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# Studies on Magnetic Properties of $MnTi_{1-x}Nb_xO_3$ System

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**Synthesis and characterization of electrical and magnetic properties of ilmenite phases of the type $MnTi_{1-x}Nb_xO_3$ have been carried out. Single phase materials could be obtained for $0.0 \le x \le 0.25$. The electrical conductivity increases with increasing Nb content. Magnetic susceptibility studies show that the phases exhibit 2D antiferromagnetic behavior. The magnetic susceptibility data has been analyzed using Fisher's specific heat to determine the long range ordering temperature.** © 1998 Academic Press

## INTRODUCTION

The magnetic properties of ilmenite oxides have been investigated extensively (1–17). The compounds $ATiO_3$ ($A$ = Mn, Fe, Co, Ni) are antiferromagnetic insulators. However, the magnetic properties of $MnTiO_3$ are quite different from those of $FeTiO_3$ and $NiTiO_3$. Neutron diffraction studies have revealed that in $MnTiO_3$ below the Neel temperature ($T_N = 64$ K), the $Mn^{2+}$ spins align antiferromagnetically both along the $c$-axis and in the $c$-plane. This is in contrast to that of the other ilmenites, $FeTiO_3$ and $NiTiO_3$, where the $Fe^{2+}$ or $Ni^{2+}$ spins order ferromagnetically in the $c$-plane. This difference in the spin structure below the ordering temperature results in interesting spin glass behavior for certain compositions of the solid solution $Fe_{1-x}Mn_xTiO_3$ or $Ni_{1-x}Mn_xTiO_3$ (18–37). Goodenough and Stickler (9) have used crystal field, superexchange, and molecular field theories to explain the observed magnetic behavior of the ilmenite oxides. They have proposed an exciton-exchange mechanism to explain the difference in the spin structure.

In addition to the difference in interactions in $MnTiO_3$ compared to the other ilmenite oxides, the susceptibility as a function of temperature also exhibits a peculiar behavior. The static magnetic susceptibility results of Akimitsu *et al.* (12) on single crystal samples and of Stickler *et al.* (8) on powdered samples of $MnTiO_3$ exhibit typical two-dimensional (2D) characteristics; that is, no anomaly at $T_N$ (64 K), but a broad maximum at about 90 K, which are in quite contrast with the behavior of other antiferromagnetic ilmenite oxides, $FeTiO_3$, $CoTiO_3$, and $NiTiO_3$. The paramagnetic-to-antiferromagnetic transition is quite sharp in the case of Fe, Co, Ni titanates with $T_N$ values 56 K, 38 K, and 23 K respectively (8). However, later studies on single-crystal $MnTiO_3$ by Yamauchi *et al.* (15) show that the $\chi_{\parallel}$ exhibits a change of slope at $T_N$, but the anisotropy of $\chi$ does not disappear at $T_N$ but persists up to 95 K.

Antiferromagnetic resonance studies by Stickler *et al.* (8) have shown that the magnetic anisotropy of $MnTiO_3$ is small, and the ratio of the anisotropy field, $H_A$, to the exchange field, $H_E$, was estimated to be $1.2 \times 10^{-3}$. Neutron quasielastic scattering studies near $T_N$ indicated strong anisotropoy in spin correlations (14, 38). The ratio of effective interlayer interaction to intralayer interaction is estimated to be rather small ($0.034 \pm 0.005$) (Spin dynamics studies by Todate *et al.* (17) reveal a slightly higher value, viz., $0.042 \pm 0.006$ for this ratio). However, the critical exponent, $\beta$, characteristic of the sublattice magnetization $[M = M_0(T_N - T)^{\beta}]$ has a value of $0.32 \pm 0.01$ just below $T_N$ which is the same value as for a 3D Heisenberg magnet. The neutron paramagnetic scattering from powdered $MnTiO_3$ shows that the interlayer interaction is not negligible compared with the intralayer interaction (39).

