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# Magnetic field-temperature phase diagram, exchange constants and specific heat exponents of the antiferromagnet $\text{MnNb}_2\text{O}_6$

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## Abstract

This work presents the magnetic field-temperature ( $H$ - $T$ ) phase diagram, exchange constants, specific heat ( $C_p$ ) exponents and magnetic ground state of the antiferromagnetic  $\text{MnNb}_2\text{O}_6$  polycrystals. Temperature dependence of the magnetic susceptibility  $\chi (= M/H)$  yields the Néel temperature  $T_N = 4.33$  K determined from the peak in the computed  $\partial(\chi T)/\partial T$  vs.  $T$  plot in agreement with the transition in the  $C_p$  vs.  $T$  data at  $T_N = 4.36$  K. The experimental data of  $C_p$  vs.  $T$  near  $T_N$  is fitted to  $C_p = A/T - T_N^{-\alpha}$  yielding the critical exponent  $\alpha = 0.12$  (0.15) for  $T > T_N$  ( $T < T_N$ ). The best fit of  $\chi$  vs.  $T$  data for  $T > 50$  K to  $\chi = \chi_0 + C/(T - \Theta)$  with  $\chi_0 = -1.85 \times 10^{-4} \text{ emu.mol}^{-1}\text{Oe}^{-1}$  yields  $\Theta = -17$  K, and  $C = 4.385 \text{ emuKmol}^{-1}\text{Oe}^{-1}$ , the later giving magnetic moment  $\mu = 5.920 \mu_B$  per  $\text{Mn}^{2+}$  ion. This confirms the effective spin  $S = 5/2$  and  $g = 2.001$  for  $\text{Mn}^{2+}$  and the dominant exchange interaction being antiferromagnetic in nature. Using the magnitudes of  $\Theta$  and  $T_N$  and molecular field theory (MFT), the exchange constants  $J_{\parallel}/k_B = -1.08$  K for  $\text{Mn}^{2+}$  ions along the chain  $c$ -axis and  $J_{\perp}/k_B = -0.61$  K as the interchain coupling perpendicular to  $c$ -axis are determined. These exchange constants are consistent with the expected  $\chi$  vs.  $T$  variation for the Heisenberg linear chain. The  $H$ - $T$  phase diagram, mapped using the  $M$ - $H$  isotherms and  $M$ - $T$  data at different  $H$  combined with the reported data of Nielsen *et al.*, yields a triple-point  $T_{TP}(H, T) = (18 \text{ kOe}, 4.06 \text{ K})$ . The spin-flopped state above  $T_{TP}$  and the forced ferromagnetism for  $H > 192$  kOe are used to estimate the anisotropy energy  $H_A \approx 0.8$  kOe.

## 1.Introduction

The four transition metal niobates  $\text{MNb}_2\text{O}_6$  ( $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{and Ni}$ ) crystallize in the columbite structure (space group  $D_{2h}^{14}-Pbcn$ ) with orthorhombic unit cell containing 4 molecules per unit cell. For  $\text{MnNb}_2\text{O}_6$ , the lattice parameters are:  $a = 14.4204 \text{ \AA}$ ,  $b = 5.7566 \text{ \AA}$  and  $c = 5.078 \text{ \AA}$  [1-3] and for  $\text{M} = \text{Fe}, \text{Co}$  and  $\text{Ni}$ , the lattice parameters decrease nearly linearly with decreasing ionic size of  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions in that order [4-13]. This crystal structure has zig-zag like chains of  $\text{M}^{2+}$  ions along the  $c$ -axis containing two crystallographically inequivalent  $\text{M}^{2+}$  ions and isosceles triangular arrangement of  $\text{Mn}^{2+}$  ions in the  $ab$  plane. A schematic diagram of this structure based on available literature [1-13] is shown in figure 1. Consequently, the Hamiltonian describing the exchange coupling among  $\text{M}^{2+}$  ions in these systems can be written as [6,7,13,14]:

$$H = -J_0 \sum_i S_i^z S_{i+1}^z - J_1 \sum_{ij} \vec{S}_i \cdot \vec{S}_j - J_2 \sum_{ij} \vec{S}_i \cdot \vec{S}_j \quad \text{--- (1)}$$

In Eq. (1), the sum is over nearest-neighbours (nn) along the  $c$ -axis for  $J_0$ , over nn along the  $b$ -axis for  $J_1$ , and over next-nn for  $J_2$  in the  $ab$  plane (see figure 1). When independent determination of  $J_1$  and  $J_2$  is not possible, they are replaced by an average  $J_\perp$  as the interchain exchange coupling [12].

