y, z based on \mathbf{a}, \mathbf{b} and \mathbf{c} are calculated from the orthorhombic coordinates X, Y, Z using the relations $x = (X + Y)/2$, $y = (Y - X)/2$ and $z = Z$. Symmetry operations are also converted into the formula based on a C lattice with \mathbf{a}, \mathbf{b} and \mathbf{c} : generator sets are $\frac{1}{2} + x, \frac{1}{2} + y, z$; y, x, z ; $\frac{3}{4} - y, \frac{1}{4} - x, \frac{1}{2} + z$. Reflection conditions change to $h + k = 2n$ (for hkl), $h + l = 2n$ (for $h\bar{h}l$) and $l = 2n$ (for $00l$).

In the early stage of the refinement only the 1556 reflections of the major group are used. Six twin domains have been considered after some trials. The twin operations are, respectively, x, y, z , y, z, x , z, x, y , $x, -y, -z$, $-y, -z, x$ and $-z, x, -y$. R_F is 0.101 using 36 structural parameters (25 atomic coordinates and 11 isotropic thermal parameters) and six scale factors (9.9,

Table 3. Atomic and domain parameters with e.s.d.s in parentheses

Atomic parameters based on the cell with $a = b = 9.9073$, $c = 9.8703$ Å, $\alpha = \beta = 90$, $\gamma = 90.642^\circ$, $Z = 4$. Coordinates of equivalent positions: $x, y, z, y, x, z, \frac{1}{4} - x, \frac{3}{4} - y, \frac{1}{2} + z, \frac{3}{4} - y, \frac{1}{4} - x, \frac{1}{2} + z, \frac{1}{2} + x, \frac{1}{2} + y, z, \frac{3}{4} - x, \frac{1}{4} - y, \frac{1}{2} + z, \frac{1}{4} - y, \frac{3}{4} - x, \frac{1}{2} + z$.

	x	y	z	U^{11}	U^{12}	U^{13}	U^{22}	U^{23}	U^{33}	U_{eq}		
Ge1	0.1247 (2)	0.1247	0.5	0.005 (1)	0.003 (1)	0.001 (1)	0.005	0.001	0.016 (3)	0.009 (1)		
Cu1	0.3677 (4)	0.1567 (3)	0.2493 (9)	0.027 (2)	0.002 (2)	0.011 (2)	0.015 (1)	-0.001 (2)	0.032 (3)	0.025 (1)		
Cu2	0.1534 (5)	-0.0457 (4)	0.8439 (9)	0.034 (2)	0.003 (2)	-0.003 (2)	0.022 (2)	-0.006 (2)	0.029 (3)	0.029 (1)		
Cu3	0.1735 (7)	-0.0269 (5)	0.1421 (10)	0.092 (4)	0.019 (3)	-0.010 (3)	0.025 (2)	0.007 (2)	0.032 (3)	0.049 (2)		
Cu4	0.3006 (5)	0.3006	0.0101 (13)	0.023 (2)	0.008 (2)	0.012 (3)	0.023	0.012	0.054 (5)	0.033 (2)		
Cu5	0.3646 (5)	0.3646	0.4685 (10)	0.028 (2)	-0.012 (3)	0.005 (2)	0.028	0.005	0.016 (4)	0.024 (2)		
S1	0.4991 (6)	0.2573 (6)	0.8792 (11)	0.010 (3)	0.004 (2)	-0.002 (2)	0.009 (3)	-0.002 (2)	0.015 (5)	0.011 (2)		
S2	-0.0002 (7)	-0.0002	0.6368 (13)	0.008 (2)	-0.002 (3)	0.002 (3)	0.008	0.002	0.012 (5)	0.010 (2)		
S3	0.2488 (7)	0.2488	0.6331 (13)	0.007 (2)	0.002 (3)	-0.002 (2)	0.007	-0.002	0.013 (5)	0.009 (2)		
S4	0.3876 (6)	0.3876	0.2441 (17)	0.009 (2)	-0.002 (3)	-0.006 (3)	0.009	-0.006	0.038 (8)	0.018 (3)		
S5	0.1357 (5)	0.1357	-0.0073 (15)	0.008(2)	-0.007 (3)	-0.001 (2)	0.008	-0.007	0.017 (6)	0.011 (2)		
Domain	1	2	3	4	5	6	7	8	9	10	11	12
Scale factor	10.09 (8)	7.14 (7)	6.76 (7)	4.18 (9)	4.15 (9)	4.55 (9)	2.32 (9)	1.72 (10)	1.72 (10)	0.98 (15)	1.49 (12)	1.71 (11)
Volume ratio	106	53	48	18	18	21	6	3	3	1	2	3

