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Magnetic Properties of $CoAs_xS_{2-x}$*

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Magnetization and susceptibility measurements were made on polycrystalline powders of solid solutions of $CoAs_xS_{2-x}$ from 4.2 to 500°K and to 9.5 kOe. A ferromagnetic region is observed for at least the region $0 \leqslant x \leqslant 0.3$; the Curie temperature appears to be a linear function of composition, decreasing from a value of 122°K for $x = 0$ at a rate of 10°K per mol% As. The saturation magnetization decreases slightly from 40 emu/g for $x = 0$ to 38 emu/g for $x = 0.125$ and then decreases linearly at the rate of 4 emu/g per mol% As. The paramagnetic data indicate that the P^2_{eff} decreases linearly with increasing arsenic content, i.e., as $(1 - x)$ 4.5 μB^2. The Weiss constant decreases initially from 150°K for $x = 0$ to 85°K for $x = 0.30$ and then decreases to near zero for CoAsS. The magnetic properties of this system are compared with those of the systems $Co_{1-x}Fe_xS_2$ and $CoSe_xS_{2-x}$.

Introduction

The physical properties of transition metal compounds with the pyrite structure have been the subject of several recent studies. Of particular importance to this study is the effect of cation- and anion-substitution on the ferromagnetic properties of CoS_2. The magnetic and transport properties of CoS_2 have been attributed to a partially filled and isolated σ^* band, which is spontaneously magnetized at low temperatures (*1*, *2*). The interpretation of the properties reported for the system $CoAs_xS_{2-x}$ will be based on the existence of this narrow isolated antibonding band.

The cation-substituted system $Co_xFe_{1-x}S_2$ exhibited (metallic) ferromagnetism for $x \geqslant 0.05$ (*1*). The square of the effective paramagnetic moment P^2_{eff} increased linearly with cobalt concentration. The ferromagnetic moment was proportional to the cobalt concentration over the range $0 \leqslant x \leqslant 0.95$; a reduced moment was observed for larger values of x, resulting in a 10% reduction in the moment for pure CoS_2. The reduction in moment was hypothesized to be the result of an overlap of the spin-up and spin-down bands below the Fermi energy for x greater than 0.95. The Curie temperature did not exhibit a monotonic increase with cobalt substitution, but rather an unexplained maximum at $x = 0.80$.

The isoelectronic anion-substituted system $CoSe_xS_{2-x}$ exhibited ferromagnetism throughout only a small portion of the compositional region, i.e., $x \leqslant 0.25$; the remaining members of the series to $CoSe_2$ were apparently antiferromagnetic (*2*, *3*). However, recent neutron diffraction measurements have failed to indicate an antiferromagnetic ordering in $CoSe_2$ to 4.2°K (*4*). It was reported that the selenium substitution introduced strong next-nearest neighbor antiferromagnetic interactions (*5*). In the ferromagnetic region the Curie temperature (*2*) and Weiss constant (*3*) decreased linearly with composition. The paramagnetic moment remained practically constant throughout the entire region $0 \leqslant x \leqslant 2.0$ (*3*); however, the ferromagnetic moment remained constant at the reduced value of 0.88 μB only to $x = 0.22$, and then decreased very rapidly. This decrease in the ordered moment, in contrast to the constant paramagnetic moment, implies the onset of a complicated spin configuration, presumably leading to antiferromagnetism for $x \geqslant 0.30$. Although no clear Neel peak was observed in the susceptibility curves, anomalies were observed in the inverse susceptibility data (*2*), indicating the possibility of antiferromagnetism.

The study of the additional anion-substituted system $CoAs_xS_{2-x}$ was undertaken in order to help

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develop a unified picture of the magnetic interactions involved in substituted-CoS_2 systems. Since $CoAs_xS_{2-x}$ is isoelectronic with $Co_{1-x}Fe_xS_2$, the paramagnetic and ferromagnetic moments should behave similarly for the two systems; any differences would tend to illustrate the role of the anions in the determination of the spin structure. Since selenium and arsenic are neighbors in the periodic table, comparison of the behavior of these two systems should lead to a better understanding of the role of the anion in magnetic interactions.

Preparation of Materials

Polycrystalline samples of $CoAs_xS_{2-x}$ were prepared directly from the elements Co (99.999%), As (99.999%), and S (99.999%) (supplied by Atomergic Chemical Co., N.Y.) or by the reaction of CoS and additional sulfur and arsenic. The latter method resulted in more complete reaction and greater homogeneity of the products. Initially, the cobalt was reduced under an atmosphere of 15% H_2–85% Ar at 650°C for 4 hr. The sintered product was broken up into usable size pieces and then further reduced at 950°C for 5–10 hr; this resulted in little further sintering. The arsenic was heated in a vacuum at 190°C in order to sublime off any volatile oxide (As_2O_3). The sulfur was sifted and only pieces larger than 40 mesh were used; this facilitated handling and quantitative transfer. CoS was prepared from the elements in sealed evacuated silica tubes at 700–800°C and ground and annealed to ensure homogeneity.

