

TABLE 2

Magnetic Properties of  $\text{Cr}_x\text{Co}_{1-x}\text{S}_2$  Compositions

Cell Constant (Å)	Formula	$T_c$ , °K	$\sigma_s$ , emu/g	$\mu_B$ (BM)	$x(5)$	$x(3)$
5.5345	$\text{CoS}_2$	118- 124	40.86	0.90		
5.5376	$\text{Cr}_{0.05}\text{Co}_{0.95}\text{S}_2$	170	36.53	0.77	0.05	0.08
5.538	$\text{Cr}_{0.06}\text{Co}_{0.94}\text{S}_2$	170	30.58	0.67	0.07	0.11
5.540	$\text{Cr}_{0.09}\text{Co}_{0.91}\text{S}_2$	210	30.1	0.66	0.07	0.11
5.540	$\text{Cr}_{0.09}\text{Co}_{0.91}\text{S}_2$	160	27.8	0.61	0.08	0.13
5.5422	$\text{Cr}_{0.13}\text{Co}_{0.87}\text{S}_2$	255	24.70	0.54	0.09	0.15
5.5439	$\text{Cr}_{0.16}\text{Co}_{0.84}\text{S}_2$	260	17.63	0.38	0.12	0.21
5.5452	$\text{Cr}_{0.18}\text{Co}_{0.82}\text{S}_2$	300	20.40	0.43	0.11	0.19
5.5456	$\text{Cr}_{0.19}\text{Co}_{0.81}\text{S}_2$	290	20.75	0.45	0.11	0.18
5.5477	$\text{Cr}_{0.22}\text{Co}_{0.78}\text{S}_2$	325	16.70	0.36	0.13	0.21
5.5494	$\text{Cr}_{0.25}\text{Co}_{0.75}\text{S}_2$	335	16.32	0.35	0.13	0.22
5.5508	$\text{Cr}_{0.27}\text{Co}_{0.73}\text{S}_2$	330	16.20	0.35	0.13	0.22
5.5532	$\text{Cr}_{0.31}\text{Co}_{0.69}\text{S}_2$	350	9.69	0.21		
5.558	$\text{Cr}_{0.39}\text{Co}_{0.61}\text{S}_2$	275	18.2	0.39		

such as (1) deviation of the dependence of cell dimensions on composition from the linearity assumed, (2) nonstoichiometry from the ideal  $\text{Cr}_x\text{Co}_{1-x}\text{S}_2$  formulation due to the presence of  $\text{Cr}^{+3}$ , (3) small variations in the Cr:Co ratio within a sample, and (4) dilution caused by undetected  $\text{Cr}_2\text{S}_3$ . Despite these uncertainties, the data do indicate significant features of the substitution.

The scatter of magnetic data (Table 2) from a reasonable compositional dependence is apparent. Nevertheless, two general trends in the data are evident: (1) Curie temperatures within the system increase rapidly with increasing  $x$  from 118°K (for  $x = 0$ ) to a maximum that is above room temperature for  $x \approx 0.25$ -0.30, and (2) saturation magnetizations decrease over a

comparable compositional interval. The decrease in  $\sigma_s$  suggests that the electron spins on Cr are antiparallel to those of the host; the rate of that decrease should be indicative of the number of electron spins associated with each chromium. For  $\text{CoS}_2$ , the saturated value of magnetization corresponds to  $0.9 \mu_B$  (4,5). In the system  $\text{Cr}_x\text{Co}_{1-x}\text{S}_2$  that value should decrease at the rate of approximately  $5x$  if high-spin  $\text{Cr}^{++}$  is antiparallel to the  $\text{Co}^{++}$  moment, at  $3x$  if antiparallel  $\text{Cr}^{++}$  is low-spin. If part of the Cr is present as  $\text{Cr}^{+3}$ , it should also decrease by  $3x$  since one cation vacancy would be present for every two  $\text{Cr}^{+3}$  ions. In Table 2, columns  $x(5)$  and  $x(3)$  are calculated values of  $x$  assuming that  $\mu_B$  ( $\text{CoS}_2$ ) is decreased by  $5x$  and  $3x$ , respectively. It would appear that the assumption of low-spin  $\text{Cr}^{++}$  gives generally better agreement with values of  $x$  determined from the x-ray data, but no clear-cut conclusion can be drawn.

The problems associated with compositional definition in the present study reflect difficulties that are encountered at times in syntheses at high pressures where sample volume is necessarily small and where severe gradients in both temperature and pressure may occur. In the present case, these gradients resulted in multiphase formation. Although this further reduced the effective sample size of the resultant pyrite products, significant information has been derived from the magnetic measurements made thereon. It is of interest that the divalent state of chromium can be stabilized in a pyrite structure by application of external pressure and that substitution of this ion dramatically increases the Curie temperature of  $\text{CoS}_2$ . Compositions in the solid solution system  $\text{Cr}_x\text{Co}_{1-x}\text{S}_2$  as reported in this paper are the only known examples of pyrites that are magnetic at room temperature.