

## Magnetic, Structural, and Mössbauer Effect Study of $MnGd_2S_4$

L. BEN-DOR\* AND I. SHILO†

*Department of Inorganic & Analytical Chemistry, The Hebrew University of Jerusalem, Israel*

AND I. FELNER

*Racah Institute of Physics, The Hebrew University of Jerusalem, Israel*

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The compound  $MnGd_2S_4$  has the cubic  $Th_3P_4$  structure with  $a_0 = 8.360 \text{ \AA}$  and with an  $x$  parameter equal to  $0.070 \pm 0.003$ . Magnetic susceptibility shows no magnetic order to liquid He temperature and a temperature dependence that is the simple sum of the theoretical contributions for  $Mn^{2+}$  and  $Gd^{3+}$  ions. Similar results were obtained from Mössbauer studies.

### Introduction

In the family of compounds of the general formula  $AB_2S_4$  various types of structures are found when different combinations of cations are chosen. Some representative structures for  $A =$  alkali earth metals and  $B =$  rare earth elements are: orthorhombic, cubic spinel, cubic  $Th_3P_4$  (1, 2); for  $A =$  divalent-transition metals and  $B$  as above possible structures are cubic spinel and  $NiAs$  (3). It is possible to relate the type of crystallization to the intrinsic properties of the ions, crystal radii and electronegativities, and predict with a certain amount of assurance the crystal structure of an unknown compound of this stoichiometry (1). Some  $MnLn_2S_4$ , for  $Ln =$  heavy lanthanides, have been investigated (4, 5) and found to have the spinel structure, some of them transforming to the cubic  $Th_3P_4$  structure under pressure.

This cubic structure has also been found for  $CdGd_2S_4$ ,  $EuLn_2S_4$  ( $Ln =$  light lanthanides)

\* To whom correspondence should be addressed.

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(6) and for  $MLn_2S_4$  ( $M = Ca, Sr, Ba, Mg; Ln =$  as above approx) (7). Certainly, the most extensive work in this field in which the largest number of compounds with this general formula has been prepared and studied is by Flahaut and his collaborators (8).

In this study we report structural and magnetic data for  $MnGd_2S_4$  as part of a larger research program on a series of  $ALn_2S_4$  compounds.

### Experimental

The starting material for obtaining  $MnGd_2S_4$  was 99.9995% S (Ventron Alfa Products), 99.9% Mn (BDH Reagents), and 99.9%  $Gd_2O_3$  (Research Chemicals). In the first step  $MnS$  was synthesized from its elements,  $Gd_2O_3$  was converted to  $Gd_2S_3$  and, subsequently,  $MnGd_2S_4$  was prepared.

1a. Appropriate amounts of the reactants, manganese and sulfur, were sealed in an evacuated silica ampoule without premixing. The ampoule was placed in a cold furnace and its temperature raised slowly to  $400^\circ C$  and

kept at that temperature for 24 hr. Subsequently, the temperature was raised to 900°C and held constant for 4 days. Slow raising of the temperature is crucial, as otherwise the ampoule tends to explode. The ampoule was taken from the furnace and quenched in air at room temperature.  $\alpha$ -MnS is greenish and has the rock salt structure.

*1b.* Gd<sub>2</sub>O<sub>3</sub> was placed in a quartz boat within a Vycor tube and CS<sub>2</sub> with He as carrier gas was passed through the tube (9). The material was thus treated at 1100°C for 26 hr, the result being reddish-brown orthorhombic Gd<sub>2</sub>S<sub>3</sub>. The material was left to cool within the furnace after switching off the current and under flow of the above gas mixture.

2. A stoichiometric ground mixture of MnS and Gd<sub>2</sub>S<sub>3</sub> was placed in a quartz ampoule and sealed under a vacuum of 10<sup>-4</sup> Torr. The ampoule was heated to 800°C for 14 hr and at 1100°C for 16 hr. The ampoule was cooled within the furnace after switching off the current. The material obtained was orange-brown and was X-ray identified as MnGd<sub>2</sub>S<sub>4</sub>.

X-ray powder diffraction patterns were taken with a Philips Diffractometer using Ni-filtered CuK $\alpha$  radiation. The scanning speed was  $\frac{1}{3}^\circ$  per minute.

The magnetic susceptibility was measured with an Alpha Magnetometer in the temperature range of 80 to 320°K and field strength of ca. 7.6 kOe. The absolute value was determined by the use of Co[Hg(SCN)<sub>4</sub>] as standard. In the temperature range of 4.2 to 65°K and field strengths of 2.5, 5, and 10 kOe the magnetization was measured using a small pendulum magnetometer developed in the laboratory (10).

