

Magnetic properties of $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$ [†]

A K GANGULI and J GOPALAKRISHNAN*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

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 ~ 1050 K *in vacuo*. These oxides provide a rich variety of systems for investigating the magnetic properties of Fe^{3+} and 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

[†] Contribution No. 398 from the Solid State and Structural Chemistry Unit

* To whom all correspondence should be addressed

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 θ_p increases with increasing 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 θ_p values is reversed in samples (4)–(6); θ_p becomes more negative with increasing 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 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) (~ 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)	θ_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; θ_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 Mn^{3+} ordered in O and SP layers and 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 O' - orthorhombic structure of LaMnO_3 and related perovskites (Goodenough *et al* 1961) and in 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 Fe^{3+} in samples (4) and (5). In sample (4), the O sites are occupied by both Mn^{3+} and 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 Mn^{3+} do not show a definite ordering. The increase of negative θ_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.

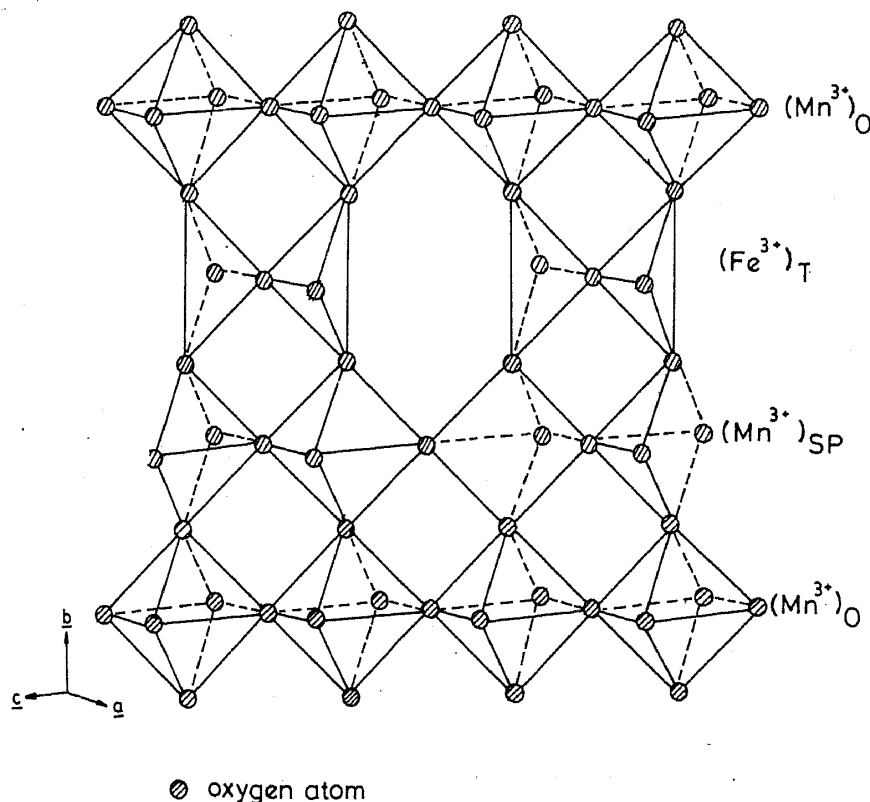


Figure 1. Schematic structure of $\text{Ca}_3\text{FeMn}_2\text{O}_{7.5}$ showing O, T and SP layers.

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

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

^a 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.

References

- Ferey G, Varret F and Coey M 1979 *J. Phys.* **C12** 1531
 Goodenough J B, Wold A, Arnott R J and Menyuk N 1961 *Phys. Rev.* **124** 373
 Grenier J C, Pouchard M and Georges R 1973 *Mater. Res. Bull.* **8** 1413
 Kanamori J 1959 *J. Phys. Chem. Solids* **10** 87
 Nguyen N, Calage Y, Varret F, Ferey G, Caignaert V, Hervieu M and Raveau B 1984 *J. Solid State Chem.* **53** 398
 Poeppelmeier K R, Leonowicz M E and Longo J M 1982 *J. Solid State Chem.* **44** 89
 Rao C N R, Gopalakrishnan J, Vidyasagar K, Ganguli A K, Ramanan A and Ganapathi L 1986 *J. Mater. Res.* **1** 280
 Vidyasagar K, Ganapathi L, Gopalakrishnan J and Rao C N R 1986 *J. Chem. Soc. Chem. Commun.* 449
 Wollan E O, Child H R, Koehler W C and Wilkinson M K 1959 *Phys. Rev.* **112** 1132