Contribution from the Department of Chemistry and Division of Engineering,
Brown University, Providence, Rhode Island 02912

High Pressure Synthesis and Properties of CoXY Compounds (X = P, As, Sb; Y = S, Se)[1]

R. HENRY, J. STEGER, H. NAHIGIAN, and A. WOLD*

Received May 7, 1975 AIC50311C

The CoXY compounds, where X = P, As, or Sb and Y = S or Se, were subjected to elevated temperatures and pressures. CoSbS transformed from the orthorhombic structure (space group *Pbca*) to form a cubic pyrite type structure at 1150°C, 60 kbars pressure; and a similar transformation occurred for CoPSe at 1500°C, 60 kbars pressure. CoAsSe transformed partially from the orthorhombic marcasite structure (space group *Pnn*2) to the cubic pyrite type structure at 1600°C, 60 kbars pressure. Ordering of the mixed anion pairs was observed for cubic CoSbS (space group $P2_13$), whereas no anion ordering was found for cubic CoPSe (space group *Pa*3). No structural transformation was observed for CoSbSe which retained the marcasite structure up to 1600°C, 60 kbars pressure. Lattice parameters and density values were also determined for the CoXY compounds. Magnetic susceptibility measurements determined over the temperature range from 77 to 292°K showed temperature-independent diamagnetic behavior for cubic CoSbS.

Introduction

In recent years, a number of studies have been reported on the cobalt and nickel dichalcogenides and their anion- and cation-substituted systems.[2-10] These studies have attempted to relate the magnetic and electrical properties with the crystallography of the systems.

The compounds of the general formula CoXY, where X = P, As, or Sb and Y = S or Se, have been found to exist in three closely related crystallographic structures: pyrite, which is cubic (space group *Pa*3), anomalous marcasite, which is orthorhombic (space group *Pnn*2), and pararammelsbergite, which is orthorhombic (space group *Pbca*). The relationship between the structures can best be seen by comparing the coordination of the cation octahedra.[11] The pyrite octahedra are characterized by corner sharing. Each corner of a pyrite octahedron shares corners with two neighboring octahedra, giving a total sharing of corners with twelve neighboring octahedra (Figure 1). The marcasite structure is characterized by linear chains of edge-shared octahedra that run parallel to the orthorhombic *c* axis. A marcasite octahedron shares two parallel and opposite edges with two neighboring octahedra and corners with eight additional neighboring octahedra (Figure 2). The combination of both the pyrite and the marcasite stacking sequence of the octahedra results in the pararammelsbergite structure. In this structure, each octahedron shares an edge with one neighboring octahedron and shares corners with ten additional neighboring octahedra[12] (Figure 3).

Some transition metal chalcogenides and pnictides, which are closely related to the CoXY compounds, form with the cubic pyrite structure when synthesized at elevated temperatures and pressures. For example, $NiAs_2$, when prepared at ambient pressure, has a similar electronic configuration and is isostructural to CoSbS and to CoPSe. However, when $NiAs_2$ is synthesized using high-pressure techniques, the pyrite structure is formed.[4] $FeTe_2$ is isostructural with CoAsSe and with CoSbSe when prepared at ambient pressure. However, when synthesized at elevated temperatures and pressures,[5] a cubic pyrite structure is formed. Since the CoXY compounds are related both structurally and electronically to $NiAs_2$ and $FeTe_2$, it appeared possible that cubic phases of the CoXY compounds might also form at elevated temperatures and pressures.

Table I. Synthetic Conditions for CoXY Compounds

	P	As	Sb
S	Low-pressure phase, tetragonal; only a slight distortion from cubic *Pa*3	Low-pressure phase, cubic *Pa*3	60 kbars, 1150°C, 20 min; complete transformation from orthohombic *Pbca* to cubic $P2_13$
Se	60 kbars, 1500°C, 30 min; complete transformation from orthorhombic *Pbca* to cubic *Pa*3	60 kbars, 1600°C, 30 min; partial transformation from orthorhombic *Pnn*2 to cubic *Pa*3 or $P2_13$	60 kbars, 1600°C, 30 min; no transformation from orthorhombic *Pnn*2

