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$GeCd_4S_6$, a New Defect Tetrahedral Structure Type[1]

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The crystal structure of $GeCd_4S_6$ is monoclinic *Cc*, with $a = 12.346$ (2) Å, $b = 7.084$ (1) Å, $c = 12.378$ (2) Å, $\beta = 110.20$ (2)° at 25.0 (5)° and $Z = 4$. A stationary-counter, stationary-crystal technique with Mo K radiation and balanced filters was used to collect three-dimensional data to $2\theta = 60°$ and of the 1530 accessible reflections 1255 were nonzero. The refinement proceeded to a conventional $R = 0.0715$ for the observed $F(hkl)$. The structure consists of two interpenetrating body-centered sulfur icosahedra with the Cd^{2+} and Ge^{4+} in tetrahedral coordination. The GeS_4 tetrahedron is regular with average Ge–S = 2.20 (1) Å; the CdS_4 tetrahedra are somewhat distorted and the Cd–S distances vary from 2.50 to 2.69 Å. The compound is a defect tetrahedral structure whose formula can be written as $4_102_46_6$.

Introduction

In the preparation of compounds AB_2S_4 which might have olivine and K_2SO_4-type crystal structures[2] a new phase was observed from a 1:2:2 reaction mixture of Ge–CdS–S. We initiated a structure determination on the basis of the formula $GeCd_2S_4$ but it became quickly evident that this was not the correct stoichiometry and the analysis showed that the compound was $GeCd_4S_6$. A review of the literature revealed that there has been considerable confusion about this compound. Hahn and DeLorent[3] reported this compound as $GeCd_2S_4$. Nitsche[4] undertook to grow single crystals of this material and reported its stoichiometry as $GeCd_4S_5$ on the basis of chemical analysis although his unit cell dimensions agreed with ours. Kaldis and Widmer[5] grew large single crystals of this material and reported that a chemical analysis showed that the formula was $GeCd_4S_6$. Recently Serment, Perez, and Hagenmuller[6] investigated the systems SiS_2–MS and GeS_2–MS (M = Cd, Hg) and reported unit cell dimensions and space groups for the four isostructural compounds $GeCd_4S_6$, $GeHg_4S_6$, $SiCd_4S_6$, and $SiHg_4S_6$ but did not carry out a determination of the crystal structure. They also indicated the possibility of a solid solution $Ge_{1+x}Cd_4Si_{6+2x}$ where x can vary continuously from 0 to 1. Kaldis, Krausbauer, and Widmer[7] have also grown crystals of $SiCd_4Se_6$ which is isostructural with the other compounds.

Experimental Section

The preparative conditions for AB_2S_4-type materials have been previously described[2] and the crystal which was used in this analysis came from a reactant mixture of Ge–2CdS–2S. The powder X-ray diffraction diagram showed lines all of which were later indexed on the basis of the unit cell dimensions determined from single-crystal photographs and any other phases were either present in very small amounts or as a glass. The powder diagram strongly resembled the pattern expected from a cubic spinel phase and many of the lines could be indexed on a 10-Å lattice constant.

Single-crystal Weissenberg and precession diffraction photographs showed a true diffraction symmetry of $2/m$, with systematic absences hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, consistent with the space groups *Cc* and *C2/c*. The reciprocal lattice has a pseudo threefold axis of symmetry and a pseudocubic unit cell of about 10 Å can be chosen which corresponds to a value expected for a spinel sulfide. Also a pseudohexagonal cell with dimensions $a_h = 7.0$ Å and $c_h = 34.5$ Å can be used successfully to index the powder diffraction diagram.[6] The value of c_h is twice the [111] of the spinel cube and the corresponding rhombohedral cell to this hexagonal cell has $a_{rh} = 12.25$ Å which is the [211] of the cubic cell. The intersection of two [211] vectors forms an angle of 70°, *i.e.*, the supplement of the monoclinic angle. These two [211] are a and c of the true monoclinic cell and b is $^1/_2$[110] of the cubic cell.

An irregularly shaped crystal having approximate dimensions 0.2 × 0.2 × 0.1 mm was mounted along the unique axis and placed on a quarter-circle orienter. The diffractometer was set at a 1° takeoff angle with a 0.05° receiving slit and 55 reflections having 2θ values between 7 and 60° were measured at room temperature, 25.0 (5)°, using Mo Kα radiation (λ 0.7093 Å). These values were used in a least-squares determination of lattice parameters yielding $a = 12.346$ (2) Å, $b = 7.084$ (1) Å, $c = 12.378$ (2) Å, $\beta = 110.20$ (2)°, and $Z = 4$.

