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# Preparation and Properties of Several Indium Thiospinels*

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Indium thiospinels of the type $AB_2X_4$ have been prepared by direct combination of the elements. Four of these compounds have the composition $MIn_2S_4$ (M = Mn, Fe, Co, Ni). Selenium has also been substituted into indium thiospinels of the type $MIn_2S_{4-x}Se_x$ (M = Mn, Fe, Ni and $0 \leqslant x \leqslant 1.0$). Electrical resistivity measurements, at room temperature, on pressed bars indicate that all of these compounds are semiconductors with resistivities greater than $10^5$ Ω cm. The moments obtained from paramagnetic measurements were found in many cases to be equivalent to the values calculated from the spin only moments of the paramagnetic ions. However, the observed paramagnetic moment is lower for $Mn^{+2}$ compounds and $CoIn_2S_4$ shows a larger moment than expected for $Co^{+2}$. Compounds of the type $MIn_2S_4$ (M = Mn, Fe, Co, Ni) and $MIn_2S_{4-x}Se_x$ (M = Mn, Fe, Ni) are paramagnetic down to 4.2°K. The magnetic interactions that occur in compounds of the series $MIn_2S_4$ (M = Mn, Fe, Co, Ni), $MIn_2S_{4-x}Se_x$ (M = Mn, Fe, Ni) are primarily antiferromagnetic with negative ($\theta$) Weiss constants. However, their magnetic properties cannot be interpreted by the simple exchange rules if nearest-neighbor interactions are dominant.

## Introduction

Hahn (*1*) first prepared a series of indium thiospinels by direct combination of the binary sulfides, and in 1961 Flahaut (*2*) reported the preparation of the thiospinel $CrIn_2S_4$. However, they were only concerned with the synthesis and structure determinations of these compounds. In 1967, Yagnik (*3*) and Eibschutz (*4*) studied the magnetic susceptibility and Mössbauer spectrum of $FeIn_2S_4$. They demonstrated that it was paramagnetic from room temperature to liquid-nitrogen temperature. The results of the Mössbauer studies indicate that iron has a formal valence state of II and occupies the octahedral site which is, however, trigonally distorted. From this work it can be concluded that $FeIn_2S_4$ is an inverse spinel.

Recently, Darcy (*5*) reported $MnInCrS_4$ to be a normal spinel ($Mn^{+2}$ are located on the A sites) and therefore direct Mn–Cr interactions, on the B sites, could not be studied. In addition, Robbins (*6*) prepared a series of compounds with the composition $Cd_{1-x}In_x[M_xCr_{2-x}]S_4$ (M = Co, Ni). He reported that the Curie temperature of $CdCr_2S_4$ is lowered when part of the $Cr^{+3}$ is replaced by either $Co^{+2}$ or $Ni^{+2}$. In addition, Robbins indicated that the introduction of $In^{+3}$ for $Cd^{+2}$ on the tetrahedral site affects the more distant neighbor interactions and this also contributes to the lowering of $T_c$.

It is apparent from this brief review of the literature that the magnetic properties of the indium thiospinels should be studied in more detail. It would be of considerable interest to compare the spin-only moments of the divalent ions ($M$), surrounded by sulfur ligands, with the moments reported for the same ions found on identical sites in oxide spinels. In addition, the magnetic properties of such compounds would be changed markedly by the partial or complete (if possible) substitution of sulfur by selenium. It has already been shown (*7, 8*) that such substitution increases the Curie temperature of the ferromagnetic spinels $CdCr_2S_4$ and $HgCr_2S_4$. Partial substitution of sulfur by selenium or tellurium has been reported in several other series. Pickardt (*9*) has studied the system $CdCr_2(S_{1-x}Se_x)_4$ ($1 > x > 0$); Riedel (*10*) reported on the systems $ZnCr_2(S_{1-x}Se_x)_4$ ($1 \geqslant x \geqslant 0$) and $ZnCr_2(Se_{1-x}Te_x)_4$ ($0.2 \geqslant x \geqslant 0$). It would, therefore, be most interesting to study the effect on the magnetic properties of the substitution of sulfur by selenium in the series of compounds $MIn_2S_4$.