Experimental Section

Preparation. Ambient Pressure Synthesis. Polycrystalline powders were prepared initially by direct combination of the elements. Spectroscopic grade Co, P, As, Sb, S, and Se were obtained from Atomergic Chemical Co., Division of Gallard-Schlesinger Chemical Corp., New York, N.Y. The high-purity cobalt (99.999%) was reduced (850°C for 8 hr) in a 15% hydrogen–85% argon atmosphere. High-purity arsenic was heated for 3 hr at 200°C under a dynamic vacuum to remove any volatile impurities. Elemental phosphorus, antimony, sulfur, and selenium were used as supplied. Stoichiometric quantities of the elements were allowed to react in evacuated sealed silica tubes three times at 800°C with two intermediate grindings under a dry nitrogen atmosphere. Reaction completeness was determined by both microscopic observation and X-ray analysis. Complete reaction was easier to achieve if the temperature gradient across the length of the sample tube was minimized to avoid segregation of the components.

High-Pressure Synthesis. Reactions were carried out using a belt apparatus of the type described by Hall.[13] Figure 4 shows a schematic of the sample cell. A graphite sleeve functions as the internal heater while pyrophyllite or lava stone serves as the pressure-transmitting medium.

A major problem associated with the high-pressure synthesis of sulfides is sample contamination. Boron nitride was used initially for the reaction container; however, it was difficult to isolate the sample from the boron nitride crucible. Consequently, boron nitride was replaced by Pyrex which neither reacted with nor adhered to the sample.

Prereacted polycrystalline samples were packed in Pyrex capsules and treated at pressures of 60 kbars and temperatures ranging from 1000 to 1700°C. Reaction times ranged from 20 min to 2 hr. The sample temperatures were then reduced, over a period of 4 hr, to 600°C, followed by a more rapid cooling (<15 min) to room temperature. After the samples had cooled, the pressure was reduced from 60 kbars to ambient pressure. Table I lists the conditions of preparation for each of the compounds studied.

X-Ray Analysis and Characterization. Powder diffraction patterns were obtained with a Norelco diffractometer using monochromated high-intensity Cu Kα radiation (λ 1.5405 Å). Fast scans of 1° (2θ)/min were recorded to examine materials for the possible presence of extra phases. Slow scans of 1° (2θ)/4 min were obtained for all single-phase samples in the range $12^\circ \le 2\theta \le 130^\circ$. Lattice parameters were determined using high-angle reflections ($2\theta > 70^\circ$) corrected relative to an internal MgO standard.

Density Determinations. Sample densities were determined using

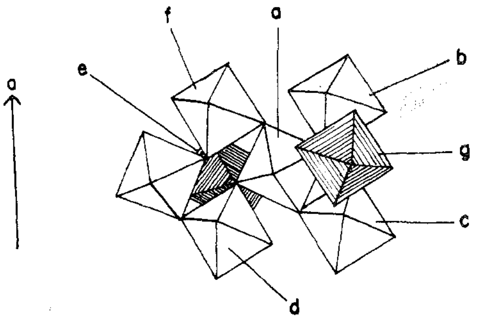

Figure 1. Coordination of the cation octahedra of pyrite. Octahedron a shares corners with octahedra b, c, d, e, f, g (shown) and six additional octahedra (not shown).

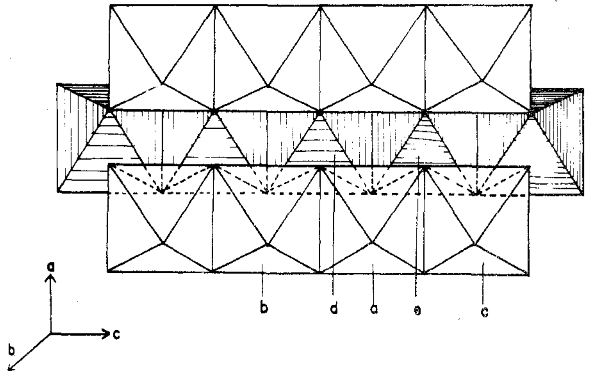

Figure 2. Coordination of the cation octahedra of marcasite. Octahedron a shares edges with octahedra b and c and corners with octahedra d and e (shown) and octahedron a also shares corners with six additional octahedra (not shown).

