

$\eta_{nlm\sigma}(r, \theta, \phi)$,⁹ we may realize that their type is the same except the parts of the normalization constants and exponents and they do not have the same radial nodes that the hydrogenic wave functions, $\Psi_{nlm\sigma}(r, \theta, \phi)$ ¹⁰ have *i.e.* they have no radial nodes for the orbitals; 2s, 3s, 3p, 4s, 4p, 4d, 5s etc. Therefore, they are not a good description of the self-consistent field (SCF) method.^{11,12}

Author has orthonormalized the conventional STO's.⁴ But their analytic expression for the two-electron integrals in the two, three, and four-centers cases are very complex so that author has generalized and orthonormalized the conventional GTO's by using of Eq.(5) and (6). The orthogonalized GTO and orthonormalized GTO are listed in Table 2 and 3, respectively.

These GTO's have the same radial nodes and the same nodal numbers, $n - (l + 1)$ that the hydrogenic orbitals, $\Psi_{nlm\sigma}(r, \theta, \phi)$, have. Therefore they are another good representations of the SCF and have very simple analytic expression for the integrals mentioned above.

Also two of $g_{nlm\sigma}^{\circ}(r, \theta, \phi)$ which are different from each other only in their quantum numbers, are orthogonal, so that the 465 overlap integrals between any two orbitals of 31 $g_{nlm\sigma}^{\circ}(r, \theta, \phi)$ with only one different value among n, l, m and σ go to zero, and in the case of $g_{nlm\sigma}^{\circ}(r, \theta, \phi)$, those integrals have only unit or zero value because they are orthonormalized from each other by the next equation.

$$(g_{nlm\sigma}^{\circ}(r, \theta, \phi) / g_{n'l'm'\sigma'}^{\circ}(r, \theta, \phi)) = \delta_{nlm\sigma} \delta_{n'l'm'\sigma'} \quad (7)$$

where $g_{nlm\sigma}^{\circ}(r, \theta, \phi)$ and $g_{n'l'm'\sigma'}^{\circ}(r, \theta, \phi)$ are located at the same center in the molecule, and $\delta_{nlm\sigma}$ represents Kronecker delta.

Eventually, author has generalized the conventional GTO's

which have no regular form for each atomic orbital with legal quantum numbers to obtain the $g_{nlm\sigma}^{\circ}(r, \theta, \phi)$ and $g_{nlm\sigma}^{\circ}(r, \theta, \phi)$ which are the closest in the GTO's form to the hydrogenic orbitals.

These new GTO's shall be intensively utilized in ab-initio MO procedures in the near future because of their regular atomic orbital form and simple analytic representation of the integrals which must be evaluated in the ab-initio molecular orbital calculation. These integrals based on the orthonormalized Gaussian type orbitals, $g_{nlm\sigma}^{\circ}(r, \theta, \phi)$ shall have been determined in the series of our following papers.

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Preparation and Properties of $\text{Co}_{1-x}\text{M}_x\text{S}_8$ (M = Ni, Rh, Ru, and Fe)

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Samples with the nominal composition of $\text{Co}_{1-x}\text{M}_x\text{S}_8$ (M = Ni, Rh, Ru, and Fe) were prepared, and their magnetic properties were measured. X-ray diffraction analysis showed that small amount of the elements Ni, Rh, and Fe could be incorporated into Co_9S_8 forming a homogeneous π -phase, whereas the Ru-incorporated sample could not be prepared in a single phase. The lattice parameter was observed to increase as other elements were incorporated into Co_9S_8 . Samples incorporated with the elements of Ni, Rh, and Ru showed Pauli-paramagnetism while the Fe-incorporated sample exhibited weak ferromagnetism. The values of magnetic susceptibility for the Ni, Rh, Ru-incorporated samples were nearly the same as that of pure Co_9S_8 .

