JOURNAL OF SOLID STATE CHEMISTRY 35, 103–106 (1980)

Magnetic Behavior in Solid Solution Systems: II. (MnMg)Gd_2S_4 and (MnMg)Yb_2S_4

L. BEN-DOR AND I. SHILO*

Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel

Received December 11, 1979

The solid solutions in the systems (MnMg)Gd_2S_4 and (MnMg)Yb_2S_4 have the cubic Th_3P_4 (space group $I\bar{4}3d$) and the cubic spinel (space group $Fd3m$) structure, respectively. All materials are paramagnetic above 77 K. The spinel (higher symmetry) family shows a downward curvature to the origin below 60 K. The Th_3P_4 family exhibits two differing behaviors: for $x = 0,1$ the Curie–Weiss law is obeyed down to 4.2 K; for $0 < x < 1$ some magnetic ordering is observed.

Introduction

In Part I (*1*) the orthorhombic system (MnMg)Tb_2S_4 was studied and dilution of the magnetic system helped in evaluating exchange interactions. Here two similar systems, cubic in structure, are studied whereby Tb is exchanged for Yb or Gd. In each case the crystal structure is maintained throughout and the magnetic behavior is studied by dilution of the Mn^{2+} by Mg^{2+} ions.

The pure component materials in the case of Yb had been prepared by the Flahaut school (*2*) but they were unsuccessful at that time in obtaining pure material in the case of Gd. Magnetic properties of $MnYb_2S_4$ were studied by various authors (*3–6*) and those of $MgYb_2S_4$ were reported by Hirota *et al.* (*6*). Other relevant materials studied for their magnetic properties were $MnSc_2S_4$ (*5*); $MgTm_2S_4$ and $MnTm_2S_4$ (*6*); and $MnEr_2S_4$, $MgEr_2S_4$, and (MnMg)Y_2S_4 (*7*).

Experimental and Results

The appropriate sulfides MnS, MgS, Yb_2S_3, Gd_2S_3 were weighed, ground and mixed, and introduced into a quartz ampoule. The ampoule was evacuated, sealed, and heated at 1100°C for 48 hr. After quenching the ampoule was broken open and chemical analysis for manganese and magnesium was performed by atomic absorption spectrometry. Stoichiometry was proven to within 0.5% compared to the weighed composition.

Only one phase was observed by X-ray diffraction for all the materials obtained. In the spinel family (MnMg)Yb_2S_4 the values of the cell parameters were as follows:

	a (Å)			
$x = 1$	$x = 0.5$	$x = 0.333$	$x = 0.167$	$x = 0$
10.955 10.95(*3,4*) 10.949(*9,10*)	10.961	10.963	10.964	10.967 10.957(*8*)

* In partial fulfillment of the Ph.D. degree. Present address: Ames Laboratory, Iowa State University, Ames, Iowa 50011.

0022-4596/80/130103-04$02.00/0

TABLE I

MEASURED AND CALCULATED RESULTS OF X-RAY DIFFRACTION DATA FOR $MgYb_2S_4$

$d_{obs.}$	$d_{calc.}$	$h\ k\ l$	$I_{obs.}$	$I_{calc.}$
6.3391	6.3318	111	89.0	89.4
3.8883	3.8774	220	2.3	1.3
3.3070	3.3067	311	99.6	100
3.1677	3.1659	222	38.5	36.5
2.7409	2.7417	400	100	85.2
2.5183	2.5160	331	27.6	34.1
2.1132	2.1106	511, 333	43.4	39.2
1.9375	1.9387	440	90.3	77.5
1.8526	1.8537	531	27.5	26.2
1.6723	1.6724	533	13.6	14.8
1.6537	1.6533	622	21.3	19.9
1.5824	1.5829	444	24.2	21.9
1.5359	1.5357	551, 711	13.5	14.5
1.4283	1.4278	731, 553	19.1	26.8
1.3717	1.3709	800	12.1	12.5
1.2653	1.2663	751, 555	11.6	13.5
1.2582	1.2580	662	6.4	8.3
1.2256	1.2261	840	24.6	28.6
1.2035	1.2037	753, 911	7.5	7.2
1.1502	1.1496	931	8.1	8.4

In the case of the cubic Th_3P_4 family the cell parameters for all values of x were in fact identical and were found to be 8.360 Å for $MnGd_2S_4$ and 8.359 Å for $MgGd_2S_4$. These two compounds have not been reported in literature (cf. (*10*, *11*)). The powder diffraction data for $MgYb_2S_4$ and $MgGd_2S_4$ are shown in Tables I and II.

The magnetic susceptibility of the two systems was measured and for temperatures above 77 K all the materials were paramagnetic. Table III gives the magnetic data for all materials obeying the Curie–Weiss law.

