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THE SYNTHESIS OF COPPER DISULFIDE

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The Synthesis of Copper Disulfide

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Over the years there have been a number of reported syntheses of copper polysulfides.¹ Gattow and Rosenberg,² who investigated these claims roentgenographically, conclude that all hitherto reported compounds of composition $\text{CuS}_{>1}$ were mixtures of CuS and sulfur and not distinct compounds of copper. In no case was synthesis attempted at both elevated temperature and pressure. This synthesis was carried out in the "belt" superpressure apparatus³ 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 were determined from the readings of a Pt—Pt-10% Rh thermocouple present during some of the runs. When a sample consisting of

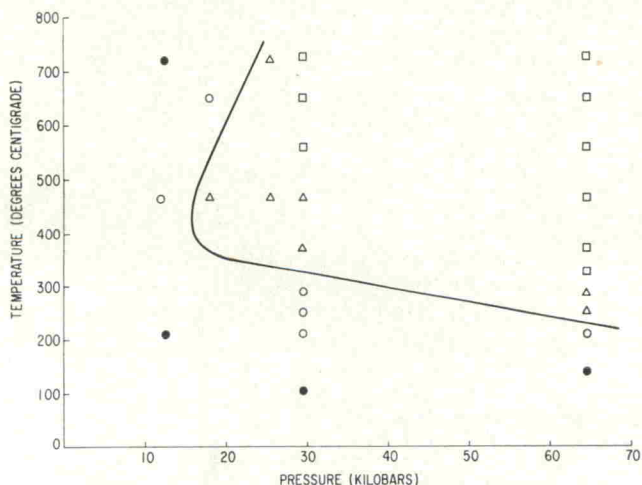


Figure 1.—Pressure-temperature diagram for the reaction of sulfur with covellite to form cubic copper disulfide. Two-minute runs produce the pyrite structure only, $\square$; mostly pyrite structure, Δ ; mostly covellite, $\circ$; and no reaction, $\bullet$.

(1) "Gmelins Handbuch der Anorganischen Chemie," Verlag Chemie, Weinheim/Bergstrasse, 1958, pp 483, 484.

(2) G. Gattow and O. Rosenberg, *Naturwissenschaften*, **51**, 213 (1964).

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

TABLE I
SPACING AND INDEXING OF THE REFLECTIONS OF
CUBIC COPPER DISULFIDE^a

<i>d</i> , Å	<i>hkl</i>	Intens	<i>d</i> , Å	<i>hkl</i>	Intens
3.32	111	m	1.054	521	m
2.89	200	vs	1.022	440	m
2.57	210	ms	1.005	522	w
2.35	211	ms	0.990	530	vw
2.04	220	s	0.978	531	m
1.92	300	w	0.963	600	m
~~1.86~~	~~310~~	~~vw~~	0.950	610	vw
1.73	311	s	0.939	611	m
1.66	222	m	0.913	620	m
1.59	320	m	0.903	621	m
1.54	321	m	0.895	541	w
1.40	410	mw	0.883	533	m
1.36	411	w	0.873	622	m
1.325	331	m	0.864	630	vw
1.291	420	m	0.854	631	m
1.260	421	m	0.828	700	m
1.231	332	w	0.819	710	m
1.180	422	mw	0.811	711	mw
1.158	500	w	0.804	640	ms
1.132	510	w	0.796	720	mw
1.112	511	ms	0.788	721	mw
1.073	520	m			

^a Copper $K\alpha_1$ nickel-filtered radiation employed with a Norelco camera of diameter 114.59 mm.

a mixture of CuS (covellite) and sulfur in a 1:1.2 mole ratio was subjected to the appropriate temperature and pressure conditions (Figure 1) and then washed with boiling CS_2 to extract the excess sulfur, a dark purplish red material was obtained. Chemical analysis indicated the formula $\text{CuS}_{1.9}$ and the X-ray reflections (Table I) showed that it had the cubic (NiS_2) pyrite structure, $a = 5.796$ Å. The calculated density is 4.44 g cm^{-3} . The low pycnometric density, $4.24 \pm 0.10 \text{ g cm}^{-3}$, may be ascribed to sulfur vacancies in the lattice. Between 200 and 300° in an inert atmosphere, CuS_2 decomposes to yield covellite, some digenite, and somewhat more than 1 mole of sulfur per mole of CuS_2 . Further decomposition, which occurs between 400 and 475°, produces Cu_2S (chalcocite) and nearly 0.5 mole of sulfur.

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