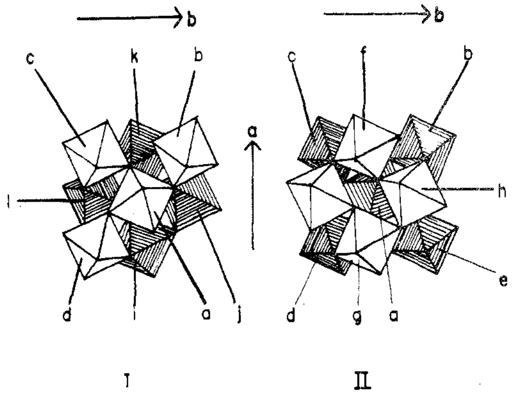

Figure 3. Coordination of the cation octahedra of pararammelsbergite. The lower octahedra in I are identical with the upper octahedra in II. Octahedron a shares corners with octahedra b, c, d, e, f, g, i, j, k and l and shares an edge with octahedron h.

a hydrostatic technique[14] employing a Mettler H54 analytical balance. The density medium perfluoro(1-methyldecalin) was chosen because of its relatively low vapor pressure and its ability to wet the samples. A high-purity silicon crystal (ρ = 2.328 g/cm^3) was used for calibrating the density fluid. In order to obtain reproducible results, care was taken to outgas the samples thoroughly prior to density measurements.

Magnetic Measurements. Magnetic susceptibility data were obtained using a Faraday balance[15] equipped with a Cahn RG Electrobalance, over the temperature range 77–292°K. Measurements were performed at field strengths of 6.25 and 10.30 kOe. The balance was calibrated using a platinum wire ($\chi_g = 0.991 \times 10^{-6}$ emu/g at 297°K). No corrections were made for core diamagnetism because of the large uncertainty in the magnitude of the corrections relative to the magnitude of the susceptibility of the various materials studied.

Results and Discussion

CoSbS, when prepared under ambient pressure, crystallized in the orthorhombic space group *Pbca* (α-CoSbS). When subjected to conditions (Table I) of elevated temperature and pressure, CoSbS undergoes a crystallographic transformation. The resulting metastable phase crystallizes with the cubic ullmanite structure, space group $P2_13$ (β-CoSbS). Lattice parameters and densities are given in Table II. The X-ray data for β-CoSbS are given in Table III.

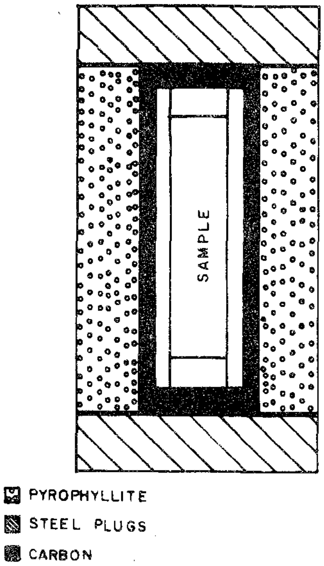

Figure 4. High-pressure sample cell.

Table II. Densities, Lattice Parameters, and Space Groups for Some MXY Compounds

Compd	ρ_{obsd}, g/cm^3	ρ_{calcd}, g/cm^3	Lattice parameters, A	Space group
α-CoSbS[a]	6.96 (2)	6.98	a_0 = 5.834 (9) b_0 = 5.953 (5) c_0 = 11.664 (5)	*Pbca*
β-CoSbS[b]	7.05 (2)	7.08	a_0 = 5.844 (2)	$P2_13$
α-CoPSe	6.31 (2)	6.33	a_0 = 5.548 (9) b_0 = 5.659 (5) c_0 = 11.185 (5)	*Pbca*
β-CoPSe			a_0 = 5.63 (1)	*Pa*3
α-CoAsSe	7.26 (2)	7.25	a_0 = 4.751 (5) b_0 = 5.753 (5) c_0 = 3.584 (5)	*Pnn*2
β-CoAsSe				*Pa*3 or $P2_13$
α-CoSbSe (no transformation)	7.67 (2)	7.68	a_0 = 5.056 (5) b_0 = 6.031 (5) c_0 = 3.686 (5)	*Pnn*2

[a] α = ambient-pressure phase. [b] β = high-pressure phase.