In the present study, compounds of the type $MnTi_{1-x}Nb_xO_3$ have been synthesized and their electrical and magnetic properties have been studied. Doping with $Nb^{4+}$ is expected to improve the electrical conductivity. Since $Nb^{4+}$, which is paramagnetic, is introduced in the diamagnetic TiO layer of the ilmenite structure, it is expected to affect the quasi-2D antiferromagnetic behavior of $MnTiO_3$.

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## EXPERIMENTAL

The compounds are prepared by high temperature solid state reaction of MnO (Cerac, UK), $TiO_2$ (Cerac, UK), and $NbO_2$ in evacuated and sealed quartz ampoules at 1000°C. $NbO_2$ is prepared from $Nb_2O_5$ and Nb metal in stoichiometric proportion heated at 800°C in evacuated and sealed quartz ampoules. Phase formation is confirmed by powder X-ray diffraction (Rich Seifert, Germany). The electrical resistivity of the Nb-doped samples is measured using a two probe apparatus in Ar atmosphere. DC magnetic susceptibility studies are carried out on $MnTiO_3$ and $MnTi_{0.75}Nb_{0.25}O_3$ using a SQUID magnetometer (Quantum Design, UK). AC susceptibility measurements are carried out on $MnTi_{0.9}Nb_{0.1}O_3$ and $MnTi_{0.8}Nb_{0.2}O_3$ using a AC susceptometer (Lake Shore, USA).

## RESULTS AND DISCUSSION

Single phase materials could be obtained for $0.0 \leq x \leq 0.25$. Typical XRD patterns are shown in Fig. 1. The hexagonal lattice parameters calculated by least squares fitting of the high angle reflections show an increase with $Nb^{4+}$ content and are tabulated in Table 1. The room temperature electrical resistivity of the $Nb^{+}$ doped phases systematically decreases with increasing $Nb^{4+}$ content. The electrical resistivity for all the compositions shows an Arrhenius type behavior, and the activation energy systematically decreases with Nb content. The log $\sigma$ vs $1000/T$ plot for the compound $MnTi_{0.75}Nb_{0.25}O_3$ is shown in Fig. 2, and the activation energy calculated from the slope of the linear plot is $\sim 0.2$ eV.

**TABLE 1**
**Hexagonal Lattice Parameters for $MnTi_{1-x}Nb_xO_3$ System**

| Composition | $a$ (Å) | $c$ (Å) |
|---|---|---|
| 0.00 | 5.133 | 14.27 |
| 0.10 | 5.148 | 14.32 |
| 0.20 | 5.157 | 14.33 |
| 0.25 | 5.170 | 14.35 |
| 0.33* | 5.176 | 14.36 |
| 0.40* | 5.186 | 14.38 |

*Multiphasic.

Figure 3 shows the static magnetic susceptibility ($\chi$) vs temperature plots for $MnTiO_3$ and $MnTi_{0.75}Nb_{0.25}O_3$. Figure 4 shows the ac susceptibility vs temperature plots for $MnTi_{0.9}Nb_{0.1}O_3$ and $MnTi_{0.8}Nb_{0.2}O_3$. $MnTiO_3$ exhibits a broad peak around 90 K and does not show any marked anomaly at $T_N$ (64 K) (Fig. 3). The data compares well with that reported in the literature (7). Careful examination of the curve does reveal a slight change in the slope at $T_N$. Since the measurements were made on powdered samples, the slope change is not as pronounced as observed by Yamauchi *et al.* (15) for single-crystal $MnTiO_3$. From Figs. 3 and 4, it is evident that the broad peak shifts toward lower temperatures with increasing Nb content. Further, $\chi$ increases at lower temperatures. This can be due to canting of spins. A similar observation has been made in the case of $KMnPO_4 \cdot H_2O$ by Visser *et al.* (40). The susceptibility is reported to follow Curie-Weiss behavior up to 100 K. At 27 K, a broad maximum is observed in the $\chi$–$T$ curve, which is characteristic of 2D magnetic interactions. Below 18 K, the susceptibility increases. This behavior has been attributed to spin canting by the authors. In the present case,

