

## Magnetic properties of $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$ <sup>†</sup>

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MS received 26 November 1986

**Abstract.** Magnetic susceptibility of  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  members crystallizing in two different structures, one having octahedral (O), tetrahedral (T) and square-pyramidal (SP) coordination of transition metal atoms (OTSP structure) and the other having octahedral and tetrahedral coordination (OT structure), has been investigated. Susceptibility behaviour of the oxides with OTSP structure is different from that of the oxides with OT structure.  $\text{Ca}_2\text{Fe}_{1.33}\text{Mn}_{0.67}\text{O}_5$  with OTSP structure shows an antiferromagnetic ordering while the corresponding oxide with OT structure shows weak ferromagnetism.

**Keywords.**  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$ ; magnetic susceptibility.

### 1. Introduction

We have recently synthesized a new series of oxides of the general formula  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  employing the carbonate solid-solutions  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x(\text{CO}_3)_4$  as precursors (Vidyasagar *et al* 1986). The oxides crystallize in an orthorhombic structure related to brownmillerite (B.M.) and  $\text{Ca}_2\text{Mn}_2\text{O}_5$ . Electron diffraction investigations of these oxides (Rao *et al* 1986) revealed a novel oxygen vacancy ordering derived from the perovskite structure indicating the presence of three different coordination polyhedra [octahedra (O), tetrahedra (T) and square-pyramids (SP)] around the transition metal atoms (OTSP structure).  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  with OTSP structure transform to the brownmillerite structure (OT structure) on heating at  $\sim 1050$  K *in vacuo*. These oxides provide a rich variety of systems for investigating the magnetic properties of  $\text{Fe}^{3+}$  and  $\text{Mn}^{3+}$  in different oxygen coordinations. In this communication, we briefly report magnetic susceptibility studies of  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  in both the structures over the temperature range 40–800 K.

### 2. Experimental

$\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  ( $x = 0.67, 1.00$  and  $1.33$ ) in OTSP and OT structures were prepared as described earlier (Vidyasagar *et al* 1986). Magnetic susceptibilities were measured by the Faraday method using a Cahn RG electrobalance. For measurements in the 300–800 K range, the sample held *in vacuo* at  $\sim 10^{-3}$  torr was

<sup>†</sup> Contribution No. 398 from the Solid State and Structural Chemistry Unit

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heated using a microfurnace. For measurements in the 40–300 K range, a closed cycle helium cryostat (Air Products Displex) was employed.  $\text{HgCo}(\text{NCS})_4$  was used as the calibrant and the susceptibilities were corrected for diamagnetism.

### 3. Results and discussion

Magnetic susceptibility data of  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  are given in table 1. We see clearly an antiferromagnetic ordering around 570 K in  $\text{Ca}_2\text{Fe}_{1.33}\text{Mn}_{0.67}\text{O}_5$  (1) and  $\text{Ca}_2\text{FeMnO}_5$  (2), while in  $\text{Ca}_2\text{Fe}_{0.67}\text{Mn}_{1.33}\text{O}_5$  (3) the antiferromagnetic ordering is significantly missing. Instead, the last oxide shows a weak ferromagnetism, the susceptibility increasing sharply around 680 K. Sample (1) shows an additional susceptibility maximum around 140 K. The paramagnetic Curie temperature  $\theta_p$  increases with increasing  $\text{Mn}^{3+}$  content.

The susceptibility behaviour of  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  changes drastically on transforming to the brownmillerite (OT) structure. Significantly, the antiferromagnetic ordering noticed in samples (1) and (2) is missing in samples (4) and (5); instead, the latter show a weak ferromagnetism. Moreover, the trend in  $\theta_p$  values is reversed in samples (4)–(6);  $\theta_p$  becomes more negative with increasing  $\text{Mn}^{3+}$  content.

