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Crystal Growth and Magnetic Properties of Compositions in the CoS_2:$CoSe_2$ System†

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The growth of relatively large single crystals of several compositions in the CoS_2:$CoSe_2$ system has been accomplished by chloride chemical transport. Further details of the low temperature ($4.2 \leqslant T \leqslant 300$°K) magnetic properties of members of the series were explored to complement previous studies by the present authors and other workers. In particular, the temperature dependence of the magnetization for $CoSe_{0.07}S_{1.93}$, $CoSe_{0.15}S_{1.85}$, and CoS_2 at several values of the applied magnetic field, and the field dependence of the magnetization at temperatures close to T_c for the same samples have been determined. The results strongly suggest first-order ferro- to paramagnetic transitions for the solid solutions. The magnetic properties of the entire system obtained in this study and by other workers are presented and compared. Peculiarities in the properties are also pointed out. Finally, a brief discussion of the bonding in the compounds, insofar as the magnetic properties allow inferences, is given.

Introduction

The transition metal dichalcogenides with the pyrite (FeS_2) structure have been the subject of numerous recent investigations. Interest in these compounds has been generated by the fact that they combine a simple structure (Fig. 1) with a wide variety of magnetic and electrical properties (*1*). CoS_2, a large range of the FeS_2:CoS_2 solid solution system, and a narrow range at the cobalt-rich end of the NiS_2:CoS_2 system are metallic ferromagnets (*2*). The metallic conduction has been attributed to a partially filled and isolated $\sigma^* e_g$ band which is also thought to be the spontaneously magnetized band (*3*). This particular combination of properties therefore renders these series well-suited for more detailed studies of itinerant *d*-electron magnetism (*2*, *4*).

The above-mentioned series of metallic ferromagnets can be further extended by way of members of the anion-substituted system, CoS_2:$CoSe_2$. This system has the advantages that the magnetic atom is not changed and, for all compositions, the number of electrons in the $\sigma^* e_g$ band should be the same on the basis of any reasonable bonding model. Furthermore, it might be expected that substitution of the more polarizable Se atom for S should lead to a greater degree of covalence, hence, increased bandwidth for the $\sigma^* e_g$ band. The magnetic properties themselves ought to reflect these effects.

Abbreviated reports of the magnetic properties of the CoS_2:$CoSe_2$ system have been given previously by Adachi and coworkers (*5*) and by the present authors (*6*). The high-temperature ($300 \leqslant T \leqslant 800$°K) properties of powder samples and some of the low-temperature properties have also been reported more recently by Adachi, Sato, and Takeda (*7*). The purpose of this paper is to present a more complete study of the low-temperature ($4.2 \leqslant T \leqslant 300$°K) properties of members of the series emphasizing single crystal studies and results not contained in the previous reports. Establishment of a complete

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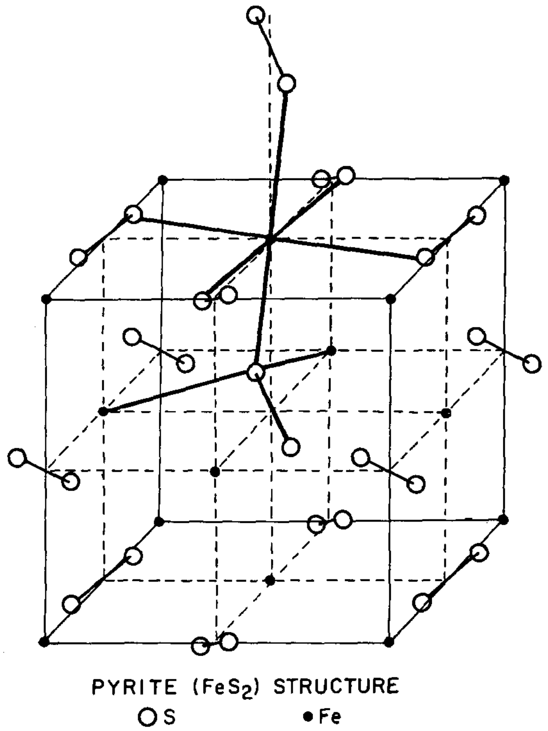

FIG. 1. Pyrite structure—the coordination of the metal and nonmetal atoms is indicated by the heavy black lines. The metal atoms and anion pairs occupy interpenetrating FCC networks as in NaCl. The axes of the anion pairs lie along [111] directions.

set of reliable experimental data is considered worthwhile in view of their likely theoretical significance.

