

## Structural Behavior of the Ferromagnetic Spinel $Al_xMo_2S_4$ and $Ga_xMo_2S_4$ , Containing Tetrahedral Clusters of Molybdenum Atoms

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The structure of the ferromagnetic spinels  $Al_xMo_2S_4$  and  $Ga_xMo_2S_4$  ( $x \sim 0.5$ ) was determined from powder diffraction data. The Al and Ga atoms order on the tetrahedral sites. The space group is  $F\bar{4}3m$ ;  $a = 9.726 \text{ \AA}$  for  $Al_xMo_2S_4$  and  $9.739 \text{ \AA}$  for  $Ga_xMo_2S_4$ . The Mo atoms were found to shift towards the tetrahedral site vacancies, created by the lower Al and Ga concentrations. This results in tetrahedral clusters of Mo around the vacancies. Their semiconducting and magnetic behavior was explained on the basis of the structural behavior of the molybdenum lattice in these spinel compounds.

### Introduction

Since Barz (1) reported the existence of the new ferromagnetic spinels  $Ga_xMo_2S_4$  and  $Ga_xMo_2Se_4$  ( $x \sim 0.5-0.7$ ), considerable effort has been directed to determine their structural and magnetic properties. Several other spinel compounds with similar compositions have been prepared, such as  $Ga_xV_2S_4$ ,  $Al_xMo_2S_4$ , and  $Ga_xCr_2S_4$  (2). X-ray diffraction shows that these spinels contain vacancies on the tetrahedral sites created by the lower Al and Ga concentrations. Attention was therefore focused on their magnetic superexchange interactions (2). The present X-ray study of the Mo spinels was undertaken to give a more detailed description of their structure in order to get a better understanding of their semiconducting and weakly ferromagnetic behavior.

### Experimental and Structural Data

The powder samples were prepared from the elements; the detailed experimental procedure has been previously described (2). Based on X-ray identification, single phases were obtained at the compositions  $Al_{0.75}Mo_2-$

$S_4$  and  $Ga_{0.67}Mo_2S_4$ . The lattice constants are listed in Table I. Diffractograms were made with a Philips X-ray diffractometer, using  $CuK\alpha$  radiation. The intensities were measured with a planimeter. As previously reported (2), the intensities unambiguously showed the compounds to be normal spinels with Al and Ga on the tetrahedral sites and Mo on the octahedral sites. The space group of the spinel structure is  $Fd\bar{3}m$ . The presence of the extra reflections  $hk0$ ,  $h+k=2n$ , which do not occur for a stoichiometric spinel  $AB_2S_4$ , lead to the lower-symmetric space group  $F\bar{4}3m$ . The ideal atomic positions with the equivalent positions  $(0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0)$  are as follows:

4 Al(Ga) in (4a):  $0, 0, 0$ ;  
 $(8x-4) \square$  in (4c):  $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ ;  
 16 Mo in (16e):  $x, x, x; x, \bar{x}, \bar{x}; \bar{x}, x, \bar{x}; \bar{x}, \bar{x}, x$ ;  
 $x = 5/8$ ;  
 16  $S_I$  in (16e):  $x, x, x$ ; etc.;  $x = 3/8$ ;  
 16  $S_{II}$  in (16e):  $x, x, x$ ; etc.;  $x = 7/8$ .

The eightfold tetrahedral position (8a,  $Fd\bar{3}m$ ) of the spinel splits into two fourfold tetrahedral positions (4a, 4c) in the lower-symmetric space group  $F\bar{4}3m$ . The Al and Ga atoms are crystallographically ordered on the position (4a), with the vacancies  $\square$  on (4c). The ordering would be complete for  $x = 0.5$ .

