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The Magnetic Susceptibilities of the Cobalt–Sulfur System[1]

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The magnetic susceptibilities of various sulfides of cobalt were determined as functions of temperature up to 1300°K. Co_4S_3, CoS, and Co_3S_4 were found to be temperature-independent paramagnetic, and Co_9S_8 antiferromagnetic with a Néel temperature above the decomposition temperature. CoS_2 is ferromagnetic with a Curie temperature of 116°K. Based on the susceptibilities, a partial phase diagram was drawn for the cobalt–sulfur system.

Introduction

Because of the electrons in the partially filled d subshells, the transition metals and their compounds are an interesting group for magnetic studies. From the magnetic susceptibilities it should be possible to evaluate the phase relationships which exist in a family of compounds formed between some transition metal and an electronegative constituent.

A great deal of work has been reported in the literature on the phase diagram of the cobalt–sulfur system. Of particular note is the admirable work of Rosenqvist[2a] and the more recent work of Kuznetsov and his coworkers.[2b] The only systematic magnetic phase investigation of this system was undertaken by Haraldsen,[3] but his results are over a limited temperature region. Other studies of magnetic properties of cobalt sulfides have been confined to small ranges of temperature and/or composition.[4–9]

Experimental Section

(A) Measurement of Susceptibilities.—Susceptibilities were determined by a Faraday method using a Sartorius balance as previously described.[10] Powder samples about 250 mg. in weight were sealed in evacuated thin-walled Vycor capsules. The diamagnetic susceptibilities of several empty capsules were determined to evaluate the magnitude of the capsule corrections to be applied. Measurements were made at fields of about 1000, 1500, and 2000 oersteds. In some cases the samples had field dependent susceptibilities at lower temperatures. The results for these were extrapolated to infinite field strength.

(B) Preparation of Samples.—The samples were prepared either directly from the elements or by treatment of CoO with hydrogen sulfide. In the latter method the oxide used as the starting material was a Baker product labeled Co_2O_3. On analysis by electrolysis this proved to be nonuniform with a cobalt content consistently higher than the theoretical value for Co_2O_3. The only stable oxide of cobalt above 1000° is reported to be CoO.[11–13] Batches of CoO were made by heating the Baker oxide to constant weight at 1100°. To prepare the sulfides, a given weight of CoO was treated in a stream of hydrogen sulfide at 600° until, from the increase in weight, it was determined that an excess of sulfur was present. The excess of sulfur was removed by heating the sample *in vacuo*.

Johnson-Matthey and Co. cobalt, estimated to be better than 99.9% purity, and Fisher sublimed sulfur were used in the direct combination method. Carefully weighed portions of the two elements were sealed in evacuated Vycor tubes. The reaction was initiated with a burner flame. After this treatment the samples richer in sulfur than CoS had unreacted sulfur which was taken up only after prolonged heating at 500°. Each sample, after the reaction was apparently complete, was ground and reheated at 700° for 48 hr. Finally the samples were again ground and tempered at temperatures selected with the aid of Rosenqvist's phase diagram.

(C) Analysis of Samples.—The cobalt content of most of the samples was checked either by the standard electrodeposition method or by roasting. For the roasting method, a study was made of the thermal stability of the various oxides of cobalt. The decomposition of the commercial product labeled Co_2O_3 did not begin until above 500°. Co_3O_4 was stable between 700 and 900° with a slight loss in weight as the temperature increased. Above 1000°, CoO was the stable form with no apparent weight loss up to 1100°. These results are in general agreement with those noted in the literature with one exception. The reported decomposition temperature of Co_2O_3 is below 300°.

Analyses were performed by heating the sulfides in a gentle stream of air at temperatures which were slowly increased until the evolution of sulfur dioxide had ceased. The samples were further heated at 1100° until constant weight was attained. Quick cooling of the resulting CoO was necessary to prevent formation of Co_3O_4.

In all cases the analytical results agreed to within one part per thousand with those calculated from the initial elemental weights.

