This Freon mixture solution was exposed to ^{60}Co γ rays at 77 K for several minutes at a dose rate of 5.1×10^{17} eV min^{-1} g^{-1} to generate the cation radical of the solute.

Measurements of Electronic Spectra. Absorption spectra of samples in a quartz cell with a 1- or 10-mm optical path at room temperature were obtained on a Union-Giken SM-401 spectrophotometer. Those at 77 K were measured by using a Cary 17 spectrophotomer equipped with a liquid-nitrogen Dewar vessel with optical windows.

IR Spectrum of $Rh_2(O_2CCF_3)_4(CO)_2$. Axial ligand free $Rh_2(O_2CCF_3)_4$ (187 mg, 0.284 mmol) was kept under carbon monoxide gas of atmospheric pressure at room temperature for 1 h. The weight of the sample increased to 202 mg accompanied by a change in the color from light green to light brown, showing that the 1:2 adduct, $Rh_2(O_2CCF_3)_4(CO)_2$, was formed by absorption of 15 mg (0.55 mmol) of carbon monoxide. KBr pellets of this dicarbonyl adduct were prepared under carbon monoxide gas and transferred for measurements of its IR spectra to a JASCO A-302 infrared spectrophotometer. IR absorptions: 2150 (m), 1644 (s), 1463 (w), 1191 (vs), 862 (m), 784 (m), 739 (s), 544 (m), 527 (sh) cm^{-1}.

Registry No. $Rh_2(O_2CEt)_4(H_2O)_2$, 60801-05-0; $Rh_2(O_2CEt)_4[HC(CH_2CH_2)_3N]_2$, 83416-24-4; $Rh_2(O_2CEt)_4(PPh_3)_2$, 14781-76-1; $Rh_2(O_2CEt)_4[P(c\text{-}C_6H_{11})_3]_2$, 83398-59-8; $Rh_2(O_2CEt)_4[P(OPh)_3]_2$, 83398-60-1; $Rh_2(O_2CEt)_4[P(OMe)_3]_2$, 83398-61-2; $Rh_2(O_2CCF_3)_4(H_2O)_2$, 70084-34-3; $Rh_2(O_2CCF_3)_4[HC(CH_2CH_2)_3N]_2$, 83398-62-3; $Rh_2(O_2CCF_3)_4(PPh_3)_2$, 77966-16-6; $Rh_2(O_2CCF_3)_4[P(c\text{-}C_6H_{11})_3]_2$, 83398-63-4; $Rh_2(O_2CCF_3)_4[P(OPh)_3]_2$, 77966-17-7; $Rh_2(O_2CCF_3)_4[P(OMe)_3]_2$, 83398-64-5.

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Preparation and Properties of the Systems $Co_{1-x}Ru_xS_2$ and $Rh_{1-x}Ru_xS_2$

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Members of the systems $Co_{1-x}Ru_xS_2$ ($0 \le x \le 1$) and $Rh_{1-x}Ru_xS_2$ ($0.5 \le x \le 1$) were prepared, and their crystallographic and magnetic properties were studied. From comparison with the system $Co_{1-x}Rh_xS_2$, it appears that the 4d electrons of Rh(4d^7) are localized in the presence of Co(3d^7) but delocalized in the presence of Ru(4d^6). The magnetic susceptibility of the system $Co_{1-x}Ru_xS_2$ is sensitive to the homogeneity of the products and indicates that Ru(4d^6) behaves as a diamagnetic ion.

Introduction

Numerous studies have reported the effects of cation and anion substitution on the electrical and magnetic properties of CoS_2.[1-10] This compound crystallizes in the cubic pyrite structure (space group *Pa*3) and exhibits metallic ferromagnetism, which has been attributed to a partially filled σ^* band.[11-14] The observed ferromagnetic moment has been reported to be 10% lower than the theoretical value. The reduced moment has been attributed[6] 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.[6,7] Members of the system $Co_xFe_{1-x}S_2$ exhibit ferromagnetic behavior for $x > 0.05$ with the ferromagnetic moment proportional to the cobalt concentration over the range $0.05 < x < 1.0$. In the $Co_{1-x}Ni_xS_2$ system, antiferromagnetic behavior was observed for $x > 0.1$, although with no well-defined Nêel temperature.

Samples of $Cr_xCo_{1-x}S_2$ ($0 \le x < 0.4$) have also been made with use of a high-pressure synthesis.[10] Although the disulfide of chromium is unknown, single-phase pyrite structures were found in the composition range indicated. Magnetic studies of this system showed that the Curie temperature increased rapidly with increasing chromium concentration, to a maximum at about $x = 0.3$, and that the saturation magnetization decreased over a comparable range.

