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Crystal structure of germanite, $Cu_{26}Ge_4Fe_4S_{32}$, determined by powder X-ray diffraction

RODNEY T. TETTENHORST AND CHARLES E. CORBATÓ

Department of Geology and Mineralogy
The Ohio State University, Columbus, Ohio 43210

Abstract

The crystal structure of germanite has been refined in space group 218, $P\bar{4}3n$, to a weighted R of 3.60% from 66 powder X-ray diffraction reflections. The structure deviates only slightly from a body-centered lattice type and is a modification of the sphalerite structure. The cubic cell dimension is 10.5862(5)Å. The ideal chemical formula is $Cu_{26}Ge_4Fe_4S_{32}$, analogous to the formula proposed for colusite by Orlandi et al. (1981).

Introduction

The chemical formula and crystal structure of germanite have remained in doubt since its discovery at Tsumeb, Southwest Africa in 1920. Although Tsumeb is the primary germanite locality, a more recent discovery was reported at Bancaïroun, France by Picot et al. (1963). The exact chemical formula is uncertain because a pure substance is difficult to obtain due to its intimate association with other minerals on a microscopic scale. A literature review reveals that about a dozen independent chemical analyses and/or structural formulas have been published. Early analyses were tabulated by Murdoch (1953) and Sclar and Geier (1957). More recent analyses were presented by Picot et al. (1963) and Viaene and Moreau (1968). The most frequently cited chemical formula is $Cu_3(Ge,Fe)S_4$, originally proposed by de Jong (1930), although variations on this have been suggested. In addition, other elements, principally As, Ga, Pb and Zn, are thought to occur in the structure and these elements have been reported in amounts up to 5% in chemical analyses.

Crystal structure analysis of germanite has been hindered by a lack of any single crystals and uncertainty in the chemical formula. de Jong (1930) proposed that germanite had an isometric sphalerite-like structure with $a = 5.29$Å although he indicated that the correct cell edge length might be twice this value. Murdoch (1953) concluded that germanite, colusite and reniérite were essentially isostructural and isometric or pseudo-isometric from X-ray powder photographs. He gave a cell edge for germanite of $a = 10.58$Å and indicated that space groups for these minerals were hextetrahedral, $\bar{4}3m$, from observations of earlier workers on single crystals of colusite and reniérite. Strunz (1966) put germanite in the tetrahedrite space group, $I\bar{4}3m$. The only powder XRD data generally available is that of Murdoch which has been reproduced by the JCPDS on card 10-469. These data are assigned a low reliability by JCPDS because of many unindexed lines.

The objective of the present study was to update the powder XRD data for germanite and to ascertain its crystal structure insofar as possible. A successful refinement of the structure has been made to a reasonable degree of reliability. The refinement was aided by an insightful observation by Orlandi et al. (1981).

Experimental

A portion of a hand specimen of germanite from Tsumeb (The Ohio State University Mineralogy Museum #8246) was selected for study by powder XRD, SEM and reflecting microscopy. An X-ray fluorescence attachment to the SEM allowed for a qualitative analysis of the elements present.

XRD data were taken on material that was hand-ground to pass through a sieve whose openings were 61 μm. The powder was front loaded into a standard Al holder and numerous patterns were taken on a Philips 3100 X-ray diffractometer. The X-ray unit is equipped with copper radiation, scintillation detector, PHA, graphite monochromator and theta-compensating slit. Patterns were run from 6-154° 2θ at goniometer speeds ranging from 1/8° to 1° 2θ/min. with appropriate time constants and various chart speeds. Positions of the diffraction maxima were corrected over the entire angular range by comparison with peaks of tetradecanol for low 2θ values and a powdered silcon sample provided by Philips for angles larger than about 25° 2θ. Intensities were taken as the planimetered area under the peaks after drawing a suitable background. Three patterns were used to place all of the intensities on the same scale. Observed d-values and intensities for each (hkl) are listed in Table 1. Intensities listed in Table 1 were converted to standard intensities as given by the JCPDS by removing the effects of the theta-compensating slit and graphite monochromator.