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## Experimental

### Preparation of Materials

Compounds of the series $MIn_2S_4$ (M = Mn, Fe, Co, Ni) and $MIn_2S_{4-x}Se_x$ (M = Mn, Fe, Ni) were prepared by direct combination of stoichiometric amounts of high-purity elements (99.99%) or better. The reactants were carefully weighed out, transferred to silica tubes which were then evacuated to $2\mu$ Hg and sealed. The reactions were carried out at elevated temperatures by means of Hevi-Duty furnaces (type G-07-T). Four polycrystalline compounds of the type $MIn_2S_4$ were obtained as single phase products after three successive 48-hr heating periods; the products were ground between firings for 1 hr in an agate mortar under an atmosphere of dry nitrogen. The temperature required for the preparation of $FeIn_2S_4$, $CoIn_2S_4$, and $NiIn_2S_4$ was 800°C, whereas 1000°C was necessary in order to prepare pure $MnIn_2S_4$. For preparation of the series $MIn_2S_{4-x}Se_x$, a mixture of the elements was first heated at 600°C for 5 days followed by a second heat treatment at 800°C and then the product was annealed at 400°C for 4–15 days.

### X-Ray Analysis

X-Ray diffraction patterns were obtained from a Norelco diffractometer with monochromatic radiation (A.M.R. 202 focusing monochromator) and a high intensity copper source. The radiation used was $[\lambda(\mathrm{Cu}K\alpha_1) = 1.5405\ \text{Å}]$. For the selenium substituted compounds, in which the changes in cell parameters are of the order of 0.1 to 0.2 Å, a Guinier Camera (XDC Incentive Research and Development AB, Sweden) was used. With this instrument it was possible to obtain cell parameters with a precision of 0.001 Å; sodium chloride was used as an internal standard. Cell dimensions were refined by means of a Nelson–Riley plot (*11*). Cation distribution in these compounds was determined by comparison of the experimental intensities with the calculated intensities obtained for the 400, 422, 444, 642, and 840 reflections assuming both a normal and inverse configuration of the cations.

### Density Determination

Densities were obtained by a hydrostatic technique (*12*) using 1, 1, 2, 2-tetrachloroethane as the liquid at 25°C.

### Magnetic Measurements

Magnetic susceptibility measurements were obtained by means of a Faraday balance (*13*) over the temperature range 77–298°K. A vibrating sample magnetometer of the Foner type (Princeton Applied Research Model FM-1) was used to obtain data from 298°K to liquid helium (4.2°K); the susceptibility measurements were made with a field of 10 kOe. The data obtained from the two instruments coincided over the region of temperature overlap, viz. 77–298°K. The differences between the calculated (spin only) and experimental values of $P_{\mathrm{eff}}$ are given in Tables II and III.

### Electric Resistivity Measurements

Resistivity measurements were performed on pressed bars (98–99% of theoretical density) using a four-probe technique. Resistivity as a function of temperature was determined from liquid nitrogen (77°K) up to room temperature (298°K) for the sample $FeIn_2S_4$. The other compounds, because of their high resistivities, were measured only at room temperature.

## Results and Discussion

Compounds of the type $MIn_2S_4$ (M = Mn, Fe, Co, Ni) and $MIn_2S_{4-x}Se_x$ (M = Mn, Fe, Ni) have been obtained as single phase products. Compounds of the series $CoIn_2S_{4-x}Se_x$ could not be obtained as single phase material and, hence, were not included in this study. Table I indicates the cell parameters, average B–B distances and densities for all compounds prepared.

In the following sections, the magnetic and electrical properties of a series of related compounds are compared and discussed.

The magnetic properties for the $MIn_2S_4$ compounds are given in Fig. 1 and summarized in Table II.