(D) X-Ray Diffraction Patterns.—X-Ray powder patterns were taken of most of the samples using a North American Philips diffractometer with an iron target tube.

Results

Representative gram susceptibility *vs.* temperature plots of the sulfides are shown in Figures 1 and 2. From these figures, isotherms of susceptibility *vs.* composition at selected temperatures are plotted in Figures 3, 4, and 5.

Discussion

For a simple mixture the gram susceptibility should vary in a linear fashion with composition, ranging from one component of the mixture to the other. Within a solid solution the variation of susceptibility with com-

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[1] Assisted by grants from the National Science Foundation and the Robert A. Welch Foundation.

[2] (a) T. Rosenqvist, *J. Iron Steel Inst.*, **176**, 37 (1954); (b) V. G. Kuznetsov, A. A. Eliseev, Z. S. Shpak, K. K. Palkina, M. A. Sokolova, and A. V. Dmitriev, *Voprosy Met. Fiz. Poluprovod., Akad. Nauk SSSR, Trudy 4-go Soveshchaniya*, 159 (1961).

[3] H. Haraldsen, *Z. anorg. allgem. Chem.*, **224**, 85 (1935).

[4] R. Benoit, *J. chim. phys.*, **52**, 119 (1955).

[5] B. C. Guha, *Nature*, **155**, 364 (1945).

[6] H. Haraldsen and W. Klemm, *Z. anorg. allgem. Chem.*, **223**, 409 (1935).

[7] L. Néel and R. Benoit, *Compt. rend.*, **237**, 444 (1953).

[8] A. Serres, *J. phys. radium*, **14**, 689 (1953).

[9] F. K. Lotgering, *Philips Res. Rept.*, **11**, 337 (1956).

[10] J. J. Banewicz, R. F. Heidelberg, and R. Lindsay, *Phys. Rev.*, **117**, 736 (1960).

[11] G. Valensi, *Metaux Corrosions*, **25**, 283 (1950).

[12] T. Ando and R. Umemoto, *Bull. Osaka Ind. Res. Inst.*, **2**, 89 (1951).

[13] T. M. Ovchinnikova, E. S. Ioffe, and A. L. Rotinyan, *Dokl. Akad. Nauk SSSR*, **100**, 469 (1955).

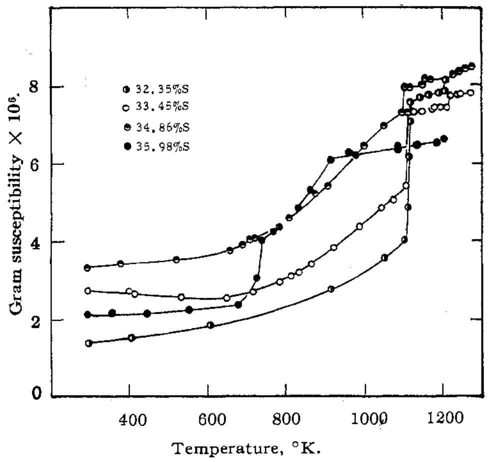

Figure 1.—Gram susceptibilities as a function of temperature of some sulfides of cobalt.

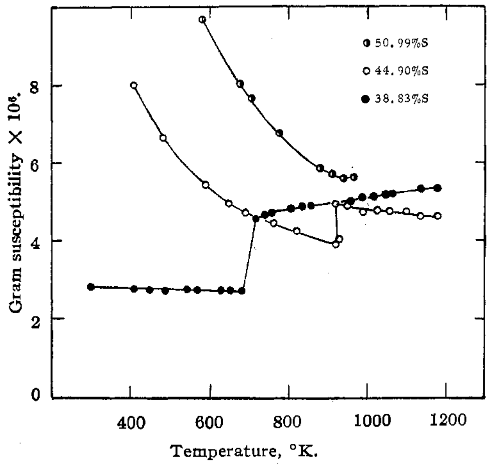

Figure 2.—Gram susceptibilities as a function of temperature of some sulfides of cobalt.