For the Yb spinel system the reciprocal susceptibility vs T for the temperature range 4.2–50 K shows a dependence steeper than that for the higher-temperature range with a break in the curve below ≈60 K. The 4.2 K magnetization dependence on field strength to 17 kOe is linear and of low value (Fig. 1). The magnetization vs temperature gives no evidence of any magnetic ordering. A Mössbauer experiment on the Yb atom in $MgYb_2S_4$ also proved that magnetic ordering was nonexistent to 4.2 K. Longo and Raccah (*3*), who studied $MnYb_2S_4$ to 4.2 K, discovered the same behavior including the break in linearity at 60 K. They attribute this behavior to the Yb ions (*12*). Barthelemy (*13*) observed a similar curvature in the orthorhombic MnY_2S_4 and deduced that the material is ferrimagnetic with a Curie temperature near 0 K. Heikens *et al.* (*7*), on the other hand, maintain that in the orthorhombic structure some of the Mn^{2+} ions are isolated and thus paramagnetic, but others form clusters of four to six ions and an exchange coupling exists among them which results in zero reciprocal susceptibility near 0 K.

The system studied here is of a normal spinel structure and thus only one ion, viz., Yb, occupies the octahedral site. In the case of $MgYb_2S_4$ no magnetic ordering was found to 4.2 K (Mössbauer). Adding a second magnetic ion, Mn^{2+}, in the tetrahedral site, instead of Mg^{2+}, does not alter the

TABLE II

MEASURED AND CALCULATED RESULTS OF X-RAY DIFFRACTION DATA FOR $MgGd_2S_4$

$d_{obs.}$	$d_{calc.}$	$h\ k\ l$	$I_{obs.}$	$I_{calc.}$
3.4102	3.4117	211	85.2	80.9
2.9535	2.9546	220	4.8	4.6
2.6404	2.6427	310	100	100
2.2325	2.2335	321	61.6	59.0
2.0877	2.0892	400	3.0	2.1
1.8679	1.8687	420	34.4	37.4
1.7809	1.7817	332	22.1	24.1
1.7050	1.7058	422	6.5	8.7
1.6385	1.6389	510, 431	28.9	29.2
1.5257	1.5257	521	4.5	6.4
1.4773	1.4773	440	1.4	2.0
1.3559	1.3557	611, 532	30.4	36.2
1.3214	1.3213	620	5.2	7.7
1.2896	1.2895	541	11.0	14.1
1.2329	1.2322	631	2.4	3.6
1.2064	1.2062	444	7.4	7.5
1.1595	1.1589	640	7.2	7.8
1.1374	1.1372	552, 633, 721	17.4	26.9

TABLE III

CURIE CONSTANT AND CURIE TEMPERATURE FOR $Mn_xMg_{1-x}Yb_2S_4$ AND $Mn_xMg_{1-x}Gd_2S_4$

$(MnMg)Yb_2S_4$				$(MnMg)Gd_2S_4$			
x	$C_{obs.}$	$C_{calc.}$	$-\theta$(K)	x	$C_{obs.}$	$C_{calc.}$	$-\theta$(K)
1	9.34	9.45	50	1	20.1(10)	20.0	13
	9.5(3)(14)		60				
	10.2(4)(15)		30	0.667	18.9	18.5	14
	10.0(6)		54				
0.5	7.39	7.28	56	0.5	17.1	17.8	10
0.333	7.06	6.55	67	0.333	17.5	17.1	13
0.167	6.60	5.80	71	0.167	16.2	16.3	7
0	5.90	5.10	81	0	15.8	15.6	11
	4.4(5)		60				

behavior. Thus it is postulated that the nonobeyance of the Curie–Weiss law for low temperature stems from the fact that the distance between the J states is large, i.e., $\Delta \gg kT$, rather than from any magnetic ordering.

In the case of the Th_3P_4 system, both pure components ($MnGd_2S_4$ and $MgGd_2S_4$) obey the Curie–Weiss law down to 4.2 K but for $0 < x < 1$ there is a deviation from linearity both in the curves of magnetization vs field (Fig. 1) and in the dependence of magnetization vs temperature an example of which is shown in Fig. 2. It was stated (*10*) that in $MnGd_2S_4$, similar to spinel $MnSc_2S_4$ (*16*), there might be a negative weak magnetic ordering of the Mn^{2+} ions below 4.2 K and also a weak Mn–Gd exchange coupling. The weak interaction is due to the comparatively large M–M distances in the Th_3P_4 structure as opposed to the much smaller distances in the spinel structure. (Mn–Mn distance in the spinel is 0.8 Å shorter than that in Th_3P_4.) In the solid solution materials which contain both Mn^{2+} and Mg^{2+}, a cooperative phenomenon

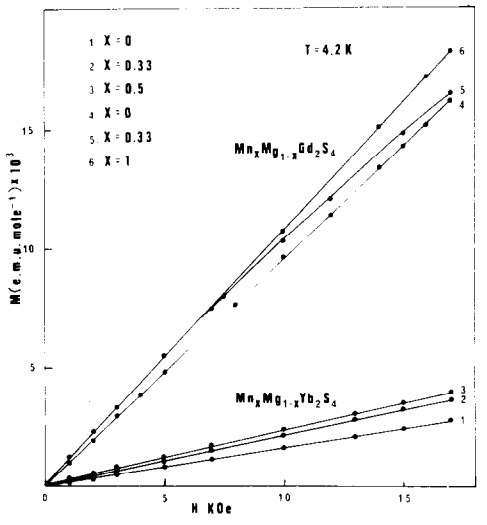

FIG. 1. Magnetization vs magnetic field for $(MnMg)Yb_2S_4$ and $(MnMg)Gd_2S_4$ at 4.2 K.

