

MAGNETIC AND ELECTRICAL PROPERTIES OF TERNARY PYRITE-TYPE  
 $\text{Cr}_x\text{Co}_{1-x}\text{S}_2$  PHASES PREPARED AT HIGH PRESSURE

P. C. Donohue, T. A. Bither, W. H. Cloud\*, and  
C. G. Frederick  
Central Research Department\*\*  
E. I. du Pont de Nemours and Company  
Experimental Station  
Wilmington, Delaware 19898

(Received February 11, 1971; Communicated by J. B. Goodenough)

ABSTRACT

New pyrite-type phases  $\text{Cr}_x\text{Co}_{1-x}\text{S}_2$  ( $0 < x < 0.4$ ) have been prepared at 65 kbars pressure in a tetrahedral anvil apparatus. Magnetic measurements indicate that the saturation magnetization decreases, while the Curie temperature increases, with increasing  $x$ .  $T_c$  reaches a maximum above room temperature at  $x \approx 0.3$ . The magnetic data favor an arrangement in which low-spin  $\text{Cr}^{+2}$  is aligned antiferromagnetically to  $\text{Co}^{+2}$ . Electrical measurements show essentially temperature-independent resistivity with  $\rho \approx 10^{-4}$  ohm-cm.

Introduction

The pyrite-type compound  $\text{CoS}_2$  is ferromagnetic (1,2) with a Curie temperature,  $T_c$ , of 118°K and a saturation magnetization,  $\sigma_s$ , of 40.8 emu/g. Solid solutions of  $\text{CoS}_2$  with  $\text{FeS}_2$  and with  $\text{NiS}_2$  have been prepared at ambient pressure (3) and their magnetic properties studied (4,5). Both  $T_c$  and  $\sigma_s$  decrease to zero with increasing Ni content. With increasing Fe content,  $T_c$  and  $\sigma_s$  initially increase slightly, and then decrease to zero. Maxima for these two parameters occur at  $T_c \approx 146^\circ\text{K}$  for  $\text{Co}_{0.75}\text{Fe}_{0.25}\text{S}_2$  and  $\sigma_s \approx 43$  emu/g for  $\text{Co}_{0.95}\text{Fe}_{0.05}\text{S}_2$ .

\*Deceased.

\*\*Contribution No. 1775.

Chromium forms a series of sulfides from CrS to  $\text{CrS}_{1.6}$ , which have crystal structures related to the NiAs type (6,7), but the disulfide is unknown. By the use of high reaction pressures, Cr was found to replace some of the Co in  $\text{CoS}_2$  so as to give pyrite-type solid solutions  $\text{Cr}_x\text{Co}_{1-x}\text{S}_2$ . The purpose of this work was to determine the range over which formation of this solid solution occurred and to investigate the magnetic properties of these Cr-substituted compositions.

#### Experimental

Reactions were carried out at 60-65 kb pressure in a tetrahedral anvil press of National Bureau of Standards design (8). Samples were contained in a cylindrical boron nitride crucible surrounded by a graphite-sleeve resistance heater inserted in a pyrophyllite tetrahedron. The calibration points used to establish the pressure developed were the transitions  $\text{Bi(I)} \rightarrow \text{Bi(II)}$  ( $25.37 \pm 0.02$  kbars),  $\text{Bi(II)} \rightarrow \text{Bi(III)}$  ( $26.96 \pm 0.18$  kbars),  $\text{Tl(II)} \rightarrow \text{Tl(III)}$  ( $36.69 \pm 0.11$  kbars), and  $\text{Ba(II)} \rightarrow \text{Ba(III)}$  ( $59.0 \pm 1.0$  kbars). All compressions were made on the assembly at room temperature. The charge was then heated to the desired temperature which was measured with a Pt-Rh thermocouple, uncorrected for pressure effects. The thermocouple was placed at the center of the surface of the boron nitride crucible. The temperature at the ends of the crucible is about 30% lower.

High purity CrS,  $\text{Cr}_2\text{S}_3$ , Co, and S were used as reactants. These were ground together in the desired ratios and were pressed into pellets. In general, a small excess of S was used to enhance crystal growth, which occurred at the ends of the pellet because of the temperature gradient.

Reactions were carried out at various conditions. Usually the pellets were pressured to 65 kbars and the temperature was then raised to  $1100^\circ$ - $1200^\circ$  and held for about 2 hours. Subsequently, the samples were either quenched or cooled about