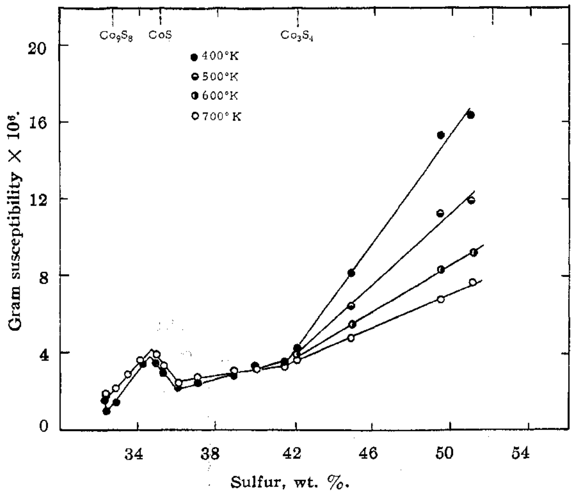

Figure 3.—Susceptibility isotherms in the cobalt–sulfur system at 400, 500, 600, and 700°K.

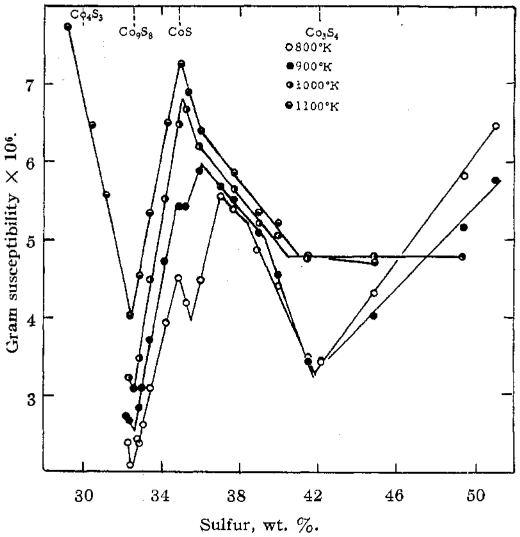

Figure 4.—Susceptibility isotherms in the cobalt–sulfur system at 800, 900, 1000, and 1100°K.

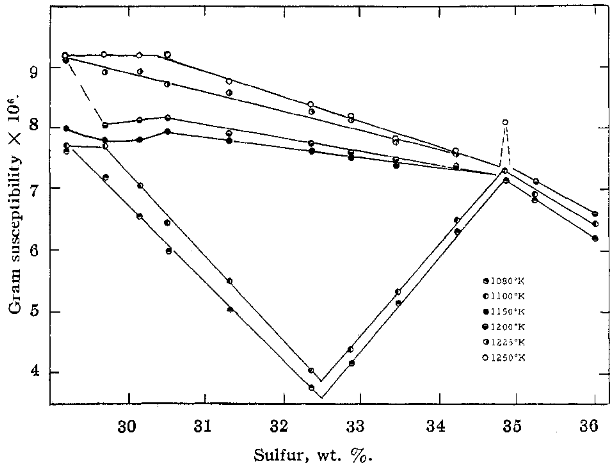

Figure 5.—Susceptibility isotherms in the cobalt–sulfur system at higher temperatures.

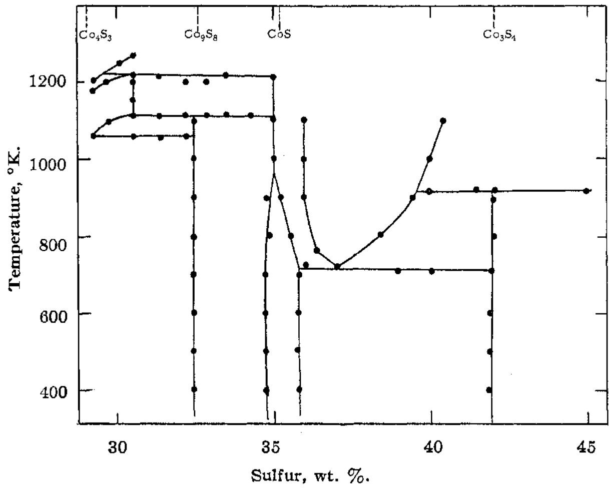

Figure 6.—Phase diagram for the cobalt–sulfur system based on magnetic susceptibilities.