It can be seen from Table II that the experimental value of $P_{\mathrm{eff}}$ for $FeIn_2S_4$ is in agreement with the calculated spin-only paramagnetic moments of the divalent ions obtained assuming an octahedral field and high-spin state. If $g = 2.2$ is used in place of the spin only $g = 2.0$, as has been observed experimentally by Gorter (*14*) in $NiFe_2O_4$, then $P_{\mathrm{eff}}(\mathrm{calcd}) = 3.11$, which is in good agreement with the observed value.

However, $CoIn_2S_4$ shows a large $P_{\mathrm{eff}}$ (4.78 $\mu$B) value compared to the calculated $P_{\mathrm{eff}}$ (3.86 $\mu$B) moment. Cossee (*15*) has reported similar values for other $Co^{+2}$ compounds, and he attributed this to be a result of incomplete quenching of the orbital angular momentum. The paramagnetic moment for $MnIn_2S_4$ is lower (5.68 $\mu$B) than the calculated value of 5.92 $\mu$B. The observed moment corresponds to

TABLE I

CRYSTALLOGRAPHIC AND DENSITY DATA FOR $MIn_2S_4$, $MInCrS_4$, AND $MIn_2S_{4-x}Se_x$ COMPOUNDS

| Compound | Cell edge (Å) | B–B (Å) | Theoretical density $D_x$ (g/cc) | Experimental density $D_m$ (g/cc) |
|---|---|---|---|---|
| $MnIn_2S_4$ | 10.72 ± 1[a] | 3.78 | 4.44 | 4.39 ± 5 |
| $FeIn_2S_4$ | 10.61 ± 1 | 3.75 | 4.59 | 4.49 ± 5 |
| $CoIn_2S_4$ | 10.58 ± 1 | 3.73 | 4.67 | 4.62 ± 5 |
| $NiIn_2S_4$ | 10.50 ± 1 | 3.71 | 4.78 | 4.71 ± 5 |
| $MnIn_2S_{3.8}Se_{0.2}$ | 10.746 ± 3[b] | 3.79 | 4.51 | 4.49 ± 5 |
| $MnIn_2S_{3.5}Se_{0.5}$ | 10.787 ± 3 | 3.81 | 4.61 | 4.55 ± 5 |
| $MnIn_2S_{3.0}Se_{1.0}$ | 10.830 ± 3 | 3.83 | 4.79 | 4.73 ± 5 |
| $FeIn_2S_{3.8}Se_{0.2}$ | 10.643 ± 3 | 3.76 | 4.65 | 4.64 ± 5 |
| $FeIn_2S_{3.5}Se_{0.5}$ | 10.670 ± 3 | 3.77 | 4.78 | 4.70 ± 5 |
| $NiIn_2S_{3.5}Se_{0.5}$ | 10.574 ± 3 | 3.73 | 4.94 | 4.93 ± 5 |

[a] Data obtained from slow scan diffraction and Debye–Scherrer films.
[b] Data obtained from slow scan diffraction and Guinier films.

4.7 electrons; Menyuk et al. (*16*) assumed for similar compounds that $Mn^{+2}$ is not completely in the ground ($^6S_{5/2}$) state, but there may also be present some excited states.

From Fig. 1 it can be seen that all of the compounds shown are paramagnetic over the temperature range studied (4.2–298°K) and obey the Curie–Weiss law. In addition, no ordering temperature is apparent. All four indium thiospinels have large negative paramagnetic Curie temperature points, or Weiss contsants ($\theta$), which indicate the presence of antiferromagnetic interactions. The slight curvature observed at low temperatures may be a result of some localized clustering of the magnetic ions.

$MnIn_2S_4$ is a mixed spinel and therefore both direct Mn–Mn and indirect Mn–S–Mn (A–X–B, 125°) magnetic interactions are present. However, since the magnetic ions are dilute, there is little opportunity for long-range order. From Goode-