Only one previous study has appeared concerning the substitution of platinum metals for cobalt in CoS_2. Members of the system $Co_{1-x}Rh_xS_2$ ($0 \le x \le 0.6$) were prepared and their magnetic properties studied.[5] It was found that both the Curie temperature and the Weiss constant decreased monotonically with increasing rhodium substitution. At low rhodium concentration, an increase in the ferromagnetic moment (with a maximum at $x = 0.3$) was found and attributed to Co(3d^7)–Rh(4d^7) ferromagnetic interactions. As the rhodium concentration was increased further, the moment decreased due to a lack of magnetic homogeneity and the possible formation of rhodium–rhodium clusters.

The purpose of this study is to investigate the magnetic properties of the systems $Co_{1-x}Ru_xS_2$ and $Rh_{1-x}Ru_xS_2$ to further understand the magnetic interactions between cobalt's 3d^7 electrons and 4d systems.

Experimental Section

Preparation of Materials. Polycrystalline samples of the systems $Co_{1-x}Ru_xS_2$ ($0 \le x \le 1$) and $Rh_{1-x}Ru_xS_2$ ($0.5 \le x \le 1$) were prepared. Attempts to prepare samples by direct combination of the elements were largely unsucessful, but samples were obtained by heating in hydrogen sulfide stoichiometric quantities of pentaamminecobalt(III) chloride and ammonium hexachlororuthenate(IV) for the preparation of members of the system $Co_{1-x}Ru_xS_2$ and ammonium hexachlororhodate(III) and ammonium hexachlororuthenate(IV) for the compositions $Rh_{1-x}Ru_xS_2$.

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 was heated at 650 °C for 4 h, ground, and further reduced at 850 °C for 8 h; Ru and Rh were reduced for 8 h 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

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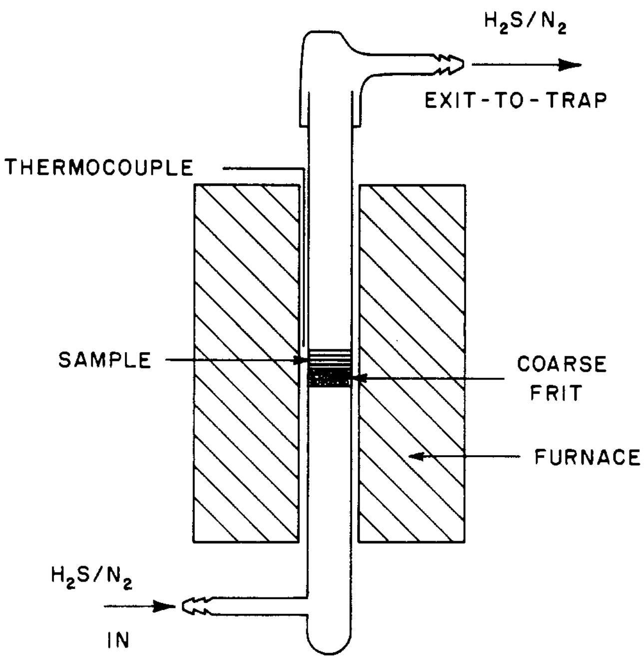

Figure 1. Flow-bed reactor for the preparation of members of the system $Co_{1-x}Ru_xS_2$ with H_2S.

tube; the tube was evacuated and sealed. Samples were slowly brought to the reaction temperature and maintained there for the stated period of time. For the system $Co_{1-x}Ru_xS_2$, only Ru-rich samples ($x \geq 0.7$) could be prepared as single-phase materials using this technique. No member of the system $Rh_{1-x}Ru_xS_2$ could be prepared as a pure homogeneous sample by this method.

Synthesis by the Precursor Method. Stoichiometric quantities of $(NH_4)_2RuCl_6$[15] and $[Co(NH_3)_5Cl]Cl_2$[16] or $(NH_4)_2RuCl_6$ and $(NH_4)_3RhCl_6$ (Engelhard Inc. 99.999%) were dissolved in 12 mL of 0.15 M NH_4OH by warming, with stirring, to 80 °C. When solution was achieved, the solvent was evaporated with use of an infrared lamp. The product was ground thoroughly and transferred into a flow-bed reactor (Figure 1) in which sulfurization took place. The system was purged at a flow rate of 55 cm^3/min with nitrogen for at least 1 h. The mixture was treated with hydrogen sulfide at a rate of 80 cm^3/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 h. The temperature was lowered to 250 °C over 1 h and then cooled to room temperature in the H_2S flow. After sulfurization, the product was extracted with methanol to remove the NH_4Cl that 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 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 Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å). Fast scans at $1°[2\theta]$/min were examined for the possible presence of extraneous phases. Slow scans at $0.25°[2\theta]$/min were obtained for all single-phase samples in the range of $26° < 2\theta < 105°$. Lattice parameters for the well-crystallized materials were determined by least-squares analysis. For members of both systems, $Co_{1-x}Ru_xS_2$ ($0 \leq x \leq 1$) and $Rh_{1-x}Ru_xS_2$ ($0.5 \leq x \leq 1$), the patterns can be indexed on the basis of a cubic pyrite structure (space group *Pa*3).

