

Preparation and Properties of the Systems $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$, $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$, and $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$

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Members of the systems $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$ ($0 \leq x \leq 0.6$) were prepared, and their crystallographic and magnetic properties studied. The observed ferromagnetic moments for compositions where $x \leq 0.2$ indicate a ferromagnetic alignment between $\text{Co}(3d^7)$ and $\text{Rh}(4d^7)$ electrons. This is the first observation of localized behavior of $4d$ electrons in the pyrite structure. Members of the systems $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$ ($0 \leq x \leq 1$) and $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$ ($0.5 \leq x \leq 1$) were also prepared and their crystallographic and magnetic properties studied. From comparison with the $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$ system, it appears that the $4d$ electrons of $\text{Rh}(4d^7)$ are localized in the presence of $\text{Co}(3d^7)$ but are delocalized in the presence of $\text{Ru}(4d^6)$. The magnetic susceptibility of the $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$ system is sensitive to the homogeneity of the products and indicates that $\text{Ru}(4d^6)$ behaves as a diamagnetic ion. © 1986 Academic Press, Inc.

Introduction

Numerous studies have reported the effects of cation and anion substitution on the electrical and magnetic properties of CoS_2 (1-9). This compound crystallizes in the cubic pyrite structure (space group $Pa\bar{3}$) and exhibits metallic ferromagnetism, which has been attributed to a partially filled σ^* band (10-13). The observed ferromagnetic moment has been reported to be 10% lower than the theoretical value. The reduced moment has been attributed (5) to an overlap of the spin-up and spin-down bands below the Fermi level.

Recently, solid solutions of FeS_2 and NiS_2 with CoS_2 have been made (5, 6). Members of the system $\text{Co}_x\text{Fe}_{1-x}\text{S}_2$ exhibit ferromagnetic behavior for $x > 0.05$ with the ferromagnetic moment proportional to

the cobalt concentration over the range $0.05 \leq x \leq 1.0$. In the $\text{Co}_{1-x}\text{Ni}_x\text{S}_2$ system, antiferromagnetic behavior was observed for $x > 0.1$ although with no well defined Néel temperature.

No magnetic studies have been made on compounds where platinum metals have been substituted for cobalt in CoS_2 . The possibility of $\text{Co}(3d^7)$ and $\text{Rh}(4d^7)$ orbital interaction and the effect of this interaction on the magnetic properties of CoS_2 have motivated this study. In addition, it is known that RhS_2 does not exist (14), and therefore the extent to which rhodium ($4d^7$) can be stabilized in the pyrite structure is of interest. Also, to further understand the magnetic interactions between cobalt's $3d^7$ and $4d$ systems, an investigation of synthesis and magnetic properties of the system $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$ was undertaken. Finally, to as-

certain the interaction of two $4d$ electron systems, measurements of the magnetic properties of $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$ were made.

Experimental

Preparation of Materials

Polycrystalline samples of the system $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$ ($0 \leq x \leq 1$) were synthesized either by direct combination of the elements in sealed evacuated silica tubes, or by heating stoichiometric quantities of pentaminechlorocobalt(III) chloride and ammonium hexachlororhodate(III) with hydrogen sulfide. Polycrystalline samples of the systems $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$ ($0 \leq x \leq 1$) and $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$ ($0.5 \leq x \leq 1$) were also prepared. However, attempts to prepare samples by direct combination of the elements were largely unsuccessful, but samples were obtained by heating in hydrogen sulfide stoichiometric quantities of pentaminecobalt(III) chloride and ammonium hexachlororuthenate(IV) for the preparation of members of the system $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$, and ammonium hexachlororhodate(III) and ammonium hexachlororuthenate(IV) for the compositions $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$.

Direct Combination of the Elements

Starting materials were pretreated as follows: the high-purity metals (Co 99.999% Leico, Inc., Ru 99.999% and Rh 99.999% Engelhard, Inc.) were reduced in a 15% H_2 /85% Ar atmosphere (Co at 650°C for 4 hr, ground, further reduced at 850°C for 8 hr; Ru and Rh were reduced for 8 hr at 800°C). Freshly sublimed sulfur was used.

