PtGeSe with Cobaltite Structure, a Ternary Variant of the Pyrite Structure

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PtGeSe crystallizes in the orthorhombic cobaltite structure, an ordered variant of the pyrite structure with $a = 6.015$ (4), $b = 6.072$ (1), $c = 5.992$ (1) Å, space group $Pca2_1$ and four formula units per cell. Intensities were measured with a four-circle automatic diffractometer and corrected for absorption ($\mu = 991$ cm^{-1}). The structure was refined by full-matrix least-squares methods to $R = 8.9\%$ (1202 reflexions) or $R = 6.7\%$ (894 reflexions, $|F| > 2\sigma$). The possible ordering variants of a ternary pyrite structure are indicated. The compounds PtGeS and PtSiSe were found to be isotypic with PtGeSe.

Introduction

Following research on binary structures similar to pyrite (Hohnke & Parthé, 1968; Parthé & Hohnke, 1970) investigations on ternary pyrites have been undertaken. El-Boragy & Schubert (1971) have published the powder patterns of PtGeSe and PtGeS which indicated a structure similar to pyrite. It seemed interesting to investigate these compounds by single-crystal work.

Experimental

The following materials were used: Pt(5*N*) from Engelhard and Si, Ge, S, Se (all 5*N*) from Fluka.

All compounds were prepared by heating the elements in evacuated quartz tubes at 600 and 900°C for about four to six weeks. Some samples were ground after one week and reheated to enhance the attainment of equilibrium. It this way PtGeS, PtGeSe and a new compound PtSiSe were synthesized. Attempts to form PtSiS and similar compounds with Pd failed. The compound PtGeS was found to be a diamagnetic semiconductor.

A crystal of PtGeSe with dimensions $0.07 \times 0.06 \times 0.05$ mm was selected. On precession photographs the systematic absences of $0kl$ with $l \neq 2n$ and of $h0l$ with $h \neq 2n$ indicated the space groups $Pca2_1$ (No. 29) or $Pcam$ (No. 57). The space group $Pca2_1$ was selected for further work because an ordered structure similar to pyrite cannot have a centre of symmetry.

From the precession photographs it appeared that the values of the lattice constants a, b and c were equal but X-ray powder photographs (Guinier–Hägg camera Cr $K\alpha_1$, $\lambda = 2.2896$ Å) showed a splitting of lines which could only be attributed to slight differences of a, b and c. Hence three values for the lattice constants were determined from the powder photograph but it was not possible to say which was a, which was b and which was c. To resolve this difficulty accurate values of the lattice constants were also determined from a single crystal on a four-circle (Philips PW1100) automatic diffractometer. Clearly the relation

between the axial lengths and the systematic absences permits the assignment of the axes unequivocally.

Crystal data

PtGeSe.
Orthorhombic; space group $Pca2_1$ (No. 29).
$a = 6.015$ (4); $b = 6.072$ (1); $c = 5.992$ (1) Å.
$U = 218.8$ Å^3; $Z = 4$.
$D_x = 10.52$ g cm^{-3}.
$\mu = 991$ cm^{-1}. $F(000) = 576$.

The intensities were collected on the automatic diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), a graphite monochromator and an ω scan. Intensities were measured for each independent, non-systematically absent reflexion with $\sin \theta / \lambda < 1.24$ Å^{-1}. (Scan speed 0.02°/sec, background measured on both sides of the reflexion; scan time variable with θ; time for measuring the background = scan time/2). 1202 reflexions were recorded of which 894 were greater than 2σ in $|F|$. Lorentz and polarization corrections were applied as usual.

The linear absorption coefficient for PtGeSe was $\mu = 991$ cm^{-1}, ($\mu R \simeq 3.5$) and it was therefore necessary to correct for absorption. The dimensions of the crystal were determined by calibrated photographs taken with a microscope. The crystal form could be described by six planes. The orientation of the crystal corresponding to the primary X-ray beam was determined by the orientation matrix and two planes. The intensities were then corrected for absorption by a program using the analytical method of de Meulenaer & Tompa (1965). The values of the transmission factor were found to lie in the range $0.04 < T < 0.15$.