position can be either linear or more complex. The abrupt changes of slope in the isothermal plots are ordinarily characteristic of either compounds or the boundaries of solid solution regions. The phase diagram shown in Figure 6 has been constructed from the isotherms in Figures 3, 4, and 5 together with additional isotherms not shown. For comparison an excellent compilation of previously reported data is given by Hansen.[14]

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[14] M. Hansen and K. Anderko, "Constitution of Binary Alloys," 2nd Ed., McGraw-Hill Book Co., New York, N. Y., 1958, p. 497.

(A) Discussion of Individual Phases. (1) Co_4S_3.—This phase has a lower temperature limit of about 1065°K. at 29.2% S rising to about 1106°K. at 30.6% S. The low sulfur limit was not observed; the upper sulfur limit appears to be around 30.6% S and independent of temperature. The susceptibility is approximately independent of composition but rises slightly with temperature from 7.6 to 8.4×10^{-6} cm.^{3}/g.$^{-1}$. The phase has an incongruent melting point at around 1206°K. and 30.6% S. The melt has a susceptibility of 9.2×10^{-6} cm.^{3}/g.$^{-1}$. All samples in this composition region were ferromagnetic below about 1070°K. The room-temperature X-ray diffraction patterns of samples in this region showed Co_9S_8 with some weak cobalt metal reflections.

(2) **Co_9S_8** has a positive susceptibility which increases with temperature from a value of 1.0×10^{-6} at 300°K. to 4.0×10^{-6} at about 1106°K. This substance is probably an antiferromagnetic below its Néel temperature. All samples in this region showed a field dependence of susceptibility, but only values corrected by extrapolation to infinite field strength are reported. Lotgering[9] has determined the magnetic susceptibility of Co_9S_8 from 150 to 300°K. and reports it to follow a Curie–Weiss behavior. Therefore there is a gross discrepancy between Lotgering's results and those reported in this paper. If the temperature of samples with compositions close to Co_9S_8 is lowered suddenly from above 1110°K. to room temperature, apparently sufficient quantities of the decomposition products of the peritectic melting of Co_9S_8 are frozen in and the susceptibilities are drastically different from the equilibrium values. In this case an apparently antiferromagnetic behavior is observed with a Néel temperature close to 300°K. and a Curie–Weiss behavior above this temperature. Treatment of the sample for prolonged periods of time at intermediate temperatures results in a gradual lowering of the susceptibility. Data shown here are on samples tempered at 350° for 1 month. The X-ray diffraction pattern of Co_9S_8 gave a cubic structure consistent with that reported by Lundqvist and Westgren[15] and Kuznetsov.[2b] The value of a found was 9.928 ± 0.004 Å.

(3) **CoS.**—There are two regions to be considered. One is an extensive solid solution region previously reported in the literature with a eutectoid decomposition temperature of 710°K. The other is a narrower region around CoS.

The larger solid solution region is the one previously reported by Rosenqvist[2a] and others. At 800°K. it appears in a narrow range from 37.0 to 38.3% S. As the temperature increases its lower sulfur limit is 35.9% at 900°K., 1000°K., and 1100°K. The sulfur-rich limit is 39.5% at 900°K., 40.0% at 1000°K., and 40.6% at 1100°K. The gram susceptibility in this region tends to increase very slightly with temperature at any composition, but drops rapidly with sulfur content from around 8×10^{-6} to below 5×10^{-6}.

The cobalt-rich side of this solid solution region has essentially the same boundaries as those reported by Rosenqvist. The sulfur-rich side is in good agreement at 800 and 900°K. but extends to somewhat higher compositions than those reported by Rosenqvist or Kuznetsov above 900°K.

