Metal-Deficient Sulphospinels

F. K. LOTGERING AND G. H. A. M. VAN DER STEEN

Philips Research Laboratories, N.V. Philips' Gloeilampenfabrieken, Eindhoven Netherlands

The authors show the existence of the metal-deficient sulphospinels $Cr_{8/9}M_{16/9}\square_{1/3}S_4$ with $M = Al$ or In as well as mixed crystals of these compounds with stoichiometric sulphospinels like $ZnCr_2S_4$ and $CuTi_2S_4$. Magnetic and electrical measurements are described. In all materials investigated, chromium is in the trivalent state, and attempts to substitute divalent chromium fail and result in the generation of metal-deficient spinels. The strong decrease of the ferromagnetic moment of $CdCr_2S_4$ as a consequence of In or Sn substitution is not caused by the substitution of divalent chromium, but by spin canting.

1. Introduction

Until recently, $In_{8/3}\square_{1/3}S_4$ ($= 4/3In_2S_3$) was the only metal-deficient sulphospinel reported in the literature (*1, 2*). Very recently an isomorphous Al_2S_3 modification (*3*) has been prepared under high pressures. In this paper, it will be shown that metal vacancies are easily formed in several sulphospinels. The starting point of the investigation was an attempt to substitute divalent chromium into sulphospinels. It appeared that such a substitution does not occur and that a metal-deficient sulphospinel is generated as may be represented by the conversion $2Cr^{2+} + S \rightarrow 2Cr^3 + \frac{3}{4}\square + S^{2-}$.

The main results of this work have been published (*4*). The present paper gives experimental details and describes some new experiments. In Section 2 it is shown that attempts to prepare the Cr^{2+}-containing spinels CrM_2S_4 ($M = Al$ or In) failed, whereas the corresponding metal-deficient spinels $Cr_{8/9}M_{16/9}\square_{1/3}S_4$ are easily generated. Section 3 gives examples of sulphospinels with varying concentration of metal vacancies. Section 4 deals with the influence of the incorporation of nonmagnetic ions or metal vacancies on the ferromagnetic spin ordering in $CdCr_2S_4$.

2. $Cr_{8/9}M_{16/9}\square_{1/3}S_4$ with $M = Al$ or In

In spinels having the composition $Cr^{2+}M_2^{3+}S_4^{2-}$ with $M = Al$ or In, as reported by Flahaut *et al.* (*5*), the chromium is expected to be divalent because a deviation from the trivalent state of Al or In is very unlikely.

We tried to prepare $CrAl_2S_4$ by heating $CrS + 2Al$ at 1250–1300°C in H_2S, as described in Ref. (*5*). We obtained far from complete conversion because the aluminium melts, and is withdrawn from reaction with the H_2S atmosphere by CrS floating on the liquid aluminium. We therefore adopted another method. The binary alloy $CrAl_2$ (*6*) was heated in a carbon crucible at 1250°C in a H_2S atmosphere. Since $CrAl_2$ melts at a much higher temperature than Al, this avoided the presence of a liquid metal phase. The sample did not show any indication of a molten phase, though the firing temperature was higher than the peritectic melting point (1170°C) reported in the literature (*6*). Using this method, we obtained a reasonably pure spinel phase with a cell edge near to that given in Ref. (*5*) (see Tables I and II, No. 1).

As a consequence of the strong affinity of Al for oxygen, it is difficult to prepare the sulphide free from oxygen. The oxygen content was checked by chemical analysis (*7*). The Al, Cr alloy contained 0.5 wt % oxygen and the final product 2–3 wt % oxygen. Further it was found from chemical analysis that the Al, Cr alloy had the composition $CrAl_{1.92}$ instead of the planned composition $CrAl_2$, and we will formulate the compositions of our samples using the composition $CrAl_{1.92}$ for this starting material.

If the spinel generated from this alloy is stoichiometric, the composition must be $Cr^{2+}Cr_{0.03}^{3+}Al_{1.97}^{3+}S_4^{2-}$. However, the properties are in disagreement with this. From paramagnetic measurements at 88 to 290°K are found a Curie–Weiss law with

TABLE I

PREPARATION OF THE SAMPLES[a]