Atomic coordinates X, Y, Z based on the orthorhombic cell with a space group $Pmn2_1$ and cell parameters $a = 7.0445$, $b = 6.9661$, $c = 9.8699$ Å can be calculated from the values of x, y, z using the relations $X = x - y$, $Y = x + y$ and $Z = z$. The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^{*2}U^{11} + 2hka^*b^*U^{12} + 2hla^*c^*U^{13} + k^2b^{*2}U^{22} + 2klb^*c^*U^{23} + l^2c^{*2}U^{33})$. $U_{eq} = B_{eq}/(8\pi^2) = (1/3)[(\mathbf{a}\cdot\mathbf{a}) a^{*2}U^{11} + (\mathbf{b}\cdot\mathbf{b}) b^{*2}U^{22} + (\mathbf{c}\cdot\mathbf{c}) c^{*2}U^{33} + 2(\mathbf{b}\cdot\mathbf{c}) b^*c^*U^{23}]$.

6.8, 6.4, 4.1, 4.0 and 4.4). The agreement of the six-domain model is fairly good.

In the next stage the minor group (248 reflections) with h', k' and l' must be added to the observed data set. Based on one common set of pseudocubic basic vectors, however, it is not possible to assign integral indexes to all of the 1804 observed reflections. After a method

proposed by Kato (1997), a six-dimensional formalism is applied using the program *FMLS*M (Kato, 1994, 1998).

3.2. Six-dimensional formalism and structure refinement

The whole reflections are assigned on the basis of two sets of pseudocubic basic vectors, $\mathbf{a}, \mathbf{b}, \mathbf{c}$ and $\mathbf{a}', \mathbf{b}', \mathbf{c}'$. Relations between the reciprocal basic vectors are $\mathbf{a}^* = -\mathbf{b}_h^* + \mathbf{c}_h^*$, $\mathbf{b}^* = \mathbf{a}_h^* + \mathbf{c}_h^*$, $\mathbf{c}^* = -\mathbf{a}_h^* + \mathbf{b}_h^* + \mathbf{c}_h^*$, $\mathbf{a}'^* = \mathbf{b}_h^* + \mathbf{c}_h^*$, $\mathbf{b}'^* = -\mathbf{a}_h^* + \mathbf{c}_h^*$, $\mathbf{c}'^* = \mathbf{a}_h^* - \mathbf{b}_h^* + \mathbf{c}_h^*$. As shown by $\mathbf{a}'^* + \mathbf{b}'^* + \mathbf{c}'^* = \mathbf{a}^* + \mathbf{b}^* + \mathbf{c}^*$, $[111]^*$ belongs to the two pseudocubic cells in common. Each reflection is expressed by $\mathbf{q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + h'\mathbf{a}'^* + k'\mathbf{b}'^* + l'\mathbf{c}'^*$. The major group (1556 reflections) is assigned by $hkl000$, while the minor group (248 reflections) is assigned by $000h'k'l'$.

Symmetry operations are also expressed in the (3 + 3)-dimensional formalism (Kato, 1997). Those for the six major domains causing the major-group reflections are given by the scheme

$$\mathbf{g} = \left[\begin{pmatrix} \mathbf{R} & \mathbf{0} \\ \mathbf{0} & \mathbf{R} \end{pmatrix} \middle| \begin{pmatrix} \mathbf{v} \\ \mathbf{v} \end{pmatrix} \right],$$

where \mathbf{R} and \mathbf{v} are, respectively, the matrix and the vector of the corresponding three-dimensional symmetry operations including the space-group operations and their products with the three-dimensional twinning operations. The symmetry operations for the six minor domains are obtained by multiplying the six-dimensional twinning operation $\mathbf{t} = \{\mathbf{T}|\mathbf{0}\}$ into the major domain symmetry operations \mathbf{g} , where \mathbf{T} is the matrix (000100|000010|000001|100000|010000|001000). The product $\mathbf{t}\cdot\mathbf{g}$ is given by the scheme

