form iridium disulfide having the orthorhombic crystal structure of iridium diselenide,[4,5] in which part of the iridium may be considered to have the +3 oxidation state. If the ratio of sulfur to iridium is increased to nearly 3:1, then a pyrite structure is formed[6] in which the +3 iridium is balanced with cation vacancies. At 60 kbars, a mixture of sulfur and iridium (3:1 mole ratio) will react at 1500° to form the same pyrite structure ($IrS_{2.9}$) observed by Biltz, *et al.*[6] (a = 5.62 Å). If, however, sulfur and iridium in a 2:1 mole ratio react at 60 kbars and 1500°, then a new pyrite phase is found ($IrS_{1.9}$) with a = 5.68 Å. Powder diffraction patterns obtained from samples having an initial composition with a mole ratio between 2 and 3 which were allowed to react under the same conditions showed the presence of both pyrite phases.

Nickel diarsenide crystallizes in an "anomalous" marcasite structure[7] which differs from the Jahn-Teller marcasite structure by having minimal angular distortion about the cation octahedra. In this sense the "anomalous" marcasites are like the pyrites; however, they differ from the pyrites in that the marcasite structure is a less dense packing arrangement. These factors suggest that materials having the "anomalous" marcasite structure might be induced to form the pyrite structure when synthesized under pressure. An intimate mixture of powdered nickel and arsenic in a 1:2.2 mole ratio after reaction at 60 kbars and 1400° was cooled at pressure to room temperature over a period of 0.5 hr. After the release of the pressure a metallic gray material was obtained which gave the X-ray reflections (Table I) of the cubic pyrite structure, a = 5.77 Å. The calculated density, 7.21 g cm^{-3}, may be compared with the pycnometric density of 7.15 ± 0.10 g cm^{-3}. These results suggest that other materials possessing the "anomalous" marcasite structure may also be synthesized in the pyrite arrangement under pressure.

Table I

Spacing and Indexing of the Reflections of Cubic Nickel Diarsenide[a]

d	hkl	Intensity	d	hkl	Intensity
2.86	200	W	1.070	432	M
2.56	210	S	1.051	521	M
2.34	211	S	1.019	440	M
2.03	220	W	0.961	600	W
1.98	221	VW	0.949	610	W
1.73	311	VS	0.936	611	M
1.66	222	W	0.911	620	VW
1.59	230	M	0.880	533	M
1.54	321	S	0.870	622	VW
1.435	400	W	0.860	630	M
1.285	420	W	0.851	631	M
1.255	421	M	0.832	444	VW
1.225	332	W	0.800	640	W
1.174	422	W	0.792	641	S
1.109	511	M	0.785	552	S

[a] Copper Kα_1 nickel-filtered radiation employed with a Norelco camera of diameter 114.6 mm.

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(4) L. B. Barricelli, *Acta Cryst.*, **11**, 75 (1958).

(5) F. Hulliger, *Nature*, **204**, 644 (1964).

(6) W. Biltz, J. Laar, P. Ehrlich, and K. Meisel, *Z. Anorg. Allgem. Chem.*, **233**, 263 (1937).

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Contribution from the General Electric Research and Development Center, Schenectady, New York

The Formation of the Skutterudite Phase in the Cobalt-Phosphorus System

By Ronald A. Munson[1] and John S. Kasper

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Relatively few compounds occur in the skutterudite structure (space group $T_h^5(Im3)$), but the existence of IrP_3 and RhP_3 as well as $CoSb_3$ and $CoAs_3$ in this structure strongly suggests that CoP_3 ought to have this arrangement also. Biltz and Heimbrecht,[2] however, were unsuccessful in preparing cobalt triphosphide with the skutterudite structure at low pressures.