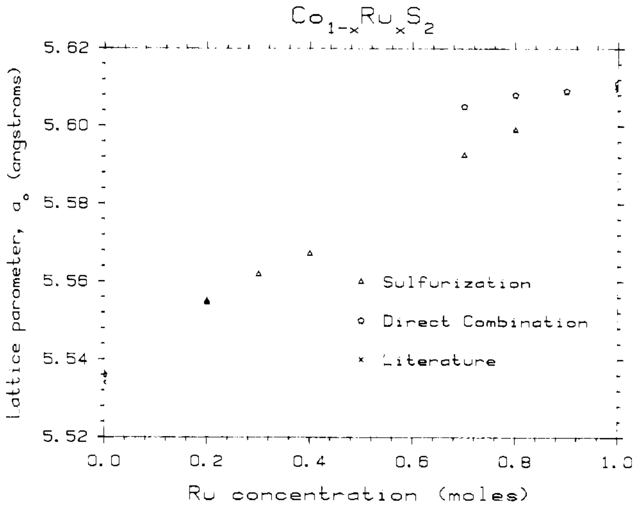

Figure 2. Variation in the lattice parameter a_0 with increasing Ru concentration.

Table I. Paramagnetic Moment of $Co_{1-x}Ru_xS_2$[a]

composition	μ_{eff},[b] μ_B/mol of CoS_2	composition	μ_{eff},[b] μ_B/mol of CoS_2
$Co_{0.8}Ru_{0.2}S_2$	2.21	$Co_{0.3}Ru_{0.7}S_2$	2.06
$Co_{0.7}Ru_{0.3}S_2$	2.19	$Co_{0.2}Ru_{0.8}S_2$	1.99
$Co_{0.6}Ru_{0.4}S_2$	2.00		

[a] Prepared from precursors and heated at 800 °C for 7 days.
[b] From susceptibility measurements for 80 K < T < 300 K.

Magnetic Measurements. Magnetic susceptibilities were measured with a Faraday balance[17] over the range from liquid-nitrogen to room temperature at a field strength of 10.4 kOe. Honda–Owen (field dependency) plots were also made to test for the presence or absence of any ferromagnetic phase. The data were then corrected for core diamagnetism.[18]

Results and Discussion

Results on Preparation. Only Ru-rich samples could be prepared with use of direct combination of cobalt, ruthenium, and sulfur, and even these samples are probably not homogeneous. Although only single phases were found for $x > 0.7$, cell parameters for these samples showed a positive deviation from ideal behavior (see Figure 2). The magnetic properties, however, did indicate that a partial solid solution between CoS_2 and RuS_2 was obtained.

The samples of both systems prepared from precursors, on the other hand, appeared from X-ray diffraction patterns to be homogeneous. Patterns for all of these samples could be interpreted on the basis of a cubic pyrite structure. Lattice parameters of members of the system $Co_{1-x}Ru_xS_2$ were found to obey Vegard's law and change linearly with composition (see Figure 2). Values of 5.537 (1) for CoS_2 and 5.610 (1) Å for RuS_2 agree well with values in the literature (5.534[19] and 5.6095 Å,[20] respectively). RhS_2 cannot be prepared, but all members of the system $Rh_{1-x}Ru_xS_2$ ($0.5 \leq x \leq 1$) gave the same cell constant, namely, 5.607 (4) Å.

Magnetic Properties. The measured effective moments for members of the system $Co_{1-x}Ru_xS_2$ (in terms of CoS_2 equivalents) are given in Table I. It can be seen that, after the samples are heated for 8 days at 800 °C, the effective moments are much higher than the calculated value of $\mu_{eff} = 1.73$ μ_B. For a determination of whether the high moments were a result of inhomogeneous products, a sample of the composition

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Table II. Effect of the Annealing of $Co_{0.2}Ru_{0.8}S_2$[a] at 800 °C

time of anneal, days	μ_{eff}, μ_B/mol of CoS_2	Θ, K	time of anneal, days	μ_{eff}, μ_B/mol 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)

[a] Prepared from precursors and heated at 800 °C for 7 days.

