overall pattern of the vibrational frequencies and the force constants for $Ru(H_2O)_6^{2+}$ and $Ru(H_2O)_6^{3+}$ correlates well with corresponding data for the better documented hexaammines. A comparison of our results with the incomplete analysis of the ruthenium hexaammines[4,10] shows the general relationship $\nu_i(Ru(NH_3)_6^{2+}) \approx \nu_2(Ru(H_2O)_6^{2+})$ and $\nu_i(Ru(NH_3)_6^{3+}) < \nu_i(Ru(H_2O)_6^{3+})$. This observation is consistent with the corresponding metal–ligand distances and with a π interaction possible for water but not for ammonia.[11]

Discussion

To our knowledge, the present study reports the first normal-coordinate analysis for the two hexaaqua ions of a redox couple. This, together with the structural data,[2] makes possible a reliable calculation of the reorganization energy of the inner coordination sphere for the $Ru(H_2O)_6^{2+}$ – $Ru(H_2O)_6^{3+}$ self-exchange reaction. Since our efforts to measure the internal $Ru(H_2O)_6^{n+}$ frequencies in solution (up to 1.5 M in $Ru(H_2O)_6^{2+}$ or $Ru(H_2O)_6^{3+}$) were unsuccessful, we use the solid-state properties as the best available vibrational data for the hexaaqua ions to estimate the redox kinetics of the dissolved species. In terms of the harmonic approximation the inner-sphere reorganization energy within the classical limit[1] is given by

$$\Delta G_{in}^{*} = \frac{3f_{II}f_{III}(\Delta r)^2}{f_{II} + f_{III}}$$

In this expression f_{II} and f_{III} represent the force constants of $Ru(H_2O)_6^{2+}$ and $Ru(H_2O)_6^{3+}$, respectively. Δr is the difference of the metal–ligand distances between the oxidized and reduced complex. Following Marcus,[12] we use the force constants F_{11} (A_{1g}) of the breathing vibration for f_{II} and f_{III}. With Δr = 0.09 (2) Å^2, f_{II} = 1.91 (1) mdyn Å^{-1}, and f_{III} = 2.98 (2) mdyn Å^{-1}, we obtain 4.1 (1.8) kcal mol^{-1} for ΔG_{in}^{*}. Within the given standard deviation the same value for Δr was determined by an EXAFS study of aqueous solutions of $Ru(H_2O)_6^{2+}$ and $Ru(H_2O)_6^{3+}$.[13] Assuming a value of 10.9 kcal mol^{-1} for the sum of the other contributions to the activation energy for electron transfer,[1] ΔG^{*}, we calculate log k = 1.82 (1.8) for the rate of the $Ru(H_2O)_6^{2+/3+}$ self-exchange. It has to be emphasized that the uncertainty in ΔG_{in}^{*} and log k is predominantly due to the error in Δr.[2] Our result in terms of the classical limit of the Marcus theory agrees well with log k = 1.78 (45) as estimated by Sutin[11] using the Marcus cross relation for a series of redox reactions. From a current study of the $Ru(H_2O)_6^{2+/3+}$ self-exchange a preliminary value of log k = 1.4 (2) is obtained.[14] The rate calculated according to the Marcus theory is fully compatible with this directly determined experimental result.

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Registry No. II, 88703-97-3; III, 88729-59-3; $Ru(H_2O)_6^{2+}$, 30251-71-9; $Ru(H_2O)_6^{3+}$, 30251-72-0.

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Low-Temperature Synthesis and Properties of Co_9S_8, Ni_3S_2, and Fe_7S_8

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Co_9S_8, Ni_3S_2, and Fe_7S_8 were prepared as single-phase polycrystalline materials by heating the appropriate metal sulfates in a controlled mixture of H_2 and H_2S at low temperature. The products were characterized by X-ray diffraction, thermogravimetric analysis, and magnetic susceptibility measurements. The X-ray diffraction pattern and field-dependent magnetic susceptibility of Fe_7S_8 were affected by the thermal history of the sample. The observed differences can be related to the vacancy ordering associated with ferrimagnetic Fe_7S_8.

Introduction

Delafosse et al.[1-4] have shown that sulfides of nickel and cobalt can be prepared by heating their anhydrous sulfates in a stream of H_2/H_2S at low temperatures. However, the experimental conditions for obtaining Ni_3S_2 and Co_9S_8 were not specified. In addition, it has been shown[5,6] that both Co_9S_8 and Ni_3S_2 permit little variation from ideal stoichiometry. For both compounds, there was no observable variation in the lattice parameter as determined from X-ray analyses. Magnetic measurements of Co_9S_8 confirmed its narrow homogeneity range.