Refinement of the structure

The refinement was carried out with the full-matrix least-squares program *ORXFLS*3 (Busing, Martin, Levy, Ellison, Hamilton, Ibers, Johnson & Thiessen, 1971). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Allowance was made for $\Delta f'$ and $\Delta f''$ for all atoms. The final agreement index was calculated as $R = \sum \Delta F_{meas}/\sum|F_{meas}|$* and the weights were set at $1/\sigma^2$ where σ is the experimental standard deviation of the $|F_{meas}|$. The relative intensity (I_{rel}), being the difference of the number of counts of the reflexion and the number of counts of the background, might be negative. If $-\sigma_{I_{rel}} \le I_{rel} \le \sigma_{I_{rel}}$ then I_{rel} is replaced by $(I_{rel} + \sigma_{I_{rel}})/2$ but if $I_{rel} < -\sigma_{I_{rel}}$ then I_{rel} is set to zero.

For the refinement, the positional parameters of FeS$_2$ [pyrite structure, space group $Pa3$ (No. 205)] referred to the setting of space group $Pca2_1$ (No. 29) were used. Without correction for absorption no value of R smaller than 25% could be obtained. After several cycles of refinement using the corrected intensities a value $R = 7 \cdot 9\%$ (894 reflexions, $|F| > 2\sigma$) was obtained but two interatomic distances Pt–Ge were smaller than the sum of the octahedral radius of Pt and the tetrahedral radius of Ge. Therefore the Ge and Se atoms were displaced in such a way that the interatomic metal–non-metal distances had their expected value. Refinement was started again and a second minimum of R was found. In the final cycle 11 parameters were allowed to vary.

The following R values were obtained: $R = 8 \cdot 9\%$ for all 1202 reflexions which are permitted according to the space group $Pca2_1$ and $R = 6,7\%$ for 894 reflexions with $|F_{meas}| > 2\sigma$. The variations of the parameters were smaller than $\frac{1}{10}$ of their e.s.d.'s which were derived from the inverse least-squares matrix. The atomic distances were then calculated with the program $ORFFE3$ (Busing, Martin, Levy, Brown, Johnson & Thiessen, 1971).

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* $\Delta F_{meas} = ||F_{meas}| - |F_{calc}||$.

The positional parameters, the isotropic temperature factors and the atomic distances with their e.s.d.'s are given in Tables 1 and 2. The values of $|F_{meas}|$ and $|F_{calc}|$ are given in Table 3.

Table 1. *Atomic coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^3$) *with their standard deviations in brackets for orthorhombic* PtGeSe *with the cobaltite structure, space group* $Pca2_1$

Atom	x/a	y/b	z/c	B
Pt	0086 (1)	7420 (1)	0*	276 (7)
Ge	3833 (4)	1364 (4)	6168 (7)	204 (25)
Se	6198 (4)	3759 (4)	3820 (7)	415 (28)

* Arbitrarily fixed.

Table 2. *Shortest interatomic distances* (Å) *with their standard deviations in brackets*

Pt –Se(1)	2·451 (3)	Pt–Ge(1)	2·527 (4)
Pt –Se(2)	2·457 (3)	Pt–Ge(2)	2·567 (3)
Pt –Se(3)	2·490 (4)	Pt–Ge(3)	2·579 (3)
Ge–Se	2·473 (3)		

Isotypic compounds

The lattice constants of PtGeSe, PtSiSe were determined from powder patterns (Guinier–Hägg camera, Cr $K\alpha_1$, $\lambda = 2 \cdot 2896$ Å). The values are:

PtGeS: $a = 5 \cdot 864$ (9), $b = 5 \cdot 902$ (9), $c = 5 \cdot 835$ (9) Å,
PtSiSe: $a = 5 \cdot 944$ (2), $b = 5 \cdot 988$ (2), $c = 5 \cdot 900$ (2) Å.