Refinement

Cell dimension

Forty-three independent reflections were indexed on the basis of an isometric cell, and the cell dimension was refined in a least-squares program minimizing the sum of

Table 1. Observed and calculated d-values, intensities and structure factors for germanite, space group 218, a = 10.5862(5)Å, V = 1186.4Å^3, calculated D = 4.47 g/cm^3. Intensities are scaled to a value of 100 for the (222) reflection. Structure factors are arbitrarily scaled. Figure of merit (Smith and Snyder, 1979): F_{30} = 18(0.030,57).

hkl	d_o	d_c	I/I_o	I_c	F_o	F_c
110	7.50A°	7.49A°	1.5	3.2	32	44
200	5.30	5.29	1.2	1.2	58	53
210	4.75	4.73	0.6	0.3	23	15
211	4.327	4.322	3.5	3.6	59	58
220	3.743	3.743	0.8	0.9	49	46
310	3.346	3.348	1.2	1.6	45	51
222	3.054	3.056	100.0	100.0	782	762
321	2.830	2.829	2.2	2.1	50	49
400	2.645	2.646	11.5	11.8	352	355
411	2.496	2.495	0.9	0.5	34	40
330				0.8	56	68
420	2.367	2.367	0.8	0.6	52	45
421	2.312	2.310	0.2	0.3	18	24
332	2.256	2.257	1.5	1.1	74	65
422	2.163	2.161	0.3	0.2	34	32
510	2.078	2.076	0.6	0.1	13	21
431				2.1	42	70
520	1.960	1.966	0.7	0.0	22	11
432				0.2	45	23
521	1.934	1.933	0.5	0.2	32	20
440	1.870	1.871	72.2	63.2	861	868
600	1.764	1.764	0.3	0.0	42	40
442				0.3	50	43
622	1.5954	1.5959	39.3	30.6	516	519
631	1.5605	1.5608	1.2	1.1	67	72
444	1.5283	1.5280	3.2	2.2	264	256
710	1.4944	1.4971	0.3	0.2	38	40
550				0.0	17	17
543				0.1	24	26
721	1.4410	1.4406	1.4	0.5	69	52
633				0.2	69	51
552				0.0	19	14
730	1.3905	1.3900	0.4	0.3	58	61
732	1.3443	1.3444	0.8	0.2	35	39
651				0.4	47	53
800	1.3229	1.3233	9.8	7.3	600	636
662	1.2141	1.2143	15.6	9.0	401	388
752	1.1987	1.1986	0.2	0.2	34	37
840	1.1836	1.1836	2.7	1.8	171	178
910	1.1700	1.1690	1.0	0.0	11	7
833				0.3	101	73
921	1.1415	1.1415	0.9	0.0	18	12
761				0.1	54	36
655				0.0	54	36
932	1.0917	1.0919	0.8	0.0	21	17
763				0.3	65	54
844	1.0802	1.0804	20.4	12.2	493	492
10 22	1.0188	1.0186	9.2	4.5	339	301
666				1.4	336	297
11 20	0.9468	0.9469	0.6	0.0	2	4
10 50				0.0	47	28
10 43				0.0	42	25
865				0.0	40	24
880	0.9357	0.9357	6.7	4.0	415	390
11 32	0.9145	0.9145	1.1	0.1	37	28
10 53				0.3	66	51
972				0.1	42	32
776				0.0	34	27
10 62	0.8946	0.8947	9.5	6.6	244	237
12 00	0.8824	0.8822	0.5	0.1	92	94
884				0.6	92	95
11 52	0.8643	0.8644	0.9	0.2	42	35
10 71				0.3	58	49
10 55				0.1	48	41
12 40	0.8370	0.8369	8.2	8.0	302	314
10 66	0.8072	0.8072	4.4	4.4	200	197

the squares of the residuals of 2θ. All reflections were assigned equal weights.

Crystal structure

Atomic positions and isotropic temperature factors were refined by standard three-dimensional least-squares techniques using the program of Sheldrick (1976). Most refinements were made using the ideal chemical formula with the Ge and Fe atoms placed on a single site occupied by one half of each atom. Atomic scattering factors from the *International Tables for X-ray Crystallography*, Volume IV, were used throughout. All observed reflections were assigned equal weights.