Synthetic samples of the low-temperature phase of Fe_7S_8 have been prepared by Lotgering,[7] and magnetic measurements confirmed the work of other investigators[8-10] that the spontaneous magnetism of Fe_7S_8 represents a ferrimagnetic structure that is based upon an ordering of iron vacancies. This can be represented by the formula

$$\overrightarrow{Fe_4}[\overleftarrow{Fe_3}\square]S_8$$

If this model is correct, then randomization of the vacancies

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Table I. Reaction Conditions

reagent	prelim drying	drying temp, °C (under N_2, 1 h)	H_2/H_2S (v/v)	temp, °C	time, h	product
$CoSO_4·7H_2O$	135 °C/4 h	250	40/1	525	4	Co_9S_8
$NiSO_4·6H_2O$	135 °C/4 h	250	40/1	525	2	Ni_3S_2
$Fe_2(SO_4)_3·nH_2O$		175	10/1	325	6	Fe_7S_8

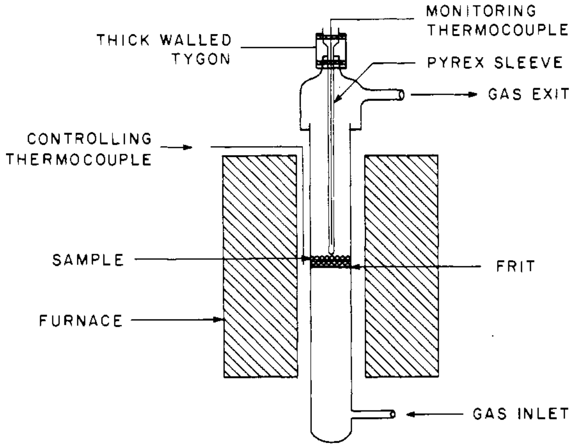

Figure 1. Reactor for the preparation of Co_9S_8, Ni_3S_2, and Fe_7S_8.

should affect markedly the observed magnetic behavior.

Since the preparation of Co_9S_8, Ni_3S_2, and Fe_7S_8 by direct combination of the elements is difficult to achieve, this paper will discuss the low-temperature synthesis involving the treatment of anhydrous sulfates in a controlled H_2/H_2S atmosphere. The homogeneous single-phase products are then characterized by X-ray diffraction analysis and magnetic susceptibility measurements.

Experimental Section

Preparation of Samples. The sulfides Co_9S_8, Ni_3S_2, and Fe_7S_8 were prepared by treating predried sulfate salts of cobalt, nickel, and iron with a mixture H_2 and H_2S in a vertical reactor (Figure 1) at 325 °C for Fe_7S_8 and 525 °C for Co_9S_8 and Ni_3S_2. Cobalt and nickel sulfates were dried initially at 135 °C; preliminary drying of ferric sulfate was unnecessary. After placement of the sulfate in the reactor tube, the system was purged with nitrogen, and a drying step followed. After 1 h of drying under a nitrogen flow, the desired flow rates for H_2 and H_2S were selected and allowed to equilibrate. At this point, the temperature was elevated to ensure complete reaction. For both Co_9S_8 and Ni_3S_2, the reactor tube was removed from the furnace at the end of the reaction and air-quenched to room temperature. The quenched samples of Fe_7S_8 were prepared in a silica reactor tube (fitted with a Vycor frit) that was cooled rapidly with ice water at the end of the reaction. An annealed sample of Fe_7S_8 was prepared by heating the quenched product in a sealed evacuated silica tube for 2 weeks at 300 °C. The tube was allowed to reach room temperature overnight. Slow-cooled samples of Fe_7S_8 were prepared by lowering the temperature of the reactor from 325 to 175 °C at a rate of 1 °C/min. The reactor tube was then removed from the furnace and allowed to reach room temperature. For all the syntheses once the reactor tube reached room temperature, the system was purged with nitrogen before the samples were removed.

The experimental conditions for the preparation of Co_9S_8, Ni_3S_2, and Fe_7S_8 are given in Table I.

Characterization of Samples. Powder diffraction patterns of the samples were obtained with a Philips diffractometer using monochromated high-intensity Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å). For qualitative identification of the phases present, the patterns were taken from $12° < 2\theta < 72°$ with a scan rate of 1° 2θ/min and a chart speed of 30 in./h. The scan rate used to obtain X-ray patterns for precision cell constant determination was 0.25° 2θ/min with a chart speed of 30 in./h. Cell parameters were determined by a least-squares refinement of the reflections.