An understanding of the complex magnetic behaviour of  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  requires a knowledge of the various magnetic interactions that are possible in these oxides. The possible interactions are  $180^\circ \text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{3+}$  and  $\text{Fe}^{3+}-\text{O}^{2-}-\text{Mn}^{3+}$  superexchanges. Of these, the  $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$  interaction is strongly antiferromagnetic (Kanamori 1959), while the  $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{3+}$  interaction could be both ferromagnetic and antiferromagnetic; this interaction becomes anisotropic when the  $e_g$  orbitals of the Jahn-Teller  $\text{Mn}^{3+}$ :  $d^4$  are ordered (Goodenough *et al* 1961).  $\text{Fe}^{3+}-\text{O}^{2-}-\text{Mn}^{3+}$  interaction also could be both ferromagnetic and antiferromagnetic. Both  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and  $\text{Ca}_2\text{Mn}_2\text{O}_5$  are known to order antiferromagnetically at 725 K and 350 K respectively (Grenier *et al* 1973; Poeppelmeier *et al* 1982). The antiferromagnetic ordering temperatures of samples (1) and (2) (table 1) ( $\sim 570$  K) are in between the ordering temperatures of the end members; the additional  $\text{Mn}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$  interaction in the solid solutions apparently lowers the Néel

Table 1. Magnetic susceptibility data of  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  oxides.

Compound number	Composition	$C_M$ (Experimental)	$C_M$ (Calculated)	$T_N$ (K)	$\theta_p$ (K)
1	$\text{Ca}_2\text{Fe}_{1.33}\text{Mn}_{0.67}\text{O}_5$	6.67	11.68	564	-384
2	$\text{Ca}_2\text{FeMnO}_5$	5.71	10.99	570	-8
3	$\text{Ca}_2\text{Fe}_{0.67}\text{Mn}_{1.33}\text{O}_5$	4.00	10.31	—	248
4	$\text{Ca}_2\text{Fe}_{1.33}\text{Mn}_{0.67}\text{O}_5$ (B.M.)	6.15	11.68	—	-104
5	$\text{Ca}_2\text{FeMnO}_5$ (B.M.)	7.62	10.99	—	-180
6	$\text{Ca}_2\text{Fe}_{0.67}\text{Mn}_{1.33}\text{O}_5$	10.66	10.31	—	-488

$C_M$  - molar Curie constant;  $T_N$  - Néel temperature;  $\theta_p$  - paramagnetic Curie temperature; B.M. - Brownmillerite.

temperature as compared to  $\text{Ca}_2\text{Fe}_2\text{O}_5$ . The magnetic behaviour of sample (3) is intriguing; there is no apparent antiferromagnetic ordering. On the contrary, the sample is weakly ferromagnetic. With  $\text{Mn}^{3+}$  ordered in O and SP layers and  $\text{Fe}^{3+}$  in T layers in the structure (figure 1), the magnetic behaviour seems to suggest that the  $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{3+}$  interaction becomes anisotropic and ferromagnetic in the layers. Anisotropic  $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{3+}$  interaction occurs in the  $\text{O}'$  - orthorhombic structure of  $\text{LaMnO}_3$  and related perovskites (Goodenough *et al* 1961) and in  $\text{MnF}_3$  (Wollan *et al* 1959).

The change in the magnetic properties of  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  on transformation to the OT structure may be understood in terms of the cation distribution in the brownmillerite structure (table 2). The T sites are most likely to be occupied exclusively by  $\text{Fe}^{3+}$  in samples (4) and (5). In sample (4), the O sites are occupied by both  $\text{Mn}^{3+}$  and  $\text{Fe}^{3+}$  providing additional  $\text{Mn}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$  interaction pathways which probably render the sample weakly ferromagnetic. Samples (5) and (6) where the octahedral sites are occupied by  $\text{Mn}^{3+}$  do not show a definite ordering. The increase of negative  $\theta_p$  values with manganese content in samples (4)–(6) indicates that the net antiferromagnetic interaction increases in the series.

The experimental molar Curie constants ( $C_M$ ) of the oxides (table 1) are much smaller than the calculated values, indicating the presence of competing interactions of varying magnitude which often lead to frustration (Ferey *et al* 1979). A small  $C_M$  value has been reported in a related oxide,  $\text{Ca}_3\text{Fe}_{1.65}\text{Mn}_{1.35}\text{O}_{8.02}$  (Nguyen *et al* 1984).

Further investigation of  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  using Mössbauer spectroscopy is in progress.