On the powder film of PtSiSe another unknown pattern was detected. Further investigations on this substance are under way.

ULLMANITE
Ni Sb S

COBALTITE
Co As S

$P2_13(T^4)$ $Pca2_1(C_{2v}^5)$ $Pn(C_s^1)\ xyz,x\bar{y}z+\frac{1}{2}$ $P1(C_1^1)$

M in 4(a): 0,0,0;
X in 4(a): $\frac{2}{3},\frac{2}{3},\frac{2}{3}$;
Y in 4(a): $\frac{5}{8},\frac{5}{8},\frac{5}{8}$

M in 4(a): 0,$\frac{1}{4}$,0;
X in 4(a): $\frac{5}{8},\frac{1}{4},\frac{1}{8}$;
Y in 4(a): $\frac{3}{8},\frac{3}{8},\frac{7}{8}$;

M$_I$ in 0,$\frac{1}{4},\frac{1}{4}$; Me$_{II}$ in $\frac{1}{4},\frac{1}{4}$,0;
X$_I$ in $\frac{5}{8},\frac{1}{8},\frac{5}{8}$; X$_{II}$ in $\frac{7}{8},\frac{5}{8},\frac{1}{8}$;
Y$_I$ in $\frac{1}{8},\frac{5}{8},\frac{5}{8}$; Y$_{II}$ in $\frac{5}{8},\frac{5}{8},\frac{5}{8}$;

M in 0,0,0; $\frac{1}{2},\frac{1}{2}$,0; $\frac{1}{2}$,0,$\frac{1}{2}$; 0,$\frac{1}{2},\frac{1}{2}$;
X in $\frac{5}{8},\frac{5}{8},\frac{5}{8}$; $\frac{1}{8},\frac{7}{8},\frac{5}{8}$;
$\frac{5}{8},\frac{1}{8},\frac{7}{8}$; $\frac{7}{8},\frac{5}{8},\frac{5}{8}$;
Y in $\frac{3}{8},\frac{3}{8},\frac{3}{8}$; $\frac{7}{8},\frac{3}{8},\frac{1}{8}$;
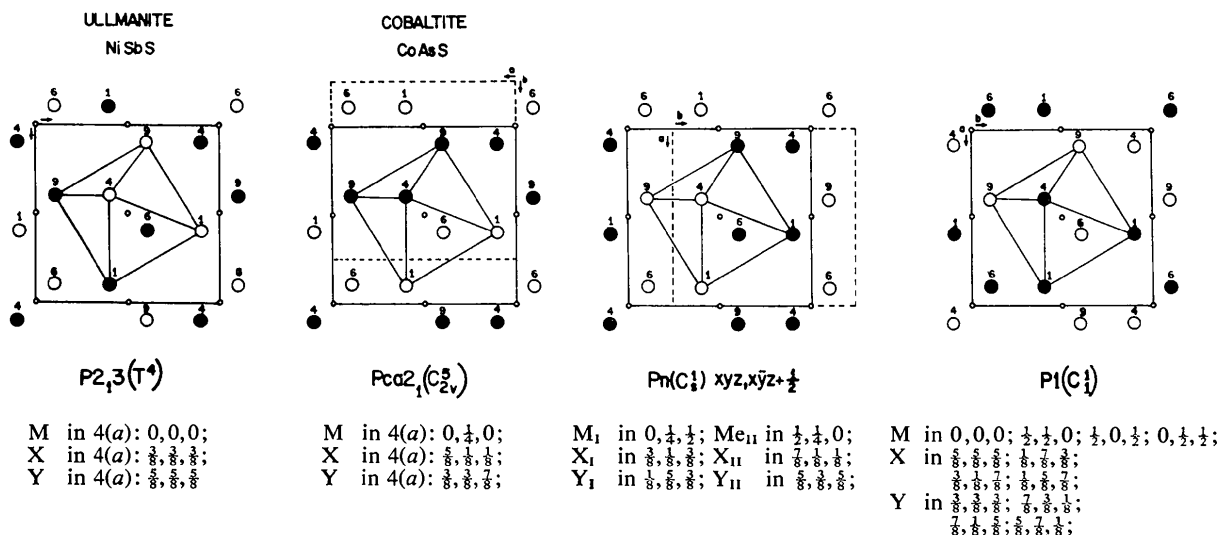$\frac{7}{8},\frac{1}{8},\frac{5}{8}$; $\frac{5}{8},\frac{7}{8},\frac{1}{8}$;