We have been able to prepare the skutterudite phase of cobalt phosphide by allowing powdered cobalt to react with phosphorus in a 3:1 mole ratio at a pressure of 60 kbars and 1400°. However, this product also contained another unidentified compound of cobalt and phosphorus. The pure skutterudite phase could be obtained only when the ratio of phosphorus to cobalt was in the vicinity of 4. Chemical analysis of the pure skutterudite phase established the empirical formula $CoP_{3.90}$ (32.8% cobalt). X-Ray reflections using cobalt Kα iron-filtered radiation indicated the body-centered-cubic structure, a = 7.711 Å. The calculated density based on CoP_4 is 3.97 g cm^{-3} which may be compared with the pycnometric density of 4.04 ± 0.10 g cm^{-3}. Initial structure factor calculations indicate agreement between the intensities listed in Table I and the assumption of random distribution of six cobalt atoms among the eight 8e skutterudite positions.

Table I

Spacing and Indexing of the Reflections of Cubic Cobalt Phosphide

d	hkl	Intensity	d	hkl	Intensity
5.4	101	MW	1.190	541	VW
3.83	200	M	1.162	622	MW
3.12	211	W	1.136	631	MW
2.71	220	M	1.113	444	MW
2.43	310	S	1.090	710	W
2.23	222	MW	1.069	640	M
2.06	321	M	1.049	721	W
1.92	400	W	1.030	642	W
1.81	330	W	1.013	730	M
1.72	420	S	0.980	732	M
1.64	332	W	0.964	800	M
1.57	422	MS	0.950	741	W
1.51	510	M	0.935	820	S
1.32	530	W	0.921	653	W
1.285	600	VW	0.909	822	S
1.219	620	MW	0.896	831	S

These preparations were carried out in the "belt"

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(1) Bureau of Mines, Metallurgy Research Center, College Park, Md. 20740.

(2) W. Biltz and M. Heimbrecht, *Z. Anorg. Allgem. Chem.*, **241**, 349 (1939).

superpressure apparatus[3] using a cell constructed of sodium chloride with a graphite heater. The cell was calibrated at room temperature with the bismuth 25.5- and 27-kbar and the barium 58-kbar transformations. Temperatures, uncorrected for pressure, were determined from a calibration of the high-pressure cell with a Pt—Pt-10% Rh thermocouple.[4]

Acknowledgment.—The authors wish to acknowledge the able assistance of R. D. Kieft and M. J. Moore in making the X-ray diffraction patterns and analyses. W. T. Doyle made the cobalt analysis.

(3) H. T. Hall, *Rev. Sci. Instr.*, **31**, 125 (1960).

(4) NOTE ADDED IN PROOF.—S. Rundqvist and E. Larsson, *Acta Chem. Scand.*, **13**, 551 (1959), report that CoP_3 (a = 7.706 Å) is isostructural with $CoAs_3$.

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Trifluoromethylsulfinyl Fluoride[1]

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Trifluoromethylsulfinyl fluoride and other alkyl- or arylsulfinyl fluorides were reported[2] as minor by-products in the synthesis of the corresponding RSF_3 compounds, as a result of reaction with the glass apparatus or traces of moisture. Supporting data were given for benzenesulfinyl fluoride which was obtained[2] in good yield by the reaction of phenylsulfur trifluoride and benzaldehyde. The CF_3SF_3 was synthesized[2] by the reaction of gaseous CS_2 or $(CF_3S)_2CS$ with AgF_2. Both reactions were exothermic and gave a mixture of products: SF_4, CF_3SF_3, CF_3SF_5, and SF_6 from CS_2; and CF_3SF_3, $(CF_3)_2S_2$, CF_3SFO, and CF_3SF_5 from $(CF_3S)_2CS$. We wish to report improved syntheses of CF_3SF_3[2–4] and CF_3SFO and some properties of the latter.

In the present investigation, we have found that liquid bis(trifluoromethyl) disulfide will, in fact, readily react further with AgF_2. The products are CF_3SF_3, CF_3SF_5, and CF_3SFO. The formation of CF_3SF_5 can be minimized by allowing the reactants to warm from −10 to 25° over several hours and by avoiding a large excess of AgF_2.[5] The formation of CF_3SFO can be minimized by using rigorously anhydrous conditions and passivated, glass-free apparatus.