Table III. X-Ray Data β-CoSbS

hkl	2θ, deg	I/I_0	*hkl*	2θ, deg	I/I_0
110[a]	21.50	20	332	76.36	11
111	26.50	13	422	80.45	4
200	30.55	17	510, 431	84.45	16
210	34.27	100	333, 511	86.54	23
211	37.18	70	432, 520	90.41	26
220	43.77	11	521	92.40	14
310[a]	49.24	13	440	96.42	18
311	51.80	58	610	106.58	8
222	54.38	21	532, 611	108.69	24
320	56.72	30	533	119.60	10
321	59.05	50	622	121.97	10
400	63.64	7	630, 542	124.32	24
411, 330	67.97	13	631	126.79	12
420	72.23	5	444	131.93	6
421	74.28	28	543, 710, 550	137.55	17

[a] Note—the presence of these reflections is indicative of space group $P2_13$.

The ullmanite structure type (Figure 5) is closely related to the pyrite structure (Figure 6). For the ullmanite structure, an ordering of the mixed anion pairs lowers the symmetry of

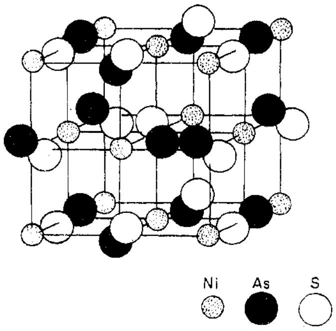

Figure 5. Ullmanite structure.

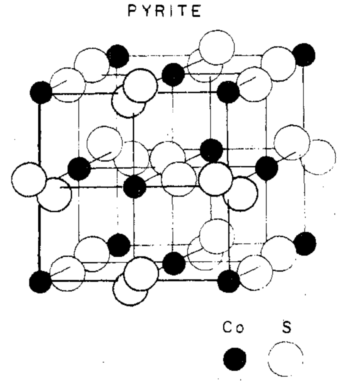

Figure 6. Pyrite structure.

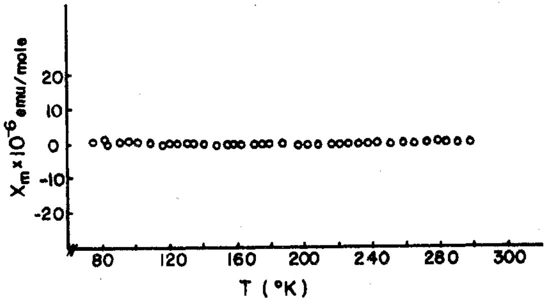

Figure 7. Molar susceptibility vs. temperature for β-CoSbS.

the pyrite. However, the essential features of the structure are unchanged. Both structures can be described as two interpenetrating face-centered cubic arrays: one face-centered cubic array of cations interpenetrating a second face-centered cubic array of anion pairs. This arrangement of atoms results in a tetrahedral coordination of the anions with three cations and one anion, whereas each cation is surrounded by six anions in a trigonally distorted octahedral arrangement. For the pyrite structural arrangement, Goodenough[16,17] has proposed a band model for correlating the properties of these compounds.

The molar susceptibility of β-CoSbS was measured as a function of both field strength and temperature. Honda–Owen[18] measurements of β-CoSbS at both 292 and 77°K gave no indication of any ferromagnetic impurities. β-CoSbS was found to exhibit temperature-independent magnetic susceptibility over the range from 77 to 292°K (Figure 7). The susceptibility of β-CoSbS resembles the susceptibility of α-CoSbS, which is slightly diamagnetic throughout the same temperature region.

The one-electron band models proposed by Goodenough for pyrite type compounds (Figure 8) can be used to interpret the results obtained. In both pyrite and marcasite structures, Goodenough has shown that for compounds with six d electrons, the t_{2g} bands are completely filled whereas the σ^*-antibonding band is empty. The magnetic properties exhibited by both α-CoSbS and β-CoSbS are consistent with those expected for a low-spin d^6 electronic configuration.