No.	Composition[b]	Starting materials	Heat treatment[c]
1	$Cr_{0.91}Al_{1.76}\square_{0.33}S_4$	$CrAl_{1.92}$	4h 1250°C (in H_2S)
			4h 1250°C (in H_2S)
2	$Zn_{0.49}Al_{0.90}Cr_{1.44}\square_{0.17}S_4$	$0.51Cr_{0.91}Al_{1.76}\square_{0.33}S_4 + 0.49ZnCr_2S_4$	72h 1000°C, q.
3	$Cu_{0.49}Al_{0.90}Ti_{0.98}Cr_{0.47}\square_{0.17}S_4$	$0.51Cr_{0.91}Al_{1.76}\square_{0.33}S_4 + 0.49CuTi_2S_4$	72h 1000°C, q.
4	$Cu_{0.30}Al_{0.99}Cr_{1.51}S_4$	$0.53Cr_{0.91}Al_{1.76}\square_{0.33}S_4 + 0.47CuCr_2S_4$	24h 650°C, q.
			48h 650°C, q.
5	$Cr_{8/9}In_{16/9}\square_{1/3}S_4$	$\frac{2}{3}In_2S_3 + \frac{1}{3}Cr_2S_3$	4 firings at 1000 to 1100°C, q.
6	$Cd_{0.73}In_{0.48}Cr_{1.70}\square_{0.09}S_4$	$0.27Cr_{8/9}In_{16/9}\square_{1/3}S_4 + 0.73CdCr_2S_4$	16h 800°C, q.
7	$Cd_{4/13}In_{16/13}Cr_{16/13}\square_{3/13}S_4$	$\frac{9}{13}Cr_{8/9}In_{16/9}\square_{1/3}S_4 + \frac{4}{13}CdCr_2S_4$	16h 800°C, q.
			4h 900°C, q.
8	"$CrIn_2S_4$"	$\frac{9}{13}Cr_{8/9}In_{16/9}\square_{1/3}S_4 + \frac{4}{13}$"$CrIn_2S_3$"	4 firings at 800 to 1150°C
9	"$Cd_{0.85}In_{0.30}Cr_{1.85}S_4$"	0.15"$CrIn_2S_4$" $+ 0.85CdCr_2S_4$	24h 800°C, q.
			16h 800°C, q.
10	"$Cd_{0.8}In_{0.4}Cr_{1.8}S_4$"	0.2"$CrIn_2S_4$" $+ 0.8CdCr_2S_4$	24h 800°C, q.
			16h 800°C, q.
11	"$Cd_{0.85}In_{0.15}Cr_2S_4$"	0.15"$InCr_2S_4$" $+ 0.85CdCr_2S_4$	24h 800°C, q.
12	"$CdSn_{0.2}Cr_{1.8}Se_4$"	mixture of CdSe, Cr, Sn and Se	24h 500°C, 24h 750°C,
			24h 800°C, q.
13	$CdCr_2S_4$	$CdS + Cr_2S_3$	60h 800°C
			24h 800°C
14	$CdIn_{0.1}Cr_{1.9}S_4$	$0.95CdS + 0.95Cr_2S_3 + 0.05CdIn_2S_4$	24h 800°C, q.
15	$CdIn_{0.2}Cr_{1.8}S_4$	$0.9CrS + 0.9Cr_2S_3 + 0.1CdIn_2S_4$	24h 800°C, q.

[a] The heating was performed in evacuated silica tubes, except for No. 1.
[b] Quotation marks: overall composition of materials assumed to be not single-phased.
[c] q = quenched.

$C_{Cr} = 1.80$ per gram atom chromium (calculated using a Cr content of 22.0 wt % as determined experimentally). This is in agreement with the spin-only value (1.87) for Cr^{3+} and much lower than the value (3.0) for Cr^{2+}. The observation of a high resistivity (Table II, No. 1) rules out the occurrence of formally divalent chromium that would be present as Cr^{3+} and a conduction electron. We, therefore, assume the substance to be a metal-deficient sulphospinel represented by $Cr_{0.91}^{3+}Al_{1.76}^{3+}\square_{0.33}S_4^{2-}$. (An attempt to prove this directly by chemical analysis failed. The Cr content calculated for the stoichiometric and metal-deficient spinel is 23.0 and 21.2 wt %, respectively. Five determinations on three samples gave a spread from 21.2 to 23.3 % with a mean value of 22.0 %).

The existence of $Cr^{2+}In_2^{3+}S_4$ and the corresponding metal-deficient spinel $Cr_{8/9}^{3+}In_{16/9}^{3+}\square_{1/3}S_4$ was investigated as follows. A mixture of pure and stoichiometric $4/9Cr_2S_3 + 8/9In_2S_3$ with the overall composition of $Cr_{8/9}In_{16/9}S_4$ was heated in an evacuated silica ampoule (Table I, No. 5). The starting materials were checked by chemical analysis

of the oxygen content (7) (0.6 wt % in Cr_2S_3 and 0.1 wt % in In_2S_3) and the metal content (52.05 ± 0.05 wt % Cr and 70.60 ± 0.05 wt % In in agreement with the calculated values of 52.0% Cr and 70.5% In). A pure spinel phase was obtained with $a = 10.47$ Å in agreement with Ref. (5). Just as in the case of $Cr_{0.91}Al_{1.76}\square_{0.33}S_4$, the Curie constant corresponds to Cr^{3+} and the electrical properties are those of a semiconductor (Table II, No. 5). Subsequently, a mixture of $Cr_{8/9}In_{16/9}S_4$ and "$CrIn_2S_3$" (a prefired mixture of $In_2S_3 + Cr$) with the overall composition of $Cr^{2+}In_2^{3+}S_4^{2-}$ was heated four times at temperatures between 800 and 1150°C (Table 1 No. 8). The X-ray diagrams of all samples exhibited a fairly large amount of unidentified phase, and for one sample we isolated an unknown phase, showing a complicated X-ray pattern. The observed Curie constant (Table II, No. 8) is much lower than that of Cr^{2+}.