Introduction

The nature of the cobalt present in sulfided cobalt molybdate catalysts has been the subject of several studies.¹⁻³ An early study by de Beer *et al.*⁴ indicated that the sulfur content present in sulfided cobalt molybdate catalysts corresponded to the value anticipated for a composition of Co_9S_8 and MoS_2 . However, since the actual catalysts were amorphous, direct evidence for the existence of those phases by the X-ray dif-

fraction patterns of the catalysts was not found. In fact, if Co_9S_8 is one of the necessary component in hydrodesulfurization (HDS) catalysts, slight modification of Co_9S_8 by the chemical substitution of cobalt with other elements may result in enhancement of the catalytic activities of the catalysts that can be caused by the possible changes in the cell size as well as in the energy levels of Co_9S_8 .

Following the above implications, we have prepared members of the Co-M-S system with a nominal composition

of $\text{Co}_{0.7}\text{M}_x\text{S}_8$ ($M = \text{Ni}, \text{Rh}, \text{Ru}$, and Fe). X-ray analysis and magnetic measurement were performed for those samples. The results were primarily compared with those of pure Co_9S_8 that were already presented in the previous works.⁵⁻⁶

Experimental

Polycrystalline samples of the series $\text{Co}_{0.7}\text{M}_x\text{S}_8$ ($M = \text{Fe}, \text{Ni}, \text{Rh}$, and Ru) were prepared by direct combination of the elements. Starting materials were pretreated as follows: the high-purity metals (Co 99.999% and Fe 99.999%, Leico Inc.; Ru 99.999% and Rh 99.999%, Englehard Inc.) were reduced in a 15% H_2 -85% Ar atmosphere (Co at 850°C for 12 h; Fe at 950°C for 24 h; Ru and Rh at 800°C for 20 h). Ni (99.999%, Gallard-Schlesinger Inc.) was heated at 400°C under an atmosphere of pure H_2 for 1 h and kept under dynamic vacuum for 30 min to remove any adsorbed H_2 . Elemental sulfur 99.9999%, Atomergic Chemical Co., was used as supplied.

Stoichiometric quantities of the elements were ground thoroughly and transferred to silica tubes. The tubes were then evacuated for one hour to a pressure below 2 μm and sealed off for reaction. The samples were reacted in a large muffle furnace with each sample positioned in the furnace so as to minimize the temperature gradient across the tubes. The samples were heated initially to 600°C and maintained at that temperature for four days. The tubes were cooled and shaken thoroughly before being reheated for one day at 700°C. Finally, the samples were annealed at 460°C for twelve days with thorough shakings every three days.

Powder diffraction patterns of the samples were obtained with a Philips diffractometer using monochromated high-intensity $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). The scan rate was 0.25° 2 θ /min with a chart speed of 30 in/hr. Cell parameters were determined by a least-squares refinement of the reflections.

Magnetic data were obtained using a Faraday balance^{7,8} equipped with a Cahn electrobalance (Model RG) over the temperature range 80-300 K. Measurements were performed at field strengths between 6.2 and 10.4 kOe. The balance was calibrated using platinum wire ($\chi_s = 0.991 \times 10^{-6} \text{ emu/g}$ at 275 K) as a standard; temperatures were measured with a Ga-As diode. The core diamagnetic correction was not applied to this measurement because of the large uncertainty in the magnitude of the correction relative to the susceptibility of the material studied.

Results and discussion

Details on the properties of Co_9S_8 have been reported in the previous publications.^{5,6} In order to compare the properties of $\text{Co}_{0.7}\text{M}_x\text{S}_8$ ($M = \text{Fe}, \text{Ni}, \text{Ru}$, and Rh) samples with those of Co_9S_8 , we will briefly summarize the results on Co_9S_8 . X-ray analyses and magnetic measurements confirmed the narrow homogeneity range of Co_9S_8 . It was observed that Co-S samples with a sulfur content greater than 47.06 atomic percent (= Co_9S_8) contained a small amount of a hexagonal phase, which could be assigned to the composition $\text{CoS}_{1.097}$.⁹ We also found that a sample with only 46.11 atomic percent sulfur contained free cobalt, as indicated by the presence of the (111) reflection of cubic cobalt, which is in agreement with the results of Lindqvist *et al.*¹⁰ The magnetic data for stoichiometric Co_9S_8 showed a field-independent susceptibility