The crystallite size was determined by the Scherrer method, and a shape factor of 0.9 was applied.[11] A computer program was used to digitize the selected X-ray (slow scan) peaks and determine the peak width.

Table II. X-ray and Thermogravimetric Analysis

sulfide	cell parameters, Å	cryst size, Å	% metal	
			obsd	calcd
Co_9S_8	$a = 9.930$ (2)	380	67.0 (2)	67.4
Ni_3S_2	$a = 5.738$ (2) $c = 7.126$ (2)	400	73.1 (2)	73.3
Fe_7S_8 (quenched)	$a = 3.447$ (2) $c = 5.747$ (2)	290	60.4 (2)	60.4

Thermogravimetric analysis was performed for each material by using a Cahn electrobalance (Model RG). Each sulfide was first heated in a stream of oxygen and then reduced to the metal in a stream of 85% Ar/15% H_2.

Magnetic data were obtained over the temperature range 80–300 K by using a Faraday balance equipped with a Cahn electrobalance (Model RG). Measurements were performed at field strengths between 6.2 and 10.4 kOe. The balance was calibrated by using platinum wire ($\chi_g = 0.991 \times 10^{-6}$ emu/g at 273 K) as a standard; temperatures were measured with a Ga-As diode. The core diamagnetic correction was not applied to these measurements because of the large uncertainty in the magnitude of the correction relative to the susceptibility of the materials studied.

Results and Discussion

Pure Co_9S_8 is difficult to prepare by direct combination of the elements.[5] Sulfur-deficient products are usually obtained and show a susceptibility that is strongly field dependent. It has been shown that the ferromagnetism observed in such products results from the formation of a small amount of cobalt metal. This problem is avoided when Co_9S_8 is prepared by heating cobalt sulfate in a stream of H_2/H_2S at 525 °C. Whereas it takes almost 2 weeks to obtain Co_9S_8 by direct combination of the elements, pure single-phase products can be obtained from the sulfate in 6 h.

Ni_3S_2 and Fe_7S_8 are also difficult to prepare by direct combination. Kullerud and Yund[6] reacted nickel and sulfur for 168 h at 500 °C, and Lotgering[7] annealed Fe_7S_8 for 1 month at 270 °C. The technique of heating sulfates in a controlled H_2/H_2S atmosphere is therefore a rapid method for obtaining homogeneous single-phase products of sulfides that resist preparation by other methods.

X-ray and thermogravimetric analyses of the products are given in Table II. Cell constants of $a = 9.930$ (2) Å for Co_9S_8 and $a = 5.738$ (2) Å and $c = 7.126$ (2) Å for Ni_3S_2 correspond with those reported previously.[12,13] The relative crystallite sizes are also given in Table II.

The magnetic susceptibility was found to be field independent for both Co_9S_8 and Ni_3S_2. This indicates the absence of any ferromagnetic impurity. In addition, the susceptibilities for both of these materials are temperature independent, and their respective values of 1.3×10^{-6} and 0.6×10^{-6} emu/g are consistent with Pauli paramagnetism.

The cell constants given in Table II for a quenched sample of Fe_7S_8, $a = 3.447$ (2) and $c = 5.747$ (2) Å, correspond to the values reported by Erd et al.[14] for the hexagonal pseudocell.

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Table III. Diffraction Data (Å) for Fe_7S_8 Samples[a]

quenched	annealed	monoclinic superlattice[b]	calcd superlattice[c]
	5.79	5.75	5.75
		5.29	5.27
		4.72	4.68
	3.11		3.13
2.98	2.97	2.97	2.97
2.87	2.85	2.84	2.85
	2.70	2.70	2.74
2.64	2.64	2.64	2.64
	2.52		2.55
	2.42		2.36
		2.27	2.25
	2.21	2.21	2.23
	2.15	2.16	2.15
2.07	2.06	2.06	2.06
		2.01	2.01
	1.971		1.973
		1.946	1.954
	1.911	1.914	1.917
1.720	1.717	1.717	1.717
	1.630	1.632	1.631
1.614	1.604	1.606	1.600
	1.561		1.565
1.491	1.498		1.496
1.478	1.487	1.488	1.488
1.442	1.442	1.439	1.438
	1.430	1.424	1.424
1.325	1.320	1.320	1.317
1.296	1.289	1.286	1.289

[a] Because of the complexity of the structure, unambiguous assignment of the Miller indices at high 2θ values is not possible from powder data. [b] Reference 14. [c] Reference 15.