Our conclusion from these experiments is that $Cr_{8/9}^{3+}In_{16/9}^{3+}\square_{1/3}S_4$ can easily be prepared, whereas the existence of $Cr^{2+}In_2^{3+}S_4$ has not been proved up to now.

TABLE II

EXPERIMENTAL DATA[a]

No.	Formula[b] (ca.)	Extra reflections (X-ray diagram)	Cell edge a (Å)	C_{Cr}[c]	θ (°K)	Seebeck coeff (μV/deg)	ρ (ohm cm) q (eV)
1	$Cr^{3+}_{0.91}Al^{3+}_{1.76}\square_{0.33}S^{2-}_4$	weak	9.93	1.80	−49		$\rho > 10^7$ at 420°K
2	$Zn^{2+}_{0.49}Al^{3+}_{0.90}Cr^{3+}_{1.44}\square_{0.17}S^{2-}_4$	pure spinel	9.95	1.87	−30		$\rho \simeq 10^5$
3	$Cu^+_{0.49}Al^{3+}_{0.90}Ti^{3+}_{0.49}Ti^{4+}_{0.49}Cr^{3+}_{0.47}\square_{0.17}S_4$	pure spinel	9.95	1.7	6	−46	$\rho \simeq 3.10^{-2}$ (77°K to r.t.)
4	$Cu^+_{0.50}Al^{3+}_{0.99}Cr^{3+}_{1.50}Cr^{4+}_{0.01}S_4$	very weak (Al_2O_3); superstr. (420)	9.93	1.70	−33		
5	$Cr^{3+}_{8/9}In^{3+}_{16/9}\square_{1/3}S^{2-}_4$	pure spinel	10.47	1.85	52	−1100	$\rho = 6.10^2$ $q = 0.23$
6	$Cd^{2+}_{0.73}In^{3+}_{0.48}Cr^{3+}_{1.70}\square_{0.09}S^{2-}_4$	idem	10.32	1.82	135	−560	$\rho = 3.10^2$ $q \simeq 0.08$
7	$Cd^{2+}_{4/13}In^{3+}_{16/13}Cr^{3+}_{16/13}\square_{3/13}S^{2-}_4$	idem	10.42	1.87	73	−600	$\rho = 2.10^2$ $q \simeq 0.05$
8	"$Cr^{2+}In^{3+}_2S_4$"	moderate	10.60	1.48	−10	−400	$\rho \simeq 10^2$ $q = 0.21$
9	"$Cd^{2+}_{0.85}In^{3+}_{0.30}Cr^{3+}_{1.70}Cr^{2+}_{0.15}S_4$"	pure spinel	10.30	—	—		
10	"$Cd^{2+}_{0.8}In^{3+}_{0.4}Cr^{3+}_{1.6}Cr^{2+}_{0.2}S_4$"	one moderate reflection of "$CrIn_2S_4$"	10.30	1.84	145	−310	$\rho \simeq 10^{-1}$ (77°K to r.t.)
11	"$Cd^{2+}_{0.85}In^{3+}_{0.15}Cr^{3+}_{1.85}Cr^{2+}_{0.15}S_4$"	pure spinel	10.22	1.84	165	−240	$\rho \simeq 1$ (100°K to r.t.)
12	"$Cd^{2+}Sn^{4+}_{0.2}Cr^{3+}_{1.6}Cr^{2+}_{0.2}Se_4$"	weak (CdSe)	10.75	1.86	181		$\rho = 8.10^{-2}$ $q = 0.034$
13	$Cd^{2+}Cr^{3+}_2S^{2-}_4$	pure spinel	10.25	1.81	172		
14	$Cd^{2+}In^{3+}_{0.1}Cr^{3+}_{1.9}S^{2-}_4$	pure spinel	10.26	—	—		
15	$Cd^{2+}In^{3+}_{0.2}Cr^{3+}_{1.8}S^{2-}_4$	pure spinel	10.28	1.80	155		

[a] C_{Cr} = Curie constant per gram atom chromium; θ = asymptotic Curie temperature; q = activation energy of the resistivity ρ.

[b] Quotation marks: hypothetical formula for single phase, which is assumed not to be the case.

[c] Susceptibilities corrected for diamagnetism using the value -2.0×10^{-4} per mole.