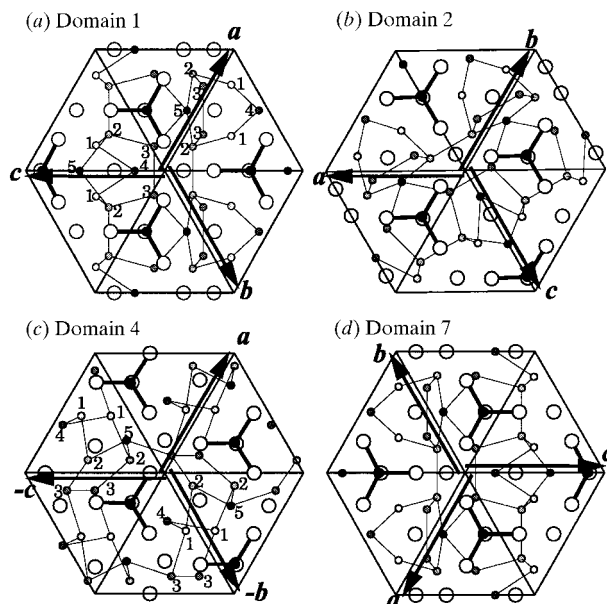


Fig. 1. Structure model of Cu_8GeS_6 (II). Large open, medium solid and small shaded circles represent S, Ge and Cu, respectively. Ge and Cu ions are joined to the nearest S ions with thick and thin rods, respectively.

Table 4. Selected interatomic distances (\AA) and angles ($^\circ$)

(1) GeS_4 tetrahedral unit			
Ge—S1 ⁽ⁱ⁾ , S1 ⁽ⁱⁱ⁾	2.176 (6)	S1 ⁽ⁱ⁾ —S1 ⁽ⁱⁱ⁾	3.638 (11)
Ge—S2	2.202 (10)	S2—S1 ⁽ⁱ⁾ , S1 ⁽ⁱⁱ⁾	3.559 (11)
Ge—S3	2.172 (10)	S3—S1 ⁽ⁱ⁾ , S1 ⁽ⁱⁱ⁾	3.567 (11)
		S2—S3	3.468 (16)
S1—Ge—S1	113.5 (5)	S1—Ge—S2	108.8 (3)
S1—Ge—S3	110.2 (3)	S2—Ge—S3	104.9 (6)
(2) Cu—S (< 2.7 \AA)			
Cu1—S1 ⁽ⁱⁱ⁾	2.362 (9)	Cu3—S5	2.219 (11)
Cu1—S3 ⁽ⁱⁱ⁾	2.341 (7)	Cu4—S1 ^(vii)	2.395 (10)
Cu1—S4	2.295 (7)	Cu4—S1 ^(viii)	2.395(10)
Cu2—S1 ⁽ⁱⁱⁱ⁾	2.491 (9)	Cu4—S4	2.608 (18)
Cu2—S2	2.590 (12)	Cu4—S5	2.304 (11)
Cu2—S4 ^(iv)	2.476 (8)	Cu5—S2 ^(ix)	2.511 (15)
Cu2—S5 ^(v)	2.330 (12)	Cu5—S3	2.290 (14)
Cu3—S1 ⁽ⁱⁱ⁾	2.470 (12)	Cu5—S4	2.239 (18)
Cu3—S2 ^(vi)	2.344 (7)		
(3) Cu—Cu (< 2.9 \AA)			
Cu1—Cu2 ⁽ⁱⁱ⁾	2.800 (7)	Cu2—Cu3 ^(xi)	2.758 (7)
Cu1—Cu3	2.838 (8)	Cu2—Cu5 ^(iv)	2.702 (6)
Cu1—Cu4	2.842 (9)	Cu3—Cu3 ^(x)	2.824 (11)
Cu2—Cu2 ^(x)	2.804 (9)	Cu3—Cu5 ⁽ⁱⁱ⁾	2.852 (9)

Symmetry codes: (i) $\frac{1}{4} - y, \frac{3}{4} - x, z - \frac{1}{2}$; (ii) $\frac{3}{4} - x, \frac{1}{4} - y, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iv) $\frac{3}{4} - x, \frac{1}{4} - y, z + \frac{1}{2}$; (v) $x, y, z + 1$; (vi) $\frac{1}{4} - x, -\frac{1}{4} - y, z - \frac{1}{2}$; (vii) $x, y, z - 1$; (viii) $y, x, z - 1$; (ix) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (x) y, x, z ; (xi) $\frac{1}{4} - x, -\frac{1}{4} - y, z + \frac{1}{2}$.

