

Magnetic susceptibility studies of $Mn_{1-x}M_xO$ ($M = Zn, Mg, Fe$)

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MS received 21 April 1982

Abstract. Magnetic susceptibility studies of $Mn_{1-x}M_xO$ ($M = Zn, x \leq 0.1$; $M = Mg, x \leq 0.12$; $M = Fe, x \leq 0.4$) in the range 77 to 300 K are reported. The methods of preparation of $Mn_{1-x}M_xO$ systems preclude the presence of trivalent ions. The $Mn_{1-x}Fe_xO$ system shows anomalous behaviour around $x = 0.2 - 0.3$. The results are discussed in terms of competition between the nearest neighbour and the next-near-neighbour interactions, dilution effects and cooperative effects of FeO_6 octahedra.

Keywords. MnO ; FeO ; magnetic susceptibility.

1. Introduction

Magnetic susceptibility of MnO and its solid solutions with other ions such as Mg , Zn and Fe have been extensively studied by several workers (Millar 1928; Foex 1948; Seino *et al* 1973; Jagadeesh and Seera 1980; Evrard 1971; Hope *et al*). Hope *et al* have investigated the system $(Mn_{1-y}Fe_y)_xO$ ($y < 1.0$) which always has a slight excess of oxygen. Murthy and coworkers (Deshapande and Murthy 1981; Deshapande *et al* 1978) have recently reported the preparation of MnO stabilized by small amounts of Zn and also $Mn_{1-x}Fe_xO$ ($x < 0.4$) which are very resistant to oxidation. Thus, the $Mn_{1-x}Fe_xO$ system has no excess oxygen for $x < 0.4$. In this paper, we report the results of our studies of the magnetic susceptibilities of $Mn_{1-x}M_xO$ ($M = Mg, Fe$ and Zn) in the 77-300 K range.

2. Experimental

The $Mn_{1-x}M_xO$ systems were prepared according to the procedure of Murthy and coworkers (Deshapande and Murthy 1981; Deshapande *et al* 1978). X-ray lattice parameters were determined using a Phillips PW 1050 diffractometer. Magnetic susceptibility measurements were carried out by the Faraday method using a Cahn RG recording vacuum electrobalance. Susceptibilities were

measured using $\text{HgCo}(\text{SCN})_4$ for calibration purposes. The field used was 3000 gauss.

3. Results and discussion

3.1. X-ray diffraction studies

Crystal structures of these solid solutions are all of the rocksalt type. The cubic unit cell parameters of these solid solutions are given in table 1. All the samples show a linear decrease in the unit cell dimensions with increasing x as expected of Vegard's law behaviour (figure 1).

3.2. Magnetic susceptibility studies

Magnetic susceptibility studies of these compounds were carried out below 300 K. All the samples showed a maximum in the susceptibility at a temperature T_{max} which could be associated with the antiferromagnetic ordering temperature T_{N_0} . The χ_{M}^{-1} vs T plots of these compounds are shown in figures 2-4. The magnetic susceptibility of the $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ and $\text{Mn}_{1-x}\text{Mg}_x\text{O}$ samples were normalised for one g atom of Mn. Such a normalisation was not carried out for the $\text{Mn}_{1-x}\text{Fe}_x\text{O}$ compounds. The values of μ_{eff} and θ calculated from the slopes of these lines above 200 K from a least squares fit are given in table 1. Because of the broad

Table 1. X-ray parameters and magnetic properties of $\text{Mn}_{1-x}\text{M}_x\text{O}$ compounds.

Compound	x	a , Å (± 0.003)	μ_{eff} B	θ (K)	T_{max} (K)
$\text{Mn}_{1-x}\text{Zn}_x\text{O}$	0.001	4.449	5.63	533	127
	0.005	..	5.77	568	125
	0.010	..	5.98	629	123
	0.050	4.443	6.14	667	119
$\text{Mn}_{1-x}\text{Mg}_x\text{O}$	0.001	4.450	5.82	573	120
	0.005	4.451	5.72	547	119
	0.010	4.449	5.73	568	118
	0.050	4.439	5.44	460	116
	0.10	4.430	5.44	440	114
	0.12	4.426	5.47	435	110
	0.15	4.419	5.45	445	100
$\text{Mn}_{1-x}\text{Fe}_x\text{O}$	0.1	4.435	5.27	358	126
	0.2	4.425	4.94	210	138
	0.3	4.412	5.20	238	130
	0.4	4.401	5.09	150	150