In connection with the stability problem of $Cr^{2+}M^{3+}_2S^{2-}_4$ (M = Al or In), the question arises as to whether a spinel In_3S_4 indeed exists as suggested by Stubbs et al. (8). According to a phase diagram given in Ref. (8), In_3S_4 would be stable between 370 and 840°C and would not mix with $In_{8/3}S_4$. This was concluded from thermal analysis, but no direct observation of the In_3S_4 phase by means of X-ray diffraction was reported. We fired a mixture of $In_2S_3 + InS$, sealed in evacuated silica ampoules, several times at temperatures between 800 and 1100°C. Two samples were annealed at 700 or 800°C and quenched; others were slowly cooled from 1000°C to 500, 400 or 300°C, and quenched. The X-ray diagrams of all samples showed considerable amounts of nonidentified phases and a spinel phase with $a = 10.75 \pm 0.05$ Å, i.e., equal to the pseudo-cubic cell edge $(10.77^{(2)}_4)$ of $In_{8/3}S_4$ within the experimental error. Our conclusion is that we did not obtain an In_3S_4 phase with spinel structure and we doubt whether such a phase exists.
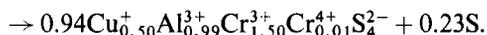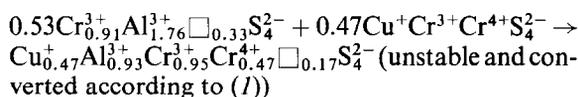
3. Mixed Crystals Containing Metal Vacancies

Powder mixtures of $Cr_{0.91}Al_{1.76}\square_{0.33}S_4$ (Section 2) with $ZnCr_2S_4$, $CoCr_2S_4$, $CuTi_2S_4$ or $CuCr_2S_4$ were heated in silica tubes (Table I, No. 2, 3 and 4). Although the differences in the cell edges of all these sulphospinels are small, the presence of two spinel phases in the starting mixtures could be observed clearly in the X-ray pattern from line splitting at larger scattering angles. After heating, this splitting disappears. From this and the difference in the magnetic behaviour before and after firing, it was

concluded that mixed crystals are generated (for example, the ferromagnetic starting component $CuCr_2S_4$ disappears during the reaction, as seen from the paramagnetic behaviour of the final product at low temperatures).

In the cases of $ZnCr_2S_4$, $CoCr_2S_4$, or $CuTi_2S_4$ as second component, the final product can be formulated as simple mixed crystals of the two starting components (Table II, Nos. 2 and 3). The reaction involving $CuCr_2S_4$ seems, however, to be more complicated. We carried out this reaction (Table I, No. 4) several times and always observed some sulphur present on the wall of the ampoule after firing, whereas no sulphur was produced during reactions with $ZnCr_2S_4$ or $CuTi_2S_4$. We attribute this to the presence of tetravalent chromium in $CuCr_2S_4$, which may be represented by $Cu^+Cr^{3+}Cr^{4+}S_4^{2-}$ according to Ref. (9)[1] and the hypothesis that Cr^{4+} is not stable in the presence of metal vacancies, but converts into Cr^{3+} due to segregation of sulphur by the reaction:

$$2Cr^{4+} + \tfrac{3}{4}\square + S^{2-} \rightarrow 2Cr^{3+} + S. \qquad (1)$$

The complete reaction equation then reads (rounded off to two decimal places):

$0.53Cr_{0.91}^{3+}Al_{1.76}^{3+}\square_{0.33}S_4^{2-} + 0.47Cu^+Cr^{3+}Cr^{4+}S_4^{2-} \rightarrow Cu_{0.47}^+Al_{0.93}^{3+}Cr_{0.95}^{3+}Cr_{0.47}^{4+}\square_{0.17}S_4^{2-}$ (unstable and converted according to (1))

$\rightarrow 0.94Cu_{0.50}^+Al_{0.99}^{3+}Cr_{1.50}^{3+}Cr_{0.01}^{4+}S_4^{2-} + 0.23S.$

The (420) reflection observed for this sample can be attributed to ionic $1:1$ ordering on the A sites (10) occupied by $0.50Cu^+$ and $0.50Al^{3+}$.

$CuTi_2S_4$ is an n-type metallic conductor, as appears from its low resistivity and the low negative Seebeck coefficient (11). This must be attributed to the presence of formally trivalent titanium according to the formula $Cu^+Ti^{3+}Ti^{4+}S_4$, though the exact conduction mechanism is not known (9). Assuming a simple mixed crystal of this compound and $Cr_{0.91}^{3+}\ Al_{1.76}^{3+}\square_{0.33}S_4$ for the material No. 3 in Table II, we expect Ti^{3+} to be present in the mixed crystal as well, but with about half the concentration found in $CuTi_2S_4$. In accordance with this, a low resistivity and a fairly low, negative Seebeck coefficient is found.