$$\mathbf{t} \cdot \mathbf{g} = \left[\begin{pmatrix} \mathbf{0} & \mathbf{R} \\ \mathbf{R} & \mathbf{0} \end{pmatrix} \middle| \begin{pmatrix} \mathbf{v} \\ \mathbf{v} \end{pmatrix} \right].$$

Relations (\mathbf{M}^*) among reciprocal bases, σ , \mathbf{Z} , \mathbf{T} matrixes, \mathbf{t} operation, symmetry and twin operations are shown together in Table 2. The three-dimensional atomic arrangement is related to a six-dimensional structure factor with the help of the matrix \mathbf{P}^{-1} derived from \mathbf{Z} and σ matrixes (Kato, 1990).

Refinement was performed on the basis of $|F|$ through a corrected version (V3.20) of *FMLSM* (Kato, 1994, 1997, 1998) with unit weight for all reflections. In the structure factor calculation a summation over three points along [000111] can be used instead of integration. Besides atomic coordinates and anisotropic thermal parameters, 12 scale factors were considered as parameters, because the volume of each domain is proportional to the square of the scale factor. The agreement was satisfactory with 77 structural parameters (25 positional parameters and 52 anisotropic thermal parameters) and 12 scale factors; $R_F = 0.083$ and $wR_F = 0.090$. The final parameters based on a pseudocubic cell are listed in Table 3.† The positional parameters are converted into those based on the orthorhombic cell with space group $Pmn2_1$ using the relations $X = x - y$, $Y = x + y$ and $Z = z$.

†Supplementary data for this paper are available from the IUCr electronic archives (Reference: OH0067). Services for accessing these data are described at the back of the journal.

4. Discussion

The refined structure model is essentially the same as the results of the Rietveld analysis (Ishii *et al.*, 1999) and it is isomorphous with Cu_8SiS_6 (Levalois & Allais, 1981), Cu_8SiSe_6 (Ishii *et al.*, 1999) and $\text{Ag}_8\text{GeSe}_6(\beta')$ (Carré *et al.*, 1980). The standard deviations of the positional parameters are about one fourth of those obtained by the Rietveld analysis. Selected interatomic distances and angles calculated based on the final parameters are listed in Table 3, and the structure model is illustrated in Fig. 1. Ge ions are coordinated tetrahedrally by 2S1, S2 and S3 to form almost regular and isolated GeS_4 units. S4 and S5 are not bonded to Ge, and they are centers of the S—S Friauf polyhedra (Kuhls *et al.*, 1978). Cu2 and Cu4 are in distorted S—S tetrahedra formed by S4, S5 and two S ions of a GeS_4 unit, and Cu1, Cu3 and Cu5 are in S—S triangle faces shared by two distorted tetrahedra. Cu ions are coordinated by each other (Cu—Cu < 2.9 \AA) and they seem to form a Cu—Cu network (Table 4).

The high-temperature phase (phase I) of Cu_8GeS_6 is considered to crystallize in the same type as $\text{Ag}_8\text{GeTe}_6(\gamma)$ (Rysanek *et al.*, 1976). Chalcogen atoms pattern two types of almost regular tetrahedral sites, one for Ge atoms and the other empty, and four types of distorted tetrahedra. In Cu_8GeS_6 (phase I), Cu ions are expected to be distributed statistically over many sites in