consistent with Pauli paramagnetism, and the reported value of $0.85 \times 10^{-6} \text{ emu/g}$ was in good agreement with the results of Knop.¹¹ Magnetic susceptibility measurements of the cobalt-rich samples showed the presence of small amounts of cobalt metal. Lattice parameters of the samples with composition close to Co_9S_8 had the same value as that obtained for a stoichiometric sample of Co_9S_8 , *i.e.*, 9.930(2) Å . Co_9S_8 has a face-centered cubic structure, generally called as the π -phase.¹²

The samples, $\text{Co}_{0.7}\text{Ni}_x\text{S}_8$ with $x = 0.9$ and $x = 1.8$, resulted in X-ray diffraction patterns of the π -phase free from foreign lines in good agreement with the result of Knop *et al.*¹² The lattice parameters (a_0) of above samples with $x = 0.9$ and $x = 1.8$ were computed to be 9.943(2) and 9.957(2) Å , respectively. Extrapolation of the curve, a_0 vs x , to $x = 0$ gives the value of 9.930 Å , which is in good agreement with the cell parameter of Co_9S_8 . This may indicate that the members of the system $\text{Co}_{0.7}\text{Ni}_x\text{S}_8$ obey the Vegard's law. That is, the lattice parameter varies linearly with the amount of Ni in $\text{Co}_{0.7}\text{Ni}_x\text{S}_8$. This observation would also indicate that the samples prepared are homogeneous. In the magnetic studies with the temperature range of 80~300 K, above samples showed the field and temperature independent susceptibilities consistent with Pauli paramagnetism. Variation of the magnetic susceptibility with temperature is shown in Figure 1. For comparison, similar data for the sample of Co_9S_8 are also represented in Figure 1. In fact, it was observed that the magnetic properties of $\text{Co}_{0.7}\text{Ni}_x\text{S}_8$ are mostly the same as those of Co_9S_8 . Moreover, it was found that the magnetic properties of $\text{Co}_{0.7}\text{Ni}_x\text{S}_8$ are nearly independent of the amount of Ni. Commercially, a metal either Co or Ni is used as the promoter in the HDS catalyst. As mentioned previously,⁵ some cobalt in the catalytic system was reported to be possibly associated with the Co_9S_8 phase. Although we could not give any concrete evidence, the fact that magnetic characters of $\text{Co}_{0.7}\text{Ni}_x\text{S}_8$ are rather similar to those of Co_9S_8 might be correlated with the use of both metals, Co and Ni, as the promoters in the HDS catalysts.

As reported by Knop *et al.*,¹² the sample, $\text{Co}_{0.7}\text{Rh}_{0.9}\text{S}_8$, prepared in this work gave X-ray diffraction pattern of the π -phase free from foreign lines. The lattice parameter of this sample was computed to be 9.978(2) Å , which is much greater than those of the 3d-element substituted $\text{Co}_{0.7}\text{M}_x\text{S}_8$ samples ($M = \text{Fe}, \text{Co}, \text{Ni}$). Magnetic studies showed that this sample has field-independent magnetism at both of liquid nitrogen and room temperatures. Variation of the magnetic susceptibility with temperature for this sample is also included in Figure 1. It can be seen from this figure that the magnetic property of Rh-substituted sample is almost the same as that of Co_9S_8 . However, a little difference can be noticed from the