The products were obtained first by heating the stoichiometric amounts of the starting materials in sealed evacuated silica tubes at 350°C to initiate reaction. The samples were reground and reheated for 1–2 weeks at 700–800°C in order to obtain complete reaction. This was determined by quenching the samples and examining the surface of the tubes with a 40× microscope. Unreacted arsenic and sulfur were observed as orange-red amorphous patches. Completely reacted samples were easier to obtain if the temperature gradient was less than 5°C across the length of the sample tube.

Samples that were observed to have reacted incompletely were heated further at 800°C until complete reaction was achieved. Single-phase products were ground in an agate mortar and pestle under dry nitrogen, outgassed at 100°C for $\frac{1}{2}$ hr, and then resealed in evacuated silica tubes for annealing at 800–850°C. Annealing periods ranged from 2 weeks to 2 months. Temperatures higher than 850°C resulted in decomposition of the product and attack of the silica.

Sample Characterization

X-Ray Diffraction

Powder diffraction patterns were obtained with a Norelco diffractometer with monochromated high intensity CuK_{α_1} radiation ($\lambda = 1.5405$ Å). All samples exhibited the cubic pyrite structure (space group *Pa*3). The K_α doublets were resolved clearly even prior to extensive annealing; such treatment of some of the higher arsenic-content samples did tend

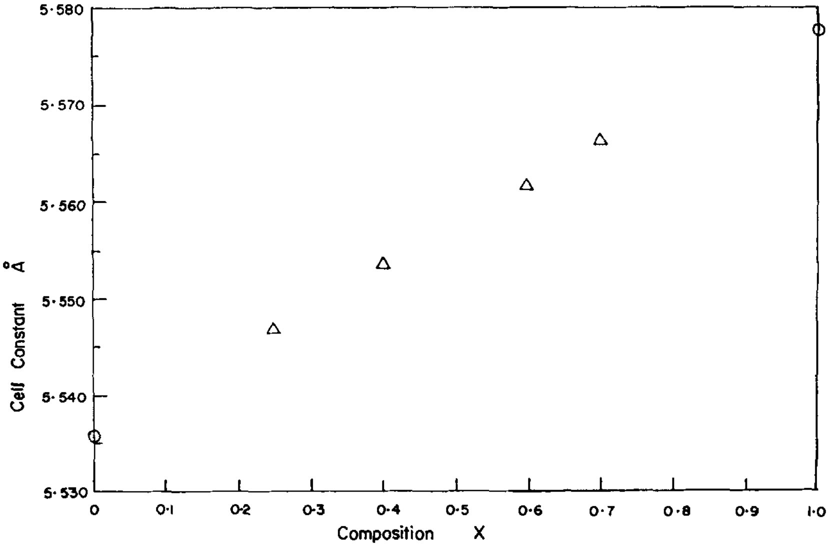

FIG. 1. Cell constant versus composition for $CoAs_xS_{2-x}$. (○) Crystals; (△) Powder.

to improve the sharpness of the diffraction peaks slightly. The cell constants were determined from Nelson–Riley plots (*6*) of high angle reflections ($90 < 2\theta < 140°$). The results of these determinations are shown in Fig. 1; there appears to be a very small, but linear, increase in the cell size with arsenic substitution.

Chemical Analysis

The samples were prepared in sealed evacuated silica tubes and, therefore, their compositions were undoubtedly those determined by the careful weighing out of the reactants. However, four random samples were chemically analyzed for cobalt and arsenic (sulfur by difference) as a check on the final compositions. Arsenic was separated from the cobalt in a solution of the sample by the precipitation of arsenic sulfide from an acid solution with thioacetamide. The cobalt was determined gravimetrically as a pyridine–thiocyanate complex and the arsenic was determined by the Volhard titration of silver from a silver arsenate precipitate (*7*). The results of these analyses are shown in Table I. The uncertainties in values of x are believed to be within 0.003. Similar accuracy in composition is assumed for other samples studied.