The cell edge and asymptotic Curie temperature for the system $Cr_{8/9}In_{16/9}\square_{1/3}S_4$-$CdCr_2S_4$ are given

[1] The formula gives the formal charges correctly. It is not necessary to use here a formula that describes the real Cr^{4+} concentration corresponding to the electronic structure given in Ref. (9).
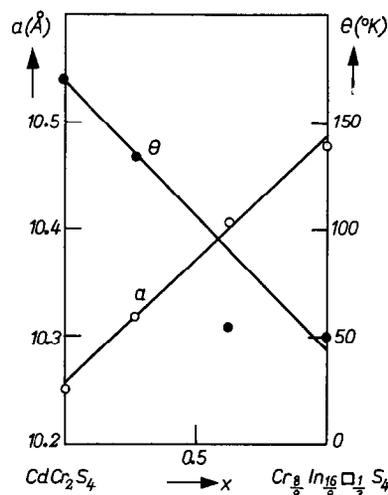

FIG. 1. $Cd_{1-x}^{2+}In_{16x/9}^{3+}Cr_{2-10x/9}^{3+}\square_{x/3}S_4^{2-}$. Cell edge a and asymtotic Curie temperature θ as a function of the composition.

as a function of the composition in Fig. 1. The linear behaviour shows that a complete series of mixed crystals exists. The Curie constant is in excellent agreement with the value for trivalent chromium (Table II, Nos. 5, 6, 7 and 13) and may be considered as a check on the planned composition.

Recently (12), we also found a series of mixed crystals between In_2S_3 and Cr_2S_3 with compositions $Cr_{8(1-x)/3}In_{8x/3}\square_{1/3}S_4$ and $\tfrac{3}{8} \leqslant x \leqslant 1$, and the existence of the sulphospinel $In_{1/2}Cr_{3/2}Sn_{1/2}\square_{1/2}S_4$ having a higher concentration of vacancies than reported so far. The existence of metal vacancies in these materials has been confirmed by the observation (12) of superstructure reflections due to vacancy ordering and by a density measurement on $Cr_{8/5}T_{16/15}\square_{1/3}S_4$.

4. Influence of In Substitution on the Ferromagnetic Ordering of $CdCr_2S_4$

Pinch and Berger (13) postulated the presence of divalent chromium in In-substituted $CdCr_2X_4$ according to the formula $Cd_{1-y}^{2+}In_y^{3+}Cr_{2-y}^{3+}Cr_y^{2+}X_4^{2-}$ with $y \leqslant 0.15$ for $X = S$ and $y \leqslant 0.20$ for $X = Se$. A strong argument was the experimental finding that the ferromagnetic moment at $4.2°K$ decreases rapidly with the In content, which was explained on the assumption that the Cr^{2+} and Cr^{3+} ions are coupled antiferromagnetically. The observed moment is roughly in agreement with the values calculated for an antiparallel alignment of the Cr^{2+} spins with respect to ferromagnetically ordered Cr^{3+} spins. Further, the magnetization curves measured at
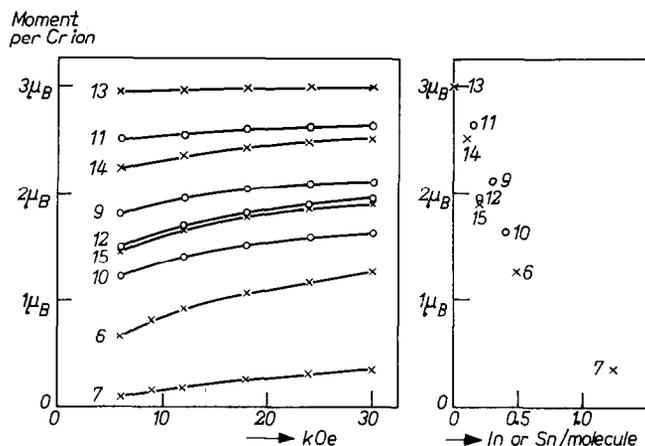
FIG. 2. $Cd^{2+}Cr_2^{3+}S_4$ (No. 13); $Cd^{2+}Cr_{2-x}^{3+}In_x^{3+}S_4$ with $x = 0.1$ (No. 14) and 0.2 (No. 15), $Cd_{1-x}^{2+}In_{16x/9}^{3+}Cr_{2-10x/9}^{3+}\square_{x/3}S_4$ with $x = 0.27$ (No. 6) and 9/13 (No. 7), "$Cd_{0.85}^{2+}In_{0.15}^{3+}Cr_{1.85}^{3+}Cr_{0.15}^{2+}S_4$" (No. 11), $Cd_{1-y}^{2+}In_{2y}^{3+}Cr_{2-2y}^{3+}Cr_y^{2+}S_4$" with $y = 0.15$ (No. 9) and 0.20 (No. 10), "$Cd^{2+}Sn_{0.2}^{4+}Cr_{1.6}^{3+}Cr_{0.2}^{2+}Se_4$" (No. 12). Magnetic moment per Cr ion at 4.2°K as a function of H (left) and of the In or Sn content for $H = 30$ kOe (right).