Initial attempts were made to refine the structure with either P or I lattices and point groups $\bar{4}3m$ and $2/m\bar{3}$. Satisfactory results were obtained only in space group 218, $P\bar{4}3n$. Models considered in detail were sphalerite-structure derivatives which contained 32 anion[1] and either 32 or 34 cation sites. Models investigated in detail in space group 218 were (Wyckoff site notation in parentheses):

A. Cu in (c), (d) and (f); (Ge,Fe) in (e); S in (e) and (i).

B. Cu in (i); (Ge,Fe) in (e); S in (c), (d), (e) and (f).

C. Cu in (i); (Ge,Fe) in (a) and (b); S in (e) and (i).

D. A combination of A and C with all cation sites half occupied. Models A and B were tried with two additional Cu atoms on site (a) as suggested by Orlandi et al. (1981) in their discussion of the crystal chemistry of colusite. All models were carried through 5 cycles of refinement.

Chemical analyses show that Ge and Fe occur in approximately equal amounts in germanite and structural formulas show that Ge and Fe sum to about 8 atoms per 32 anions (Table 4). We have arbitrarily combined Ge and Fe together and have positioned them on one 8 atom/cell site. However, they may be distributed unequally over all other sites. Our data cannot distinguish these various possibilities since the scattering factors are nearly identical for the major cations which occur in germanite.

Sixty-six reflections were used for the structure refinement. F_o values for peaks composed of multiple reflections (e.g., 411 and 330) were divided equally among the contained members. In the last stages of the refinement these F_o values were apportioned in the same ratio as their respective F_c values with the I_o for any peak held constant. The final F_c and their respective F_o values are given in Table 1.

Refinements were made by allowing parameters to vary in a stepwise manner beginning with the scale factor, then the Cu and (Ge,Fe) positions, then the S positions and finally the temperature factors. Initial isotropic temperature factors were fixed at unity. When they were allowed to vary, the temperature factors for a given chemical species were kept the same even though these atoms were distributed over more than one structural site. Our limited data did not allow an evaluation of anisotropic thermal parameters which would require 19 terms in the model finally accepted, or even allow for isotropic thermal factors for atoms at each structural site.

Discussion of results

Elements detected in the germanite specimen by SEM-XRF are Cu, Ge, Fe, S, As, Ga, Zn, Pb and Si. Hand specimen and reflecting microscope observation show the

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[1] In this paper S atoms are termed anions; all other elements are termed cations.

Table 2. Atom types, number of atoms, Wyckoff sites, fractional coordinates and isotropic thermal parameters for germanite, $P\bar{4}3n$

Atom	#	Site	x	y	z	B(Å^2)
Cu1	2	(a)	0	0	0	1.2(2)
Cu2	6	(c)	1/4	1/2	0	
Cu3	6	(d)	1/4	0	1/2	
Cu4	12	(f)	.257(2)	0	0	
(Ge,Fe)	8	(e)	.240(2)	.240(2)	.240(2)	1.3(6)
S1	8	(e)	.121(3)	.121(3)	.121(3)	1.3(2)
S2	24	(i)	.379(3)	.364(3)	.121(2)	

Numbers in parentheses represent the esd in the least significant figure.

presence of impurities, which are intimately mixed with germanite.

XRD pattern and cell dimension refinement

The observed XRD pattern is similar to that described by Murdoch (1953). Impurities identified by XRD are tennantite, sphalerite and galena. Subtraction of the impurity peaks gives a germanite pattern which can be indexed on an isometric cell. The least-squares refinement gives a = 10.5862(5)Å with an *rms* of the residuals of 2θ of 0.038°. Four of the 43 independent reflections have 2θ residuals greater than 0.05°; the largest discrepancy is 0.13°2θ. All 4 of these reflections have intensities less than unity on a scale on which the most intense peak has a value of 100. The d_c values are listed in Table 1.

