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Magnetic and Crystallographic Properties of Spinels of the Type $A_xB_2S_4$ Where A = Al, Ga, and B = Mo, V, Cr

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Spinels with the formula $Ga_{0.67}Mo_2S_4$, $Al_{0.75}Mo_2S_4$, $Ga_{0.67}Cr_2S_4$, and $Ga_{0.5}V_2S_4$ have been prepared. Since the cation to anion ratio of these spinels is less than 3:4 they must contain cation vacancies. X-ray diffraction studies indicate that the Al, Ga, and vacancies occupy the *A* (tetrahedral) sites and Mo, V, and Cr the B (octahedral) sites. All of the spinels are semiconductors and exhibit weak ferromagnetism. The magnetic porperties are explained in terms of B site ferro- and antiferromagnetic superexchange interactions. An anomaly observed in the magnetic properties of $Ga_{0.5}V_2S_4$ at ~46°K would seem to indicate a possible phase transition.

Introduction

The magnetic properties of chalcogenide spinels of the type MCr_2X_4 have been extensively studied. Spinels of the type $Cd[Cr_2]X_4$ and $Hg[Cr]_2X_4$ (where Cd and Hg occupy tetrahedral, A, sites, Cr occupies the octahedral, B, sites and X = S, Se) exhibit ferromagnetism (*1*) and are semiconductors (*2*). Since the A sites contain the nonmagnetic Cd^{2+} and Hg^{2+} ions, the magnetic properties, of these spinels, are associated with the B-site Cr–Cr interactions.

As shown in Fig. 1 each B site Cr ion is surrounded by near neighbor Cr ions (B_0–X–B_1) at a 90° angle through an intervening anion. Each Cr ion is surrounded by six such near neighbor Cr ions which interact ferromagnetically (*1*) by superexchange through the common anion.

The more distant Cr–Cr interactions (~30 in number) are antiferromagnetic (*1*, *3*). The exchange path of these interactions is more complex. Baltzer et al. (*1*) suggested that the A site cation (Cd, Hg) is included in the interaction chain Cr–X–A–X–Cr. Dwight and Menyuk (*3*) hypothesize long-range interactions of the type Cr–X–X–Cr where the superexchange is perturbed by the A site cation. These Cr–Cr interactions are more numerous and weaker than the near neighbor ferromagnetic interactions. The competition between these two superexchange interactions causes θ/Tc to vary greatly from the value of one (*1*) which is predicted for an ideal ferromagnet.

Recently, Barz (*4*) reported the existence of one of the few nonchromium containing chalcogenide spinels, $Ga_xMo_2S_4$. This spinel was reported to be ferromagnetic with Tc = 13°K. This interesting observation prompted us to initiate a further study of the preparation and properties of $Ga_xMo_2S_4$, as well as new spinel compositions of the type $Ga_xV_2S_4$, $Al_xMo_2S_4$, and $Ga_xCr_2S_4$.

Experimental

Preparation

All of the materials were prepared from appropriate mixtures of powders of the elements. The mixtures were pressed into pellet form, sealed in evacuated silica tubes, and heated to 800°C at the rate of 10–15°C/hr. Samples were held at 800°C for two days and furnace cooled to room temperature by shutting off the furnace. In order to obtain

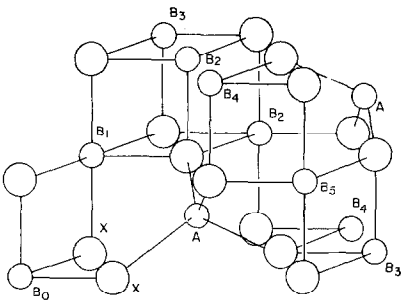

FIG. 1. Portion of spinel lattice showing nearest to fourth-nearest B–B neighbors.

single phase spinels it was necessary to reseal the samples in silica tubes and heat to 1000°C, followed by quenching in water. Single phase spinel compositions were obtained for $Ga_{0.67}Mo_2S_4$, $Al_{0.75}Mo_2S_4$, $Ga_{0.5}V_2S_4$, and $Ga_{0.67}Cr_2S_4$. All of these spinels thus contain cation vacancies. In the compositions $Ga_{0.67}Mo_2S_4$ and $Ga_{0.67}Cr_2S_4$ all of the Mo and Cr are trivalent. In $Al_{0.75}Mo_2S_4$ and $Ga_{0.5}V_2S_4$ the Mo and V must exhibit mixed valencies in order to maintain electroneutrality.