A stationary-counter, stationary-crystal method using Mo Kα radiation, balanced Zr–Y filters, a 5° takeoff angle, and wide counter aperture were employed to collect intensity data to a maximum 2θ value of 60°. The basis for accepting an intensity as statistically nonzero was a value of $\Delta I/I < 0.33$, where $\Delta I/I = (P + B)^{1/2}/(P - B)$, P is the total counts with the Zr filter in 10 sec, and B is the total background counts with the Y filter in 10 sec; of the 1530 accessible reflections about 1255 satisfied this requirement. The estimated standard deviation for $F(hkl)$ was calculated using

$$\sigma(|F_o|) = (2|F_o|LpA^{1/2})^{-1}(P + B + 0.0004P^2)^{1/2}$$

where Lp is the Lorentz and polarization corrections and A is the absorption correction. Initially the linear absorption coefficient was calculated as 151 cm^{-1} on the basis of 8 formula weights of $GeCd_2S_4$ in the unit cell but the final data set was obtained with the value of the absorption coefficient calculated for the correct formula and the transmission factor varied in that case between 0.21 and 0.65.

Structure Determination

A Wilson plot calculated on the basis of the $GeCd_2S_4$ formula showed that the intensities followed an acentric distribution so that the space group *Cc* was chosen. This choice was subsequently shown to be correct by the successful refinement of the structure and is consistent with the piezoelectric effect observed by Nitsche[4] for $GeCd_4S_6$.

A three-dimensional Patterson synthesis was calculated to locate the heavy-atom positions. Theoretically there should be $N(N - 1)$ interaction peaks in the Patterson function among N crystallographically independent atoms, and N Harker peaks, for this particular symmetry. There were 20 peaks in general position in the Patterson map with their peak heights

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[1] Research sponsored by the Robert A. Welch Foundation, Houston, Texas.

[2] K. Susa and H. Steinfink, *J. Solid State Chem.*, **3**, 75 (1971).

[3] H. Hahn and C. DeLorent, *Naturwissenschaften*, **45**, 621 (1958).

[4] R. Nitsche, *Z. Kristallogr. Kristallgeometrie, Kristallphys., Kristallchem.*, **120**, 229 (1964).

[5] E. Kaldis and R. Widmer, *J. Phys. Chem. Solids*, **26**, 1697 (1965).

[6] J. Serment, G. Perez, and P. Hagenmuller, *Bull. Soc. Chim. Fr.*, **2**, 561 (1968).

[7] E. Kaldis, L. Krausbauer, and R. Widmer, *J. Electrochem. Soc.*, **114**, 1074 (1967).