Experimental

Single Crystal Preparation

Most of the measurements were carried out on single crystals prepared by chemical transport. Initial magnetic measurements on powders of some ferromagnetic solid solutions suggested that these preparations were not homogeneous even after relatively long annealing periods. Details of the magnetic properties, especially in the vicinity of T_c, were, therefore, obscured. The growth of small single crystals of CoS_2 using iodine as the transport agent had previously been demonstrated by Morris, Johnson and Wold (*10*). Bouchard (*11*) also obtained large single crystals of CoS_2 with chlorine as the transport agent. Preparation of sufficiently large single crystals of CoS_2, $CoSe_2$ and the solid solutions for magnetic measurements by chlorine transport was therefore attempted.

The transport reactions were carried out in a three zone furnace in silica tubes charged with chlorine gas and power samples of the desired composition. Preparation of the powder samples has previously been described (*6*). An initial 12-hr period of reverse transport was employed to aid in the removal of nucleating centers from the growth zone, thereby reducing the number of nuclei that develop. This leads to a smaller number of larger crystals. The growth zone was then gradually brought to the temperature required for the desired growth gradient. The reaction conditions and results are summarized in Table I.

Sample Characterization

X-Ray Characterization. The powder diffraction patterns of the samples were obtained with a Norelco diffractometer using monochromatic radiation from a high intensity Cu source ($\lambda K\alpha_1 = 1.5405$ Å). Several small crystals from each batch were finely ground and the resulting powders studied as collodion mounts. Cell constants were determined from high-angle ($100 \leqslant 2\theta \leqslant 118°$) reflections with NaCl as internal standard. The samples were found to be single-phase preparations with the pyrite structure

TABLE I

GROWTH CONDITIONS FOR TRANSPORT REACTIONS

Composition	Cl_2 Pressure (mmHg)	T Growth (°C)	T Charge (°C)	Time	Size Crystals
CoS_2	50	850	875	7 days	3 mm
$CoSe_{0.07}S_{1.93}$	50	740	800	2 weeks	5 mm
$CoSe_{0.15}S_{1.85}$	88	775	825	3 days	2 mm
$CoSe_{0.20}S_{1.80}$	125	775	825	6 days	2 mm
$CoSe_{0.22}S_{1.78}$	62	746	800	7 days	2 mm
$CoSe_{0.25}S_{1.75}$	50	775	800	6 days	1 mm
$CoSe_2$	50	790	825	3 days	2 mm

TABLE II

CELL PARAMETERS, a_0, FOR $CoSe_xS_{2-x}$

Nominal Composition	a_0($\pm$0.001 Å)	a_0 [Adachi et al. Ref. (*7*), Å]	Chemical Analysis %Co (calcd)	%Co (found)	x
CoS_2	5.535	5.534	47.89	47.87	—
$x = 0.075$	5.548	—	46.56	46.66	0.069
0.10	5.553	5.553	46.11	46.36	0.091
0.15	5.561	—	45.28	45.50	0.138
0.20	5.570	5.569	44.49	44.58	0.195
0.22	5.573	—	44.03	44.39	0.21
0.25	5.577	—	43.69	43.88	0.24
0.30[a]	5.587	—	42.98	43.09	0.29
0.60[a]	5.639	5.638			
1.00[a]	5.710	5.704			
1.50[a]	5.787	—			
2.00($CoSe_2$)	5.859	5.861	27.14	27.00	2.018

[a] Powder samples.

and to possess sharp reflections with the Kα doublets clearly resolved at high angles. Cell constants found for CoS_2 and $CoSe_2$ are in agreement with recently published values (*3*, *11*, *12*) and are shown in Table II along with those of the solid solutions. Cell parameters reported by Adachi et al. (*7*) are also shown in Table II for comparison.

Preliminary studies were carried out on powder samples annealed at 700°C. For these powder samples with broadened diffraction peaks the decrease of the magnetization in the vicinity of the transition temperatures was not abrupt in contrast to the samples with sharp reflections. The reflections of the crystals were sharp in all cases; a fact that is probably attributable to the mineralizing effect of the Cl_2 transport agent. This effect has been discussed by Schäfer (*13*) and in the present context amounts to a leveling of concentration gradients within and among growing crystals leading to homogeneous crystals that differ negligibly in composition. It is also noteworthy that the crystals differed only slightly in composition from that of the powder *feedstock* employed in the reactions.