Stoichiometric quantities of the elements (with a 10% by weight excess of sulfur) were ground thoroughly and transferred to a silica tube; the tube was evacuated and sealed. Each sample was heated slowly to 400°C , maintained at this temperature for 12 hr, and then raised gradually to 800°C .

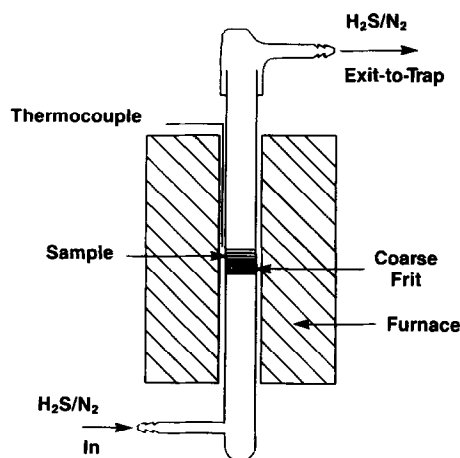


FIG. 1. Vertical sulfiding unit.

Once each week the sample was extracted with CS_2 to remove the excess sulfur. After approximately 5 weeks of heating at 800°C , single-phase products of $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$ were obtained. For the system $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$, only Ru-rich samples ($x \leq 0.7$) could be prepared as single-phase materials using this technique. No member of the system $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$ could be prepared as a pure homogeneous material by this method.

Synthesis by the Precursor Method

Stoichiometric quantities of $(\text{NH}_4)_2\text{RuCl}_6$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2^{15}$ or $(\text{NH}_4)_2\text{RuCl}_6$ and $(\text{NH}_4)_3\text{RhCl}_6$ (Engelhard, Inc. 99.999%), or $(\text{NH}_4)_3\text{RhCl}_6$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ were dissolved in 12 ml of 0.15 M NH_4OH by warming, with stirring, to 80°C . When a solution was achieved, the solvent was evaporated using an infrared lamp. The product was ground thoroughly and transferred into a flow reactor (Fig. 1) in which sulfurization took place. The system was purged at a flow rate of 55 cc/min with nitrogen for at least an hour. The mixture was treated with hydrogen sulfide at a rate of 80 cc/min for 10 min at room temperature. The system was then heated to 250°C , maintained at this temperature for 1 h, raised to 500°C , and maintained at this temperature for 2 hr.

The temperature was lowered to 250°C over an hour and then cooled to room temperature under flowing H₂S. After sulfurization, the product was extracted with methanol to remove the NH₄Cl which was formed. The product was then dried under vacuum. The products obtained after extraction and drying were annealed with 10% by weight excess sulfur and approximately 0.01 g of iodine in evacuated sealed silica tubes at 800°C. The temperature was raised from room temperature to 800°C over a period of 2 days. Samples were held at 800°C for 7 days and then cooled overnight to room temperature. The samples were then extracted with acetone to remove the iodine. Single-phase products were obtained.

Sample Characterization

X-ray diffraction. Powder diffraction patterns were obtained with a Norelco diffractometer using monochromatic high-intensity CuK α_1 radiation ($\lambda = 1.5405 \text{ \AA}$). Fast scans at $1^\circ [2\theta]/\text{min}$ were examined for the possible presence of extraneous phases. Slow scans of $0.25^\circ [2\theta]/\text{min}$ were obtained for all single-phase samples in the range of $12^\circ \leq [2\theta] \leq 120^\circ$. Lattice parameters for the well-crystallized materials were determined by least-squares analysis using $[2\theta]$ values from 26 to 105° . For members of the systems Co_{1-x}Rh_xS₂ ($0 \leq x \leq 0.6$), Co_{1-x}Ru_xS₂ ($0 \leq x \leq 1$) and Rh_{1-x}Ru_xS₂ ($0.5 \leq x \leq 1$) the patterns could be indexed on the basis of a cubic pyrite structure (space group *P3a*). Powder patterns of Co_{1-x}Rh_xS₂ composition, where $x \leq 0.6$, indicate the presence of the sulfur deficient Rh₂S₃ (16).