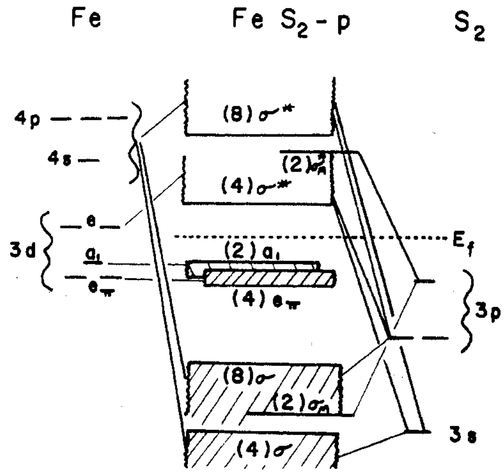

Figure 8. Energy band model for pyrite type compounds.

CoPSe. CoPSe, when prepared initially by direct combination of the elements, is orthorhombic in space group *Pbca* (α-CoPSe). α-CoPSe, treated under the conditions listed in Table I, transformed to the cubic pyrite structure in space group *Pa*3 (β-CoPSe). The lattice parameters of α-CoPSe and β-CoPSe are listed in Table II. No further measurements were made on β-CoPSe because of the presence of small amounts of other phases, namely, $CoSe_2$.

CoAsSe and CoSbSe. Both CoAsSe and CoSbSe, when prepared via direct combination of the elements at ambient pressure, are orthorhombic with space group *Pnn*2. CoAsSe, treated at elevated temperatures and pressures (see Table I) partially transformed to a cubic structure (β-CoAsSe), whereas CoSbSe, reacting under the same conditions, remained structurally unchanged. Because of the similarity of the scattering factors of As and Se, it was not possible to conclude from the powder diffraction data whether β-CoAsSe formed the pyrite structure with disordered anions, as found for β-CoPSe, or the ullmanite structure with ordered anions, as with β-CoSbS. The partial transformation of CoAsSe precluded the possibility of magnetic characterization of the high-pressure form of this material.

Registry No. CoSbS, 51021-58-0; CoPSe, 51021-57-9; CoAsSe, 51021-48-8; CoSbSe, 51021-59-1.

References and Notes

(1) This work was supported by the Army Research Office, Durham, N.C., and the Materials Research Laboratory at Brown University.
(2) H. S. Jarrett, W. H. Cloud, R. J. Bouchard, S. R. Butler, C. G. Frederick, and J. L. Gillson, *Phys. Rev. Lett.*, **21**, 617 (1968).
(3) K. Adachi, K. Sato, and M. Takeda, *J. Phys. Soc. Jpn.*, **26**, 631 (1969).
(4) P. C. Donohue, T. A. Bither, and H. S. Young, *Inorg. Chem.*, **7**, 998 (1968).
(5) T. A. Bither, R. J. Bouchard, W. H. Cloud, P. C. Donohue, and W. J. Siemons, *Inorg. Chem.*, **7**, 2208 (1968).
(6) J. M. Hastings and L. M. Corliss, *IBM J. Res. Develop.*, **14**, 227 (1970).
(7) S. Furuseth, A. Kjekshus, and A. F. Andresen, *Acta Chem. Scand.*, **23**, 2325 (1969).
(8) V. Johnson and A. Wold, *J. Solid State Chem.*, **2**, 209 (1970).
(9) J. Mikkelsen and A. Wold, *J. Solid State Chem.*, **3**, 39 (1971).
(10) H. Nahigian, J. Steger, R. J. Arnott, and A. Wold, *J. Phys. Chem. Solids*, **35**, 1349 (1974).
(11) H. Nahigian, J. J. Steger, H. L. McKinzie, R. J. Arnott, and A. Wold, *Inorg. Chem.*, **13**, 1498 (1974).
(12) W. N. Stassen and R. D. Heyding, *Can. J. Chem.*, **46**, 2159 (1968).
(13) H. T. Hall, *Rev. Sci. Instrum.*, **31**, 125 (1960).
(14) R. Adams, Ph.D. Thesis, Brown University, 1973.
(15) B. Morris and A. Wold, *Rev. Sci. Instrum.*, **39**, 1937 (1968).
(16) J. B. Goodenough, *J. Solid State Chem.*, **3**, 26 (1971).
(17) J. B. Goodenough, *J. Appl. Phys.*, **38**, 1054 (1967).
(18) K. Honda, *Ann. Phys. (Leipzig)*, **32**, (337), 1048 (1910); M. Owen, *ibid.*, **37** (342), 657 (1912).