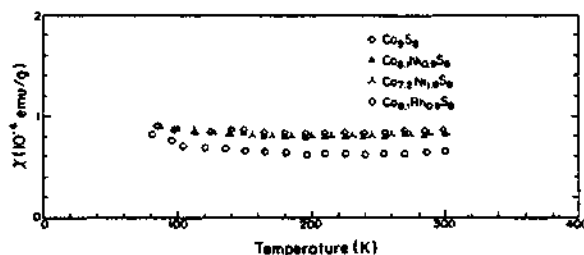


Figure 1. Thermal variation of the magnetic susceptibility (χ) for the samples of Co_9S_8 , $\text{Co}_{0.7}\text{Ni}_{0.9}\text{S}_8$, $\text{Co}_{0.7}\text{Ni}_{1.8}\text{S}_8$, and $\text{Co}_{0.7}\text{Rh}_{0.9}\text{S}_8$.

figure. At low temperature region, the χ vs T plot for the sample of $\text{Co}_{0.1}\text{Rh}_{0.9}\text{S}_8$ exhibited a small curvature. That may indicate the possible existence of the paramagnetic impurities at low temperature. The cause of curvature may also be related to the drastic expansion of the cell size which occurs as Rh is incorporated into Co_xS_8 . According to Lindqvist *et al.*,¹⁰ four Co_xS_8 formula units constitute one unit cell. The 36 cobalt atoms are distributed over two sets of equivalent lattice sites, one containing 32, and the other 4 atoms. Similarly the 32 sulfur atoms are split up into a set of 8 and a set of 24 atoms. Later, Geller reported that one of the two kinds of cobalt atoms is surrounded by a regular octahedron of sulfur atoms, and the other is surrounded by a tetrahedron of S atoms.¹³ Each of the cobalt atoms with tetrahedral sulfur coordination was reported to be also linked to three similarly coordinated cobalt atoms whose distance is essentially the Co-Co distance in the elementary cobalts. In these respects, it is more likely that the drastic expansion of the cell size of $\text{Co}_{0.1}\text{Rh}_{0.9}\text{S}_8$ in comparison with that of Co_xS_8 induces significant increase of the energy barrier between the two different structural sites, tetrahedral and octahedral. If this model is correct, the number of localized electrons should increase as temperature is lowered, rendering the sample to exhibit paramagnetic behavior at low temperature. That is, increase of the Co-Co distance as Rh incorporates into Co_xS_8 would reduce the Co^{2+} - Co^{2+} interaction resulting in more localized electrons to be available as temperature decreases. The localized $\text{Co}(3d^7)$ electrons may then contribute to paramagnetism of the sample. Nevertheless, we could not provide at this time any concrete evidence on the correctness of above model. Accordingly, further extensive studies seem to be needed to elucidate more firmly the nature of such a peculiar behavior.

The sample with a nominal composition of $\text{Co}_{0.1}\text{Ru}_{0.9}\text{S}_8$ could not be prepared in a single phase. The extra phases could be assigned as due to RuS_2 and unreacted Ru metal. Regardless of the homogeneity of the sample, the lattice parameter of the π -phase was computed to be 9.934(2) Å. The small increase in the cell size with respect to that of Co_xS_8 would certainly indicate the formation of some $\text{Co}_{0.1}\text{Ru}_{0.9}\text{S}_8$. Nevertheless, the limit of existence of $\text{Co}_{0.1}\text{Ru}_{0.9}\text{S}_8$ should be very narrow. Since RuS_2 and Ru are both diamagnetic materials, their existence would not contribute much to the magnetic properties of the sample prepared. The magnetic

data showed field and temperature independency suggesting that $\text{Co}_{0.1}\text{Ru}_{0.9}\text{S}_8$ is Pauli-paramagnetic. Moreover, the measured magnetic susceptibility was similar to that of Co_xS_8 .