$Co_{0.2}Ru_{0.8}S_2$ 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 $Co_{0.2}Ru_{0.8}S_2$ 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 $\mu_{eff} = 1.70\ \mu_B$ 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 indicated single-phase formation for all the products reported.

Susceptibility measurements of members of the system $Rh_{1-x}Ru_xS_2$ ($0.5 \le x \le 1$), as a function of temperature from 80 to 300 K, gave values that were temperature independent and varied from 0.8×10^{-4} to 1.1×10^{-4} emu/mol.

For pure CoS_2, the moment corresponds to approximately one unpaired electron on the cobalt atom, which is present as low-spin Co(II). Goodenough[13,14] has shown that the observed metallic conductivity and ferromagnetic moment are due to partially filled σ^*e_g states. He indicated that, in this compound, the σ^*e_g states constitute a band. The occurrence of an energy difference between the t_{2g} and σ^*e_g states that is larger than the intraatomic exchange energy gives rise to the low-spin-state configuration of cobalt(II). For the system $Co_{1-x}Rh_xS_2$, it was shown that, for compositions where $x \le 0.2$, the 4d electron associated with $Rh(4d^7)$ are localized and there is a ferromagnetic alignment between $Co(3d^7)$ and $Rh(4d^7)$ electrons. For such an interaction to occur, the relative energies of the cobalt 3d and rhodium 4d manifolds must be similar. Magnetic susceptibility measurements for members of the system $Co_{1-x}Ru_xS_2$ indicate that $Ru(4d^6)$ 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 $Rh(4d^7)$ appear to be localized in the system $Co_{1-x}Rh_xS_2$, the observed Pauli paramagnetic behavior for the system $Rh_{1-x}Ru_xS_2$ indicates that, in the absence of localized cobalt electrons, rhodium 4d electrons are delocalized.

Conclusion

Synthesis of members of the $Co_{1-x}Ru_xS_2$ and $Rh_{1-x}Ru_xS_2$ systems has been accomplished by the sulfurization of mixtures of $(NH_4)_2RuCl_6$ and $[Co(NH_3)_5Cl]Cl_2$ or $(NH_4)_2RuCl_6$ and $(NH_4)_3RhCl_6$. The magnetic properties of these systems are dependent on the degree of localization of the 4d electrons. In the presence of $Co(3d^7)$, rhodium 4d electrons appear to be localized; but if only 4d states are present, then the rhodium 4d electrons are delocalized. Members of these systems are difficult to prepare as single homogeneous products, but magnetic susceptibility measurements can be used to determine when such products are obtained.

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Registry No. RuS_2, 12166-20-0; CoS_2, 12013-10-4; RhS_2, 12038-73-2.

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A Highly Siliceous Structural Analogue of Zeolite Y: High-Resolution Solid-State ^{29}Si and ^{27}Al NMR Studies

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Reaction of synthetic zeolite Na–Y with $SiCl_4$ vapor at 560 °C yields an essentially aluminum-free faujasite structure, which is highly crystalline and which, when studied by ^{29}Si NMR spectroscopy with magic-angle spinning, gives a spectrum consisting of a single sharp peak characteristic of regular, Si(4Si), lattice ordering. The ^{27}Al MAS NMR spectrum of the dry dealuminated material shows two peaks, one corresponding to residual lattice aluminum and one due to $AlCl_4^-$. The ^{27}Al MAS NMR spectrum of washed dealuminated zeolite Y contains two peaks: one due to residual aluminum still on tetrahedral sites in the lattice and an additional peak due to octahedrally coordinated cationic aluminum in the zeolitic channels. The latter can be successively removed by washing, the intensity of the octahedral peak greatly decreasing. ^{27}Al NMR is a valuable tool in probing the coordination, quantity, and location of aluminum atoms in chemically treated zeolites.

Introduction

The catalytic activity of the hydrogenic form of zeolites is known to increase with increasing Si/Al ratio.[2] It is, therefore, desirable to be able to prepare zeolites with high—and preferably variable—silicon contents, especially since thermal stability increases as zeolites become more siliceous. Considerable efforts channeled in this direction culminated, in the mid-1970s, in the synthesis of zeolite ZSM-5, an active catalyst in a number of reactions.[3]

Probably the most well-established method of preparing highly siliceous faujasites consists of hydrothermal treatment of ammonium-exchanged zeolite Y.[4] Aluminum leaves the

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