Magnetic measurements. Magnetic measurements were made with a PAR FM-1 vibrating-sample magnetometer (Princeton Applied Research Co.) in conjunction with a variable temperature control dewar which is described elsewhere (3). Field-dependent measurements were made with fields up to 8 kOe using a 9-inch Varian magnet (V3400, Varian Associates). The magnetometer was

calibrated relative to a cylinder of high-purity nickel single crystal obtained from Material Research Corp. Nickel has temperature-dependent values of magnetic moment of 58.57 emu/g at absolute zero, 58.2 emu/g at 77.3 K, and 55.8 emu/g at 293 K (17), which were the values used for the calibration. Temperature-dependent magnetization plots were taken with the use of a solid-state temperature controller (type MPXY Thermac Controller, R.I. Controls) to program the temperature at a desired rate from 4.2 to 300 K. The temperature was measured with a 0.005-in. Teflon-coated Au + 0.07% Fe versus Chromel-P thermocouple (Sigmund Cohn). The thermocouple was located on the outside of the sample chamber and within 6.5 mm of the sample.

In addition, magnetic susceptibility measurements were made from 77 to 540 K with a Faraday balance described elsewhere (18). Measurements were performed at field strengths between 6.22 and 10.40 kOe. The balance was calibrated using platinum wire ($x_g = 0.991 \times 10^{-6} \text{ emu/g}$ at 275 K). To ensure no loss of sulfur upon heating, each sample was encapsulated in a silica bubble under vacuum. To supplement these measurements, susceptibilities were also calculated from magnetometer measurements made in the range of 4.2 to 77 K.

Results and Discussions

Results on preparation. Two methods have been used for the preparation of members of the system Co_{1-x}Rh_xS₂. Direct reaction of stoichiometric mixtures of cobalt, rhodium, and sulfur in sealed evacuated tubes gave products similar in properties to those obtained by the sulfurization of a mixture of (NH₄)₃RhCl₆ and [Co(NH₃)₅Cl]Cl₂.

CoS₂ crystallizes in the cubic pyrite structure (space group *P3a*). A value of 5.538(2) Å was obtained for the cell parameter which compares well with the literature values of 5.534 Å (19) and 5.536 Å

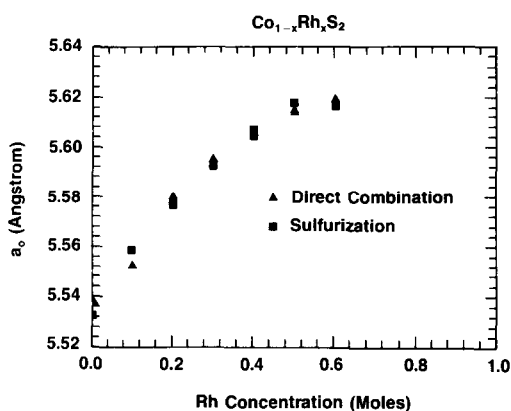


FIG. 2. Variation in A_0 for $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$.

(20). The system $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$ was reported by Hulliger (14) to have a pyrite structure for $0 \leq x \leq 0.7$. In this study, both direct combination of the elements and sulfurization of stoichiometric mixtures of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $(\text{NH}_4)_3\text{RhCl}_6$ yielded single-phase materials for $x \leq 0.6$. X-ray diffraction patterns of all products were therefore interpreted on the basis of a cubic unit cell. Figure 2 shows the variation of the cell constant as a function of composition. For values greater than $x = 0.6$, the orthorhombic phase Rh_2S_3 (space group *Pbcn*) (16) can be detected as an impurity. This is consistent with the findings of Hulliger (14), whose attempts to synthesize RhS_2 gave Rh_2S_3 as well as other sulfur-deficient phases.

For $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$, only Ru-rich samples could be prepared using direct combination of cobalt, ruthenium, and sulfur. Even these samples are probably not homogeneous. Although only single phases were found for $x \leq 0.7$, cell parameters for these samples showed a positive deviation from ideal behavior (see Fig. 3). The magnetic properties, however, did indicate that a partial solid solution of CoS_2 and RuS_2 was obtained.