Chemical Analysis. Samples were analyzed thermogravimetrically by conversion of the dichalcogenide to the monoxide following the phase diagram of Fisher and Tannhauser (*14*), or by reduction to the metal. Values of x for the samples examined are shown in Table II and are estimated to be uncertain to ± 0.01.

Magnetic Measurements. With the exception of $CoSe_2$ and $CoSe_{0.30}S_{1.70}$, the magnetic measurements were performed on single crystal specimens to assure sample homogeneity. The crystals weighed 12–30 mg. Paramagnetic data for CoS_2 were taken on powder samples. A vibrating sample magnetometer was used for most measurements. A stainless-steel dewar (Andonian Associates) utilizing a controllable flow of cryogenic fluid from the fluid well through a capillary into the sample chamber allowed variation and close control of the sample temperature. By matching the fluid flow with the output of the sample heater on the outer wall of the Be–Cu sample chamber, a desired temperature could be obtained. Two calibrated copper-constantan thermocouples attached to the outer wall of the sample chamber were used for temperature measurement. Measurements at 4.2 and 77°K were carried out with the sample in liquid helium and nitrogen, respectively. Intermediate temperatures were obtained by manual or automatic control of the heater input at a constant fluid flow rate.

Magnetic moments were determined with respect to samples of high purity nickel using the revised value ($\alpha_{\infty,0} = 58.57 \pm 0.03$ emu/g) of the saturation magnetization of Ni recently published by Danan et al. (*15*). A Faraday balance (*16*) was used for the susceptibility determinations of $CoSe_2$ and $CoSe_{0.25}S_{1.75}$.

Results

Ferromagnetic Samples

The magnetic properties observed for a 17.7-mg single crystal of CoS_2 are compared with the other reported values in Table III. The discrepancies

TABLE III

MAGNETIC PARAMETERS REPORTED FOR CoS_2

T_c(°K)	n_0(μB)	p_{eff}(μB)	θ(°K)	Comments	Ref.
122 ± 1	0.88 ± 0.02	2.18 ± 0.08	128 ± 6	crystal & powder	*a*
110	0.84	1.85	161		*b*
116	—	2.17	153		*c*
120	0.90	2.01 $T < 400°$ 1.81 $T < 400°$	—		*d*
118	0.89	1.84	193	crystal	*e*
130	0.96	1.80		crystal	*f*
124	0.84	2.13	220	powder	*g*
124	0.84	1.76	220	powder	*h*

[a] This work.

[b] R. BENOIT, *J. Chim. Phys.* **52**, 119 (1955).

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[f] S. MIYAHARA AND T. TERANISHI, *J. Appl. Phys.* **39**, 896 (1968).

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[h] K. ADACHI, K. SATO, AND M. TAKEDA, *J. Phys. Soc. Japan* **76**, 631 (1969).

among the values reported for T_c are most likely due to both differences in sample purity and inconsistency in the definition of T_c. Our value of 122°K has been obtained from the inflection point of a low-field (100 Oe) σ, T curve and is consistent with the results obtained for powder samples by the same method and reported elsewhere (*10*). Values between 118–124°K seem to be most representative. With the exception of the 0.96 μB reported by Miyahara and Teranishi (*17*), all values found for the ferromagnetic moment of CoS_2 show a reduction of from 10 to 16% from the spin-only moment of 1 μB/Co atom ($= g_{Co}S_{Co}\ \mu$B) that would be expected for divalent low-spin cobalt with $g = 2$. There is a rather large spread in the values of the paramagnetic parameters, p_{eff} and θ found for CoS_2. This is probably due to differences in the temperature intervals from which these parameters have been determined by different workers. Jarrett et al. (*2*) point out that a change in the slope of the inverse susceptibility of CoS_2 occurs at ~ 400°K. The single-crystal data of Miyahara et al. (*17*) also suggest this. Parameters determined from data above and below 400°K will, therefore, differ.