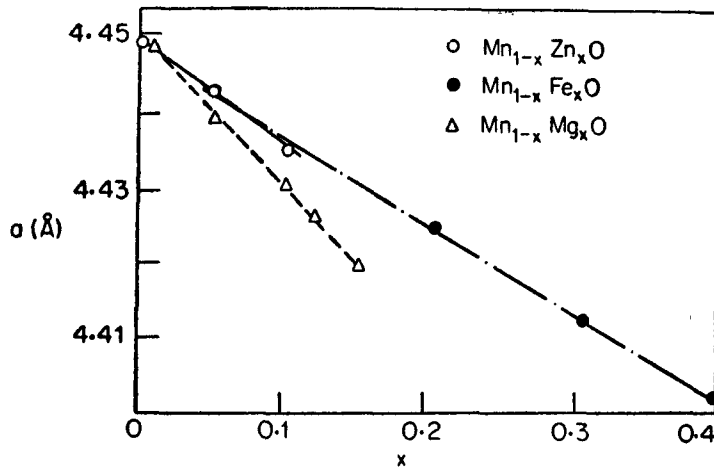


Figure 1. Variation of unit cell parameter with increasing x for the $Mn_{1-x}M_xO$ system.

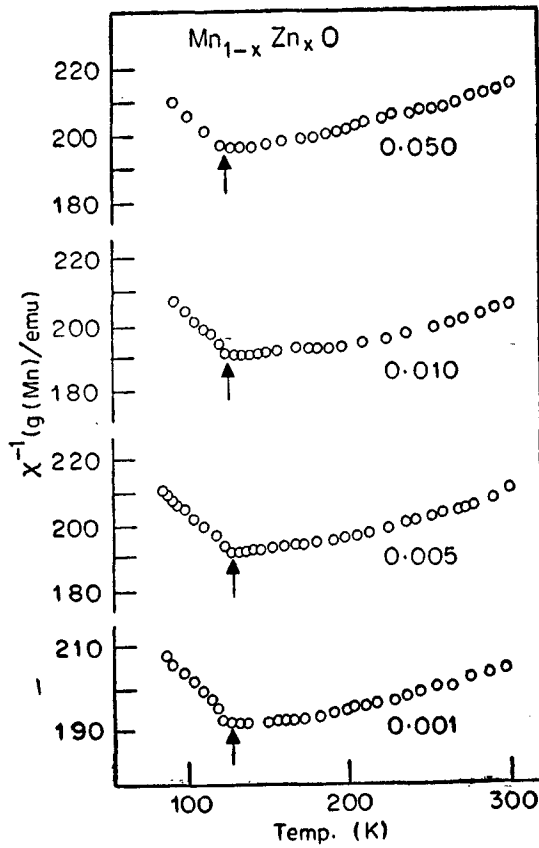


Figure 2. χ^{-1} vs T plots of $Mn_{1-x}Zn_xO$.

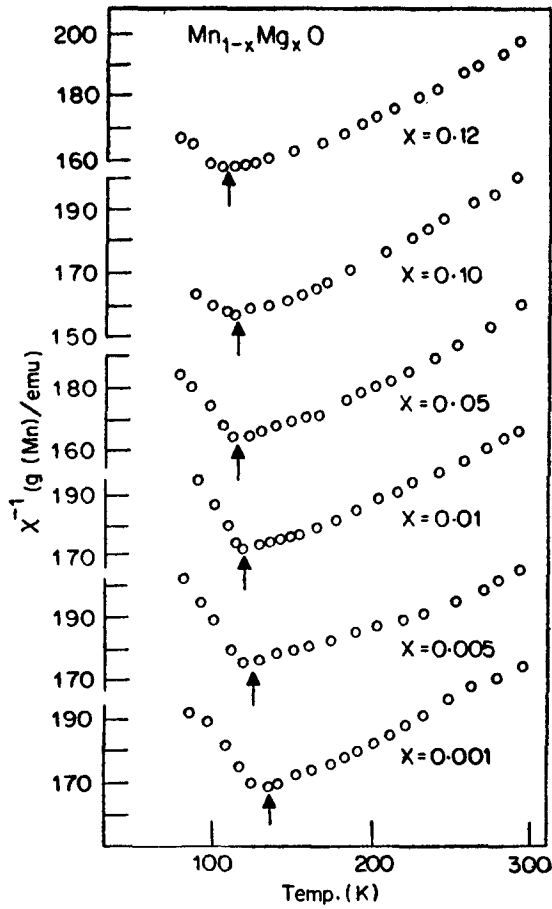


Figure 3. χ^{-1} vs T plots of Mn_{1-x}Mg_xO.