Magnetic Measurements

Magnetization measurements were made with a PAR FM-1 vibrating sample magnetometer (Princeton Applied Research Co., Princeton, New Jersey) in conjunction with a modular stainless steel dewar with variable temperature control (Andonian Associates) which is described elsewhere (*2*). Field dependent measurements were made with fields up to 9.5 kOe using a 9-in. Varian Magnet (V3400) (Varian Associates, Waltham, Mass.). The magnetometer was calibrated relative to a sphere of high purity nickel obtained from the Jarrell–Ash Company. Temperature dependent X–Y plots were taken automatically with the use of a solid state temperature controller (type MPRY Thermac Controller, R. I. Controls, Minneapolis, Minnesota) to program the temperature at a desired rate from 4.2 to 150°K, using both liquid helium and liquid nitrogen as refrigerants. The temperature was measured with two calibrated Cu-constantan thermocouples located on the outside of the sample chamber and within $\frac{1}{4}$ in. of the sample.

TABLE I

SUMMARY OF CHEMICAL ANALYSIS OF $CoAs_xS_{2-x}$

Nominal composition	% Co_{found}	% Co_{calcd}	% As_{found}	% As_{calcd}
$CoAs_{0.05}S_{1.95}$	46.70 ± .10	47.07	2.93 ± .02	2.99
$CoAs_{0.35}S_{1.65}$	42.51 ± .07	42.69	18.91 ± .04	18.99
$CoAs_{0.70}S_{1.30}$	38.32 ± .08	38.50	34.22 ± .09	34.26
$CoAs_{1.0}S_{1.0}$	35.34 ± .07	35.52	45.02 ± .11	45.16

Susceptibility measurements 77–300°K were made on a Faraday balance described elsewhere (*8*). A furnace was used to make measurements up to 650°K with the same balance arrangement. The furnace was calibrated and the temperature measured during each run with a Cu–constantan thermocouple. To supplement these measurements, susceptibilities were calculated from magnetization measurements made on the magnetometer in the range 4.2–77°K.

Results

Paramagnetic Phase

In Fig. 2 are shown representative inverse susceptibility curves for $CoAs_xS_{2-x}$. The data was taken at a field of 10 kG. There was negligible field-dependence of the susceptibility above 120°K. However, at lower temperatures there was a noticeable increase in the field-dependence, probably a result of short-range order as the Curie point is approached. The data in Fig. 2 were not corrected for this field dependence. However, the correction would have resulted in higher values of the inverse susceptibility and greater deviation from the straight line extrapolated from high temperatures. Linear behavior would still exist from 120 to 500°K.

The data shown in Fig. 2 were corrected for core diamagnetism with nominal values (*9*) of −12, −10, −9, and -38×10^{-6} cgs/mol for Co^{2+}, Co^{3+}, As^{3+}, and S^{2-}, respectively. The value for As^{3+} is probably a lower limit for As^{3-} but it was used regardless; the value of the S_2^{2-} unit is unknown, but the value of -76×10^{-6} cgs/mol was used. The application of the temperature independent correction eliminated the apparent "breaks" in the inverse susceptibility curves near 300–400°K. In particular, the break reported for CoS_2 (*1*, *10*) at 400°K was not observed in the corrected data. The diamagnetic correction decreased the slope of the inverse susceptibility curves above 300°K, resulting in higher observed values of P_{eff}^2 and lower values of the Weiss constant. For example, the uncorrected susceptibility for CoS_2 obtained in this study yielded 4.15 μB^2.

The values of P_{eff}^2 derived for $CoAs_xS_{2-x}$ are shown in Fig. 3. There is a linear decrease in P_{eff}^2

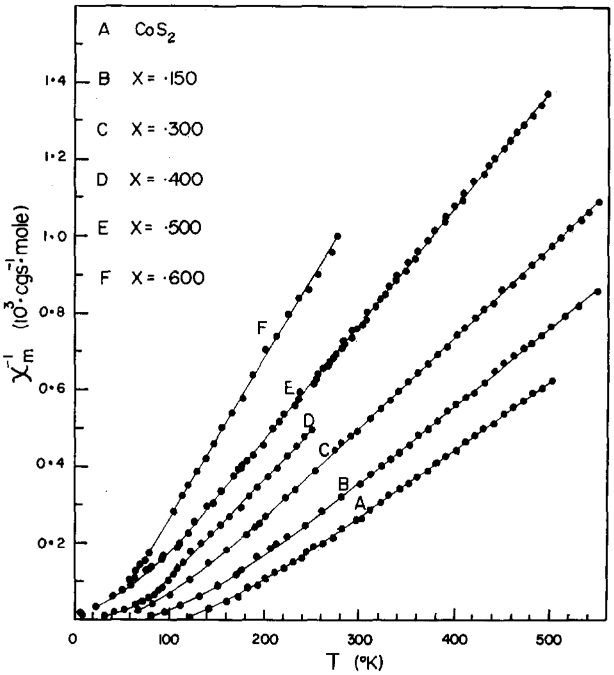

FIG. 2. Inverse molar susceptibility versus temperature for $CoAs_xS_{2-x}$.

with increased arsenic substitution, with the squared moment equal to 4.5 $(1-x)$ μB^2. The corresponding values of the Weiss constants are shown in Fig. 4. Initially there is an apparent linear decrease in θ with arsenic substitution; beyond $x = 0.4$ there is increased concave curvature resulting in a smooth decrease of θ. For the sample of CoAsS reported in Fig. 4, a small positive temperature dependent paramagnetism was observed and the θ value was nearly zero. The small moment measured was probably related to deviation from stoichiometry.