The X-ray pattern of an annealed Fe_7S_8 yields *d* spacings that correspond to those reported by Erd et al.[14] and calculated from the monoclinic superlattice reported by Tokanami et al.[15] These *d* values are compared in Table III. It can be seen that annealing of Fe_7S_8 samples generates an ordered monoclinic cell. A sample of Fe_7S_8 was slow cooled at 1 °C/min from 325 to 175 °C and then quenched to room temperature. The resulting X-ray diffraction pattern showed the onset of ordering, as indicated by the appearance of some of the superlattice peaks.

Magnetic susceptibility measurements were also able to follow the ordering process in Fe_7S_8. Quenched samples from 325 °C showed field-independent magnetic susceptibility, whereas the annealed sample indicated strong field dependency. The results of these studies are shown in Figure 2. Here, the intercept gives the magnitude of the susceptibility of a sample, and the slope is proportional to its spontaneous magnetization.

Bertaut[9] discussed the ferrimagnetic behavior of naturally occurring Fe_7S_8 samples in terms of the ordering of iron vacancies as well as of spins. In this study, the quenched Fe_7S_8 shows a temperature-independent susceptibility from liquid nitrogen to room temperature, which is consistent with a random distribution of iron vacancies. The observed magnitude of 25×10^{-6} emu/g for the susceptibility of the quenched sample is what would be anticipated for an antiferromagnet well below T_N. Observation of field dependency for annealed samples of Fe_7S_8 coincides with the appearance of superlattice lines in the X-ray diffraction patterns.

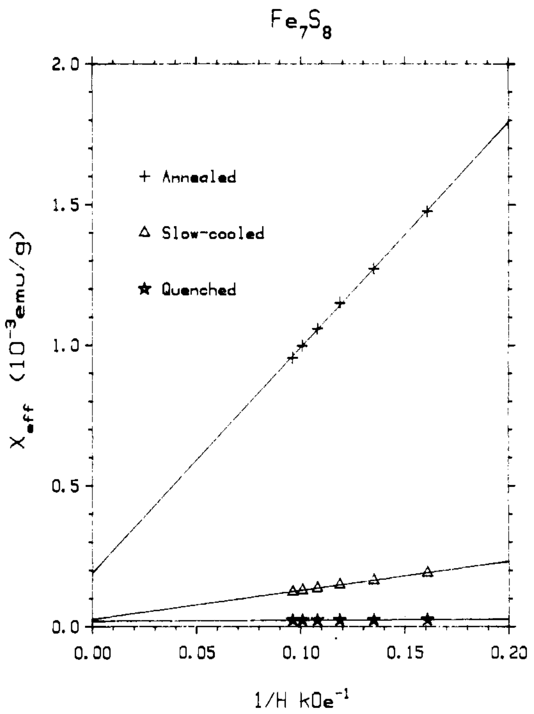

Figure 2. Magnetic susceptibility vs. reciprocal field for Fe_7S_8 samples.

Summary

The treatment of the sulfate salts of cobalt, nickel, and iron with a controlled mixture of H_2 and H_2S at low temperatures yielded Co_9S_8, Ni_3S_2, and Fe_7S_8. The sulfides prepared here were characterized by X-ray diffraction, magnetic susceptibility, and thermogravimetric analysis. The method of preparation was found to yield single-phase materials that were free of ferromagnetic impurities. Co_9S_8 and Ni_3S_2 exhibited temperature-independent magnetic susceptibility that is consistent with Pauli paramagnetism.

The field-dependent magnetic susceptibility measurements for Fe_7S_8 were sensitive to the thermal history of the sample. Annealed samples showed strong field-dependent behavior (i.e., large spontaneous magnetization), whereas quenched samples did not. Slow-cooled samples exhibited less field-dependent behavior than the annealed samples, which indicated less ordering of the vacancies. These observations are consistent with the Bertaut model for vacancy ordering in ferrimagnetic Fe_7S_8.

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Registry No. Co_9S_8, 12017-76-4; Ni_3S_2, 12035-72-2; Fe_7S_8, 12063-66-0; $CoSO_4\cdot 7H_2O$, 10026-24-1; $NiSO_4\cdot 6H_2O$, 10101-97-0; $Fe_2(SO_4)_3\cdot nH_2O$, 15244-10-7; H_2S, 7783-06-4; H_2, 1333-74-0.

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