Mössbauer studies of the 86.5-keV  $\gamma$ -ray of <sup>155</sup>Gd in MnGd<sub>2</sub>S<sub>4</sub> were performed at 4.2°K using a <sup>155</sup>SmPd<sub>3</sub> source.

## Results and Discussion

MnGd<sub>2</sub>S<sub>4</sub> has the Th<sub>3</sub>P<sub>4</sub> structure belonging to the space group  $I43d-T_d^2$ , which is a body-centred cubic structure, with four molecules in

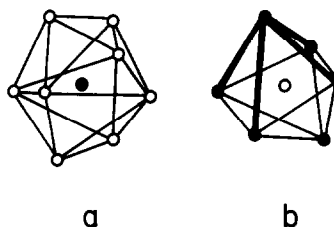


FIG. 1. The cubic Th<sub>3</sub>P<sub>4</sub> polyhedra; (a) the [ThP<sub>8</sub>] octaverticon; (b) the [PTh<sub>6</sub>] distorted octahedron.

the unit cell and  $a_0 = 8.360$  Å. The structure was discovered by Meisel (11) and the first detailed description given by Kripyakevich (12). The Th atom (Mn and Gd) occupies the 12(a) position and is surrounded by eight P atoms (S) in the 16(c) positions. This maximum coordination is obtained by a parameter  $x \approx \frac{1}{12}$ . The [ThP<sub>8</sub>] is an octaverticon containing triangular faces and surrounded by 8 identical polyhedra. The [PTh<sub>6</sub>] is a distorted octahedron surrounded by 11 similar polyhedra (Figs. 1a and b). The Th<sub>3</sub>P<sub>4</sub> structure has similarities with other structures containing octahedra, in the first place with the NaCl type.

The relative X-ray diffraction intensities were measured and the structural parameters refined with the aid of a FORTRAN program<sup>1</sup> to obtain a minimum value for the factor  $R$  defined as

$$R = \frac{\sum_{hkl} |I_{\text{obs}}(hkl) - I_{\text{calc}}(hkl)|}{\sum_{hkl} I_{\text{obs}}(hkl)} \times 100.$$

A comparison of observed and calculated intensities, based on a random metal distribution, is presented in Table I. The final refinement of parameters gave an  $R = 10.4$  value based on a sulfur  $x$  parameter of  $0.070 \pm 0.003$ . When using the accepted value of  $x = 0.083$  for Th<sub>3</sub>P<sub>4</sub>, this gives an  $R$  value close to 16. The interatomic distances as obtained with

<sup>1</sup>A FORTRAN program for calculating X-ray powder diffraction patterns (1963) by D. K. Smith, University of California.

TABLE I  
 X-RAY DATA FOR MnGe<sub>2</sub>S<sub>4</sub><sup>a</sup>

$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{obs}}$	$I_{\text{calc}}$
3.415	3.412	2 1 1	78.3	90.4
2.956	2.955	2 2 0	4.3	5.6
2.644	2.643	3 1 0	100	100
2.235	2.234	3 2 1	59.3	58.9
2.089	2.090	4 0 0	2.4	2.3
1.869	1.869	4 2 0	40.9	38.9
1.782	1.782	3 3 2	24.9	25.0
1.705	1.706	4 2 2	8.9	8.7
1.639	1.639	5 1 0, 4 3 1	27.7	30.5
1.526	1.526	5 2 1	6.1	6.8
	1.477	4 4 0	n.o. <sup>b</sup>	2.1
1.356	1.356	6 1 1, 5 3 2	31.6	36.6
1.322	1.321	6 2 0	6.7	7.5
1.290	1.289	5 4 1	9.3	14.0
	1.232	6 3 1	n.o. <sup>b</sup>	3.7
1.206	1.206	4 4 4	5.1	7.5
	1.182	7 1 0, 5 4 3	n.o. <sup>b</sup>	0.1
1.159	1.159	6 4 0	5.6	7.9
1.137	1.137	5 5 2, 6 3 3, 7 2 1	22.5	27.0

<sup>a</sup>  $a_0 = 8.360 \text{ \AA}$ .  $R = 10.4$ .  $x = 0.070 \pm 0.003$ .

<sup>b</sup> n.o.—Not observed.

the aid of the SADIAN program are given in Table II to within  $\pm 0.003 \text{ \AA}$ .