Temperature-dependent magnetization measurements indicated that a significant region of the system $CoAs_xS_{2-x}$ ordered ferromagnetically below 122°K. In general, the decrease in the magnetization near the Curie temperature was quite sharp; annealing the samples did tend to increase this sharpness slightly, and this was also evident in the X-ray patterns. However, no significant change was observed on prolonged annealing of the samples at 800°C.

Shown in Fig. 5 are the 100 Oe magnetization curves for the various solid solutions, which were

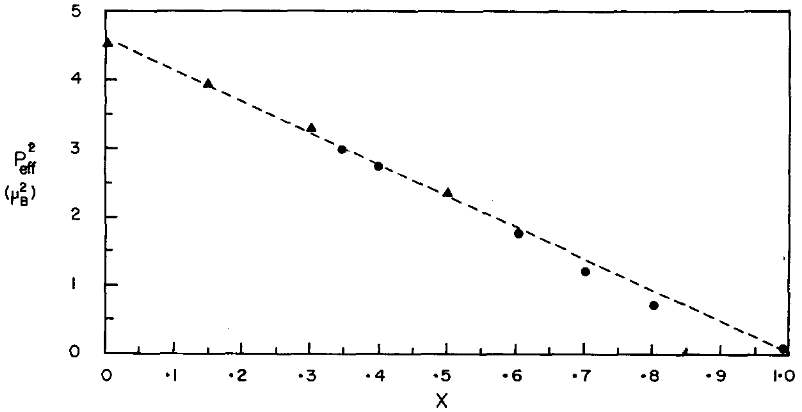

FIG. 3. P_{eff}^2 versus composition for $CoAs_xS_{2-x}$ from susceptibility data in $T_c \leqslant T \leqslant 500°K$ (▲); $77°K \leqslant T \leqslant 300°K$ (●).

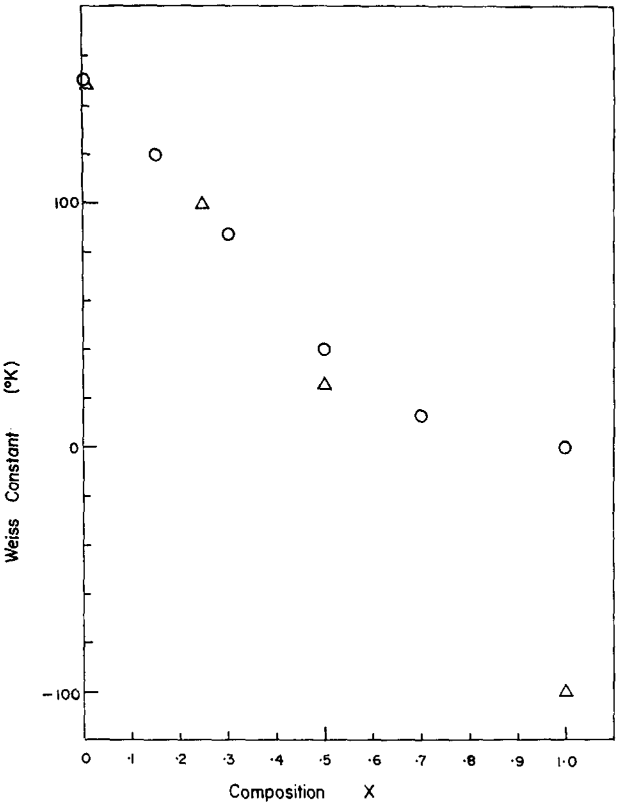

FIG. 4. Weiss constant versus composition for $CoAs_xS_{2-x}$, (○); $CoSe_xS_{2-x}$, (△).

used to determine the Curie temperatures from respective inflection points. There is an apparent broadening of the magnetization curves with arsenic substitution, particularly for values of x greater than 0.20. It is likely that this effect is caused by compositional inhomogeneities, which increase with greater arsenic substitution. X-Ray diffraction patterns of these compounds indicate the presence