Most (39 of 43) of the reflections can be indexed with $h+k+l = 2n$. The remaining 4 reflections have low intensities which indicate that the germanite cell is nearly body centered. One very weak observed peak with a d-value of about 10Å and indexed by Murdoch (1953) as the (100) of germanite is not attributed to germanite or any of the impurities listed above. We attribute this reflection to a minor amount of a mica-type phase based on the presence of Si in our chemical analysis.

Structure refinement

Crystal structure refinements that were tried and abandoned as unsatisfactory include: models A, B and C which give negative thermal parameters for the S atoms, model D which gives a weighted R of 29% and model B with Cu at the origin (an (a) site) which gives unstable and unrealistic thermal factors. Model A with 2 additional Cu atoms in the cell on (a) sites converges rapidly to a weighted R of 4.2% with reasonable temperature factors. Following a reapportionment of the F_o values in the ratio of the F_c values for the multiple-reflection peaks, this model converges to a weighted R of 3.60% and is accepted as the correct description of the structure. Position and thermal parameters for this structure are listed in Table 2; interatomic distances and bond angles are given in Table 3.

At this stage of refinement attempts were made to vary site occupancies one at a time along with all of the other parameters. Site occupancies of Cu2, Cu3 and (Ge,Fe) give unsatisfactory increases to values greater than unity. Reasonable changes in site occupancies were observed for Cu1, Cu4 and S1 with slight improvement in weighted R; all site occupancies decreased slightly. These results suggest that the sum of the cations/cell may be 33.5–34 and the anion sum 31.4–32/cell. Alternatively, these results may indicate the presence of atoms with scattering factors lower than Cu and S or may be an artifact of our limited data. Most of the cations attributed to germanite, as noted in the literature, have similar atomic scattering factors (within 4 atomic numbers of Cu) and our X-ray observations cannot distinguish between them. Therefore assignment of germanium and iron jointly in an (e) site is arbitrary and does not imply that we have evidence for this assignment.

Calculation of structural formulas for germanite based on 32 S atoms/cell from 11 analyses given in the literature shows that 9 of the 11 give cation totals which range from 33.2 to 35.4 with a mean of 34/cell. Two analyses on supposedly very pure germanites (numbers 7 and 8 from Viaene and Moreau, 1968) from Bancaïroun and Tsumeb

Table 3. Significant interatomic distances and bond angles

Distances

Cu1	- S1	2.21(3)Å
Cu2	- S2	2.36(3)
Cu3	- S2	2.18(3)
Cu4	- S1	2.31(3)
	- S2	2.32(3)
(Ge,Fe)	- S1	2.18(3)
	- S2	2.35(3)

Polyhedra: Edge Lengths and Angles

	Center	Vertices	n	Edge Length	Central Angle
Tetrahedra:	Cu1	S1, S1	6	3.61(4)Å	109.5(0)°
	Cu2	S2, S2	4	3.86(4)	109.6(9)
		S2, S2	2	3.85(4)	109.1(10)
	Cu3	S2, S2	4	3.52(4)	180.0(10)
		S2, S2	2	3.62(4)	112.4(10)
	Cu4	S1, S1	1	3.61(4)	102.9(12)
		S1, S2	2	3.85(4)	112.7(10)
		S1, S2	2	3.75(4)	108.1(10)
		S2, S2	1	3.84(4)	112.1(12)
	(Ge,Fe)	S1, S2	3	3.76(4)	112.3(12)
		S2, S2	3	3.76(4)	106.5(12)
	S2	Cu2, Cu3	1	3.74(0)	111.1(11)
		Cu2, Cu4	1	3.69(1)	104.2(11)
		Cu2, (Ge,Fe)	1	3.75(2)	105.5(12)
		Cu3, Cu4	1	3.69(1)	110.5(13)
		Cu3, (Ge,Fe)	1	3.75(2)	111.8(13)
		Cu4, (Ge,Fe)	1	3.90(3)	113.4(12)
Trigonal dipyramid:	S1	Cu1, Cu4	3	2.72(2)	73.8(10)
		Cu4, Cu4	3	3.85(2)	112.6(13)
		Cu4, (Ge,Fe)	3	3.59(2)	106.2(13)
Octahedron:	Cu1	Cu4, Cu4	12	3.85(2)	90.0(0)

Numbers in parentheses represent the esd in the least significant figure.