A summary of the magnetic properties of the solid solutions, $CoSe_xS_{2-x}$ obtained in this study is shown in Table IV along with the results of Adachi et al. (*7*). The results are also shown graphically in Fig. 2. Apart from the low values of $n_0(0.84)$ and T_c for $CoSe_{0.20}S_{1.80}$, the two sets of ferromagnetic data are reasonably consistent. The apparent discrepancies in the paramagnetic parameters arise

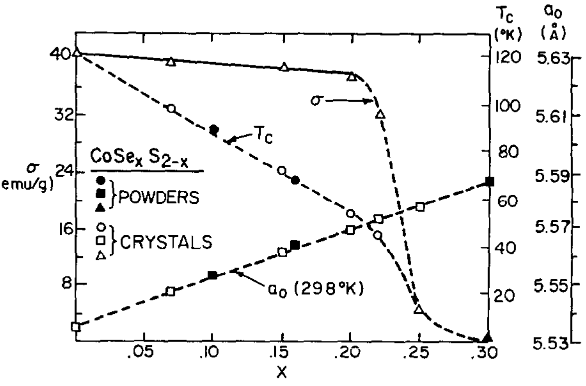

FIG. 2. $CoSe_xS_{2-x}$—compositional dependence of σ, T_c and a_0.

TABLE IV

MAGNETIC PARAMETERS FOR $CoSe_xS_{2-x}$

Composition	σ (±0.5 emu/g)	n_0 (μB/Co atom)	T_c (±1°K)	T_t[a] (°K)	θ (°K)	p_{eff} (μB/Co atom)
CoS_2	40.1	0.88(0.84)[b]	122(124)	—	128 ± 6 (220)	2.18 ± 0.08 (1.76)
$x = 0.07$	39.4	0.89	98.5			
0.10	—	(0.84)	91(94)		(195)	(1.78)
0.15	38.5	0.90	74			
0.16	—	—	69			
0.20	37.4	0.88(0.84)	54(42)		(140)	(1.72)
0.22	32.1	0.77	42	~85		
0.25	4.6	0.11	17	~85	62 ± 10	2.3 ± 0.1
0.30	—	—	—	~85	34 ± 10	2.35 ± 0.15
$CoSe_2$	—	—	—	30 – 60 (90)	−370 ± 40 (−160)	2.32 ± 0.04 (1.72)

[a] T_t refer to observed maxima in the susceptibilities, in some cases above lower transition temperatures.

[b] Values in brackets refer to those obtained by Adachi et al. (*7*).

from the fact that they were derived from different temperature intervals. This will be discussed further below.

A significant feature of the results is the fact that the ferromagnetic moment is insensitive to the Se concentration for the ferromagnetic samples. In fact, the 12% reduction in the spin-only moment observed for CoS_2 (see Table III) is also observed for all the ferromagnetic members of the $CoSe_xS_{2-x}$ series. Samples with $x = 0.22$ and $x = 0.25$ show much reduced moments (0.77 and 0.11, respectively). In this compositional range the moment changes rapidly with Se concentration so that slight sample inhomogeneity could drastically affect the results. The temperatures at which the observed low-temperature moments for these two samples disorder are shown in Table IV and Fig. 2 as T_c but it is not certain that these represent ferro- to paramagnetic transition temperatures.

For the ferromagnetic samples the decrease of the magnetization close to T_c is quite abrupt (Fig. 3) as has been found by Adachi et al. (*7*). For $x = 0.15$ and 0.20 (the latter not shown in Fig. 3), the temperature dependence of the magnetization approaches behavior more characteristic of a first-order transition than the usual second-order ferro- to paramagnetic transition. No large (1°K) hysteresis effects were found for either of these two samples, however.

The sharp transitions observed for the ferromagnets prompted measurements of the field dependence of the magnetization close to T_c. The results are shown for CoS_2, and $x = 0.07$ in Fig. 4. At temperatures just below T_c, σ varies with H in the manner typical of ferromagnets. Just above T_c, *metamagnetic-like* behavior is observed for $x = 0.07$ and 0.15, but not for CoS_2. For the former two samples above T_c and at low fields the magnetization varies approximately linearly with H and then saturates abruptly at a critical field which increases with increasing temperature. At ~ 5°K above T_c, only a marked curvature is observed in the σ,H curve. For $x = 0.07$ the temperature dependence of