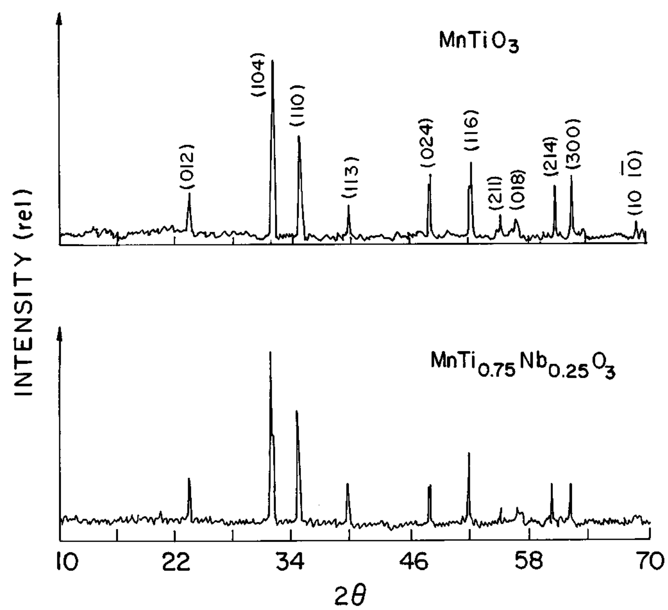


**FIG. 1.** Powder XRD patterns for $MnTi_{1-x}Nb_xO_3$ system.

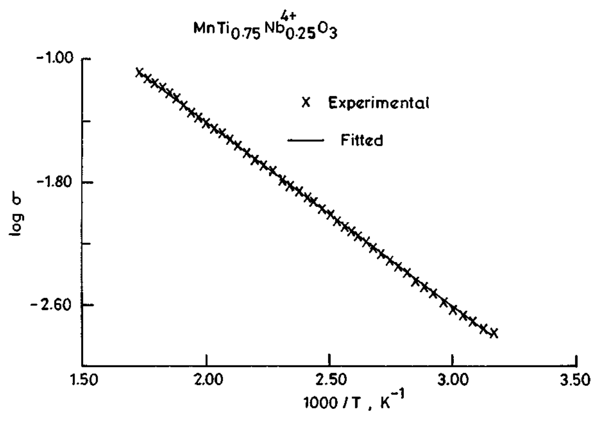


**FIG. 2.** Arrhenius plot (log $\sigma$ vs $1/T$) for $MnTi_{0.75}Nb_{0.25}O_3$.

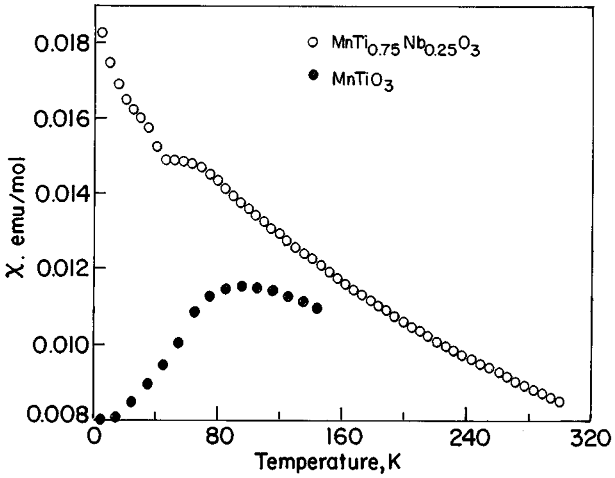


**FIG. 3.** Variation of static (DC) magnetic susceptibility with temperature for $MnTiO_3$ and $MnTi_{0.75}Nb_{0.25}O_3$.

the upward trend is believed not due to impurities since XRD does not show any impurity reflections. Also, none of the known binary or ternary phases of Mn have any ordering below 40 K. The transition to the spin-canting state is manifested as a sharp peak in the ac susceptibility curves for the $x = 0.1$ and 0.2 samples (Fig. 4).

