Magnetic Behavior in Solid Solution Systems: I. (MnMg)Tb₂S₄

L. BEN-DOR AND I. SHILO*

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

The solid solutions in the system $Mn_xMg_{1-x}Tb_2S_4$ for $0 \leq x \leq 1$ all have the orthorhombic MnY_2S_4 structure, space group $Cmc2_1$. In the temperature range 77–300 K the materials are paramagnetic and the Curie–Weiss law is obeyed. At low temperatures, ca. 20 K, there is a deviation from linearity of the curve of χ^{-1} vs T. The curves of magnetization as a function of the magnetic field at 4.2 K are reminiscent of saturation curves, especially for low values of x. The magnetic interactions between the metal ions are discussed.

Introduction

Compounds of the general formula AB_2X_4 for A, B metal ions and $X = O$, S can have one of ten structures. Steinfink *et al.* (*1, 2*) tried to outline a correlation between the crystal structure and some intrinsic properties of the metal ions such as rA/rB and K_{AB}, which is a function of χ_A and χ_B, the electronegativity of A and B, respectively, and r_e, which is the equilibrium distance. In the map showing the boundaries of the different possible structures, the cubic spinel, the cubic Th_3P_4, and the orthorhombic MnY_2S_4 lie in a comparatively small area and have boundaries of mutual existence. These structures occur for the heavier lanthanides (B ions), i.e., smaller-radius ions, and for medium-sized active metal ions: Mg^{2+}, Mn^{2+}, Cd^{2+} (A ions).

The system $(MnMg)Tb_2S_4$ was chosen in order to study the effect of diluting the

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

magnetic ion Mn by Mg while keeping the crystal structure unchanged. The component materials of this system, viz., $MnTb_2S_4$ and $MgTb_2S_4$, both crystallize in the orthorhombic MnY_2S_4 structure with about the same cell parameters at room temperature. A similar study was carried out by Heikens *et al.* for the systems $(MnMg)Y_2S_4$ (*3*) and $(MnMg)S$ (*4*).

Experimental and Results

The appropriate sulfides MnS, MgS, Tb_2S_3 were weighed, ground, and mixed and introduced into a quartz ampoule. The ampoule was evacuated and sealed under a vacuum and heated at 1100°C for 48 hr. After quenching, the ampoule was broken open and chemical analysis by atomic absorption spectrometry was carried out on the various materials. Stoichiometry was proven to within 1%.

X-Ray diffraction patterns showed the existence of only one pure orthorhombic phase, MnY_2S_4, with the space group $Cmc2_1$ for the entire range $0 \leq x \leq 1$.

Patrie and Chevalier (5) have reported the crystal structure of the two pure components within a family of orthorhombic compounds. Table I gives the cell parameters found and compares them to those given in the literature. As seen from Table I the differences between the cell parameters are within 0.01 Å and thus for all practical purposes it is assumed that the cell constants are identical for the two pure components and for the solid solutions obtained therefrom.

Magnetic data were collected for all the materials in a high- and a low-temperature range: 77–300 and 4.2–50 K. All the materials are paramagnetic and they obey the Curie–Weiss law in the high-temperature range. The Curie constant, C, and the Curie temperature, θ, are shown in Table II. The effective moment of Tb^{3+} is 9.72 μ_B and of Mn^{2+}, 5.92 μ_B.

The Curie constant was calculated from the relative weights of the magnetic ions in the compound:

$$C_{calc.} = \frac{x \cdot \mu_{eff}^2(Mn^{2+}) + 2 \cdot \mu_{eff}^2(Tb^{+3})}{8.06}.$$

For low temperatures an unexpected phenomenon is observed. At 4.2 K and for field strengths up to 15 kOe the magnetization M vs field H curves show a stronger approach to saturation for $x = 0$, viz., for $MgTb_2S_4$, and a very weak one for $x = 1$, viz., for $MnTb_2S_4$, while all other intermediate x's are arranged between the two extremes (Fig. 1). The reciprocal molar susceptibility vs temperature in the range