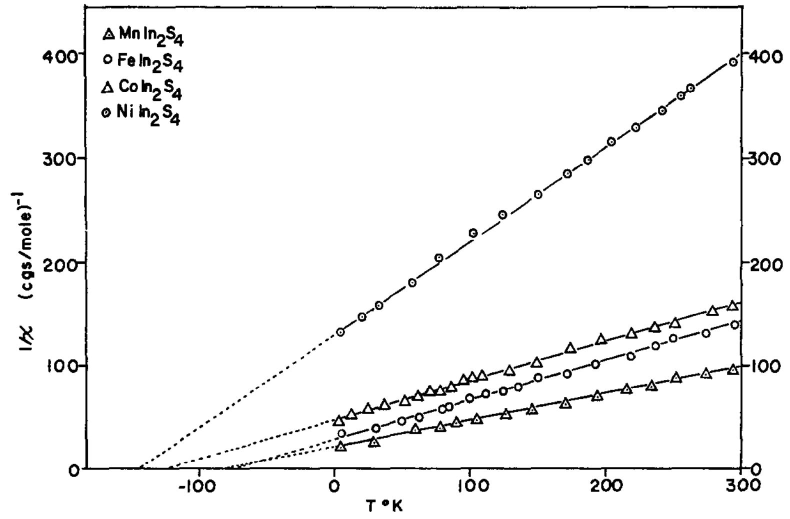

FIG. 1. Inverse susceptibility vs. temperature for compounds of the type $MIn_2S_4$ (M = Mn, Fe, Co, Ni).

TABLE II

MAGNETIC PROPERTIES OF $MIn_2S_4$ COMPOUNDS[a]

| Compound | $C_M$ | $\theta$(°K) | $P_{eff}$ (calcd) (spin only) ($\mu$B) | $P_{eff}$ (exptl) ($\mu$B) | $P_{eff}$ exptl / $P_{eff}$ calcd | $n$ calcd | $n$ exptl |
|---|---|---|---|---|---|---|---|
| $MnIn_2S_4$ | 4.00 | −78 | 5.92 | 5.68 | 0.96 | 5 | 4.7 |
| $FeIn_2S_4$ | 3.10 | −76 | 4.90 | 4.98 | 1.01 | 4 | 4.1 |
| $CoIn_2S_4$ | 2.84 | −134 | 3.86 | 4.78 | 1.23 | 3 | 3.9 |
| $NiIn_2S_4$ | 1.16 | −144 | 2.83 | 3.06 | 1.07 | 2 | 2.2 |

[a] $C$ = Curie constant; $\theta$ = Weiss constant; $P$ = paramagnetic moment; $n$ = number of unpaired electrons.

nough's rules (*17*) all the interactions present are negative, and this is consistent with the observed values for $\theta$.

It can be seen from Table II, that for other members of the series $MIn_2S_4$ (M = Fe, Co, Ni) the negative $\theta$ values increase with increasing occupancy of the $t_{2g}$ levels. On the basis of $M^{+2}$–S–$M^{+2}$ superexchange, it would seem that $NiIn_2S_4$ should have the strongest interactions. Furthermore, for $Ni^{+2}(d^8)$, the $t_{2g}$ orbitals are completely filled and, hence, the direct $t_{2g}$–$t_{2g}$ interactions are negligible. However, the 90° $Ni^{+2}(t_{2g})$–S–$Ni^{+2}(e_g)$ interaction between a filled $t_{2g}$ and half-filled $e_g$ is presumably ferromagnetic. Since there are no A-site $Ni^{+2}$ ions, the large negative $\theta$ is therefore puzzling, unless some of the next-nearest-neighbor interactions or interactions involving the diamagnetic $In^{+3}$ determine the sign and magnitude of the $\theta$ value.

The resistivities of these compounds were found to range between $10^5$–$10^8$ Ω cm at room temperature. These high values made it extremely difficult to measure the change in resistivity as a function of