Akimitsu and Ishikawa (14) postulated that the 2D behavior of $MnTiO_3$ is due to the accidental cancellation of the interlayer interactions. Figure 5 shows the ilmenite structure and the various magnetic interactions. As can be seen from the figure, $J_1$ and $J_2$ are the intralayer interactions and $J_3$, $J_4$, and $J'_4$ are the interlayer interactions. The values of $J_2$, $J_4$, and $J'_4$ are small compared to $J_1$ and $J_3$, since two

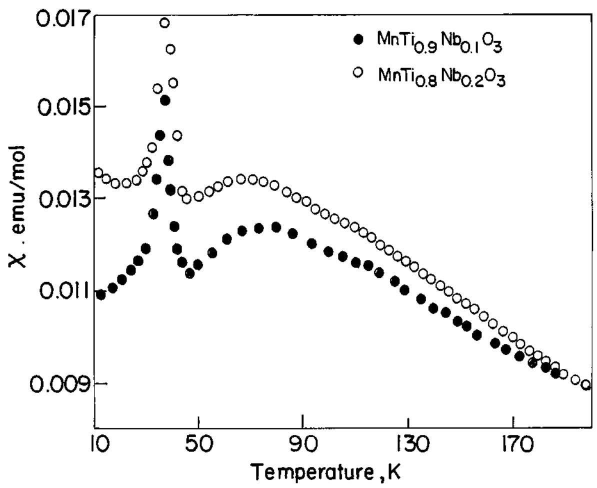


**FIG. 4.** Variation of AC magnetic susceptibility with temperature for $MnTi_{0.9}Nb_{0.1}O_3$ and $MnTi_{0.8}Nb_{0.2}O_3$.

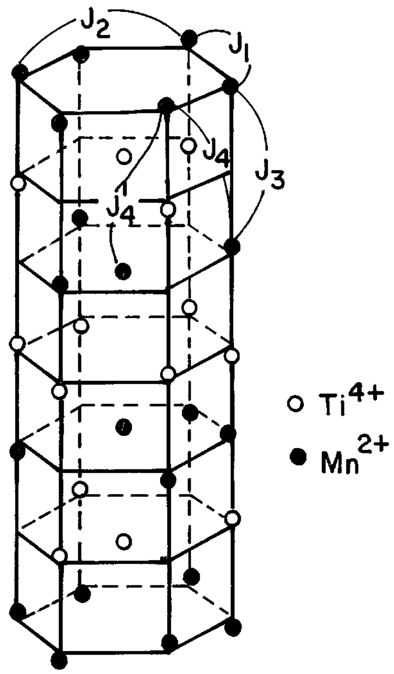


**FIG. 5.** Hexagonal unit cell of $MnTiO_3$ showing the various magnetic interactions. Only Mn and Ti atoms are shown.

oxygen atoms intervene in the interaction pathways. The 2D character of $MnTiO_3$ is due to the accidental cancellation of the relatively large interlayer interaction $J_3$ with the other interlayer interactions, $J_4$ and $J'_4$. Hence, $MnTiO_3$ can be termed a quasi-2D antiferromagnet.

The Hamiltonian for a 2D system with a small interlayer exchange interaction can be written as

$$H = -2J \sum_{\text{intralayer}} (S_i S_j) - 2JR \sum_{\text{intralayer}} (S_i S_j),$$

where $0 < R < 1$.

This system will be essentially 2D even for $R \neq 0$ at high temperatures, although 3D character will be emphasized at temperatures very close to the critical temperature. Hence, a crossover behavior is expected. If $R$ is not so small, the 3D critical region persists over a wide range of temperature. From neutron scattering studies (14), the value of $R$ is found to be $0.034 \pm 0.005$. However, the scattering profiles indicate that the short range correlations are in only two dimensions above 80 K. This shows crossover behavior from the 3D to the 2D region. It is above this crossover temperature that the broad peak maximum in the $\chi$–$T$ curve of $MnTiO_3$ begins to develop.