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TABLE I  
STRUCTURAL PARAMETERS AND MAGNETIC DATA

Al <sub>x</sub> Mo <sub>2</sub> S <sub>4</sub>		Ga <sub>x</sub> Mo <sub>2</sub> S <sub>4</sub>	
<i>a</i> (Å)	9.72 <sub>6</sub>	<i>a</i> (Å)	9.73 <sub>9</sub>
<i>x</i> (Al)	0.55	<i>x</i> (Ga)	0.52
<i>x</i> <sub>Mo</sub>	0.60 <sub>5</sub>	<i>x</i> <sub>Mo</sub>	0.60 <sub>3</sub>
<i>x</i> <sub>S<sub>I</sub></sub>	0.36 <sub>3</sub>	<i>x</i> <sub>S<sub>I</sub></sub>	0.36 <sub>0</sub>
<i>x</i> <sub>S<sub>II</sub></sub>	0.86 <sub>8</sub>	<i>x</i> <sub>S<sub>II</sub></sub>	0.86 <sub>5</sub>
<i>R</i> (%)	13.4	<i>R</i> (%)	10.3
<i>P</i> <sub>eff</sub> /4Mo	1.81 μ <sub>B</sub>	<i>P</i> <sub>eff</sub> /4Mo	1.84 μ <sub>B</sub>
Curie Temp.	18 K	Curie Temp.	18 K

Also, because of the lower symmetry of the space group, the positional parameter *x* of Mo is now variable and the 32-fold position ((32*a*) in *Fd3m*) of the anions splits into two 16-fold positions whose *x* parameters vary independently.

A special program was designed to minimize these parameters. Within the last few years a technique has been developed which showed that it was possible to determine the *u*-parameter(s) of different space groups by analysis of X-ray diffraction data. Raccach et al. (3) developed a computer program which gives this analysis for the spinel structure (space group *Fd3m*). As an extension of this it was thought that the related but more general space group *F43m* would lend itself to a similar type of analysis.

By means of a Fortran Program developed in this study it was possible to calculate theoretical relative intensities and thereby generate an agreement factor *R* similar to the one described by Raccach et al. (3). By inserting different *x*-parameters (*x*<sub>Mo</sub>, *x*<sub>S<sub>I</sub></sub>, *x*<sub>S<sub>II</sub></sub>), varying the composition and degrees of site mixing, and correcting for the Lorentz polarization, multiplicity, and anomalous dispersion, the theoretical intensities (*I*<sub>calcd</sub>) were calculated. The program then takes  $\sum I_{calcd}$  and  $\sum I_{obsd}$  and generates a scaling factor ( $S = \sum I_{obsd} / \sum I_{calcd}$ ). The proper choice of variables was selected by minimizing the *R* parameter:

$$R = \frac{\sum |I_c - I_o|}{\sum I_o}$$

Starting with the ideal positions for Mo (*x* = 5/8) and S(*x* = 3/8; 7/8), *x*<sub>Mo</sub> was varied while holding the other variables constant until the *R*-parameter was minimized with respect to *x*<sub>Mo</sub>. Next, *x*<sub>S<sub>I</sub></sub> and then *x*<sub>S<sub>II</sub></sub> were varied to reduce *R* further, and finally different compositions and degrees of site mixing were used to minimize *R* and thereby get the best agreement between *I*<sub>calcd</sub> and *I*<sub>obsd</sub>. The final atomic parameters are listed in Table I and, based on these parameters, a comparison of observed and calculated intensities is given in Table II.

### Discussion

The structure shows some interesting features. The atomic parameters show that the S<sub>I</sub> atoms, out of their ideal positions, shift away from the vacancies along the body diagonals of the octant of the unit cell (Fig. 1). In the same way the S<sub>II</sub> atoms shift away from the Al or Ga atoms. The interatomic distances are listed in Table III. The Mo positions, however, are the most interesting aspect of the structure. The Mo atoms shift considerably from their ideal positions towards the vacancies □ on the tetrahedral sites (Fig. 1). This results in tetrahedral clusters of Mo around the vacancies. The Mo–Mo distances within the clusters is very short, ~2.85 Å. The shortest Mo–Mo distance between the clusters is very large, ~4.00 Å.