4.2°K exhibit a marked slope, and the substances were far from saturated at $H = 10$ kOe. This was also attributed to the occurrence of Cr^{2+} ions, which are expected to contribute strongly to the magneto-crystalline anisotropy.

We prepared $Cd_{0.85}In_{0.15}Cr_2S_4$ according to specifications given in Ref. (13), and three other substances that would be expected to contain Cr^{2+} if they were single-phased, namely, $Cd_{0.85}^{2+}In_{0.30}^{3+}Cr_{1.70}^{3+}Cr_{0.15}^{2+}S_4^{2-}$, $Cd_{0.8}^{2+}In_{0.4}^{3+}Cr_{1.6}^{3+}Cr_{0.2}^{2+}S_4$ and $Cd^{2+}Sn_{0.2}^{4+}Cr_{0.6}^{3+}Cr_{0.2}^{2+}Se_4$ (Tables I and II, Nos. 9, 10, 11 and 12). Figure 2 gives magnetization curves at 4.2°K and the magnetic moment per Cr ion for $H = 30$ kOe as a function of the concentration of the substituted ions. These measurements confirm the behaviour described in Ref. (13) and mentioned above. Further, we carried out the same measurements on the materials $Cd_{1-x}^{2+}In_{16x/9}^{3+}Cr_{2-10x/9}^{3+}\square_{x/3}S_4^{2-}$ with $x = 0.27$ and 9/13 discussed in Section 2, and on $Cd^{2+}In_x^{3+}Cr_{2-x}^{3+}S_4^{2-}$ with $x = 0.1$ and 0.2, in which Cr^{3+} is replaced by In^{3+} (Tables I and II, Nos. 6, 7, 14 and 15). Although the latter series of substances contains the chromium exclusively as trivalent ions (as confirmed by the Curie constants, see Table II), the magnetic behaviour is essentially equal to that of the first series, i.e., a marked slope of the magnetization curve at 4.2°K and a rapid decrease of the moment for $H = 30$ kOe with the In content is likewise found (Fig. 2). The magnetic behaviour cannot therefore be considered as an indication of the presence of Cr^{2+}.

Figure 3 gives the magnetization at temperatures below T_C and the reciprocal susceptibility at temperatures above T_C as a function of T/θ measured on two of the materials, which certainly contain no Cr^{2+} (Nos. 13 and 15), and on two substances in which Cr^{2+} might be present (Nos. 11 and 12). If the low moment at 4.2°K of the latter arises from an antiparallel alignment of the Cr^{2+} and the Cr^{3+} spins, the materials would in fact be ferrimagnetic. A fundamental property of a ferrimagnet is that θ lies below T_C and that the $\chi^{-1} - T$ curve shows a curvature concave with respect to the T axis in a region above T_C. There are no indications for such behaviour in Fig. 3 as there is hardly any difference in the shapes of the $\chi^{-1} - T/\theta$ curves, which are all of the type of that for $CdCr_2S_4$ (Fig. 3, No. 13).