According to Fisher (41), the magnetic specific heat can be approximated as

$$C_m(T) \approx A\partial(\chi T)/\partial T,$$

where the constant of proportionality ($A$) is a relatively slowly varying function of temperature. Thus, any specific heat anomaly will be associated with a similar anomaly in $\partial(\chi T)/\partial T$. Thus, from a plot of $\partial(\chi T)/\partial T$ vs $T$, one can determine the transition temperature for long range order. This method has been recently used by Nakua and Greedan (42) to determine the transition temperature for $Fe_2As_4O_{12}$.

Figure 6 shows the $\partial(\chi T)/\partial T$ vs $T$ plots for $MnTiO_3$ and $MnTi_{0.75}Nb_{0.25}O_3$. The plot shows a peak around 60 K for $MnTiO_3$. The agreement of this temperature with the value of $T_N$ reported in the literature is quite striking. Thus, Fisher's analysis provides a simple method to determine $T_N$ in the case of 2D antiferromagnets. The Fisher specific heat plot for the $Nb_{0.25}$-doped sample shows a lower value for the $T_N$ (52.5 K). The temperature of the broad maximum in the $\chi$–$T$ curve of $MnTiO_3$ differs from the actual $T_N$ extracted from the $\partial(\chi T)/\partial T$ vs $T$ plot by about 30 K. This is in sharp contrast to that observed in the case of the $Nb_{0.25}$-doped sample, for which the two temperature values almost coincide. Thus, $Nb^{4+}$ doping in $MnTiO_3$ induces improved 3D character in the magnetic properties.

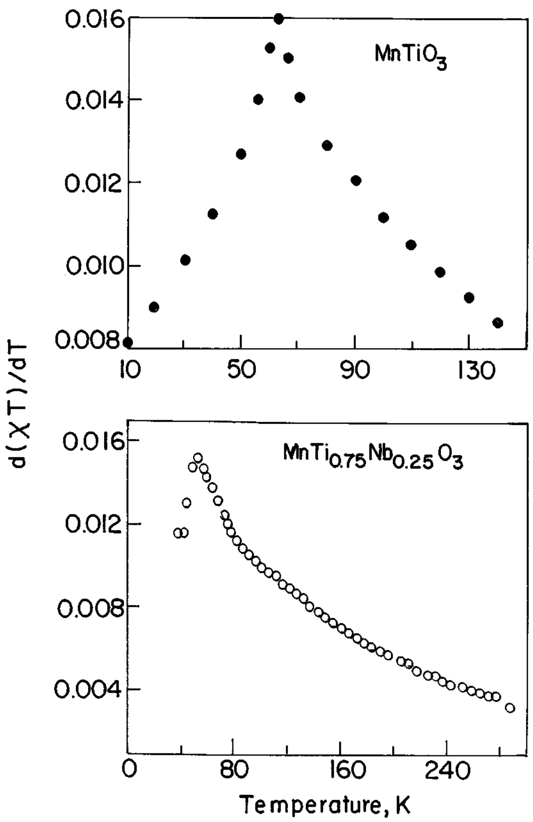


**FIG. 6.** Variation of Fisher specific heat $[\partial(\chi T)/\partial T]$ with temperature for $MnTiO_3$ and $MnTi_{0.75}Nb_{0.25}O_3$. The temperature corresponding to the cusp is the temperature for long range ordering ($T_N$).

## CONCLUSIONS

The electrical and magnetic properties of the phases $MnTi_{1-x}Nb_xO_3$ have been studied. $Nb^{4+}$ doping improves the electrical conductivity. All the samples examined show 2D antiferromagnetic behavior, although Nb doping induces improved 3D character. Fisher analysis of susceptibility is found to provide a simple method for determining the long range ordering temperature. The long range ordering temperature is found to decrease with increasing Nb content.

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