X-Ray Measurements

A Guinier de Wolff camera (Cu$K\alpha$ radiation) was used for preliminary sample identification. As stated previously, the four compositions which formed as single phase spinels, within the limits of resolution, are $Ga_{0.67}Mo_2S_4$, $Al_{0.75}Mo_2S_4$, $Ga_{0.5}V_2S_4$, and $Ga_{0.67}Cr_2S_4$. Changes in Al and Ga composition lead to mixed phases of spinels (with no change in cell parameter) and the appearance of binary sulfide phases.

TABLE I

SOME PROPERTIES OF THE SPINELS $A_xB_2S_4$

Spinel	Unit cell size (a Å)	Curie temperature (15 300 Oe) (Tc °K)	Curie–Weiss (θ °K)
$Ga_{0.67}Mo_2S_4$	9.73_9	18	17
$Al_{0.75}Mo_2S_4$	9.72_6	18[a]	18
$Ga_{0.5}V_2S_4$	9.66_3	13	—
$Ga_{0.67}Cr_2S_4$	9.88_7	56	≈40

[a] Zero field $Tc = 9.5$°K.

Unit cell parameters, obtained from diffractometer patterns using Cu$K\alpha$ radiation, are listed in Table I. The X-ray patterns also revealed extra reflections which could be indexed as 200, 420, 600, and 640. In the spinel structure, which belongs to the space group $Fd3m$, there are two crystallographically inequivalent A (tetrahedral) sites which yield the selection rule that for any $hk0$, $h + k = 4n$. Crystallographic ordering on the A sites would lead to the appearance of $hk0$ reflections where $h + k \neq 4n$ and hence to the space group $F\bar{4}3m$. Since the primary factors in cation site ordering are differences in electrostatic properties (i.e., valence) and in cation size it is reasonable to assume that the ordering observed in the $A_xB_2S_4$ ($A_x\square_{1-x}B_2S_4$) spinels arises from the presence of cations and cation vacancies on the A sites. The most complete ordering for the composition $A_x\square_{1-x}B_2S_4$ would yield the following atomic positions:

4 A: 0, 0, 0 (4 a);
$(8x - 4)$ A: 1/4, 1/4, 1/4 (4 c)
16 B: x, x, x (16 e); $x = 5/8$
16 S_I: x, x, x (16 e); $x = 3/8$
16 S_{II}: x, x, x (16 e); $x = 7/8$.

Both the Mo and V containing materials exhibited the extra reflections. They were not observed for Cr containing samples. Although the samples exhibiting the extra reflections no longer have the spinel space group we will continue to refer to them as spinels for the sake of simplicity.

In order to determine site occupancies in $Al_{0.75}[Mo_2]S_4$, the observed diffractometer peak intensities were compared to the calculated intensities. Theoretical intensities were calculated for spinels where: (a) A (tetrahedral) sites contain Al plus vacancies (□) and the B (octahedral) sites contain Mo ($Al_{0.75}\square_{0.25}[Mo_2]S_4$); (b) $Al_{0.75-x}Mo_x\square_{0.25}[Al_xMo_{2-x}]S_4$ where $x = 0.375$ and 0.75 (50 and 100% Al displacement to the B sites). Table II shows the observed intensities with those calculated for Al A site occupancy and 50% Al displacement. It can be seen that intensity comparison favors model (a), for a normal spinel. Similar analyses were made for

TABLE II

CALCULATED VS OBSERVED INTENSITIES FOR $Al_{0.75}Mo_2S_4$

		I_{calcd}	
$h\,k\,l$	I_{obsd}	$Al_{0.75}\square_{0.25}[Mo_2]S_4$ (Normal)	$Al_{0.375}Mo_{0.375}\square_{0.25}(Al_{0.375}Mo_{1.625})S_4$ (50% inverse)
1 1 1	87	100	30
2 0 0	15	25	67
2 2 0	6	4	26
3 1 1	56	59	100
2 2 2	0	4	11
4 0 0	96	90	53
3 3 1	35	33	31
4 2 0	0	2	1
4 2 2	37	18	20
3 3 3	60	48	68
5 1 1			
4 4 0	64	62	70
5 3 1	6	6	1
4 4 2	7	9	13
6 0 0			
6 2 0	0	0	1
5 3 3	0	3	7
6 2 2	0	0	2
4 4 4	16	15	8
5 5 1	19	16	10
7 1 1			
6 4 0	7	11	17
6 4 2	13	7	12
5 5 3	6	16	21
7 3 1			
8 0 0	6	7	8

$Ga_{0.67}Mo_2S_4$ and $Ga_{0.5}V_2S_4$ with comparable results. A refinement of the structures of $Al_xMo_2S_4$ and $Ga_xMo_2S_4$ is in progress (*5*).