The narrower region is perplexing. From the susceptibility isotherm a solid solution extending from 34.8 to 35.7% S at lower temperatures is suggested. According to Rosenqvist below 700°K., CoS should be a mixture of Co_9S_8 and Co_3S_4. In agreement with this, the only reflections observed in the X-ray diffraction patterns were those of Co_9S_8 and Co_3S_4 with no shift in lattice parameters to indicate solid solution. However, the sharp "break" in susceptibility at about 700°K., when the large solid solution region first becomes stable, is noted only for these samples with sulfur content in excess of 35.7%. No thermal hysteresis or any indication of lack of equilibrium was observed in any of the samples, even those containing less than 35.7% S.

Similar anomalies have been found in other systems, for example in the titanium–oxygen work of Ehrlich, as noted by Selwood.[16] Selwood has suggested that in this case the results are due to a strongly antiferromagnetic Ti_2O_3 diluted by a diamagnetic, but not isomorphous, TiO_2. Perhaps the behavior in the vicinity of CoS is due to the magnetic dilution of antiferromagnetic Co_9S_8 by temperature-independent paramagnetic Co_3S_4.

(4) **Co_3S_4** is a phase with a narrow homogeneity range. Co_3S_4 has a temperature-independent paramagnetism of 3.4×10^{-6}. The slight increase in susceptibility with decreasing temperature is probably due to extremely small amounts of ferromagnetic CoS_2. Co_3S_4 decomposes at 914°K. Lotgering has also reported on the susceptibility of Co_3S_4, indicating it to be paramagnetic. The susceptibilities of samples with sulfur content greater than that of Co_3S_4 were found by us to show a variation with temperature, particularly at lower temperatures. As the sulfur content diminishes, so also does the magnitude of the variation of susceptibility with temperature. Below $Co_3S_{3.9}$ there is no appreciable temperature dependence. While still present in $Co_3S_{4.0}$, it is thought that the effect is due to traces of CoS_2. This is borne out by the isotherms shown in Figure 5. Therefore, the statement that Co_3S_4 is temperature-independent paramagnetic in behavior is made. The X-ray diffraction pattern of Co_3S_4 was in good agreement with that previously reported with a value of a equal to 9.391 ± 0.004 Å.[14]

(5) **CoS_2.**—The diffraction patterns of the samples containing more sulfur than Co_3S_4 showed them to be mixtures of Co_3S_4 and CoS_2. The pattern for CoS_2 agreed with that of Lundqvist and Westgren with a value of a of 5.527 ± 0.005 Å.

Although pure CoS_2 could not be prepared even after prolonged treatment of samples with excess sulfur at

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(15) D. Lundqvist and A. Westgren, *Z. anorg. allgem. Chem.*, **239**, 85 (1938).

(16) P. W. Selwood, "Magnetochemistry," 2nd Ed., p. 342, Interscience Publishers, New York, N. Y., 1956.

TABLE I

Temp., °K.	150	200	300	400	500	600
Gram susceptibility $\times 10^6$	225	69.7	31.2	18.2	13.2	9.9
Temp., °K.	700	800	900	1000	1100	
Gram susceptibility $\times 10^6$	8.2	6.71	5.75	4.87	4.36	

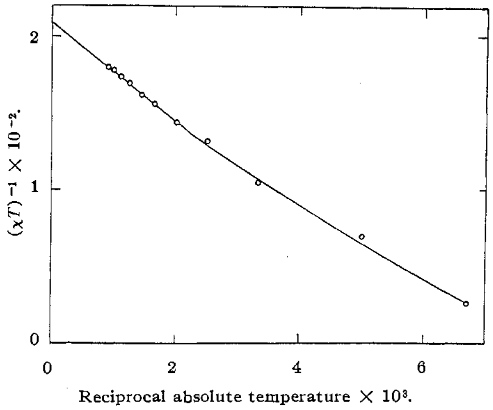

Figure 7.—Reciprocal of the product of gram susceptibility and absolute temperature for CoS_2 plotted as a function of reciprocal absolute temperature.

various temperatures, the susceptibility of the phase was calculated by extrapolation of isotherms similar to those in Figures 3 and 4 to the composition corresponding to CoS_2. The values obtained are listed in Table I.