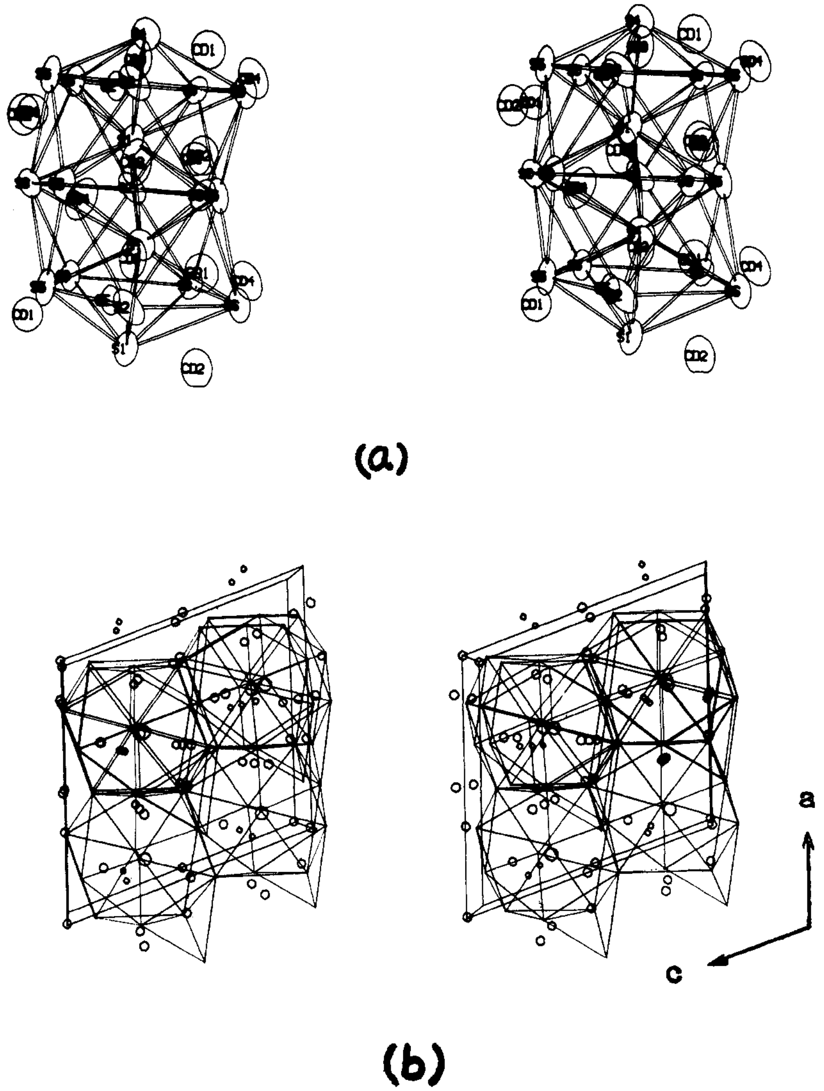

Figure 1.—(a) View along the *a* axis showing the interpenetration of two icosahedra. (b) View of the cell contents along the *b* axis. The smallest circles represent Ge atoms, the next larger circles are Cd atoms, and the largest circles in the centers of the icosahedra are sulfur. The icosahedra are formed by S atoms.

ranging from 512 to 1441 on an arbitrary scale. This accounted for interactions among five heavy atoms, including overlapping interactions between the heavy atoms and sulfur atoms, indicating that the chemical composition might not be as assumed. The x and z coordinates of the heavy atom can be fixed arbitrarily, but not y. From a Harker peak in the section (0, $2y$, $^1/_2$) the y coordinate for one heavy atom was chosen as 0.101. Four additional heavy atoms could now be located from the Patterson map and a three-dimensional electron density map was calculated using phases based on the coordinates of five heavy atoms. The Fourier map showed six peaks which could be assigned to sulfur, and no other features were observed that might have been indicative of additional atoms. The formula corresponding to the unit cell content was $GeCd_4S_6$ and a literature search quickly confirmed this stoichiometry.

A least-squares refinement of the structure was carried out using $1/\sigma^2$ as weights for the structure factors. Atomic scattering factors[8] corrected for the real and imaginary parts and anisotropic temperature factors were used and with the parameters shown in Table I the final R is 0.0715 and $wR = 0.0903$ for 1255 reflections ($R = \Sigma||F_o| - F_c||/\Sigma|F_o|$, $wR = [\Sigma w \cdot (|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$). The absolute configuration was checked by refining a new set of structure factors using negative values of $\Delta f''$ and R was 0.0729. Hamilton's significance criterion[9] was applied to the ratio of the two R values and from $R_{1,1050,0.005} = 1.0196$ the hypothesis that the structure with $\bar{x}\bar{y}\bar{z}$ is the correct one can be rejected at the 0.5% significance level. Table II lists the observed and calculated structure factors.[10] The standard deviation of an observation of unit weight is 1.24. A difference Fourier map showed no meaningful peaks and those that did occur corresponded to heights of 2–3 $e^-/\text{Å}^3$.

Discussion of the Structure

The sulfur atoms form two interpenetrating body-centered icosahedra which are illustrated in Figure 1a

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(8) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

(9) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(10) Table II, a listing of structure factor amplitudes, will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

TABLE I

ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS × 10^4 FOR $GeCd_4S_6$[a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cd1	6559 (3)	8939 (3)	9970 (2)	35 (1)	87 (3)	26 (1)	−8 (2)	13 (1)	−2 (2)
Cd2	0	9184 (3)	0	31 (1)	102 (4)	24 (1)	−4 (2)	17 (1)	−1 (2)
Cd3	1848 (2)	8843 (3)	8089 (2)	24 (1)	129 (4)	20 (1)	−1 (2)	11 (1)	4 (2)
Cd4	8665 (3)	6967 (3)	6552 (3)	26 (1)	117 (4)	26 (1)	−2 (2)	7 (1)	20 (2)
Ge	4336 (3)	7301 (3)	7466 (3)	14 (2)	56 (4)	9 (2)	−1 (2)	5 (1)	−1 (2)
S1	8582 (6)	9815 (9)	7962 (6)	32 (4)	72 (10)	15 (4)	−15 (6)	9 (3)	6 (5)
S2	6222 (6)	7361 (9)	8002 (6)	13 (4)	74 (11)	21 (4)	−2 (5)	8 (3)	−19 (5)
S3	6776 (6)	7550 (9)	4937 (6)	27 (4)	59 (9)	14 (3)	−5 (5)	8 (3)	−7 (5)
S4	8898 (6)	4829 (8)	8291 (6)	22 (4)	70 (10)	20 (4)	4 (5)	16 (3)	−5 (5)
S5	8575 (6)	2783 (9)	5601 (6)	19 (4)	90 (11)	10 (3)	6 (5)	7 (3)	7 (5)
S6	5512 (5)	2763 (8)	6146 (6)	20 (4)	76 (10)	12 (4)	5 (5)	8 (3)	3 (5)