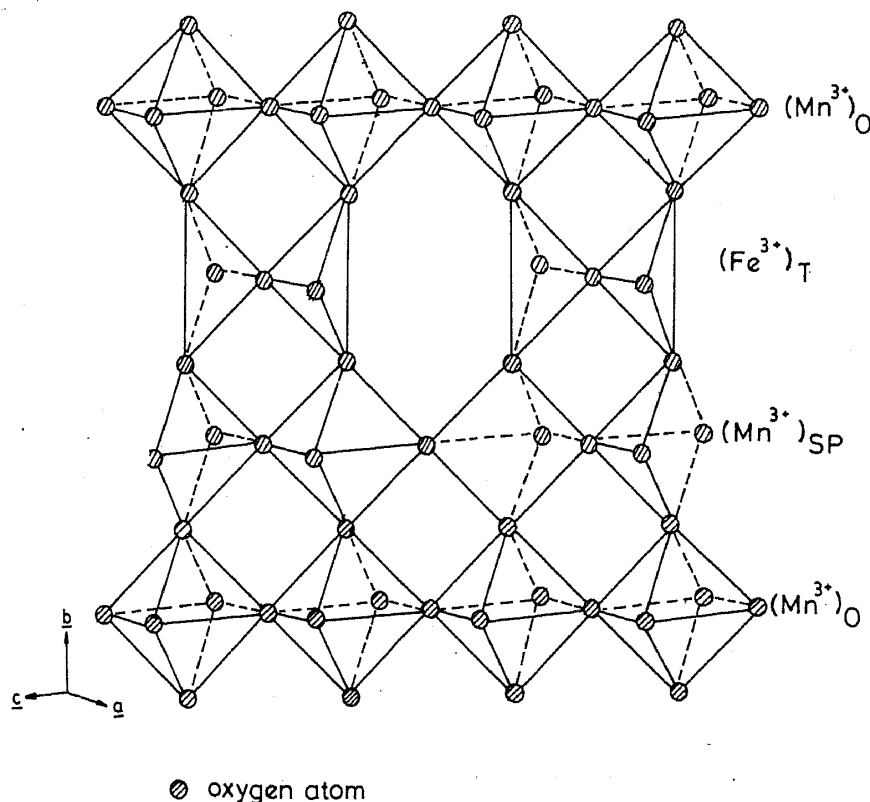


Figure 1. Schematic structure of  $\text{Ca}_3\text{FeMn}_2\text{O}_{7.5}$  showing O, T and SP layers.

Table 2. Probable cation distribution of  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  oxides.

Compound number <sup>a</sup>	Composition	Cation distribution <sup>a</sup>
1	$\text{Ca}_2\text{Fe}_{1.33}\text{Mn}_{0.67}\text{O}_5$ ( $\text{Ca}_3\text{Fe}_2\text{MnO}_{7.5}$ )	$(\text{Fe}^{3+})_{\text{O}}(\text{Fe}^{3+})_{\text{T}}(\text{Mn}^{3+})_{\text{SP}}$
2	$\text{Ca}_2\text{FeMnO}_5$ ( $\text{Ca}_3\text{Fe}_{1.5}\text{Mn}_{1.5}\text{O}_{7.5}$ )	$(\text{Fe}^{3+}\text{Mn}^{3+})_{\text{O}}(\text{Fe}^{3+})_{\text{T}}(\text{Mn}^{3+})_{\text{SP}}$
3	$\text{Ca}_2\text{Fe}_{0.67}\text{Mn}_{1.33}\text{O}_5$ ( $\text{Ca}_3\text{FeMn}_2\text{O}_{7.5}$ )	$(\text{Mn}^{3+})_{\text{O}}(\text{Fe}^{3+})_{\text{T}}(\text{Mn}^{3+})_{\text{SP}}$
4	$\text{Ca}_2\text{Fe}_{1.33}\text{Mn}_{0.67}\text{O}_5$ (B.M.)	$(\text{Fe}_{0.33}^{3+}\text{Mn}_{0.67}^{3+})_{\text{O}}(\text{Fe}^{3+})_{\text{T}}$
5	$\text{Ca}_2\text{FeMnO}_5$ (B.M.)	$(\text{Mn}^{3+})_{\text{O}}(\text{Fe}^{3+})_{\text{T}}$
6	$\text{Ca}_2\text{Fe}_{0.67}\text{Mn}_{1.33}\text{O}_5$	—

<sup>a</sup> Subscripts O, T and SP denote respectively octahedral, tetrahedral and square-pyramidal sites.

### Acknowledgements

The authors thank Professor C N R Rao, FRS for valuable discussion and advice. Thanks are also due to the University Grants Commission, New Delhi, and the Department of Science and Technology, Government of India, for support of this research. One of us (AKG) thanks the CSIR, New Delhi, for the award of a Fellowship.

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