Our conclusion is that no experimental evidence for the occurrence of Cr^{2+} in sulphospinels can be obtained from the magnetic properties. We attribute the magnetic behaviour, as given in Fig. 2, to local spin distortions caused by the presence of nonmagnetic B site ions or vacancies. It is well known (see, for instance, Ref. (14)) that positive nearest-neighbour interactions (of type CrXCr) and negative next-near-neighbour interactions (of type CrXXCr) occur in sulpho- and selenospinels. A Cr^{3+} ion in $CdCr_2S_4$ has six nearest-neighbours that are coupled ferromagnetically via the central Cr^{3+} ion, and antiferromagnetically by CrSSCr interactions. If the central Cr^{3+} ion is replaced by an In^{3+} ion, the ferromagnetic coupling of its neighbours via the central Cr^{3+} ion falls off whereas the antiferromagnetic coupling by CrSSCr exchange remains. This can cause canting of the six spins under consideration. A quantitative analysis of such a
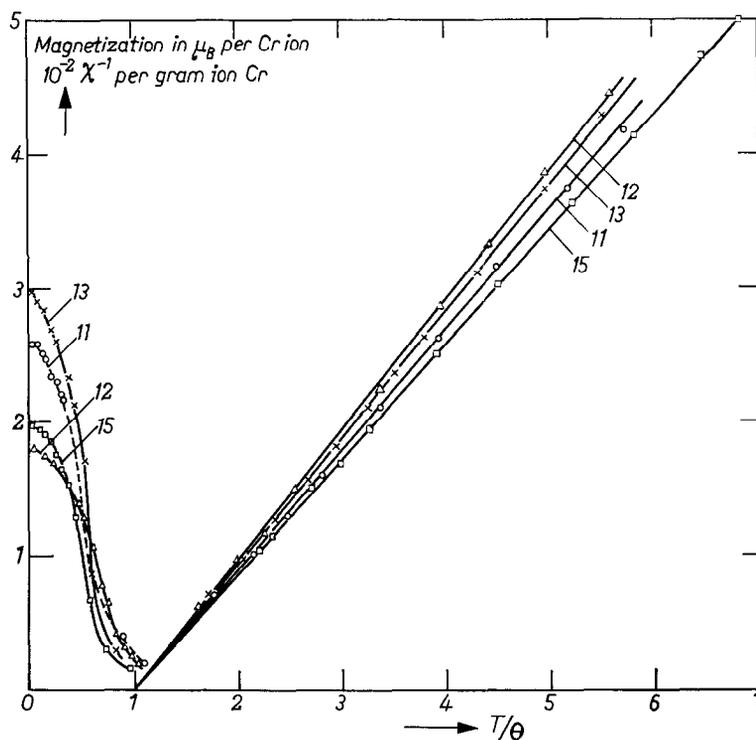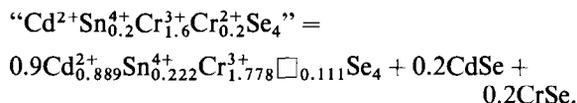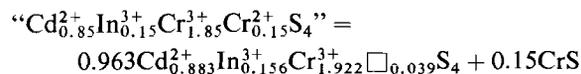
Fig. 3. $Cd^{2+}Cr_2^{3+}S_4$ (No. 13), $Cd^{2+}In_{0.2}^{3+}Cr_{1.8}^{3+}S_4$ (No. 15), "$Cd_{0.85}^{2+}In_{0.15}^{3+}Cr_{1.85}^{3+}Cr_{0.15}^{2+}S_4$" (No. 11) and "$Cd^{2+}Sn_{0.2}^{4+}Cr_{1.6}^{3+}Cr_{0.2}^{2+}Se_4$" (No. 12). Magnetization for $H = 18$ kOe (left) and reciprocal susceptibility (right) as a function of T/θ, where $\theta = 172, 155, 165,$ and $181°K$, respectively (applied diamagnetic correction: -2.0×10^{-4} per mole).

local spin distortion is known to be very difficult, because it is necessary, in addition, to envisage canting of the spins at a greater distance from the centre in a realistic model (15). Further, the interactions between different distortion centres cannot be neglected, even for $Cd^{2+}In_{0.1}^{3+}Cr_{1.9}^{3+}S_4^{2-}$ in which as much as 30% of the B sites are occupied by Cr^{3+} ions that are nearest neighbours of an In^{3+} ion. It is known (16) that the ferromagnetic ordering in $CdCr_2Se_4$ collapses as a consequence of negative CrSeSeCr interactions in the series $Cd_{1-x}Zn_xCr_2Se_4$. Such an indirect perturbation of the ferromagnetic order due to the replacement of one diamagnetic ion by another makes it plausible that a direct perturbation due to removal of magnetic ions can give local spin distortions as proposed above. In our model, the slope of the magnetization curve at $4.2°K$ arises from a lining up of canted spins in the external field against the exchange forces. In the cases Nos. 9, 10, 11 and 12 (Tables I and II), the samples are assumed not to be single-phased and to contain a metal-deficient spinel phase. Possible compositions for, e.g., Nos. 11 and 12, are:

$$\text{"}Cd_{0.85}^{2+}In_{0.15}^{3+}Cr_{1.85}^{3+}Cr_{0.15}^{2+}S_4\text{"} =$$
$$0.963Cd_{0.883}^{2+}In_{0.156}^{3+}Cr_{1.922}^{3+}\square_{0.039}S_4 + 0.15CrS$$

$$\text{"}Cd^{2+}Sn_{0.2}^{4+}Cr_{1.6}^{3+}Cr_{0.2}^{2+}Se_4\text{"} =$$
$$0.9Cd_{0.889}^{2+}Sn_{0.222}^{4+}Cr_{1.778}^{3+}\square_{0.111}Se_4 + 0.2CdSe + 0.2CrSe.$$

According to these hypothetical compositions, the samples would contain 3.7 wt % CrS and 4.8 wt % CrSe, which may escape detection in the X-ray pattern. We found indeed that the CrS phase was not observable in the X-ray diagram of a mixture of 97% $CdCr_2S_4$ and 3% CrS. According to the formula given above, the material should contain 7 wt % CdSe; the presence of CdSe was actually established (Table II, No. 12).