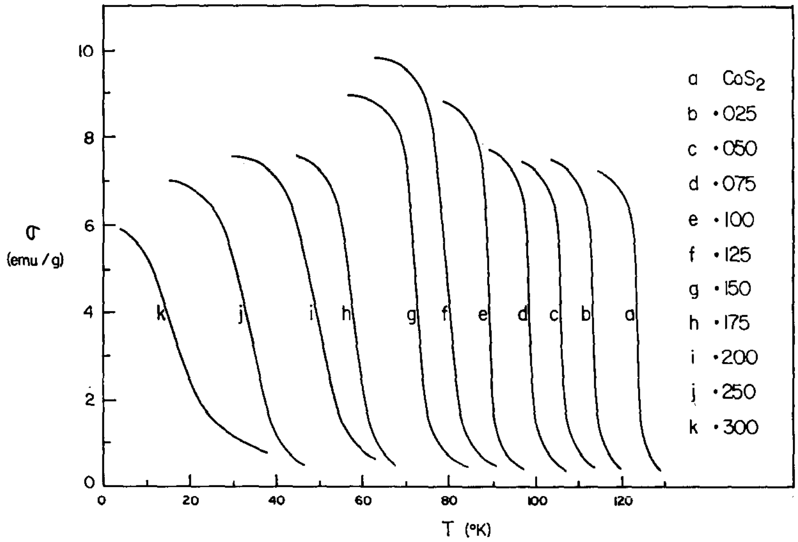

FIG. 5. $CoAs_xS_{2-x}$: magnetization versus temperature in applied field of 100 Oe.

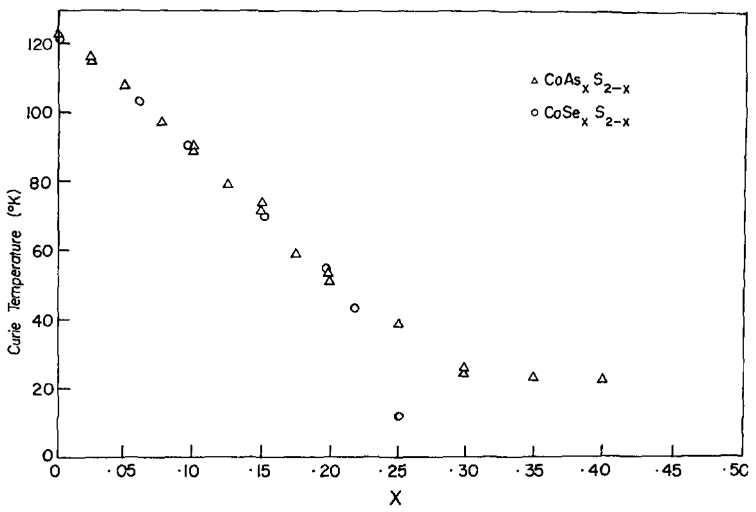

FIG. 6. Curie temperature versus composition for $CoAs_xS_{2-x}$ (△) and $CoSe_xS_{2-x}$ (○).

of a single phase; however, the small differences in the cell constants for members of this series with similar compositions probably would not result in appreciable line broadening of the peaks. For values of x greater than 0.30 there was no clear leveling-off of the low-field magnetization curves at 4.2°K, and therefore it was not possible to assign accurate values of the Curie temperatures for these compositions. It was also difficult to measure and control the temperature below 20°K, precluding accurate Curie temperature measurement. To assist in the Curie temperature determinations for the higher arsenic substituted samples, σ^2 versus H/σ plots were made, defining the Curie temperature as the isotherm passing through the origin (*11*).

The compositional dependence of the Curie temperature for $CoAs_xS_{2-x}$ for x less than 0.50 is shown in Fig. 6. Whereas the values for x greater than 0.30 can be questioned if the materials are not completely homogeneous, these values may still be compared with those obtained for members of the series $CoSe_xS_{2-x}$ and $Fe_xCo_{1-x}S_2$. There appears to be an initial linear decrease in the Curie temperature with arsenic substitution at the rate of 10°K/mol%. As to near $CoAs_{0.30}S_{1.70}$; beyond that composition, the decrease appears to be much slower, paralleling the behavior of the Weiss constant reported above.

Isothermal magnetization measurements as a function of applied field over a wide temperature