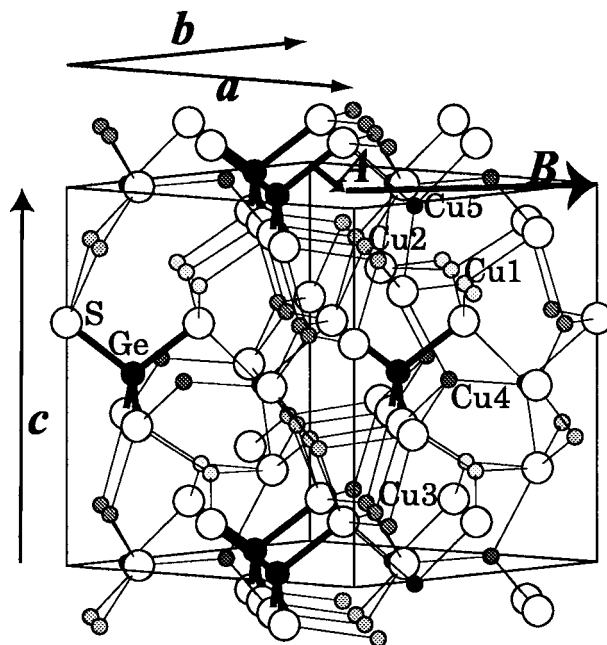


Fig. 2. Bounded projection ($0.77 < x + y + z < 1.1$) of Cu_8GeS_6 (II) along the pseudocubic [111]. (a), (b), (c) and (d) correspond to twin domains 1, 2, 4 and 7, respectively. Ge ions are joined with thick rods to the nearest S ions and Cu—Cu distances less than 2.9 \AA are shown by thin rods. Small numbers 1, 2, ..., 5 indicate Cu1, Cu2, ..., Cu5, respectively.

S—S distorted tetrahedra and S—S triangular faces. On cooling through the phase-transition temperature, the crystal can be converted into a multiple twin of phase II. Cu ions are transferred to five types of independent sites shown in Table 3 from the statistical distribution state, while Ge and S arrangements are essentially retained. The bounded projections along pseudocubic [111] of some twin domains adopted in the present refinement are shown in Fig. 2. Among the twin domains 1–6, the GeS_6 frameworks can be superposed to each other in principle and only Cu—Cu network directions differ. The minor twin domains 7–12 are respectively related to the major domains 1–6 by a twofold rotation on [111]. The present twin model is quite acceptable and it can explain the discrepancies in the assignments of the single-crystal and powder X-ray patterns of Cu_8GeS_6 (phase II) mentioned by Wang & Viaene (1974) and Khanafer *et al.* (1974).

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References

- Carré, D., Ollitrault-Fichet, R. & Flahaut, J. (1980). *Acta Cryst.* **B36**, 245–249.
- Chen, X.-A., Onoda, M., Wada, H., Sato, A. & Nozaki, H. (1999). *J. Solid State Chem.* **145**, 204–211.
- De Chalbaud, L. M., de Delgado, G. D., Delgado, J. M., Mora, A. E. & Sagredo, V. (1997). *Mater. Res. Bull.* **32**, 1371–1376.
- Goertz (1988). *Inst. Krist. Der Aachen*, JCPDS Grant-in Aid Report; JCPDS 39-1202, 40-1190.
- Hahn, H., Schulze, H. & Sechster, L. (1965). *Naturwissenschaften*, **52**, 451.
- Ishii, M., Onoda, M. & Shibata, K. (1999). *Solid State Ion.* **121**, 11–18.
- Kato, K. (1990). *Acta Cryst.* **B46**, 39–44.
- Kato, K. (1994). *Acta Cryst.* **A50**, 351–357.
- Kato, K. (1997). *Z. Kristallogr.* **212**, 423–427.
- Kato, K. (1998). *FMLSM*. Version 3.20. National Institute for Research in Inorganic Materials, Namiki, Tsukuba, Japan.
- Khanafer, M., Gorochoy, O. & Rivet, J. (1974). *Mater. Res. Bull.* **9**, 1543–1552.
- Khanafer, M., Rivet, J. & Flahaut, J. (1973). *Bull. Soc. Chim. Fr.* **3**, 859–862.
- Kuhs, W. F., Nische, R. & Scheunemann, K. (1978). *Acta Cryst.* **B34**, 64–70.
- Kuhs, W. F., Nische, R. & Scheunemann, K. (1979). *Mater. Res. Bull.* **14**, 241–248.
- Levalois, M. & Allais, G. (1981). *Acta Cryst.* **B37**, 1816–1819.
- Rysanek, N., Laruelle, P. & Katty, A. (1976). *Acta Cryst.* **B32**, 692–696.
- Wang, N. (1976). *Neues Jahrb. Mineral. Monatsh.* **6**, 241–247.
- Wang, N. & Viaene, W. (1974). *Neues Jahrb. Mineral. Monatsh.* **10**, 442–446.