It is well known that Mo, particularly among halides, chalcogenides, and pnictides, shows a strong tendency towards intermetallic bonding by forming clusters with distances in the range of 2.70–2.95 Å. For instance pairs of Mo occur in MoCl<sub>3</sub> (4), octahedral clusters (5) in MoX<sub>2</sub> (X = Cl, Br, I) and chains of Mo in MoBr<sub>3</sub> (6). They are diamagnetic or weakly temperature-dependent paramagnetic (4); their physical properties are mainly determined by the bonding mechanism within the clusters (7).

Among the chalcogenides and pnictides Mo forms for instance zigzag chains in compounds such as Mo<sub>2</sub>S<sub>3</sub> (8), CoMo<sub>2</sub>S<sub>4</sub> (9), and Mo<sub>2</sub>As<sub>3</sub> (10), triangular clusters in MoN (11) and octahedral clusters in Mo<sub>3</sub>Se<sub>4</sub> (12) and PbMo<sub>6</sub>S<sub>8</sub> (13); the phosphides show a

TABLE II  
 OBSERVED AND CALCULATED POWDER DIFFRACTION DATA

$\text{Al}_x\text{Mo}_2\text{S}_4$					$\text{Ga}_x\text{Mo}_2\text{S}_4$				
$hkl$	$10^4\sin^2\theta_o$	$10^4\sin^2\theta_c$	$I_o$	$I_c$	$hkl$	$10^4\sin^2\theta_o$	$10^4\sin^2\theta_c$	$I_o$	$I_c$
1 1 1	189	188	86.8	100	1 1 1	187	188	71.1	78.9
2 0 0	252	252	14.7	13.3	2 0 0	249	251	30.0	32.8
2 2 0	503	503	6.4	5.3	2 2 0	499	501	17.4	20.6
3 1 1	692	691	56.2	67.4	3 1 1	687	689	94.8	100.0
2 2 2	756	754	2.0	4.8	2 2 2	750	752	9.5	9.2
4 0 0	1007	1005	96.2	94.3	4 0 0	1001	1002	93.2	90.6
3 3 1	1195	1194	35.4	37.7	3 3 1	1188	1190	47.4	45.1
4 2 0	1257	1256	1.0	0.7	4 2 0		1253	0	0.3
4 2 2	1508	1508	37.4	35.6	4 2 2	1500	1504	51.4	55.7
3 3 3	1697	1696	60.0	51.5	3 3 3	1687	1691	93.2	80.3
5 1 1					5 1 1				
4 4 0	2010	2010	64.2	64.0	4 4 0	1999	2005	88.5	79.8
5 3 1	2200	2199	6.0	5.4	5 3 1	2197	2193	1.6	1.3
4 4 2	2259	2258	6.7	5.0	4 4 2	2251	2252	11.1	7.8
6 0 0					6 0 0				
6 2 0		2509	0	0.6	6 2 0		2502	0	0.2
5 3 3	2698	2697	1.5	2.5	5 3 3	2690	2690	3.9	3.9
6 2 2		2760	0	0.1	6 2 2		2752	0	0.4
4 4 4	3013	3011	16.4	14.4	4 4 4	3002	3002	13.4	12.1
5 5 1	3201	3199	19.1	16.7	5 5 1	3189	3190	16.6	18.7
7 1 1					7 1 1				
6 4 0	3265	3261	7.0	4.9	6 4 0	3252	3253	11.7	7.8
6 4 2	3514	3512	13.3	13.5	6 4 2	3501	3503	20.5	22.7
5 5 3	3702	3700	18.3	19.2	7 3 1	3689	3690	22.1	24.9
7 3 1					5 5 3				
8 0 0	4013	4014	5.5	6.6	8 0 0	4003	4003	7.9	7.4
7 3 3	4202	4202	13.5	12.9	7 3 3	4190	4191	14.2	16.2
6 4 4		4265	0	1.5	6 4 4		4253	0	1.2
8 2 0					8 2 0				
6 6 0	4516	4516	26.8	21.8	6 6 0	4503	4504	33.2	34.3
8 2 2					8 2 2				
5 5 5	4704	4704	4.0	5.4	7 5 1	4690	4691	6.3	7.9
7 5 1					5 5 5				
6 6 2	4765	4766	1.0	0.6	6 6 2	4749	4753	1.6	1.8
8 4 0	5018	5017	10.7	12.9	8 4 0	5003	5004	8.7	8.5
7 5 3	5206	5206	1.5	4.5	7 5 3	5192	5192	2.0	5.0
9 1 1					9 1 1				
8 4 2		5268	0	2.5	8 4 2	5252	5254	2.4	3.5
6 6 4	5518	5519	1.5	4.2	6 6 4	5505	5505	4.0	5.2
9 3 1	5707	5707	1.5	3.2	9 3 1	5693	5692	6.3	5.6
8 4 4	6017	6017	9.5	13.6	8 4 4	6004	6005	15.0	14.7