Holtzberg and Methfessel (13) calculated interatomic distances for the polyhedron having Th<sub>3</sub>P<sub>4</sub> structure for the  $x$  parameter in the range  $0 \leq x < \frac{1}{4}$ . For  $x = \frac{1}{2}$  the anions occupy the midpoints of the polyhedra (Fig. 1a); for  $x \neq \frac{1}{2}$  the anion is shifted along the  $1\bar{1}\bar{1}$  axis and the interatomic distances are changed. As a result of such a distortion two distances of sulfur-metal are formed: a shorter one S-3M = 2.777 Å and a longer one S-3M = 3.018 Å. For the sulfur-sulfur three different distances

are obtained: S-3S = 3.227 Å; S-2S = 3.619 Å; S-6S = 3.980 Å. These are distances between the centro-shifted sulfur in one polyhedron to the sulfur atoms on crystallographic axes emerging through the polyhedron faces.

Concerning the metal-metal distances, here, too, a shorter and a longer one are obtained. Since the Th<sub>3</sub>P<sub>4</sub> structure contains only one metal site, 12a, the metal distribution is per force a random one. Thus one cannot assign the distances to specific cations as has been suggested by Lugscheider *et al.* (6).

The reciprocal magnetic susceptibility vs temperature for the range 80–320°K gave a straight line with a slope-Curie constant  $-19.5 \pm 0.3 \text{ emu/mole}$  and Curie temperature  $\theta(^{\circ}\text{K}) = -18$ .

Magnetization vs magnetic field for the low-temperature range (4.2–60°K) gave also straight lines with the Curie constant  $C = 20.6 \pm 0.8 \text{ emu/mole}$  and  $\theta(^{\circ}\text{K}) = -15.1$ . The theoretical Curie constant when calculated from the individual contributions of Mn<sup>2+</sup> ( $S = \frac{5}{2}$ ) and Gd<sup>3+</sup> ( $S = \frac{7}{2}$ ) and bearing in mind that

$$C = \frac{P_{\text{eff}}^2(\text{Mn}^{2+}) + 2P_{\text{eff}}^2(\text{Gd}^{3+})}{2.84^2}$$

$$\text{is } \frac{5.92^2 + 2 \times 7.94^2}{2.84^2} = 20.0 \text{ emu/mole.}$$

The experimental values 19.5 emu/mole for the high-temperature range, and 20.6 emu/mole for the low-temperature range are in good agreement with the calculated constant: 20.0 emu/mole. This means that down to He temperature the curves obey a Curie-Weiss law and only paramagnetic behavior is observed. It was anticipated that interactions between the magnetic metal ions would be observed owing to the appreciable covalent character of the sulfur anions to give cooperative phenomena but this does not happen above 4.2°K. The same was observed for a whole family of compounds of the general formula EuLn<sub>2</sub>S<sub>4</sub>, where a low-magnetic-ordering temperature was obtained (6). All these compounds as well as EuGd<sub>2</sub>S<sub>4</sub>

 TABLE II  
 INTERATOMIC DISTANCES IN MnGd<sub>2</sub>S<sub>4</sub> (Å)

M-M	3.910
M-M	4.673
S-S	3.227
S-S	3.619
S-S	3.980
M-S	2.777
M-S	3.018

(14) and  $MTm_2S_4$  and  $MYb_2S_4$  ( $M = Mn, Mg$ ) in the  $Th_3P_4$  high-pressure phase (5) show a good fit of the individual contributions of the two relevant metals to the magnetization.

The Mössbauer spectrum is shown in Fig. 2. Least-squares computer calculations fit the experimental spectra assuming only a pure quadrupole hyperfine interaction. Magnetic hyperfine interactions have not been taken into account indicating that the  $Gd^{3+}$  ions are paramagnetic at 4.2°K. The isomer shift (I.S.) and the electric field gradient ( $eqQ$ ) derived from the spectra are 0.44(1) mm/sec, relative to the source, and 165 mHz, respectively. The value of I.S. indicates that the  $s$  electron density at the Gd nucleus is appreciably reduced in the  $MnGd_2S_4$  with respect to the metallic source mainly because of the ionic character of the Gd-S bond, in accordance with the interatomic distances obtained from the crystallographic data. The  $eqQ$  obtained is

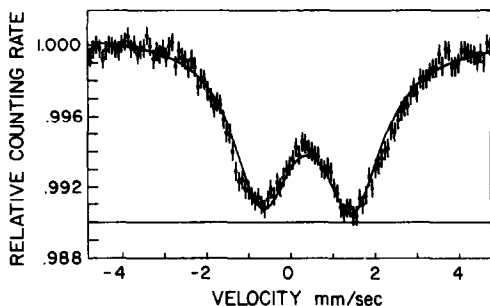


FIG. 2. Recoilless absorption spectrum of  $^{153}Gd$  in  $MnGd_2S_4$ . The theoretical smooth curve was obtained by a least-squares computer program which fits the experimental points.

due to the asymmetric electric environment acting on the  $Gd^{3+}$  ions in the 12(a) sites in the  $Th_3P_4$ -type structure.

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