Fig. 1. The four possible atom arrangements for ternary ordered pyrite structures. The metal atoms form a face-centred lattice and are indicated by small circles. The two non-metals are shown respectively by filled and unfilled large circles. The heights of the non-metal atoms above the plane of projection are indicated in units of tenths of the cell dimension perpendicular to the plane of projection.

Discussion

If one looks for the possible arrangement of the non-metals in an ordered ternary pyrite structure one finds the four arrangements shown in Fig. 1. It was assumed that Pauling's electrostatic valence rule is fulfilled, no bonds between equal anions are formed, and the cell has the same size as the pyrite cell.

The arrangement with the highest symmetry is the cubic ullmanite structure type (Takeuchi, 1957). The structure of the mineral cobaltite CoAsS has to be described in terms of an orthorhombical cell in spite of

Table 3. *Observed and calculated structure factors for* PtGeSe

Reading from left to the right the columns contain the values h, k, l, $|F_{meas}|$ and $|F_{calc}|$.

the equal values of the lattice constants (Giese & Kerr, 1965). In Table 4 the *hkl* values of the reflexions are given which might be observed in the powder patterns of a pyrite, ullmanite and a cobaltite structure. In the case of the compound CoAsS very few lines allow a distinction between the cobaltite and the ullmanite structure type. In the case of PtGeSe the splitting of the cubic powder pattern corresponding to the orthorhombic distortion could be easily observed. Examples for the two other variants with low symmetry have not yet been found.

Table 4. *The hkl values of the reflexions which might be observed in the powder patterns of a pyrite, ullmanite and a cobaltite structure*

Pyrite	Ullmanite	Cobaltite
—	—	010
—	110	110
111	111	111
200	200	200
		020
		002
210	210	210
		120
		201
		012
211	211	211
		121
		112
220	220	220
		202
		022
—	—	030
221	221	221
		212
		122
310	310	310
		130
311	311	311
		131
		113
222	222	222

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Structure Cristalline de l'Iodure de Chrome: CrI2

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CrI2 crystallizes in space group Cmc2₁. The unit-cell dimensions are $a = 3\cdot915$, $b = 7\cdot560$, $c = 13\cdot553$ Å. There are four formula units per unit cell. Least-squares refinement was made with a final R of 11 %. The structure shows layers of deformed octahedra CrI6 due to the Jahn–Teller effect.

La structure de l'iodure de chrome CrI2 a été étudiée par Tracy, Gregory, Stewart & Lingafelter (1962).

Après avoir essayé de nombreux cristaux, dont certains présentaient des taches de diffraction supplémentaires, ces auteurs ont décrit la structure du cristal donnant le diagramme le plus simple. Mais l'existence d'autres phases n'était pas exclue.

Guen, Alléaume, Eholie & Flahaut (1972) ont repris la préparation du composé selon la méthode indiquée par Tracy *et al.*, et en employant également d'autres

méthodes. Tous les produits ainsi obtenus ont conduit au même diagramme de diffraction de rayons X.

Ce diagramme ne pouvait être interprété à partir de la maille monoclinique décrite par Tracy *et al.*, et correspondait donc à une phase différente, dont nous avons entrepris l'étude.

Préparation

L'iodure de chrome est préparé à partir des éléments pris en proportions stoechiométriques. Le mélange est