more complicated structural behavior but similar metallic networks are formed (14). In all these compounds the nearest-neighbor Mo-Mo distances vary from very short ones within the clusters to distances between the

clusters about 15-20% larger than in molybdenum metal. These are still metallic distances, in the range 3.20-3.30 Å. At least a two-dimensional metallic Mo lattice is maintained. The  $d$  electrons of Mo are delocalized

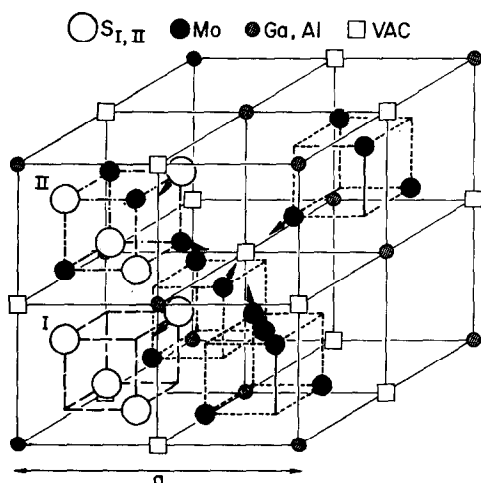


FIG. 1. Structure of the ordered spinels  $\text{Al}_{0.5}\text{Mo}_2\text{S}_4$  and  $\text{Ga}_{0.5}\text{Mo}_2\text{S}_4$ . For some of the S and Mo atoms deviations from the ideal positions are indicated by arrows. The 16  $\text{S}_{\text{II}}$  atoms occupy the same octants as Mo and four of them are indicated in one octant as II. Four of the 16  $\text{S}_{\text{I}}$  atoms, which occupy the remaining four octants, are indicated in one octant as I.

TABLE III  
INTERATOMIC DISTANCES ( $\text{\AA}$ )

$\text{Al}_x\text{Mo}_2\text{S}_4$		$\text{Ga}_x\text{Mo}_2\text{S}_4$	
Al- $4\text{S}_{\text{II}}$	2.22	Ga- $4\text{S}_{\text{II}}$	2.28
Mo- $3\text{S}_{\text{I}}$	2.37	Mo- $3\text{S}_{\text{I}}$	2.42
Mo- $3\text{S}_{\text{II}}$	2.58	Mo- $3\text{S}_{\text{II}}$	2.59
Mo- $3\text{Mo}$	2.89	Mo- $3\text{Mo}$	2.84
Mo- $3\text{Mo}$	3.99	Mo- $3\text{Mo}$	4.05
$\text{S}_{\text{I}}$ - $3\text{S}_{\text{I}}$	3.11	$\text{S}_{\text{I}}$ - $3\text{S}_{\text{I}}$	3.03
$\text{S}_{\text{I}}$ - $3\text{S}_{\text{I}}$	3.77	$\text{S}_{\text{I}}$ - $3\text{S}_{\text{I}}$	3.86
$\text{S}_{\text{I}}$ - $6\text{S}_{\text{II}}$	3.45	$\text{S}_{\text{I}}$ - $6\text{S}_{\text{II}}$	3.46
$\text{S}_{\text{II}}$ - $3\text{S}_{\text{II}}$	3.25	$\text{S}_{\text{II}}$ - $3\text{S}_{\text{II}}$	3.17
$\text{S}_{\text{II}}$ - $3\text{S}_{\text{II}}$	3.63	$\text{S}_{\text{II}}$ - $3\text{S}_{\text{II}}$	3.72
$\text{S}_{\text{II}}$ - $6\text{S}_{\text{I}}$	3.45	$\text{S}_{\text{II}}$ - $6\text{S}_{\text{I}}$	3.46

and the compounds are metallic, or semi-conducting if the  $d$  band is filled. None of them shows a localized magnetic behavior of Mo. The molybdenum spinels are the first ones among these compounds where molybdenum clusters and at the same time shows a localized moment with a weakly ferromagnetic interaction (2). Looking at the crystal structure