Table 4. Chemical analyses and number of atoms based on 32 sulfur atoms per cell for germanite samples from Tsumeb

	Analysis*		Number of Atoms	
Element	#4	#8	#4	#8
Cu	42.12	43.60	21.85	23.44
Fe	7.80	6.40	4.61	3.92
Zn	3.93	3.10	1.98	1.62
Ge	10.19	9.00	4.63	4.24
Ga	1.85	—	0.87	--
Pb	0.96	—	—	—
As	1.37	4.70	0.60	2.14
S	31.27	30.03	32.00	32.00
Rem	--	0.88		
Total	99.49	97.71		

*Analyses and heading numbers are from Viaene and Moreau, 1968. The number of atoms for #4 has been corrected for the presence of PbS

give 34.7 and 35.4 cations/cell, respectively, for 32 S atoms. Admittedly, some or all of the analyses may not have been done on pure germanite. Two chemical analyses and structural formulas for supposedly pure germanite from Tsumeb (numbers 4 and 8 given by Viaene and Moreau, 1968) are presented in Table 4. The structural formulas shown in Table 4 agree reasonably well with the results of our structure analysis. We do not believe a chemical analysis of our sample by microprobe would yield any additional meaningful information due to the intimate mixing with impurities and the fact that the X-ray data were taken on a "bulk" sample. Accurate correlation of the structure and chemistry of germanite by X-ray diffraction and microprobe awaits the finding of single crystals which lack inclusions of other phases.

Our results suggest that germanite, like colusite (Orlandi et al., 1981), contains about 34 cations/cell with 32 S atoms/cell. Certain elements which are frequently observed in the chemical analyses, such as As, have been assigned previously to the anion sites. This assignment causes a decrease in the number of cations/cell to 32 or less for 32 anion sites. Our data do not agree with such an assignment. We believe that additional elements present in the chemical analyses such as As, Ga and Zn, if not attributable to other mineral impurities, proxy for Cu and/or (Ge,Fe) in germanite. We suggest the ideal formula for germanite is $Cu_{26}Ge_4Fe_4S_{32}$.

Parallel refinements were run in which all of the unobserved reflections (182 in space group 218) were included but were given negligible weights. This was done to ascertain which of these reflections give F_c greater than F_o. F_o values for the unobserved reflections were set at what we consider to be our detection limit based on the intensities of the weakest observable peaks. Most of the unobserved reflections give F_c less than F_o or coincide with a reflection attributed to an impurity. Unobserved reflections which showed F_c values significantly larger than F_o were those for which $h^2 + k^2 + l^2 = 66, 74, 114, 154, 170$ and 176. The imprecise knowledge of the germanite composition and our inability to refine with anisotropic thermal parameters are probably responsible for these discrepancies.

The fractional coordinates and thermal parameters given in Table 2 and the interatomic distances and bond angles given in Table 3 were taken from the final cycle of refinement for the ideal chemical composition, $Cu_{26}Ge_4Fe_4S_{32}$. The structure is nearly body centered as shown by the atomic positions in Table 2. A body-centered cell for the atom sites requires only that x = y for the S2 site.

Description of polyhedra

Cu1 atoms are situated at sites whose symmetry is 23 and they are coordinated to 4 S1 atoms which form a regular tetrahedron about Cu1. The Cu1–S1 distance of 2.21Å is the second smallest cation–anion distance. Cu1 atoms are also surrounded by 6 Cu4 atoms which are situated at the corners of a regular octahedron at 2.72Å from the central Cu1. This distance is smaller by about 1Å than any other cation–cation distance in the unit cell. The short Cu1–S1 distance may thereby provide an effective shield of anions which are interposed between the Cu1 and Cu4 atoms.