The samples, $\text{Co}_{0.1}\text{Fe}_x\text{S}_8$ with $x = 0.525$ and $x = 0.90$, appeared to be homogeneous based on the X-ray diffraction patterns. The patterns for these samples could be interpreted on the basis of π -phase. However, the sample with a nominal composition $\text{Co}_x\text{Fe}_x\text{S}_8$ was observed to have a small amount of extra phases, which could be assigned to troilite and pyrrhotite. Nevertheless, lattice parameters of members of the system $\text{Co}_{0.1}\text{Fe}_x\text{S}_8$ were found to obey Vegard's law and change linearly with composition including the sample of $\text{Co}_x\text{Fe}_x\text{S}_8$. The cell constants (a_0) of $\text{Co}_{0.1}\text{Fe}_x\text{S}_8$ with $x = 0.525$ and $x = 0.90$ are 9.939(2) and 9.946(2) Å, respectively. Extrapolation of the plots of a_0 vs x , to $x = 0$ gives the value of 9.930 Å, which agrees well to the cell parameter of Co_xS_8 as reported previously.⁵ This may be an indirect evidence for the fact that the members of the system $\text{Co}_{0.1}\text{Fe}_x\text{S}_8$ obey the Vegard's law. The magnetic data for $\text{Co}_{0.1}\text{Fe}_x\text{S}_8$ showed slightly field dependent magnetism at both of liquid nitrogen and room temperatures. The magnetic moment was observed to increase with the amount of Fe in $\text{Co}_{0.1}\text{Fe}_x\text{S}_8$. The observed ferromagnetism might be, however, due to the inhomogeneity of the samples. As we have reported previously,⁸ magnetic measurement may be used as a powerful tool in determining the homogeneity of the samples especially when the X-ray diffraction patterns indicate single-phase formation of the products. In this respect, the samples of $\text{Co}_{0.1}\text{Fe}_x\text{S}_8$ were annealed at 460°C for varying periods of time. Annealing up to 15 days did not change, however, the observed magnetic moment appreciably. Hence, samples with either an excess or a deficiency of sulfur were also prepared and their magnetic properties were measured. All the products exhibited field dependent behavior. In specific, a sample with the nominal composition $\text{Co}_{0.1}\text{Fe}_{0.9}\text{S}_7$, was very strongly field dependent. This sample seemed to be dominated by ferromagnetic components, which themselves are virtually independent of temperature. Such temperature independence implies a very high Curie temperature, well above 300 K, and suggests that the ferromagnetism observed in this sample probably results from the formation of a small amount of cobalt and/or iron metals. On the other hand, it was observed that the sample with a nominal composition of $\text{Co}_{0.1}\text{Fe}_{0.9}\text{S}_{8.1}$ contained a small amount of a hexagonal phase, which could be assigned to the composition $\text{Co}_{1.2}\text{Fe}_2\text{S}_{10.97}$ as the case of the Co-S binary system.⁹ This sample exhibited a weaker ferromagnetism, however, in comparison with the sulfur-

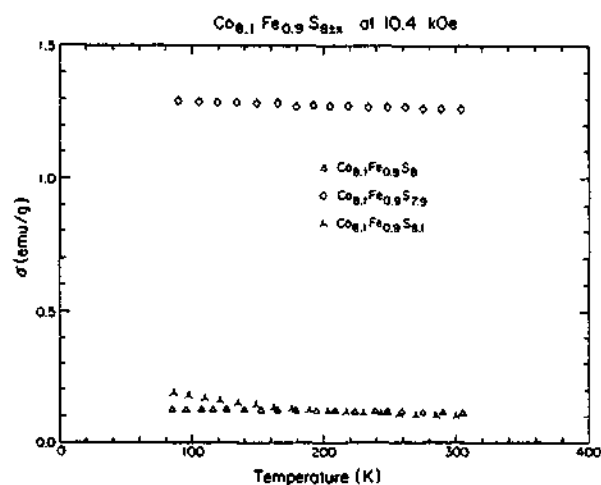


Figure 2. Thermal variation of the magnetization (σ) for compositions in the vicinity of $\text{Co}_{0.1}\text{Fe}_{0.9}\text{S}_8$ (47.06 atomic percent sulfur).