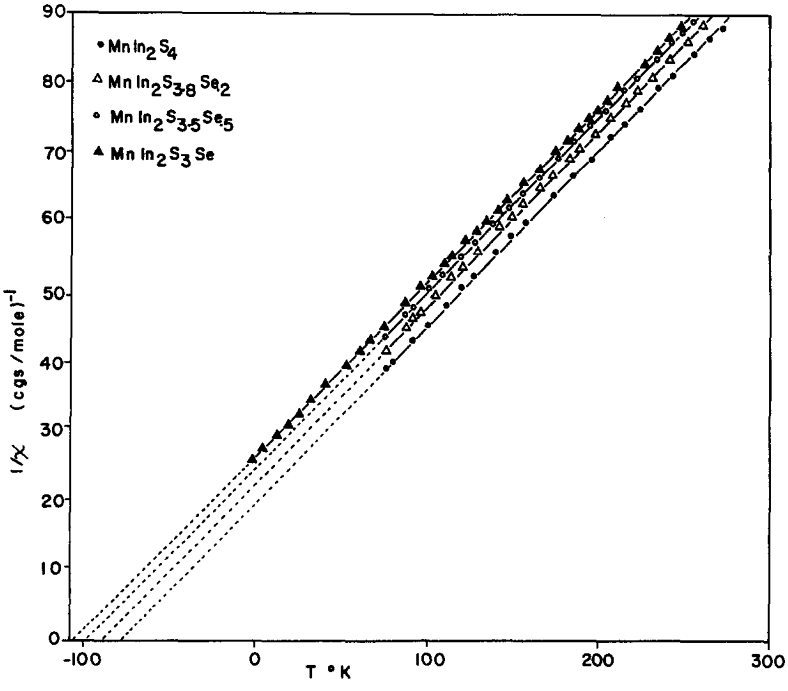

FIG. 2. Inverse susceptibility vs. temperature for compounds of the composition $MnIn_2S_{4-x}Se_x$.

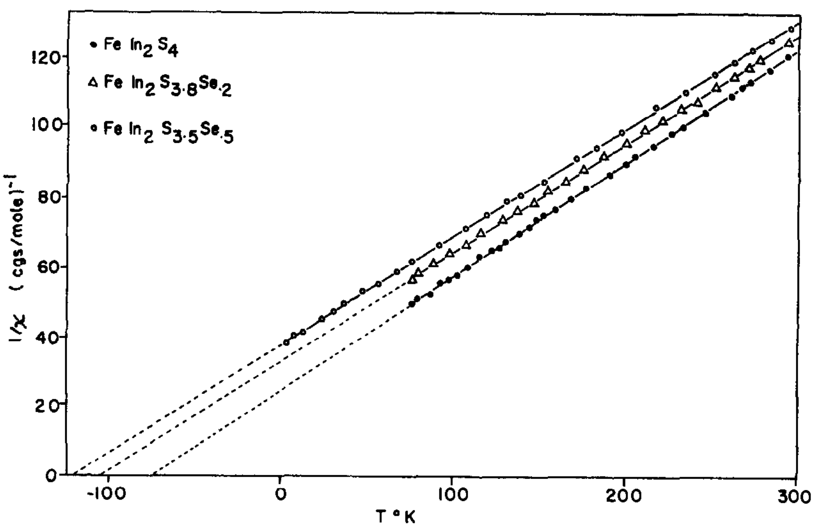

FIG. 3. Inverse susceptibility vs. temperature for compounds of the composition $FeIn_2S_{4-x}Se_x$.

temperature. However, they were found to behave as broad band gap semiconductors.

The substitution of sulfur by selenium results in an increase of the interatomic B–B distance (Table I) and, therefore, a decrease in the strength of the direct B–B interactions would be anticipated. However, it has been shown by previous investigators (*8*, *19*) that it is also necessary to consider the weaker, but nevertheless important, *n-n-n* interactions. Bertaut (*20*) has indicated that these interactions are negative and contribute to the sum of all the interactions present. If interactions with more distant neighbors play a dominant role, then substitution of Se for S should increase the magnitude of $\theta$.

Lotgering (*18*) and Dwight (*19*) demonstrated that for $ZnCr_2S_4$ the *n-n-n* antiferromagnetic interactions are significant and therefore the substitution of sulfur by the more polarizable selenium increases the relative strength of the *n-n-n* interactions.