[a] Numbers in parentheses are standard deviations in the last significant figures. The temperature factor expression is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

TABLE III

BOND DISTANCES AND ANGLES WITH STANDARD DEVIATIONS IN THE LAST SIGNIFICANT FIGURE SHOWN IN PARENTHESES

Atom set	Distance, Å	Atom set	Angle, deg
Cd1–S3	2.50 (1)	S3–Cd1–S6	123.8 (4)
Cd1–S6	2.56 (1)	S3–Cd1–S2	113.5 (4)
Cd1–S2	2.58 (1)	S3–Cd1–S5	111.7 (4)
Cd1–S5	2.64 (1)	S6–Cd1–S2	112.6 (4)
		S6–Cd1–S5	103.0 (4)
		S2–Cd1–S5	84.7 (4)
Cd2–S3	2.54 (1)	S3–Cd2–S6	112.2 (4)
Cd2–S6	2.54 (1)	S3–Cd2–S5	115.8 (4)
Cd2–S5	2.55 (1)	S3–Cd2–S1	110.9 (4)
Cd2–S1	2.57 (1)	S6–Cd2–S5	111.5 (4)
		S6–Cd2–S1	110.8 (4)
		S5–Cd2–S1	94.4 (4)
Cd3–S3	2.52 (1)	S3–Cd3–S6	122.1 (4)
Cd3–S6	2.52 (1)	S3–Cd3–S4	111.2 (4)
Cd3–S4	2.55 (1)	S3–Cd3–S2	108.0 (4)
Cd3–S2	2.60 (1)	S6–CdC–S4	118.5 (4)
		S6–Cd3–S2	99.5 (4)
		S4–Cd3–S2	90.7 (4)
Cd4–S3	2.53 (1)	S3–Cd4–S6	116.7 (4)
Cd4–S6	2.56 (1)	S3–Cd4–S4	134.4 (4)
Cd4–S4	2.57 (1)	S3–Cd4–S1	99.1 (4)
Cd4–S1	2.69 (1)	S6–Cd4–S4	116.5 (4)
		S6–Cd4–S1	101.4 (4)
		S4–Cd4–S1	85.2 (4)
Ge–S1	2.18 (1)	S1–Ge–S2	116.3 (5)
Ge–S2	2.19 (1)	S1–Ge–S5	110.6 (5)
Ge–S5	2.20 (1)	S1–Ge–S4	109.1 (5)
Ge–S4	2.22 (1)	S2–Ge–S5	109.9 (5)
		S2–Ge–S4	104.3 (5)
		S5–Ge–S4	105.9 (5)

and the unit cell content is shown in Figure 1b. The sulfur atoms are related by a center of symmetry and atoms S1 and S4 in the centers of the icosahedra are almost at the centric positions. None of the heavy atoms in the tetrahedral interstices, however, is related in such a manner and therefore the overall structure is acentric. The approximate relationship among the unit cell dimensions, $a = c = \sqrt{3}b$, $\beta = 110°$, permits the selection of an orthogonal cell with dimensions a, b, $3d_{001}$, where $3d_{001} = c_h$ as previously mentioned. Two cadmium atoms, Cd1 and Cd2, have their positions $^1/_3$ of a unit cell apart which with C-centering symmetry creates an almost perfect hexagon parallel to the ab plane. All of these factors help to emphasize the pseudo threefold symmetry.

Bond distances and bond angles are listed in Table III. The germanium atoms, as expected, are in almost perfect tetrahedral coordination while the Cd tetrahedra are considerably distorted. Values for Ge–S and Cd–S bond distances are similar to those found in the compounds CdS and GeS_2.

This compound can be classified as a tetrahedral structure using Parthe's scheme.[11] The electron to atom ratio, $N_E/N_A = 8$, makes it a normal valence compound and the valence electron concentration, VEC = 4.36, classifies it as a defect tetrahedral structure whose formula can be written as $4_1 0 2_4 6_6$, where there are four nonbonding orbitals per formula unit. Each sulfur ion surrounding a vacant tetrahedral interstice has one nonbonding orbital directed toward this vacancy and only cation–anion bonds occur in the structure.

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(11) J. H. Westbrook, Ed., "Intermetallic Compounds," Wiley, New York, N. Y., 1967, Chapter 11.