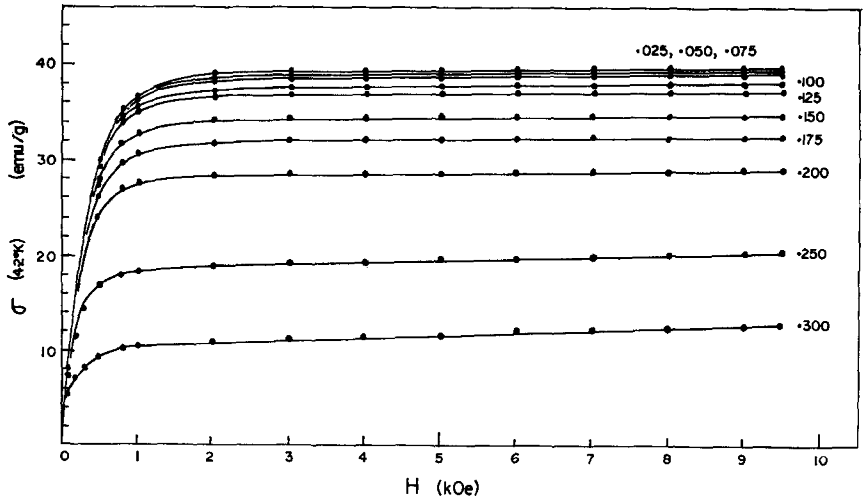

FIG. 7. $CoAs_xS_{2-x}$: magnetization versus field at 4.2°K.

range near the Curie temperature were made. There was no noticeable hysteresis; neither was there any unusual shape to the magnetization curve, such as metamagnetic behavior above the Curie temperature.

The field dependence at 4.2°K was determined for samples of $CoAs_xS_{2-x}$ and the results are shown in Fig. 7. No magnetic hysteresis was observed for any of the samples. Samples with compositions of x greater than 0.20 did not show saturation at 9.5 kOe, and extrapolation of $1/H$ curves to zero was used in order to obtain an estimate of the saturation magnetization. The magnetization measurements appeared insensitive to prolonged annealing of the samples.

The values of the saturation magnetization for $CoAs_xS_{2-x}$ are shown in Fig. 8. There is little change in the magnetization for the region $0 \leqslant x \leqslant 0.125$; further arsenic substitution results in a decrease of 6 emu g^{-1}/mol% As to $CoAs_{0.30}S_{1.70}$. Further arsenic substitution results in a much slower decrease in the moment, but the values plotted were obtained for samples that may not be completely homogeneous. A similar trend was observed for the Curie temperature.

Discussion

Paramagnetic Moment

The paramagnetic data are independent of any complicated magnetic ordering and, therefore, should be interpreted readily. The compositional dependence of P_{eff}^2 decreased linearly with composition. This indicated a squared moment of 4.5 μB^2 per formal divalent cobalt atom. Although this is in contrast to the 3.9 μB^2 per cobalt atom reported for the system $Co_xFe_{1-x}S_2$ (*1*), the discrepancy is believed to result from the diamagnetic corrections made in this study; this tends to increase the observed values of the paramagnetic moment (and decrease the values of the Weiss constants). It is therefore felt that both systems exhibit identical behavior of the paramagnetic moment, and that regardless of anion or cation substitution, this behavior reflects the formal decrease in the total number of electrons in the systems. The single unpaired electron of CoS_2 is reported to fill one-quarter of a narrow isolated antibonding band (*12*), and the similarities of the iron and arsenic substituted CoS_2 systems indicate that the electron population in this band is apparently independent of the manner in which the electron concentration is reduced in the band.

Weiss Constants

In addition to the plot of Weiss constants versus composition for the system $CoAs_xS_{2-x}$ shown in Fig. 4, the results of measurements on samples of $CoSe_xS_{2-x}$ made under identical experimental conditions with diamagnetic corrections (-48×10^{-6} cgs/mol for selenium) are included. Initially, there is identical behavior for the two systems, with linear decrease in the Weiss constants with anion substitution. There is apparently a continued linear decrease in θ_{Se} with negative values observed for values of x greater than 0.6; a value of approximately −100°K is observed for CoSeS. There were no negative Weiss constants for members of the

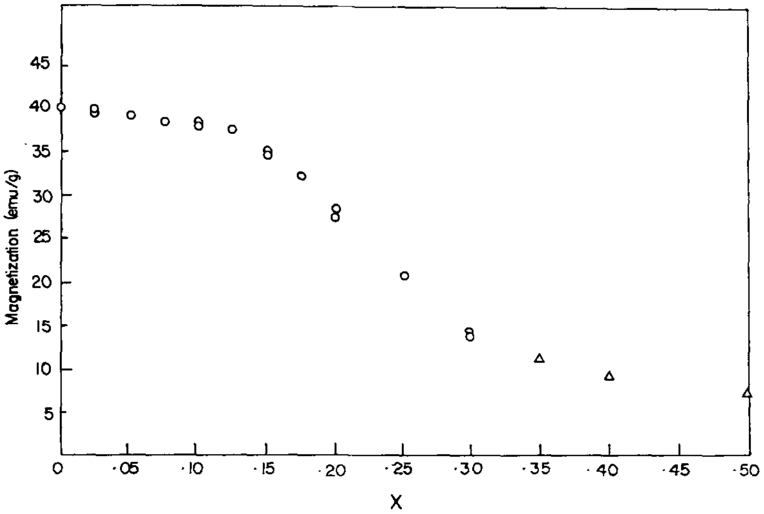

FIG. 8. Magnetization (4.2°K and infinite H) versus composition for $CoAs_xS_{2-x}$.