Magnetic Measurements

All of the magnetic measurements were carried out on a pendulum magnetometer between room temperature and 1.5°K. Figure 2 illustrates the type of measurements performed using the composition $Ga_{0.67}Mo_2S_4$. Curie temperatures (*Tc*) were obtained from the inflection point of the magnetization vs temperature curves using an external field of 15 300 Oe. The measured magnetic properties of materials investigated are shown in Table I. By extrapolation of low field (1–15 Oe) magnetic ordering temperature measurements, a zero field *Tc* of 9.5°K was obtained for $Al_{0.75}Mo_2S_4$. Both the Mo and Cr containing spinels appeared to exhibit high anisotropies and could not be saturated in a field of 15 300 Oe. Extrapolation of the inverse susceptibility vs temperature curves for these spinels show that they exhibit positive temperature intercepts (Curie–Weiss θ).

The results of magnetic measurements on the material $Ga_{0.5}V_2S_4$ are shown in Fig. 3. It can be seen in the inverse susceptibility curve, and to a lesser degree in the magnetization vs *T* curve, that an anomaly occurs at about 46°K which is above *Tc*(~13°K). This

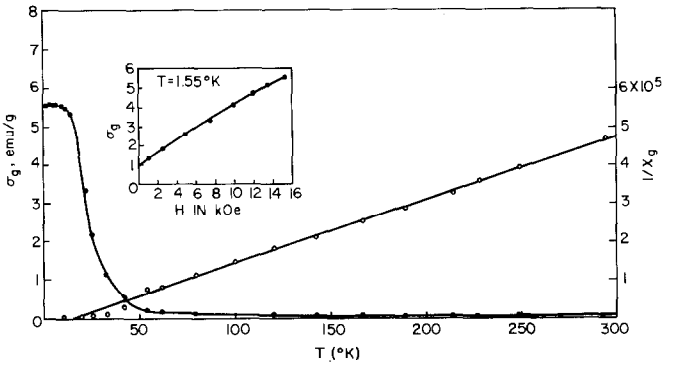

FIG. 2. Magnetic measurements on $Ga_{0.67}Mo_2S_4$.

spinel differs from the others in that it seems to saturate in a field of 15 300 Oe.

Electrical Measurements

A sample of $Al_{0.75}Mo_2S_4$ was pressure sintered at 800°C and 20 000 psi to give a pellet which was 98% of theoretical (X-ray) density. X-ray diffraction measurements showed that the structure had been maintained. Measurements were made on a rod 0.13 × 0.16 × 0.57 cm to which four leads were affixed with indium solder. Resistivities were measured using a standard four-terminal method.

Figure 4 shows log resistivity vs temperature between 4.2 and 350°K. The material exhibits a negative temperature coefficient of resistivity. Below 50°K the resistivity was too large for accurate measurement with the available instruments. However, we were able to establish that the resistivity in the temperature region 4.2°–50°K ($Tc = 9.5$°K) was greater than 10^7 Ω-cm.

Crude measurements on cold pressed (60–70% of theoretical density) pellets of the other materials show that all of them exhibit semiconductor-like behavior between room and liquid nitrogen temperatures.

Discussion

As shown by X-ray analysis the spinel A sites are occupied by the nonmagnetic Al or Ga ions and cation vacancies which order crystallographically. The magnetic ions occupy the B sites. The materials were also found to be semiconducting. These facts indicate that the magnetic properties of these spinels are due to superexchange interactions on the B sites. The low values of θ and Tc (compared to those