(Fig. 1) it is obvious why this happens. The tetrahedral clusters of Mo are isolated, because the distance from one cluster to the other is at least  $4.00 \text{\AA}$ , which is no longer a metallic distance. In this way the magnetic moment is located on the isolated tetrahedral clusters. An interesting contrast appears in the superconducting compound  $\text{PbMo}_6\text{S}_8$  (15). As previously discussed (11), in this compound Mo forms octahedral clusters; the distances between the clusters are about 15% larger than in molybdenum metal. So, while in  $\text{PbMo}_6\text{S}_8$  the Mo clusters are still connected into a three-dimensional metallic lattice, this is not so for the spinels where the tetrahedral clusters are isolated.

The crystallographic results show that the concentrations of Al and Ga are close to  $x = 0.5$ . A definite minimum for the  $R$  value was observed at  $x \approx 0.5$ , which is lower than the value of  $x$  obtained from preparation and X-ray identification; it corresponds to a complete ordering on the tetrahedral sites. This is also a more realistic value, because Mo is found to shift specifically towards the empty tetrahedral sites. This site is only completely vacant for  $x = 0.5$ .

The magnetic susceptibilities ( $1/\chi$  vs  $T$ ) of both spinels have a slope corresponding to a very low magnetic moment per Mo atom (2). However, if the magnetic moment is calculated per  $\text{Mo}_4$  cluster and the concentrations  $x$  are assumed to be 0.5, then the effect magnetic moments are  $1.81$  and  $1.84 \mu_B$  (16) for  $\text{AlMo}_4\text{S}_8$  and  $\text{GaMo}_4\text{S}_8$ , respectively (Table I). This corresponds to one unpaired electron located on the  $\text{Mo}_4$  cluster. If the valencies in these ordered systems are balanced, then their formal valence states are  $\text{Al}^{3+}(\text{Mo}^{3+})_3\text{Mo}^{4+}\text{S}_8$  and  $\text{Ga}^{3+}(\text{Mo}^{3+})_3\text{Mo}^{4+}\text{S}_8$ . The total number of  $d$  electrons on the  $\text{Mo}_4$  clusters is 11, an odd number. Apparently, ten of the  $d$  electrons are involved in intermetallic Mo-Mo bonds within the clusters and one  $d$  electron remains unpaired. This is similar to the behavior of cluster compounds of the transition-metal halides such as the  $(\text{Mo}_6\text{X}_{12})^{3+}$  and  $(\text{Ta}_6\text{X}_{12})^{3+}$  species, where an odd number of  $d$  electrons leaves one unpaired electron on the metal clusters (7, 17). In all these compounds and also in the spinels low-spin metal clusters,

bridged by anions, are formed. The intercluster ferromagnetic interaction in the Mo spinels could be compared to the weak intercluster ferromagnetic spin coupling between nickel bridged tetramers in organometallic complexes (18). However, while in the molybdenum spinels the magnetic moment is already located on the low-spin state cluster, in the nickel complexes high-spin aligned states are created on the clusters at low temperatures, which then interact ferromagnetically through intercluster spin coupling (19).