system $CoAs_xS_{2-x}$, and a value near zero was obtained for the composition close to CoAsS. In the selenium system, minima were observed in the inverse susceptibility curves indicating the likely presence of antiferromagnetism (*2*). Since such an anomaly was not observed for the system $CoAs_xS_{2-x}$, there is probably an absence of antiferromagnetic order in the arsenic system. The decrease in net ferromagnetic interactions, is observed by a decrease in the Weiss constant and Curie temperature for $CoAs_xS_{2-x}$ may result simply from the dilution of magnetic moments associated with divalent cobalt ions rather than the introduction of antiferromagnetic interactions resulting from arsenic substitution. However, the absence of long-range antiferromagnetic order does not preclude the possible existence of antiferromagnetic interactions.

For a qualitative understanding of the difference in microscopic interactions implied by identical initial-compositional dependence of the Weiss constants for $CoAs_xS_{2-x}$ and $CoSe_xS_{2-x}$, consider the molecular field definition of the Weiss constant: $\theta = \gamma C$, where C is the Curie constant and γ is the Weiss molecular field constant. C is independent of composition for $CoSe_xS_{2-x}$, but decreases linearly with composition as $(1-x)$ for $CoAs_xS_{2-x}$ as demonstrated by the squared paramagnetic moment. Therefore if both systems show identical behavior of the Weiss constant, then γ_{Se} must decrease much more rapidly with anion substitution than γ_{As}, consistent with the apparent introduction of antiferromagnetic interactions with selenium substitutions.

Ferromagnetic Moment

The interpretation of the behavior of the ferromagnetic moment is complicated by the apparent existence of an undetermined spin configuration. In the case of $Co_xFe_{1-x}S_2$ there was a reduced moment only over a small portion of the compositional range, i.e., $0.95 \leqslant x \leqslant 1.00$. It was postulated that the reduced moment was caused by an overlap of the spin-up and spin-down bands below the Fermi energy (*1*). Although the paramagnetic behavior of these two systems appears identical, the ferromagnetic moment for $CoAs_xS_{2-x}$ shown in Fig. 9 is lower than the expected Bohr magneton per divalent cobalt ion throughout most of the compositional region. If the explanation of band overlap, invoked for the reduced moment in $Co_xFe_{1-x}S_2$, is valid in the system $CoAs_xS_{2-x}$, there appears to be such band overlap below the Fermi energy for a large part of the ferromagnetic region.

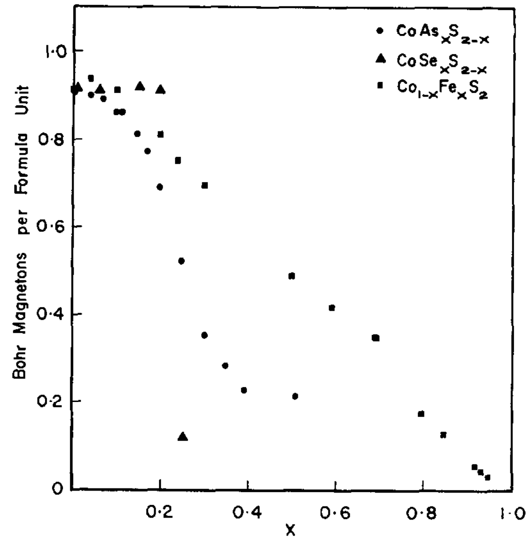

FIG. 9. Ferromagnetic moment versus composition for $CoAs_xS_{2-x}$(●), $CoSe_xS_{2-x}$(▲), $Co_{1-x}Fe_xS_2$(■).

To more clearly observe the reduction in moment, the ratio of observed to expected moment was calculated. The expected moment was defined as $(1-x)$ μB per formula unit, consistent with the observed compositional dependence of the paramagnetic moment. The results are shown in Fig. 10. Only at composition $x = 0.125$ is the full expected moment observed. Below this value of x there is a linear decrease in the ratio to the value of 0.88 observed for CoS_2. For arsenic concentrations