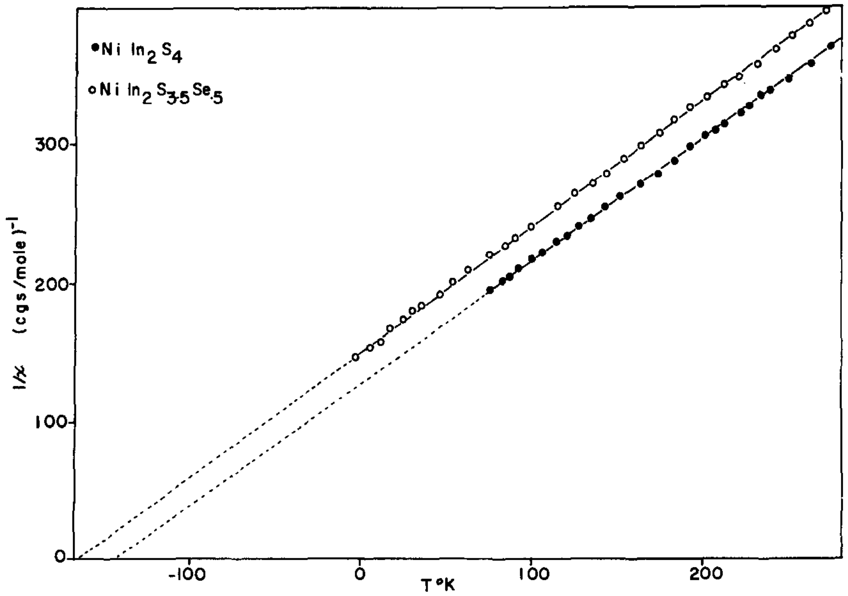

FIG. 4. Inverse susceptibility vs. temperature for compounds of the composition $NiIn_2S_{4-x}Se_x$.

TABLE III

MAGNETIC PROPERTIES OF THE $MIn_2S_{4-x}Se_x$ SYSTEM

| Compound | $C_M$ | $\theta$(°K) | $P_{eff}$ (exptl) ($\mu$B) | $P_{eff}$ (calcd) ($\mu$B) | $P_{eff}$ exptl / $P_{eff}$ calcd | $n$ (calcd) | $n$ (exptl) |
|---|---|---|---|---|---|---|---|
| $MnIn_2S_{3.8}Se_{0.2}$ | 4.00 | −90 | 5.68 | 5.92 | 0.96 | 5 | 4.7 |
| $MnIn_2S_{3.5}Se_{0.5}$ | 4.00 | −100 | 5.68 | 5.92 | 0.96 | 5 | 4.7 |
| $MnIn_2S_{3.0}Se_{1.0}$ | 4.00 | −108 | 5.68 | 5.92 | 0.96 | 5 | 4.7 |
| $FeIn_2S_{3.8}Se_{0.2}$ | 3.23 | −108 | 5.10 | 4.90 | 1.02 | 4 | 4.2 |
| $FeIn_2S_{3.5}Se_{0.5}$ | 3.23 | −121 | 5.10 | 4.90 | 1.02 | 4 | 4.2 |
| $NiIn_2S_{3.5}Se_{0.5}$ | 1.16 | −168 | 3.06 | 2.83 | 1.07 | 2 | 2.2 |

(where $C$ = Curie constant, $\theta$ = Weiss constant, $P$ = paramagnetic moment; $n$ = number of unpaired electrons).

Hence, there is a net increase in the strength of the antiferromagnetic $n$–$n$–$n$ superexchange interactions. This is consistent with the increase with Se content in the absolute values of $\theta$ reported in Table III. Despite the presence of appreciable antiferromagnetic interactions, there is no apparent long-range order down to 4.2°K. This is probably due to the fact that only one-half of the B sites are occupied by magnetic ions.

In conclusion, it can be seen that for the thiospinels studied ($MIn_2S_4$ and $MIn_2S_{4-x}Se_x$), the sign and magnitude of the observed magnetic interactions cannot be accounted for by simple exchange rules for the nearest-neighbor interactions, and there is evidence that the $e_g$–$e_g$ interactions between more distant neighbors play a dominant role.

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