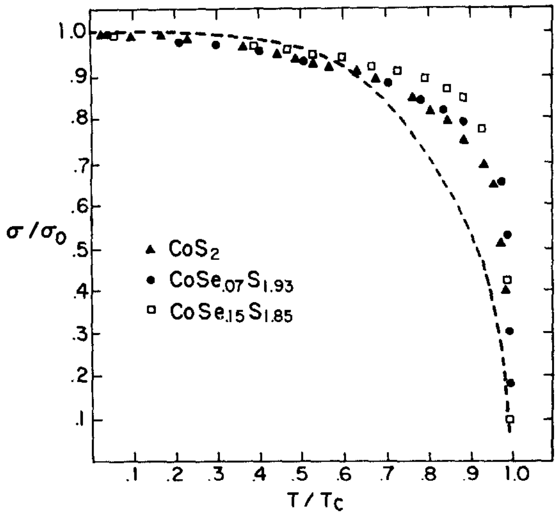

FIG. 3. σ/σ_0 vs T/T_c for single crystals. The dashed curve is the $S = 1/2$ Brillouin function.

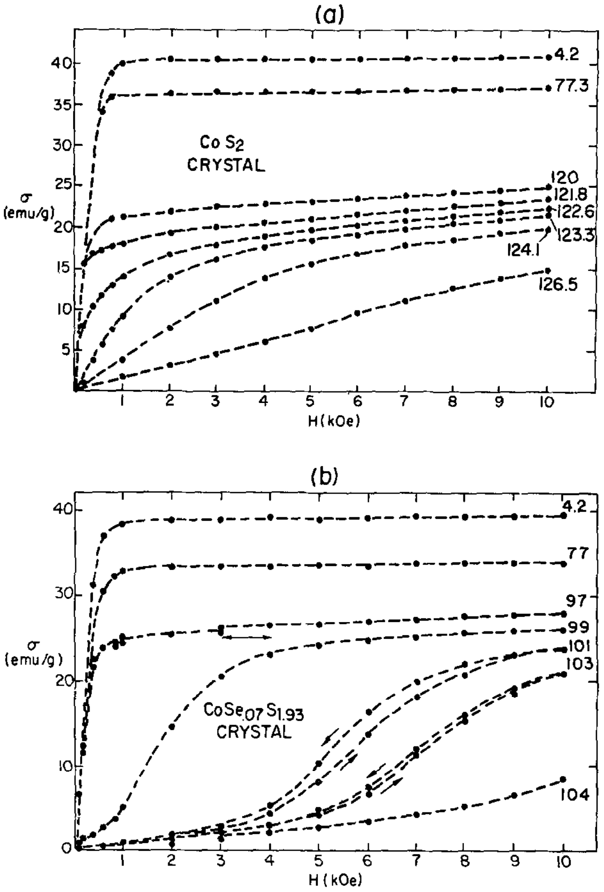

FIG. 4. σ vs H at the temperatures (°K) shown on the right: (a) CoS_2 (17.7-mg single crystal); (b) $CoSe_{0.07}S_{1.93}$ (26-mg single crystal).

the magnetization at different fields (*18*) reveals apparent Curie temperature shifts with the applied magnetic field—a result that is consistent with the isothermal magnetization curves shown in Fig. 4.

Susceptibility. The inverse susceptibility for samples of CoS_2 (powder), $CoSe_{0.25}S_{1.75}$, $CoSe_{0.30}S_{1.70}$ (powder) and $CoSe_2$ (powder) are shown in Fig. 5. The susceptibilities have not been corrected for diamagnetism. A maximum in the susceptibility of $CoSe_{0.25}S_{1.75}$ occurs at ~ 85°K. This behavior was also observed for $CoSe_{0.22}S_{1.78}$ as reported previously (*6*). $CoSe_{0.30}S_{1.70}$ also shows a maximum at the same temperature but this sample does not order ferromagnetically at or above 4.2°K. For the above compositions the reciprocal susceptibilities indicate positive θ values.

The susceptibility data for $CoSe_2$ (Fig. 6) show no obvious anomaly at the reported Néel temperature of 90°K; however, the increase of the susceptibility between this temperature and 4.2°K is unusually small. The reciprocal susceptibility suggests a Néel temperature between 30–60°K. The parameters θ and p_{eff} shown in Table III for $CoSe_2$ are in fair agreement with those reported by Bohm et al. (*12*) for (90° ⩽ T ⩽ 723°K). The parameters reported by Adachi et al. were determined over a higher temperature interval so that the results obtained here are not strictly comparable with theirs.