Measurements in this composition region were made down to liquid nitrogen temperatures and the CoS_2 was found to be ferromagnetic with a Curie temperature of 116°K., in fair agreement with the 110°K. reported previously.[7]

TABLE II

TRANSITION TEMPERATURES IN THE COBALT–SULFUR SYSTEM

Transition	No. of observations	Transition temp., °K. This work	Hansen	Kuznetsov
Co_9S_8 decomposes	8	1106 ± 3	1106, 1108	1103
Co_4S_3 eutectoid	3	1065 ± 5	1053	1058
Co_4S_3 peritectic	8	1206 ± 6	1203, 1205	1208
Co_1S_1 eutectoid	3	710 ± 10	About 733	748
Co_3S_4 decomposes	4	914 ± 2	About 898	

In Figure 7, the reciprocal of the product of the gram susceptibility and the absolute temperature, $(\chi T)^{-1}$, is plotted against the reciprocal absolute temperature, T^{-1}. Danielian[17] has recently suggested that a graph of this kind is more advantageous than the usual χ^{-1} *vs.* T plot for the determination of the Curie constant. The Curie constant, obtained as the reciprocal of the value of the intercept at T^{-1} equal to zero, is 0.59 on a molar basis for CoS_2. The gram susceptibilities used in Figure 7 were corrected for the diamagnetic contributions of the constituent ions by the addition of 0.68×10^{-6}. The Curie constant gives a value of the magnetic moment of 2.17 B.M. compared with the 1.85 found by Néel and Benoit. This magnetic moment corresponds to that of one unpaired electron with a partially quenched orbital contribution.

From the linear portion of Figure 7 at high temperatures the Weiss constant is 153°. Néel and Benoit found 161° for the Weiss constant. The deviation from linearity observed at lower temperatures signals the breakdown of the model taking into account nearest neighbor interactions only.

(B) **Transition Temperatures.**—The various transition temperatures observed in this work, compared with values compiled by Hansen and those of Kuznetsov, are shown in Table II.

[17] A. Danielian, *Proc. Phys. Soc.* (London), **80**, 981 (1962).

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Formation of a Monobromo Complex of Nickel(II) in 2-Methoxyethanol

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The formation of a monobromo complex of nickel(II) in 2-methoxyethanol solution has been demonstrated by a spectrophotometric study. The absorption spectrum of the complex indicates that it is a solvated, octahedral species of the type $Ni(solv)_5Br^+$.

Introduction

Studies of halide complexes of nickel(II) in organic solvents have shown that the formation of complexes with up to four coordinated halides can occur, the lower complexes being octahedral and the higher complexes tetrahedral. The higher, tetrahedral complexes have been well-characterized,[1-4] but the picture with respect to the lower complexes is still not clear.

A number of workers have obtained evidence for the possible formation of an octahedral monohalo complex of nickel(II) in organic solvents.[5-10] The situation is

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[1] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

[2] C. Furlani and G. Morpurgo, *Z. physik. Chem.*, **28**, 93 (1961).

[3] D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

[4] D. A. Fine, *Inorg. Chem.*, **4**, 345 (1965).

[5] S. A. Shchukarev and O. A. Lobaneva, *Dokl. Akad. Nauk SSSR*, **105**, 741 (1955).

[6] M. Baaz, V. Gutmann, G. Hampel, and J. R. Masaguer, *Monatsh.*, **93**, 1416 (1962).

[7] H. Hubacek, B. Stančić, and V. Gutmann, *ibid.*, **94**, 1118 (1963).

[8] I. V. Nelson and R. T. Iwamoto, *J. Electroanal. Chem.*, **6**, 234 (1963).

[9] T. Šramko, *Chem. Zvesti*, **17**, 725 (1963).

[10] C. P. Nash and M. S. Jenkins, *J. Phys. Chem.*, **68**, 356 (1964).