From a structural point of view the formation of clusters in the spinels shows similarity to the cubane-like metal clusters, studied by Dahl et al. (20). These occur in metal complexes of the composition  $\text{M}_4\text{X}_4\text{L}_{4n}$ , where  $\text{X} = \text{Cl}^-$ ,  $\text{S}^{2-}$ ,  $\text{OH}^-$ , etc., and  $\text{L} =$  organic ligand. In the  $\text{M}_4\text{X}_4$  core the metal atoms and anions  $\text{X}$  occupy alternate corners of a cube, resulting from two interpenetrating tetrahedra of  $\text{M}$  and  $\text{X}$ . In these complexes, the clusters form isolated units. Similar cubanes can be recognized in the spinels; however, they are not isolated and share corners. Two different types of cubanes can be distinguished in  $\text{Al}_x\text{Mo}_2\text{S}_4$  and  $\text{Ga}_x\text{Mo}_2\text{S}_4$ . For convenience we consider the Al spinel only. One  $\text{Mo}_4(\text{S}_I)_4$  cubane is centered around each vacancy and can be easily visualized around vacancy in center of unit cell (Fig. 1). It has four short Mo–Mo bonds of 2.89 Å, 12 Mo– $\text{S}_I$  bonds of 2.37 Å and long  $\text{S}\cdots\text{S}$  contacts of 3.77 Å. Bonding of each formally  $[\text{Mo}_4(\text{S}_I)_4]^{5+}$  cubane in  $\text{Al}^{3+}\text{Mo}_4\text{S}_8^{2-}$  can be described as follows. There are 11 electrons ( $= 4 \times 6$  (4*d* electrons of Mo) –  $4 \times 2$  (of  $\text{S}^{2-}$ ) – 5) on the  $\text{Mo}_4$  cluster, all Mo oxidation states being equal. One expects the four Mo–Mo bonds to be of bond order  $\sim 1$  and one unpaired electron equally distributed among the 4 Mo atoms.

Each bonding  $\text{Mo}_4(\text{S}_I)_4$  cubane, centered around each vacancy, is surrounded by (a) four nonbonding  $\text{Mo}_4(\text{S}_{II})_4$  cubanes of the second type (upper left octant in Fig. 1); they have four Mo $\cdots$ Mo contacts of 3.99 Å, 12 Mo– $\text{S}_{II}$  bonds of 2.58 Å and four  $\text{S}_{II}\cdots\text{S}_{II}$  contacts of 3.25 Å, (b) four  $(\text{S}_I)_4$  units with  $\text{S}_I\cdots\text{S}_I$  contacts of 3.11 Å (lower left octant in Fig. 1).

As inherent in the spinel structure, each Mo is a member of one bonding and one nonbonding  $\text{Mo}_4\text{S}_4$  cubane, each  $\text{S}_I$  is a member of one bonding  $\text{Mo}_4(\text{S}_I)_4$  cubane and one  $(\text{S}_I)_4$  unit and each  $\text{S}_{II}$  is just a member of one nonbonding  $\text{Mo}_4(\text{S}_{II})_4$  cubane. Each Mo is surrounded by six S atoms, assuming octahedral coordination and  $d^2sp^3$  hybridization. The clustering of Mo can be better understood by comparing it with a more simple example such as  $\text{NbCl}_4$  (4) and  $\alpha\text{-NbI}_4$  (21). In these compounds the  $\text{NbCl}_6$  octahedra form chains by sharing edges; the  $\text{Nb}^{4+}$  ions have one unpaired *d* electron. Within these chains bonding  $\text{Nb}_2\text{Cl}_2$  dimers with a short Nb–Nb distance of 3  $d_\pi$  type bonding involving two 3*d* electrons of two  $\text{Nb}^{4+}$  and nonbonding  $\text{Nb}_2\text{Cl}_2$  dimers with a long Nb–Nb distance alternate; they share the two Cl atoms through an edge. In the same way bonding and nonbonding  $\text{Mo}_4\text{S}_4$  cubanes alternate in a three-dimensional network, sharing corners.

Recently, Burger and Dahl (22) discovered cubanes in the complex compound  $(h^5\text{-C}_5\text{H}_5)_4\text{-Mo}_4\text{S}_4$  with short Mo–Mo distances of about 2.80 Å. The bonding in the cubane-like systems is discussed by Dahl et al. (20); the bonding in a three-dimensional network of cubanes as occurring in the spinels is a more complicated matter. However, it is extremely interesting to find similar structural behavior in spinels of transition metal chalcogenides and organometallic compounds.

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