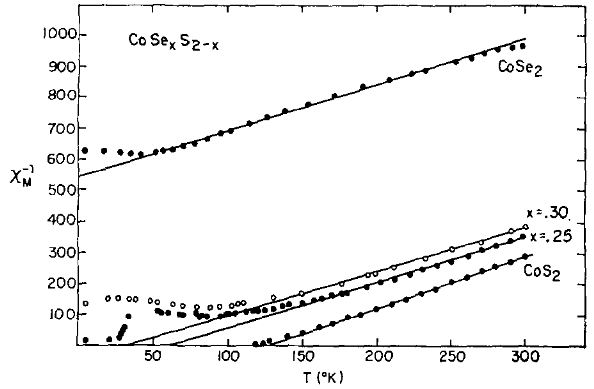

FIG. 5. $CoSe_xS_{2-x}$—inverse susceptibility, χ_M^{-1}, versus temperature.

Discussion

Low Temperature Results

For the compositional range, $0 \leqslant x \leqslant 0.20$, of the $CoSe_xS_{2-x}$ solid solution series, the moment at the cobalt atom, n_0, is constant at the value found for CoS_2, 0.88 ± 0.02 μB. This moment corresponds to approximately one unpaired electron on the Co atom, and allows the electronic configuration of the atom to be inferred. In the case of CoS_2, the moment

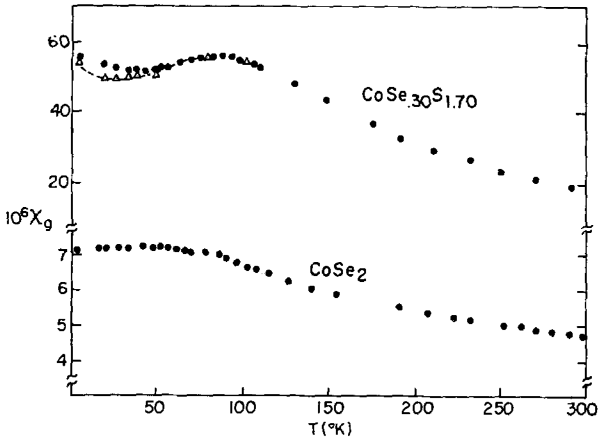

FIG. 6. $CoSe_2$ and $CoSe_{0.03}S_{1.70}$—χ_g versus temperature.

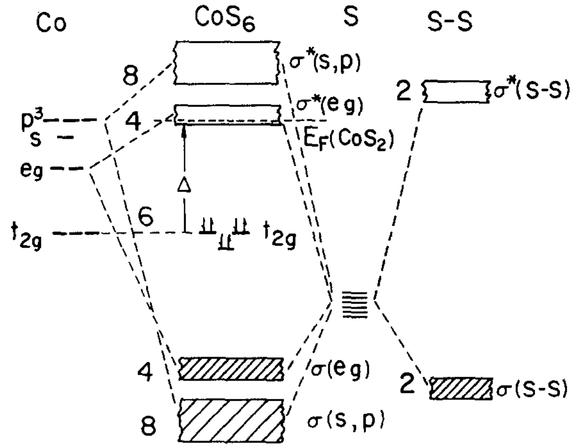

FIG. 7. Schematic molecular orbital, one-electron energy scheme for CoS_2. The scheme is also applicable to $CoSe_2$ and the solid solutions.

has previously been interpreted in terms of *low-spin* Co(II) (*1*). While this is a convenient rationalization, the ligand field description which it implies is not compatible with the known metallic conductivity of CoS_2 and the solid solutions. A more comprehensive model for CoS_2 and the sulfo- and selenopyrites in general in qualitative terms of molecular orbital theory (MOT) has been described by Bither, Bouchard, et al. (*3*). In this model, σ-d^2sp^3 orbitals on the metal atoms and sp^3 orbitals on the anions are assumed. The band scheme proposed by those authors is shown in Fig. 7. Each group VIA atom (e.g., S or Se) has 6 valence electrons that are shared among four tetrahedral bonds. Each S or Se atom contributes one electron to the S–S bond and the remaining five to the three M–S bonds. Since all the M–S bonds are equivalent, each S contributes 1 2/3 electrons to each of them. Cobalt is coordinated by six S atoms at the apices of an octahedron and these S atoms thus contribute a total of $6 \times 1\ 2/3 = 10$ electrons to the bonding in each octahedron. These ten electrons plus the two 4*s* electrons of the transition metal just fill the ground state $\sigma(s-p)$ and σe_g manifold of states. The remaining *d* electrons of the metal occupy the next-lowest available levels.