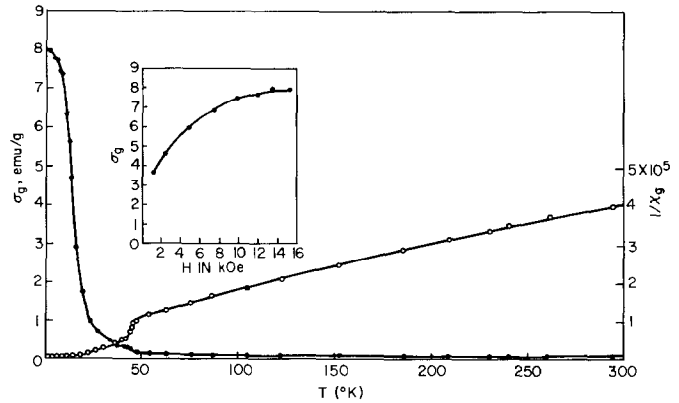

FIG. 3. Magnetic measurements on $Ga_{0.5}V_2S_4$.

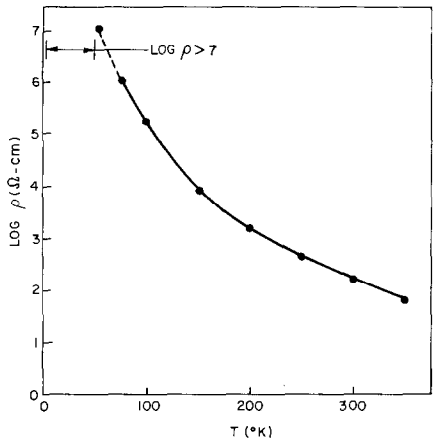

FIG. 4. Logρ vs. T for pressure sintered sample of $Al_{0.75}Mo_2S_4$.

for $CdCr_2S_4$) observed for the Mo and Cr containing spinels indicate that the near neighbor ferromagnetic interactions are relatively weak. A similar value of θ was observed for $ZnCr_2S_4$ (+18°K) which exhibits antiferromagnetism (*6*). However, the appearance of ferromagnetism in these compounds indicates that the more distant neighbor antiferromagnetic B–B interactions have also been significantly weakened. To be more quantitative, we calculated, by the method of Ref. (*1*), J/K (near neighbor interactions strength) and K/k (more distant neighbor interaction strength) for the spinel $Al_{0.75}Mo_2S_4$, using the values of θ and Tc obtained by extrapolation to zero field. The ferromagnetic interaction strength ($J/k = 1.3$°K) was found to be weak with respect to $CdCr_2S_4$ (11.3°K) (*1*). The antiferromagnetic interaction strengths ($K/k = -0.03$°K) is likewise considerably lower than $CdCr_2S_4$ (−0.33°K). Thus, as a result of the weaker antiferromagnetic interactions the ferromagnetic interactions prevail and the Mo and Cr containing spinels exhibit weak ferromagnetism.

As previously stated, one of the models (*1*) for B site antiferromagnetic interactions involves the A site cation in the superexchange path (B–S–A–S–B). If this is so then the presence of cation A site vacancies could weaken the antiferromagnetic superexchange interactions. Since the A site cations are not involved in the near neighbor B site interactions (B–S–B) the existence of the A site vacancies could not appreciably affect the ferromagnetic interaction.

The close correlation between the ferro and antiferromagnetic interactions could cause a canting of the B site moment. This effect has been observed in $HgCr_2S_4$ (*7*) in which the B site magnetic interactions are closely matched. This could explain the inability to magnetically saturate the spinels in fields up to 15 300 Oe.

The magnetic properties shown in Fig. 3 exhibit an anomaly at ~46°K. The effect as seen in the inverse susceptibility curve seems to involve most if not all of the samples. If this effect were caused by an impurity it would be a minor one since any impurity would have to be present in amounts below X-ray detection (~5–10%). A major effect would probably involve a low-temperature transition. At present, low temperature X-ray and conductivity measurements are being made to determine if a low-temperature transition is involved.

Conclusion

Materials with the formula $Ga_{0.67}Mo_2S_4$, $Al_{0.75}$ Mo_2 S_4, $Ga_{0.67}$ Cr_2 S_4 and $Ga_{0.5}$ V_2 S_4 form with the spinel structure. All are semiconductors and exhibit weak ferromagnetism (with the possible exception of $Ga_{0.5}V_2S_4$). X-ray diffraction studies show that the A sites are all occupied by nonmagnetic cations indicating that the magnetic properties of these materials originates in the B site superexchange interactions. More study involving low temperature X-ray diffraction and resistivity measurements are needed to understand the properties of $Ga_{0.5}V_2S_4$, which seems to differ from the other spinels in this study.

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