Trifluoromethylsulfinyl fluoride was obtained in good yield by simply storing small quantities of the product mixture in a glass bulb until all of the reactive CF_3SF_3 was eliminated by conversion to CF_3SFO and SiF_4. The CF_3SFO was purified by vacuum-line fractionation and identified by its gaseous molecular weight, ^{19}F nmr spectrum, mass spectrum, and an infrared spectrum, Figure 1, which is consistent with the proposed structure. The CF_3SFO is a white solid and colorless liquid or gas having a boiling point of approximately −9°. It appeared to be thermally stable in stainless steel at 135° and was unreactive with mercury at 25°. Gaseous CF_3SFO was stored in dry glass for 2 weeks without noticeable decomposition, but after 3 months in normal laboratory light all of the CF_3SFO was destroyed. Instability of sulfinyl fluorides in glass was previously noted.[2] The CF_3SFO is slowly hydrolyzed by water vapor at 25° with destruction of the CF_3 group. No reaction was observed between CsF and CF_3SFO at 120 or 135° and no complex which was stable at room temperature was formed when CF_3SFO and AsF_5 were held at −78°. The addition of F_2 to CF_3SFO at 25° produced a number of degradation products, but CF_3SO_2F and CF_4 were the major products observed from the reaction at −78°.

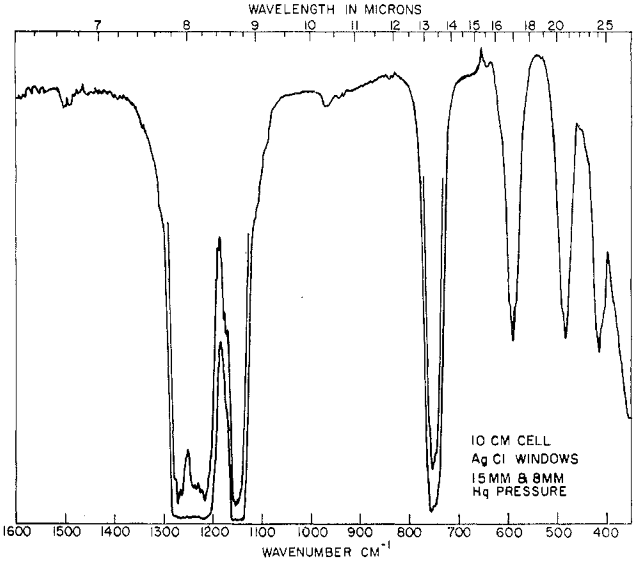

Figure 1.—Infrared spectrum of trifluoromethylsulfinyl fluoride.

Experimental Section

Preparation.—Silver difluoride (Alfa Inorganics, Inc.) and $(CF_3)_2S_2$ (Peninsular ChemResearch, Inc.) were allowed to react in a series of 11 runs utilizing 1–2 g of $(CF_3)_2S_2$ per run. The mole ratio of AgF_2 to $(CF_3)_2S_2$ was varied from 12:1 to 2:1. A valved 75-ml stainless steel cylinder was charged with AgF_2 in a drybox and the $(CF_3)_2S_2$ was condensed in at −196° in a vacuum line. Each reactant mixture was then held at a selected temperature in the range −78–50° for a time in the range 116–0.5 hr. Products were fractionated or transferred in either a glass or an all-metal and Kel-F vacuum line operating at <0.01 mm. In a typical run, the reactor was charged with an 8:1 mole ratio of AgF_2 to $(CF_3)_2S_2$, placed in a dewar containing ice, and allowed to warm to room temperature overnight. Infrared analysis of a small sample of the volatile products showed that the major product (~70%) was CF_3SF_3 with smaller amounts of CF_3SFO and CF_3SF_5 present. Quantitative ^{19}F nmr analysis (based on integration of the three CF_3 peaks) at −40° on all of the remaining volatile products gave the composition: 60% CF_3SF_3, 28% CF_3SFO, 10% CF_3SF_4, and *ca.* 2% SiF_4. No residual $(CF_3)_2S_2$ was detected by either method. However, reaction

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(1) This work was supported by the United States Air Force under Contract AF 33(615)-3954.

(2) W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3058 (1962).

(3) E. A. Tyczkowski and L. A. Bigelow, *ibid.*, **75**, 3523 (1953).

(4) R. Dresdner, *ibid.*, **79**, 69 (1957).

(5) Once formed CF_3SF_5 is resistant to further fluorination by AgF_2 at 35°.