Since Co possesses seven *d* electrons, the one unpaired electron indicated by the magnetic moment of CoS_2 suggests that the t_{2g} levels are filled with 6 electrons (spin-paired). The unpaired electron therefore occupies the $\sigma^* e_g$ state. Selenium has the same number of valence electrons as S, hence the same electronic configuration may be expected for the solid solutions. This is supported by the observation of an identical ferromagnetic moment for the solid solutions, $0 \leqslant x \leqslant 0.20$. Furthermore, the metallic conduction of CoS_2 and the solid solutions is not inconsistent with the MOT description inasmuch as it makes a natural correspondence with band theory in the tight-binding limit. In the presence of a sufficiently strong covalent interaction the $\sigma^* e_g$ level will broaden into a band of crystalline states; the electrons are no longer bound to specific sites but are free to move through the crystal under an electric field. This concept has been used extensively by Goodenough (*19*, *20*) to explain the occurrence of metallic conductivity in oxides and sulfides. The only partially filled states for the series, $CoSe_xS_{2-x}$, are the $\sigma^* e_g$ states. This implies that in these materials the $\sigma^* e_g$ states constitute a band; the degree of covalence is large. The occurrence of an energy difference between the t_{2g} and $\sigma^* e_g$ states that is larger than the intraatomic exchange energy (low-spin configurations in ligand field parlance) for the solid solutions and CoS_2 is consistent with the presence of strong covalent interactions. The stronger the bonding between the cationic e_g orbitals and the anionic orbitals, the larger will be the splitting between the t_{2g} and $\sigma^* e_g$ states. Since the t_{2g} levels are essentially nonbonding, they are little affected in energy; hence, the energy difference between the t_{2g} and $\sigma^* e_g$ states (which corresponds to the ligand field splitting, or 10Dq) becomes larger with increasing covalence.

As discussed so far, the MOT model is generally consistent with the magnetic and electrical properties of the CoS_2–$CoSe_2$ system. However, a 12% deviation of the moment of CoS_2 from the predicted 1 μB has been observed. This deviation also persists for all the ferromagnetic solid solutions in the $CoS_2:CoSe_2$ system. These results cannot be explained solely on the basis of this simplified model. Discussions of these points have been given by Jarrett and coworkers (*2*, *21*).

Above $x = 0.20$, the moment falls below 0.88, then decreases extremely rapidly with increasing x, and extrapolates to zero close to $x = 0.25$. For compositions with $x = 0.22$ and 0.25, the observed moment (0.77 and 0.11, respectively) is lower than that of CoS_2, while the paramagnetic moment does not appear to be changing proportionately. If the observed moment is intrinsic to these compositions, and does not arise from ferromagnetic clusters due to slightly inhomogeneous preparations, then the collinear spin configurations of CoS_2 (and the samples with $x \leqslant 0.20$ by inference) is being drastically modified. The reduced moments for these samples suggest possible noncollinear configurations with net ferromagnetic components. The welldefined temperatures at which the ferromagnetic components disorder appear to suggest that the moment is intrinsic and not due to sample inhomogeneity.

The monotonic decrease of T_c with increasing Se concentration contrasts the behavior of the moment. The decrease in T_c reflects a decrease in the magnitude of the net ferromagnetic interaction, either as a result of the change in cell volume with Se substitution, or of a more direct influence of the Se atoms. From the negative value of the pressure dependence of the Curie temperature observed for CoS_2, both Menyuk et al. (*22*) and Adachi and coworkers (*7*, *8*) have concluded that the decrease of T_c with Se substitution is not due purely to a volume effect. The latter workers also observed antiferromagnetism in $CoSe_2$ and CoSeS. Hattori, Adachi and Nakano (*9*) explained the experimental results on the basis of ferromagnetic nearest neighbor and antiferromagnetic next-nearest neighbor interactions; the next-nearest neighbor interactions are assumed to increase with the Se concentration. The fast decrease of T_c, observed both in this study and by Adachi and coworkers, and the apparent development of antiferromagnetism in $CoSe_{0.30}S_{1.70}$ (see Fig. 6) with $\theta > 0$ clearly justify this assumption. According to Adachi et al. (*7*), T_N for the antiferromagnets is insensitive to the Se concentration ($T_N = 90°K$ for all the antiferromagnets). The susceptibility results for $CoSe_{0.25}S_{1.75}$, $CoSe_{0.30}S_{1.70}$, and $CoSe_2$ shown in Fig. 5 on the other hand suggest a slow decrease in T_N.