Cu2 and Cu3 atoms are situated at $\bar{4}$ symmetry sites and both are coordinated to 4 S2 atoms which are arranged at the corners of a tetragonal disphenoid. The $\bar{4}$ axis intersects the two slightly smaller (3.85 vs. 3.86Å) edges of the disphenoid about Cu2 while the $\bar{4}$ axis intersects the larger (3.62 vs. 3.52Å) edges of the disphenoid about Cu3. The Cu3–S2 distance (2.18Å) is the smallest cation-anion distance in the structure and, since it appears to have no structural basis, may indicate that small atoms are present at the Cu3 site.

Cu4 atoms are located on a 2-fold symmetry axis and are coordinated to an irregular polyhedron of 2 S1 and 2 S2 atoms. The cation–anion distances are nearly equal. One pair of opposite edges of this polyhedron has lengths of 3.75Å and another pair of opposite edges has lengths of 3.85Å. The remaining pair of opposite edges which are intersected by the 2-fold axis are unequal in length (3.61 and 3.84Å). The smallest edge (S1–S1) of 3.61Å minimizes the repulsion between the unusually close Cu1 and Cu4 atoms.

The (Ge,Fe) atoms are located on a 3-fold symmetry axis and the polyhedron of 1 S1 and 3 S2 atoms about (Ge,Fe) is a regular tetrahedron all of whose edges equal 3.76Å. The (Ge,Fe) is, however, not at the center of this tetrahedron but is displaced along the 3-fold axis toward the S1.

S1 atoms are located on a 3-fold symmetry axis and are surrounded by 5 atoms, 1 Cu1, 1 (Ge,Fe) and 3 Cu4, whose positions approximate a trigonal dipyramid lacking a plane of symmetry perpendicular to the 3-fold axis. The Cu1 and (Ge,Fe) atoms lie on the 3-fold axis; the 3 Cu4 atoms lie in a plane perpendicular to the 3-fold axis but this plane is displaced from the midpoint of the Cu1–(Ge,Fe) line about 0.65Å toward the Cu1. As a consequence, the (Ge,Fe)-Cu4 edges are longer (3.59Å) than the Cu1–Cu4 edges (2.72Å).

S2 atoms are situated in a general position inside an asymmetrical four-coordinated polyhedron. The corners of this polyhedron are occupied by Cu2, Cu3, Cu4 and (Ge,Fe) atoms whose distances to the S2 atom are 2.36, 2,18, 2.32 and 2.35Å respectively.

The bonded cation–anion distances range from 2.18–2.36Å with a mean of 2.29Å. Edge lengths for tetrahedra centered on cations range from 3.52–3.90Å with a mean of 3.74Å which represents the mean S–S distance in the unit cell.

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References

de Jong, W. F. (1930) Die Kristallstrukur von germanit. Zeitschrift für Kristallographie, 73, 176–180.

Murdoch, J. (1953) X-ray investigation of colusite, germanite and reniérite. American Mineralogist, 38, 794–801.

Orlandi, P., Merlino, S., Duchi, G., and Vezzalini, G. (1981) Colusite: A new occurrence and crystal chemistry. Canadian Mineralogist, 19, 423–427.

Picot, P., Sainfeld, P., and Vernet, J. (1963) Découverte de germanite en France. Bulletin de la Société Francaise de Minéralogie et de Cristallographie, 86, 299–300.

Sclar, C. B. and Geier, B. H. (1957) The paragenetic relationships of germanite and reniérite from Tsumeb, South West Africa. Economic Geology, 57, 612–631.

Sheldrick, G. M. (1976) SHELX-76. A program for crystal structure determination. University of Cambridge, Cambridge, England.

Smith, G. S. and Snyder, R. L. (1979) F_N: A criterion for rating powder diffraction patterns and evaluating the reliability of powder-pattern indexing. Journal of Applied Crystallography, 12, 60–65.

Strunz, H. (1966) Mineralogische Tabellen. Akademische Verlagsgesellschaft, Leipzig, Germany.

Viaene, W. and Moreau, J. (1968) Contribution a l'étude de la germanite, de la reniérite et de la briartite. Annales de la Société Géologique de Belgique, 91, 127–143.

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