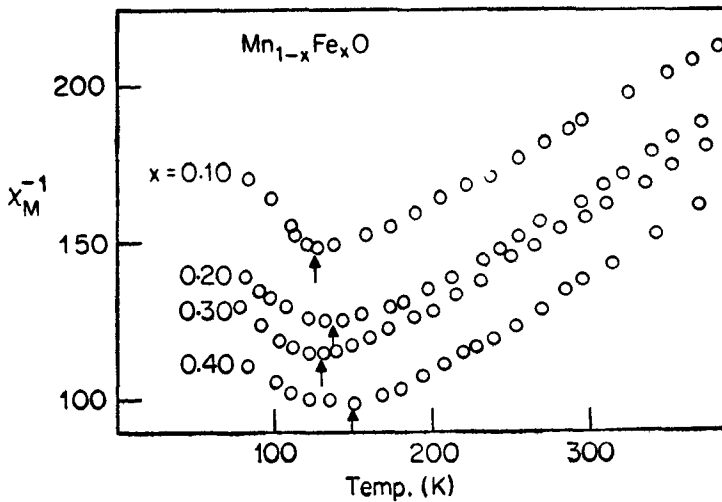


Figure 4. χ^{-1} vs. T plots of Mn_{1-x}Fe_xO.

nature of the maximum the μ_{eff} and θ values thus calculated may not represent the true high temperature values. The trends are, however, likely to be real.

MnO exhibits a broad susceptibility maximum which is slightly above the ordering temperature T_N ; T_N itself is characterized by a sharp inflection point in the susceptibility. In the rock-salt structure both the nearest neighbour cation-cation interaction J_{nn} and the next-near-neighbour cation-anion-cation interaction J_{nna} are possible. In 3d transition metal monoxides, J_{nna} is the dominant interaction and this leads to magnetic ordering of the second kind in the fcc structure (Goodenough 1963). The broad maximum in the susceptibility is probably due to competing interactions and frustrations inherent in the rock-salt structure which cannot sustain a magnetic order in which all interactions are antiferromagnetic. At T_N rhombohedral distortion takes place which reduces the unit cell length thus strengthening antiferromagnetic interactions and weakening ferromagnetic interactions between nearest neighbours. This exchange striction which is a cooperative process is likely to be damped strongly in the presence of non-magnetic impurities.

3.3. $Mn_{1-x}Mg_xO$ and $Mn_{1-x}Zn_xO$

In these compounds the sharpness of the inflection point decreases with increasing Mg or Zn concentration (figures 2 and 3). The maxima broaden considerably and T_{max} shifts to lower temperatures with increasing x . The substitution of Zn or Mg for Mn probably affects the cooperative nature of the exchange striction process so that long-range ordering is affected. The magnetic structure is broken into clusters with short-range interactions. This is the usual dilution effect.

3.4. $Mn_{1-x}Fe_xO$

Substitution of Fe for Mn leads to a decrease in θ . In FeO, $\theta/T_N \sim 1$ which is indicative of a $J_{nn} = 0$ whereas a $\theta/T_N \sim 5$ in MnO is indicative of $J_{nn} \neq 0$. The θ and μ_{eff} values of these solid solutions are given in table 1. The θ values and T_N ($\sim T_{\text{max}}$) are in reasonably good agreement with earlier results (Evrard 1971; Hope *et al.*). There is however an anomaly around $x = 0.3$ with respect to the T_{max} and θ (table 1). This sample also shows a broad minimum in the inverse susceptibility curve (figure 4). The anomalous behaviour could be representative of the solid solutions $Mn_{1-x}Fe_xO$ as distinct from the $(Mn_{1-x}Fe_xO)_yO$ ($y < 1$) studied by earlier workers (Evrard 1961; Hope *et al.*). A Mössbauer study of our samples has shown the absence of Fe^{2+} ions. The broad nature of the susceptibility around T_N for the $x = 0.3$ samples seem to show the presence of iron-rich and Mn-rich clusters. Hope *et al.* have reported the results of the quadrupole splitting, ΔE_q , at the Fe nucleus in $(Fe_{1-x}Mn_x)_yO$ systems. Their results show that for small values of x , ΔE_q is small reflecting essentially the symmetrical environment of MnO_6 octahedra. With increasing x , ΔE_q increases rapidly showing the formation of distorted FeO_6 octahedra. There seems to be some evidence of a change in the slope of the ΔE_q vs x plot around $x = 0.2-0.3$ and the ΔE_q values are very close to the value found in 'FeO' in this range. We may therefore associate the anomaly in magnetic susceptibility to the distortion of the FeO_6 octahedra which could introduce considerable anisotropy in

magnetic interactions and hence to a qualitative change in the nature of magnetic ordering.

Acknowledgement

The authors are thankful to Professor C N R. Rao for continued interest in the problem and for valuable discussions.

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