Increasing sharpness of the ferro- to paramagnetic transition with increasing Se concentration was observed and is illustrated in Fig. 3. The same effect was noted by Adachi and coworkers (*7*). Along with the magnetization data shown in Figs. 4 and 5, these data strongly suggest first-order transitions for the solid solutions. Hattori et al. (*9*) predict first-order transitions for certain ratios of the ferromagnetic first-neighbor and antiferromagnetic second-neighbor interactions; however, the details of their theoretical work have been questioned (*22*).

Susceptibilities

At $x = 0.30$ a distinct maximum (Fig. 6) in the susceptibility is suggestive of antiferromagnetism. At this composition no low temperature transition to ferromagnetism was observed, though there was an increase in the susceptibility at low temperatures. This susceptibility increase was sensitive to annealing but did not disappear after extensive annealing (one month at 800°C). On the other hand, the maximum in the susceptibility at 85°K was not sensitive to annealing. In fact, the relative magnitudes of the susceptibilities at 4.2 and 85°K increased slightly upon annealing the sample. The maximum may, therefore, be regarded as an equilibrium property of the material, and may be associated with an antiferromagnetic transition although the reciprocal susceptibility indicates a positive value of θ.

For $CoSe_2$, although θ is large and negative, the susceptibility does not allow precise identification of the Néel temperature. Small anomalies in χ and χ_M^{-1} probably indicate a transition temperature in the range 30–60°K. The neutron diffraction results of Adachi et al. (*7*) indicate an ordering temperature above 53°K. The value of θ/T_N for $CoSe_2$ is, therefore, large (~ 6). A similar value of θ/T_N has been found for $MnSe_2$ by Corliss and Hastings (*23*). Both $CoSe_2$ and $MnSe_2$ are also reported to have the same type of magnetic structure.

As mentioned previously, the inverse susceptibility of CoS_2 shows different slopes, hence different Curie–Weiss parameters, above and below 400°K (*3*). A Curie–Weiss approximation to the lower temperature region yields larger values of p_{eff} and smaller values of θ than for the high-temperature region. The susceptibility data of Adachi et al. [Fig. 3 of Ref. (*7*)] suggest similar behavior for the solid solutions and possibly for $CoSe_2$. The Curie–Weiss parameters deduced for this lower-temperature region (Fig. 6) are given in Table IV. Values of the effective paramagnetic moment and θ are larger and smaller, respectively, than those obtained by Adachi and coworkers for the higher temperature region. These paramagnetic moments also do not reflect the reduced moments found in the ferromagnetic state and as such serve to emphasize other peculiarities in the magnetic properties of this system.

Conclusion

Details of the magnetization were easily observable on homogeneous samples—a fact that illustrates the importance of minimizing the compositional fluctuations inherent in disordered solid solutions if the intrinsic properties are to be observed. The importance of mineralization processes and the value of single crystal studies are also emphasized.

Consistent with those of Adachi et al. (*7*), the results obtained in this study suggest that Se substitution introduces strong antiferromagnetic interactions between cobalt atoms. First-order ferro- to paramagnetic transitions for some of the solid solutions are suggested by both the temperature and field dependence of the magnetization in the neighborhood of T_c. Furthermore, compositions between $x = 0.20$ (ferromagnetic) and $x = 0.30$ (antiferromagnetic) appear to exhibit noncollinear magnetic structures.

A larger influence of the anion on the type of magnetic order which prevails is exhibited by this system. The exact role of the anion is not clear, however, since the observed properties cannot unambiguously separate the effects of volume changes, slight configurational changes and increased covalency (increased bandwidth) as Se is substituted for S. Nevertheless, the data do show clearly that the electronic configuration of the Co atom is not significantly changed across the series. What does change is the magnitude and/or signs of the magnetic interactions.

The magnetic properties of the $CoS_2:CoSe_2$ system do not reflect a simple monotonic increase in the strength of the ferromagnetic interaction with increasing covalence as has been observed for semiconducting systems (e.g., $CdCr_2S_4:CdCr_2Se_4$).

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