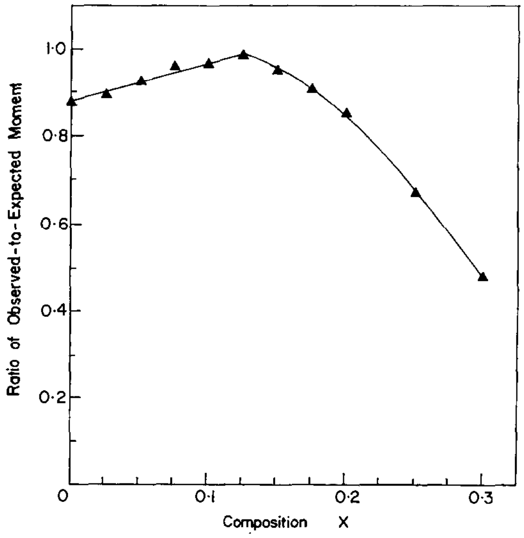

FIG. 10. Observed/expected moment versus composition for $CoAs_xS_{2-x}$.

higher than 0.125 there is a more rapid decrease in the observed:expected moment. It should be recalled that the determination of the saturation moment for x greater than 0.30 was uncertain; therefore, the ratios were not calculated for values greater than $x = 0.3$.

Contrary to the iron-substituted CoS_2 system, the arsenic-substituted system appears to exhibit spin band overlap below the Fermi energy throughout a greater part of the compositional region. For the system $CoSe_xS_{2-x}$ the moment remained constant at the reduced level of 0.88 μB until $x = 0.22$, indicating that increasing the selenium substitution does not affect appreciably the overlap of the spin-up spin-down bands. For larger Se substitution, the moment decreased very rapidly (*2*), much faster than that observed for $CoAs_xS_{2-x}$. It appears that for this system there is an apparent abrupt change from ferromagnetism to antiferromagnetism. Therefore, the rapid decrease of the ferromagnetic moment for values of $x > 0.2$ cannot be readily interpreted on the basis of increased overlap of the spin-up and spin-down bands. No such abrupt phase change occurs for the arsenic system. There is simply a smooth reduction in the ferromagnetic moment.

Ferromagnetic Curie Temperatures

The behavior of the Curie temperature for $CoAs_xS_{2-x}$ parallels the compositional dependence of the Weiss constant. There is initially a linear decrease in the Curie temperature at the rate of 10°K/mol% As to $x = 0.30$; further arsenic substitution probably results in a slower decline in the Curie temperature. The initial behavior of the Curie temperature is identical for $CoSe_xS_{2-x}$ and $CoAs_xS_{2-x}$ where linear behavior is observed. The net decrease in ferromagnetic interactions for the two systems results from two different phenomena: (1) introduction of antiferromagnetic interactions with selenium substitution, and (2) simple dilution of existing ferromagnetic interactions in the arsenic substitution, since no clear indication of antiferromagnetism exists in the latter system. The identical behavior of the Curie temperature (and Weiss constants) for the two systems is therefore likely to be coincidental.

Conclusions

Homogeneous polycrystalline samples of $CoAs_xS_{2-x}$ $(0 < x < 0.3)$ can be prepared by direct combination methods. Members of the series containing a higher arsenic content than 0.3 may not be homogeneous, although X-ray diffraction patterns do not show evidence of line broadening.

P^2_{eff} decreases linearly with an increase of the arsenic concentration; the paramagnetic data indicate that $CoAs_xS_{2-x}$ is isoelectronic with $Co_{1-x}Fe_xS_2$ .The moment associated with electrons in the isolated σ^* e_g band appears to be independent of whether cation or anion substitution is formally responsible for the reduction in total number of electrons in the system.

The rather complicated behavior of the ferromagnetic moment indicates that the arsenic substitution has a different effect on the type of low temperature ordering than either the corresponding iron or selenium substitution. Ferromagnetism is observed throughout a major portion of the compositional region, although the moment is reduced well below that expected from the value of the paramagnetic moment. The reduction in moment for $CoAs_xS_{2-x}$ is not so abrupt as for $CoSe_xS_{2-x}$; actually a ferromagnetic moment was observed for members of the arsenic substituted system beyond where the moment is presumed zero (at 0.30) for the selenium system.

The Weiss constants and Curie temperatures indicate a similar decrease in the net ferromagnetic interactions for both the arsenic and selenium systems for values of x less than 0.30. Additional substitution of arsenic results in little change in the ferromagnetic behavior, i.e., a slightly lower Curie temperature and moment, but not the apparent phase change presumed for $CoSe_xS_{2-x}$. Neither the "halt" or minimum in the inverse susceptibility curves nor magnetic hysteresis above the Curie temperatures which exist for $CoSe_xS_{2-x}$ were observed in the system $CoAs_xS_{2-x}$, further indicating an apparent lack of antiferromagnetic ordering in the latter system.

It is apparent that the precise magnetic structures, and the microscopic interactions responsible for them, cannot be uniquely determined from bulk magnetization and susceptibility measurements, and neutron diffraction experiments would be helpful in resolving this problem.

Acknowledgment

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