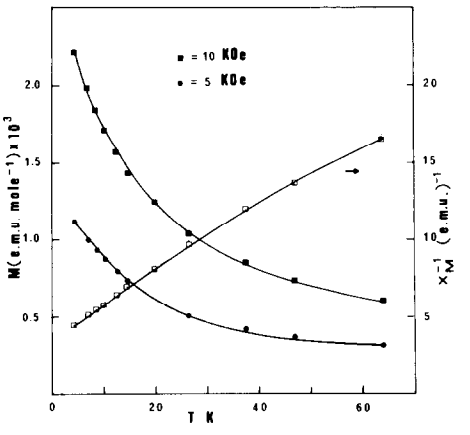

FIG. 2. Magnetization and reciprocal susceptibility vs temperature for $Mn_{0.33}Mg_{0.67}Gd_2S_4$.

is demonstrated at 4.2 K for a certain dilution of the magnetic ion.

This phenomenon is interesting and was not observed in the former solid solution system with Yb. The difference between the two systems is also demonstrated in Fig. 1—higher magnetization values for the Gd system compared to the Yb system. The explanation lies in the fact that the Gd is an S ion, not affected by the crystal field, while the Yb suffers a severe quenching of its ground Stark state. In trying to summarize the three solid solution systems,

$(MnMg)Tb_2S_4$ orthorhombic structure (*1*)
$(MnMg)Yb_2S_4$ spinel structure
$(MnMg)Gd_2S_4$ Th_3P_4 structure

there are two main points that affect the magnetic interactions: (1) symmetry and (2) metal–metal distance. The point symmetry in the orthorhombic structure is 1, in the spinel it is $\bar{3}m$, and in the Th_3P_4 it is $\bar{4}$. Also, M–M distances in the various symmetries are: orthorhombic $<Th_3P_4$ (*17*); spinel $<Th_3P_4$ (*16*).

Thus short distances and total low symmetry in the $(MnMg)Tb_2S_4$ system are associated with strong magnetic ordering. In the highly symmetrical spinel system there is no magnetic ordering (above 4.2 K) and only weak negative interaction in the magnetically diluted Th_3P_4 system.

References

1. L. BEN-DOR AND I. SHILO, *J. Solid Chem.* **35**, 99 (1980).
2. M. PATRIE AND M. R. CHEVALIER, *C.R. Acad. Sci. Paris C* **263**, 1061 (1966).
3. J. M. LONGO AND P. M. RACCAH, *Mater. Res. Bull.* **2**, 541 (1967).
4. L. SUCHOW AND A. A. ANDO, *J. Solid State Chem.* **2**, 156 (1970).
5. S. KAINUMA, *J. Phys. Soc. Japan* **30**, 1205 (1971).
6. K. HIROTA, N. KINOMURA, S. KUME, AND M. KOIZUMI, *Mater. Res. Bull.* **11**, 227 (1976).
7. H. H. HEIKENS, R. S. KUINDERSMA, C. F. VAN BRUGGEN, AND C. HAAS, *Phys. Status Solidi A* **46**, 687 (1978).
8. M. PATRIE, J. FLAHAUT, AND L. DOMANGE, *C. R. Acad. Sci. Paris* **258**, 2585 (1964).
9. M. GUITTARD, C. SOULEAU, AND H. FARSAM. *C.R. Acad. Sci. Paris* **259**, 2847 (1964).
10. L. BEN-DOR, I. SHILO, AND I. FELNER, *J. Solid State Chem.* **24**, 401 (1978).
11. J. FLAHAUT, L. DOMANGE, AND M. PATRIE, *Bull. Soc. Chim.*, 2048 (1962); J. FLAHAUT, *in* "Progress in the Science and Technology of Rare Earths" (L. Eyring, Ed.), Vol. III, Pergamon, Oxford (1968).
12. S. KERN AND P. M. RACCAH, *J. Phys. Chem. Solids* **26**, 1625 (1965).
13. E. BARTHELEMY, thesis, Paris (1971).
14. M. SHIMADE, S. KUME, AND M. KOIZUMI, *J. Amer. Ceram. Soc.* **51**, 713 (1968).
15. R. D. SCHANNON AND C. T. PREWITT, *Acta Crystallogr. B* **29**, 925 (1969).
16. P. J. WOJTOWICZ, L. DARCY, AND M. RAYL, *J. Appl. Phys.* **40**, 1023 (1969).
17. W. LUGSCHEIDER, H. PINK, K. WEBER, AND W. ZINN, *Z. Angew. Phys.* **30**, 36 (1970).