Table 1. Lattice parameters of $\text{Co}_{0.1}\text{M}_x\text{S}_8$ ^a

| Sample | Cell size (Å) ^b |
|---|----------------------------|
| Co_xS_8 | 9.930(2) |
| $\text{Co}_{0.1}\text{Fe}_{0.525}\text{S}_8$ | 9.939(2) |
| $\text{Co}_{0.1}\text{Fe}_{0.9}\text{S}_8$ | 9.946(2) |
| $\text{Co}_{0.1}\text{Ni}_{0.9}\text{S}_8$ | 9.943(2) |
| $\text{Co}_{0.1}\text{Ni}_{1.0}\text{S}_8$ | 9.957(2) |
| $\text{Co}_{0.1}\text{Rh}_{0.9}\text{S}_8$ | 9.978(2) |
| $\text{Co}_{0.1}\text{Ru}_{0.9}\text{S}_8$ ^c | 9.934(2) |

^aSee ref. (10)-(14) for the indexing of the π -phase. ^bValues in parentheses represent the uncertainties. ^cThis sample was not single phase. See text.

deficient one. Variations in the magnetization (σ) with temperature for the samples with the nominal composition $\text{Co}_{0.9}\text{Fe}_{0.1}\text{S}_8$ ($\delta = -0.1, 0, \text{ and } 0.1$) are shown in Figure 2. A small curvature in the σ vs T plot for the sample with a nominal composition of $\text{Co}_{0.9}\text{Fe}_{0.1}\text{S}_8$ might be due to the temperature-dependent paramagnetism of the hexagonal $\text{Co}_{1-x}\text{Fe}_x\text{S}_8$ which exists as an extra phase in the sample. It can be inferred from the figure that the sample with a nominal composition of $\text{Co}_{0.9}\text{Fe}_{0.1}\text{S}_8$ is indeed ferromagnetic. However, it is not clearly evident whether the Fe-incorporated π -phase has an intrinsic ferromagnetism or not, for such a behavior might have occurred from the lack of magnetic homogeneity and the possible formation of iron-iron clusters.

In conclusion, both the X-ray diffraction and magnetic data revealed that a small amount of either Ni or Rh can be incorporated into Co_9S_8 forming a homogeneous π -phase. Although the Rh-incorporated sample exhibited a weak paramagnetism at low temperature, both samples seemed to possess Pauli-paramagnetism. A weak paramagnetism of the Rh-incorporated sample at low temperature seemed to be related with the expansion of the cell size. The Ru-incorporated sample could not be prepared in a homogeneous phase. Nevertheless, this sample exhibited Pauli-paramagnetism. The observed magnetic susceptibilities of above three samples appeared rather similar to that of pure Co_9S_8 . According to the X-ray diffraction pattern, the Fe-incorporated sample was likely to form in a homogeneous π -phase. However, this sample exhibited a weak ferromagnetism. It is not yet clear whether ferromagnetism is indeed an intrinsic property of the Fe-incorporated sample or not. Such an observation might be accused due to a lack of magnetic homogeneity and the possible formation of iron-iron clusters.

The cell sizes of the samples studied in this work are summarized in Table 1. The lattice parameter of the π -phase was observed to increase as the elements Fe, Ni, Rh, and Ru are incorporated into Co_9S_8 . Among the 3d-elements, the cell sizes of the system $\text{Co}_{1-x}\text{M}_x\text{S}_8$ could be ordered with M in the sequence of $\text{Fe} > \text{Ni} > \text{Co}$. The lattice parameter seemed to vary linearly with the amount of substituting element indicating that there is not any specific preference for the substituent

atom to occupy either one of two different structural sites, tetrahedral or octahedral. Such a cell-size variation without any significant change in the magnetic property may affect the possible catalytic activity of Co_9S_8 as a promoter in HDS catalyst. It thus seems to be valuable to test the catalytic activities of the transition metal-incorporated Co_9S_8 samples.

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