Pinch and Berger (13) have also reported other experiments from which the presence of Cr^{2+} in $CdCr_2S_4(Se_4)$ was concluded. However, these data seem less convincing to us for the following reasons. The authors have observed but slight, poorly reproducible changes in moment (between 3.73 and 3.89 μ_B per molecule) after chemical treatments of a $CdCr_2S_4$ sample selected from a series of samples with moments that spread considerably (from 5.15 to 5.79 μ_B) and are substantially below the theoretical value of 6 μ_B. Such results seem to point to multiple phased rather than Cr^{2+}-containing single-phased samples. This impression is supported by our own experience as we prepared $CdCr_2S_4$ samples with a moment very near to 6 μ_B (see Fig. 2, curve 13. A moment of

5.98 μ_B per molecule is measured at 4.2°K and 30 kOe) starting from very pure and stoichiometric CdS + Cr_2S_3 but without "oxidizing" the sample by a sulphur-anneal treatment as described in Ref. (13). Further, Pinch and Berger measured a weak anisotropy on $CdCr_2S_4$ samples and observed a considerable change after annealing in H_2. This points to slight deviations from the stoichiometry of the spinel phase, but is not conclusive for the presence of Cr^{2+}, as stated by the authors themselves who suggest the presence of interstitial Cr^{3+} as an alternative explanation. For the rest, the present work does not exclude the possibility that Cr^{2+} in very low concentrations (say < 0.05 Cr^{2+} per molecule) could play a part in Pinch and Berger's experiments.

Figure 4 gives the ratio $\theta/[Cr^{3+}]$ of the asymptotic Curie temperature and the number of Cr^{3+} ions per formula unit, which is a measure of the overall interaction per pair of Cr^{3+} ions, as a function of the cell edge for sulphospinels with varying vacancy concentration. We used the data for $ZnCr_2S_4$, $Cr_{8(1-x)/3}In_{8x/3}\square_{1/3}S_4$ (12) and the data given in Table 2 with exclusion of Nos. 8–12, which are not assumed to be single-phased, and Nos. 3 and 4, in which metallic conduction may influence the interactions (9). The curves drawn in Fig. 4 for stoichiometric composition[2] and for a constant concentration of 0.33 vacancies/molecule confirm a well-known rule which states that the interaction increases in a positive sense for increasing Cr-Cr distance (see, e.g. Ref. (17)). From the relative positions of the two curves and the position of the points for intermediate vacancy concentrations between these curves, it is seen that the overall interaction changes in a negative sense with the vacancy concentration for a constant cell edge.

5. Conclusions

(1) Sulphospinels containing metal vacancies are easy to prepare. The highest vacancy concentration found occurs in $In_{1/2}Cr_{3/2}Sn_{1/2}\square_{1/2}S_4$ (Section 2).

(2) It is difficult, if not impossible, to incorporate divalent chromium in sulphospinels. This is remarkable because the occurrence of Cr^{2+} octahedrally coordinated by sulphur ions is well established in $Cr_{0.97}S$, as appears from the composition and also from the observation of a strong Jahn–Teller deformation (19). In view of the method used in the present work,

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[2] We measured $\theta = 172°K$ on $CdCr_2S_4$ (Table 2, No. 13), i.e., a much higher value than found by Baltzer et al. (18) ($\theta = 135°K$). The low values of the ferromagnetic moment (2.6 $\mu B/Cr$ ion) and the Curie constant (1.6 per gram atom Cr) reported in Ref. (18) seem to point to a far from pure sample as discussed above.
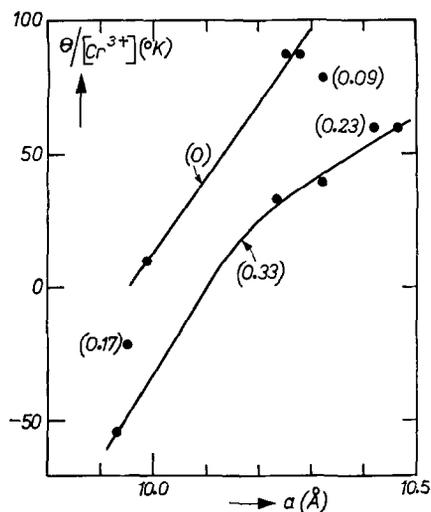

FIG. 4. Ratio of the asymptotic Curie temperature θ and the number of chromium ions $[Cr^{3+}]$ per molecule as a function of the cell edge. Figures between brackets show number of metal vacancies per molecule.

the occurrence of small amounts of Cr^{2+} (say below $0.05Cr^{2+}$ per molecule) cannot be excluded (Sections 2 and 4).

(3) The existence of a spinel phase with the composition In_3S_4 could not be confirmed (Section 2).

(4) Tetravalent chromium is unstable in metal-deficient sulphospinels (Section 3).

(5) The strong decrease of the ferromagnetic moment of $CdCr_2S_4$ upon a replacement of Cd by In (or Cr by Sn) and the slope of the magnetization curves at 4.2°K of the substituted materials arise from spin canting (Section 4).

(6) The overall interaction between the Cr^{3+} spins changes in a negative sense with the concentration of metal vacancies.

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