TABLE I

CELL PARAMETERS OF $MnTb_2S_4$ AND $MgTb_2S_4$

	a (Å)	b (Å)	c (Å)	Reference
$MnTb_2S_4$	3.79	12.76	12.65	This work
	3.78	12.76	12.63	(5)
$MgTb_2S_4$	3.79	12.76	12.64	This work
	3.78	12.74	12.62	(5)

TABLE II

C AND θ FOR $Mn_xMg_{1-x}Tb_2S_4$

	x				
	0	0.25	0.5	0.75	1.0
$C_{obs.}$	23.8	25.4	27.0	27.5	28.1
$C_{calc.}$	23.4	24.5	25.6	26.7	28.0
θ(K)	-3.0	-4.7	-4.5	-6.8	-4.0

4.2–50 K shows positive asymptotic curves with a small Curie–Weiss temperature. The magnetization vs temperature shows a tendency toward magnetic ordering, this tendency decreasing monotonously with the amount of Mn^{2+} substitution (increasing values of x) and nearly disappearing at the limit for $x = 1$. This behavior is demonstrated in Figs. 2 and 3 for $MgTb_2S_4$ and $MnTb_2S_4$, respectively, as representative examples.

Discussion

In the system $Mn_xMg_{1-x}Tb_2S_4$, as x decreases Mg^{2+} ion exchange for Mn^{2+} ions and for $x = 0$ the manganese magnetic sublattice disappears, leaving only the ter-
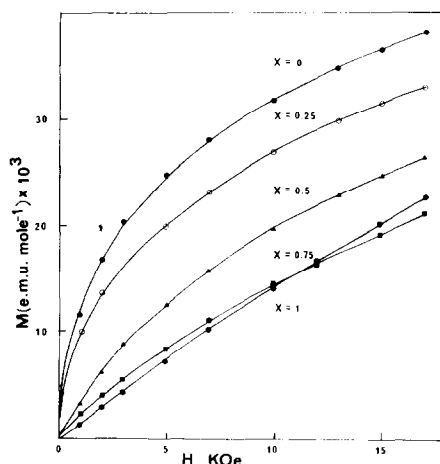

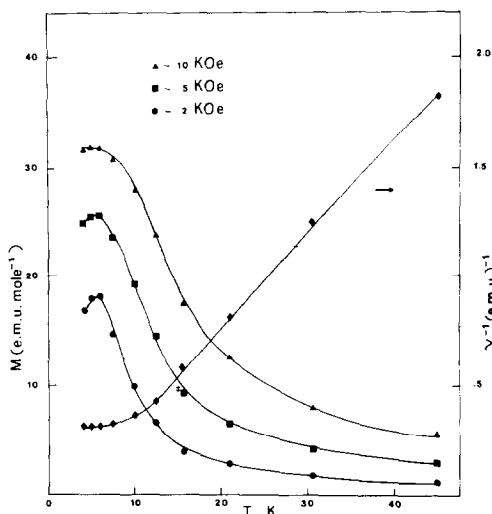FIG. 1. M vs H for the system $Mn_xMg_{1-x}Tb_2S_4$ at 4.2 K.

FIG. 2. M and χ^{-1} vs T for MgTb₂S₄ for various field strengths.

bium sublattice. For intermediate values of x both sublattices coexist. This nonmagnetic dilution makes possible the study of Mn–Tb interactions if they exist. In his thesis (6) and a subsequent report (3) Heikens studied a similar orthorhombic system containing only one magnetic ion: $Mn_xMg_{1-x}Y_2S_4$. He revealed the presence of strongly negative Mn–Mn exchange interactions for $x = 1$, while for the dilute system there existed isolated Mn ions and finite clusters, made up of four to six members of exchange-coupled Mn ions.

In Fig. 1 for small values of x the magnetization moment approaches saturation for a field of 17 kOe. Also, at low field the moment of MnTb₂S₄ reaches only ~30% of the value for MgTb₂S₄. Comparison of Figs. 2 and 3 shows that for a temperature range of 6–15 K at low field, 2 kOe, the moment for MgTb₂S₄ jumps 4.5-fold while that for MnTb₂S₄ changes by 1.5-fold only.