The samples of both systems prepared from precursors, on the other hand, ap-

peared to be homogeneous based on X-ray diffraction patterns. Patterns for all of these samples could be interpreted on the basis of a cubic pyrite structure. Lattice parameters of members of the system $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$ were found to obey Vegard's law, and change linearly with composition (see Fig. 3). Values of 5.537(1) Å for CoS_2 and 5.610(1) Å for RuS_2 agree well with values in the literature (5.534 and 5.6095 Å, respectively). RhS_2 cannot be prepared, but all members of the system $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$ ($0.5 \leq x \leq 1$) gave the same cell constant, namely, 5.607(4) Å.

Ferromagnetic region. CoS_2 is a well-known ferromagnetic material with a well-defined Curie point (T_C). A value of 123 K was measured for T_C which compares well with values in the literature of 124 K (23), 130 K (24), and 122 K (25). The observed Curie point for CoS_2 is depressed from 123 K for CoS_2 to 25 K for $\text{Co}_{0.4}\text{Rh}_{0.6}\text{S}_2$; the monotonic decrease for the system $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$ is shown in Fig. 4. This decrease in T_C is what is anticipated for a gradual decrease in the strength of the ferromagnetic interactions.

A ferromagnetic moment of 0.83 Bohr magnetons was obtained for CoS_2 which is in good agreement with the value in the literature (23, 24). The reduced moment observed for CoS_2 has been discussed in terms

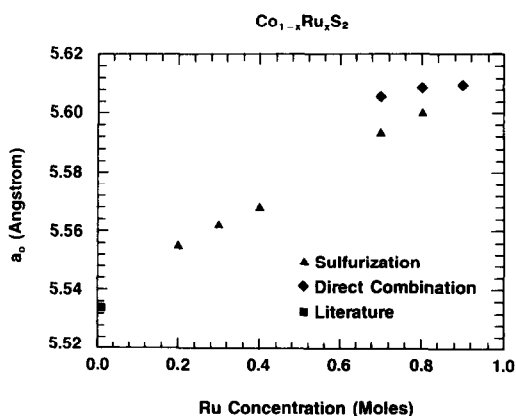
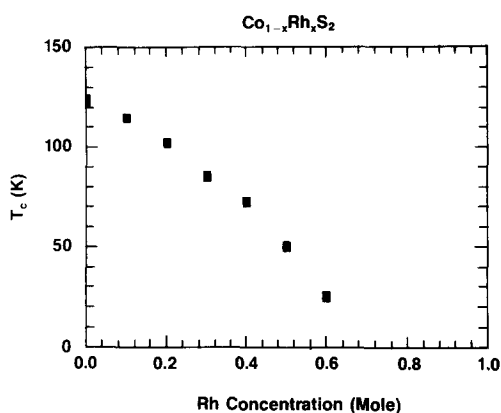
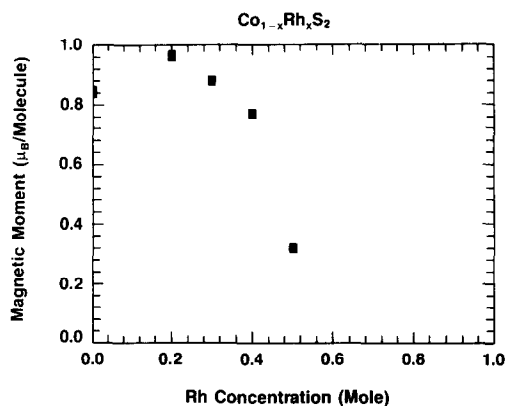


FIG. 3. Variation in A_0 for $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$.

FIG. 4. Variation in T_C (K) for $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$.

of a partial overlap in the spin-up and spin-down bands (8–10). The ferromagnetic moment versus rhodium concentration is plotted in Fig. 5. It was observed for the $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$ system that the ferromagnetic moment reaches a maximum of 0.96 Bohr magnetons per molecule at $x = 0.2$ and then decreases with increasing rhodium content. This maximum moment is larger than the value of 0.8 Bohr magnetons obtained for the end member CoS_2 , suggesting that there is a ferromagnetic interaction between the $\text{Co}(3d^7)$ and $\text{Rh}(4d^7)$ electrons, and a smaller degree of occupancy of the σ^* band.

FIG. 5. Variation in magnetic moment for $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$.