M_{sat} is the saturation moment estimated by plotting the values obtained for M from 12–17 kOe vs H^{-2} and extrapolation to H^{-2} → 0 (7). For MgTb₂S₄, M_{sat} is $\simeq 10$ μ_B and for MnTb₂S₄, $M_{sat} \simeq 5$ μ_B. The two

figures mentioned above and these estimated values justify the assumption that the Mn–Tb interaction is antiferromagnetic and that the Tb–Tb interaction is ferromagnetic or canted ferromagnetic.

The compounds under discussion are orthorhombic, of comparatively low symmetry, and the Tb ions occupy two different sites—prismatic and octahedral. Thus, it is probable that the splitting of the J level will be maximal and the Stark levels will be singlets. In other words the effective saturation moment can reach 9 μ_B at the limit only. The value of ca. 10 μ_B for two ions of Tb^{3+} in MgTb₂S₄ results from a canted ferromagnetic interaction or another positive exchange. The value of ca. 5 μ_B in the case of MnTb₂S₄ is the result of positive Tb–Tb and negative (resultant) Tb–Mn exchange. The diluted system Mn_x $Mg_{1-x}Tb_2S_4$ shows an intermediate behavior between the two extreme cases ($x = 0, x = 1$). When x decreases toward zero, the value of the magnetization as a function of the magnetic field increases. Also for low fields ≈ 1 kOe, the curves are very steep for $x = 0, 0.25$ and level off as x increases. All this substantiates the idea that while the nonmagnetic Mg^{2+} ions do not interfere
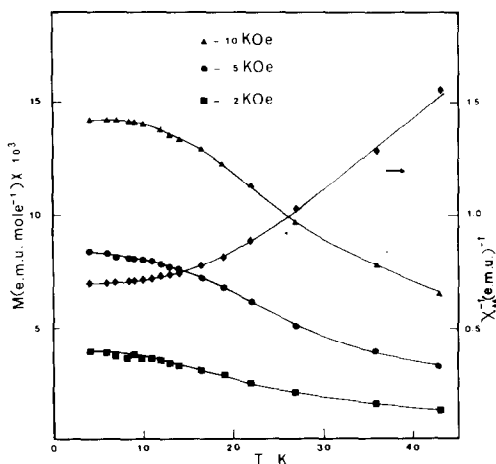

FIG. 3. M and χ^{-1} vs T for MnTb₂S₄ for various field strengths.

with the positive Tb–Tb interaction, the negative Mn–Tb interaction interferes, reducing the overall magnetization with increasing content of Mn. It cannot be ruled out that a negative Mn–Mn exchange can also exist.

In conclusion, it was shown that diluting a magnetic system helps in evaluating the exchange interactions between the magnetic species.

Acknowledgments

References

1. K. KUGIMIGA AND H. STEINFINK, *Inorg. Chem.* 7, 1762 (1968).
2. J. E. IGLESIAS AND H. STEINFINK, *J. Solid State Chem.* 6, 119 (1973).
3a. H. H. HEIKENS AND C. F. VAN BRUGGEN, *Proc. Int. Conf. Magn. ICM-73, Moscow*, 1(2), 83 (1974).
3b. H. H. HEIKENS, R. S. KUINDERSMA, C. F. VAN BRUGGEN, AND C. HAAS, *Phys. Status Solidi A* 46, 687 (1978).
4. H. H. HEIKENS, R. S. KUINDERSMA, C. F. VAN BRUGGEN, AND C. HAAS, *J. Magn. Magn. Mater.* 8, 130 (1978).
5. M. PATRIE AND M. R. CHEVALIER, *C. R. Acad. Sci. Paris C* 263, 1061 (1966).
6. H. H. HEIKENS, Ph.D. thesis, Groningen (1977).
7. K. H. J. BUSCHOW AND V. S. VAN DER GROOT, *Phys. Status Solidi* 35, 515 (1969).