For $x = 0.5$, a moment of 0.32 Bohr magnetons per molecule was measured. This moment is smaller than the expected 0.5 Bohr magnetons if only cobalt atoms contribute to the moment at the equivalent of one unpaired electron per atom. This large reduction in moment, for high rhodium concentration, can be attributed to a lack of magnetic homogeneity in these samples, with the possible formation of rhodium clusters.

Magnetic properties. The measured effective moments for members of the system $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$ (in terms of CoS_2 equivalents) are given in Table I. It can be seen that after heating the samples for 8 days at 800°C, the effective moments are much higher than the calculated value of $\mu_{\text{eff}} = 1.73\mu_B$. A second sample of $\text{Co}_{0.2}\text{Ru}_{0.8}\text{S}_2$ was annealed at 800°C for varying periods of time, and the effective moments are given in Table II. As prepared, the two samples of composition $\text{Co}_{0.2}\text{Ru}_{0.8}\text{S}_2$ initially gave effective moments of 1.99 and 2.10 μ_B . It can be seen that at the end of 8 days the measured effective moment of $\mu_{\text{eff}} = 170\mu_B$ was close to the spin-only value of 1.73 μ_B . Further annealing up to 17 days did not change the observed effective moment appreciably. The other members of the system after long annealing also gave the effective moment expected for the amount of CoS_2 present in the composition. It is evident that the observed effective moments are useful in determining the homogeneity of the samples since the X-ray diffraction patterns indi-

TABLE I
PARAMAGNETIC MOMENT OF $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$

Composition	μ_{eff} (μ_B /mole of CoS_2)	Composition	μ_{eff} (μ_B /mole of CoS_2)
$\text{Co}_{0.06}\text{Ru}_{0.2}\text{S}_2$	2.21	$\text{Co}_{0.3}\text{Ru}_{0.7}\text{S}_2$	2.06
$\text{Co}_{0.07}\text{Ru}_{0.3}\text{S}_2$	2.19	$\text{Co}_{0.2}\text{Ru}_{0.8}\text{S}_2$	1.99
$\text{Co}_{0.06}\text{Ru}_{0.4}\text{S}_2$	2.00		

TABLE II
EFFECT OF THE ANNEALING OF $\text{Co}_{0.2}\text{Ru}_{0.8}\text{S}_2$ AT 800°C

Time of anneal (days)	μ_{eff} (μ_{B} /mole of CoS_2)	Θ (K)	Time of anneal (days)	μ_{eff} (μ_{B} /mole of CoS_2)	Θ (K)
0	2.10 (2)	94 (2)	8	1.70 (2)	109 (2)
4	1.94 (2)	102 (2)	17	1.73 (2)	112 (2)

cated single phase formation for all the products reported.

Susceptibility measurement of members of the system $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$ ($0.5 \leq x \leq 1$), as a function of temperature from 80–300 K, gave values which were temperature independent and varied from 0.8 to 1.1×10^{-4} emu/mole.

Conclusion

Synthesis of members of the $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$ and $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$ systems has been accomplished by the sulfurization of mixtures of $(\text{NH}_4)_2\text{RuCl}_6$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ or $(\text{NH}_4)_3\text{RhCl}_6$. Synthesis of members of the system $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$ by direct combination of the elements gave materials whose properties were similar to those obtained by the sulfurization of stoichiometric quantities of $(\text{NH}_4)_2\text{RhCl}_6$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

For the system $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$, it was shown that for $x \leq 0.2$, the $4d$ electrons associated with $\text{Rh}(4d^7)$ are localized, and there is a ferromagnetic alignment between the $\text{Co}(3d^7)$ and $\text{Rh}(4d^7)$ electrons. For such an interaction to occur, the relative energy of the cobalt $3d$ and rhodium $4d$ manifolds must be similar. Magnetic susceptibility measurements for members of the system $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$ indicate that the ruthenium ($4d^6$) is in the low-spin state and hence diamagnetic. The observed moments of the products are due to the amount of Co (low-spin $3d^7$) present. Whereas the $4d$ electrons of $\text{Rh}(4d^7)$ appear to be localized in the system $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$, the observed Pauli para-

magnetic behavior for the system $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$ indicates that in the absence of localized cobalt electrons, rhodium $4d$ electrons are probably delocalized.

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