Despite the similarity of the crystal structure of the four niobates, the nature of magnetic ordering in these systems is sufficiently different. For  $\text{FeNb}_2\text{O}_6$ , the reported studies by Yaeger *et al* [5], Heid *et al* [6] and Sarvezuk *et al* [7] reported  $T_N \simeq 4.9 \text{ K}$  to  $5.5 \text{ K}$  with canting angle  $\Phi \sim 17^\circ$  from the easy  $a$ -axis. For  $\text{NiNb}_2\text{O}_6$ , the studies by Yaeger *et al* [4], Heid *et al* [6] and Sarvezuk *et al* [7] reported  $T_N = 5.7 \text{ K}$  with easy direction being closer to  $c$ -axis. The magnetic properties of  $\text{CoNb}_2\text{O}_6$  are somewhat different in that it is shown to be a good example of an Ising chain ferromagnet along the  $c$ -axis with effective spin  $S = 1/2$  and exchange constant  $J_0/k_B = 6.2 \text{ K}$  and the interchain antiferromagnetic exchange constants  $J_1/k_B = -0.42 \text{ K}$  and  $J_2/k_B = -0.67 \text{ K}$  [14]. The  $\text{Co}^{2+}$  moments are aligned close to  $c$ -axis with canting angle  $\Phi = \pm 31^\circ$ . In addition, for  $H // b$ -axis,  $T_C = 2.95 \text{ K}$  for  $H = 0$  reduces to absolute zero in a critical field  $H_C = 52.5 \text{ kOe}$ . For  $H > H_C$ , quantum critical fluctuations have been reported well above  $T = 0 \text{ K}$  [15,16,17,18].

The subject of this paper is magnetic properties of  $\text{MnNb}_2\text{O}_6$  on which previous magnetic studies include those of Nielsen *et al.* [1,2] and Holmes *et al.* [3] who reported  $T_N \simeq 4.4 \text{ K}$  with moments aligned close to the  $a$ -axis. The new results reported here include the following: (i) structural characterization of the sample using X-ray photoelectron spectroscopy in addition to the Rietveld refinement of the X-ray diffraction pattern; (ii) Measurements and analysis of specific heat covering the region around  $T_N$ ; (iii) Complete mapping of the  $H$ - $T$  phase diagram and determining the triple point  $T_{TP}(H,T) = (18 \text{ kOe}, 4.06 \text{ K})$  from the  $M$  vs.  $H$  and  $M$  vs.  $T$  data; (iv) Determination of the exchange constants  $J_0$  and  $J_\perp$  from the temperature dependence of magnetic susceptibility; and (v) estimating the anisotropy energies from the spin-flop field. Details of these results are presented in the following pages.

## 2. Synthesis of sample and its structural characterization:

Polycrystalline bulk samples of  $\text{MnNb}_2\text{O}_6$  were prepared using  $\text{MnO}_2$  and  $\text{Nb}_2\text{O}_5$  as precursors and the standard solid-state reaction method. Stoichiometric amounts of the precursors were first mixed in an agate mortar with pestle for 4-6 hour and then pressed into cylindrical pellets using a hydraulic press with pressure of  $20 \text{ kN/m}^2$ . These pellets were then sintered in air at  $1150^\circ\text{C}$  for 12 hours. The resulting sample was re-grinded/pelletized and then finally sintered at  $1200^\circ\text{C}$  for 24 hours in air. Re-grinding and re-sintering were found to be very important to obtain a bulk grain size  $\sim 2\mu\text{m}$  and dense polycrystalline ceramic  $\text{MnNb}_2\text{O}_6$  of ideal stoichiometric columbite structure.

The purity and crystal structure of this prepared material was investigated using the X-ray diffraction (XRD) technique employing a Rigaku X-ray diffractometer (Model-TTRAX III, Cu-K $\alpha$  radiation with wavelength  $\sim 1.54 \text{ \AA}$ ). The XRD pattern was recorded in the ' $\theta$ - $2\theta$ ' geometry between  $2\theta = 10^\circ$  and  $80^\circ$  with slow scan rate of  $1^\circ/\text{minute}$ . Figure 2 shows the XRD pattern of the prepared sample plotted along with the Rietveld refinement data performed using the FullProf program confirming the single-phase nature of the prepared  $\text{MnNb}_2\text{O}_6$  sample having stoichiometric columbite structure with lattice constants  $a = 14.4327 \text{ \AA}$ ,  $b = 5.7627 \text{ \AA}$  and  $c = 5.0819 \text{ \AA}$  and absence of any secondary impurity phase within the sensitivity of the XRD technique.

The electronic structure and chemical composition of the pelletized sample were probed using X-ray photoelectron spectroscopy (XPS). For this, we used Kratos Analytical spectrometer (model: AXIS Supra+) configured with a dual monochromatic X-ray source Al K $\alpha$  /Ag L $\alpha$  ( $2984.2 \text{ eV}$ ) with spatial resolution less than  $1 \mu\text{m}$ . The electronic spectra for Mn, Nb and Oxygen are shown in figure 3. The binding energy of carbon *C-1s* orbital ( $\sim 284.8\text{eV}$ ) was used for the calibration of all the recorded core-level spectra. The *Nb-3d* core level spectrum (figure 3(a)) exhibits two sharp peaks centred at  $207.25 \text{ eV}$  and  $210 \text{ eV}$  with binding energy separation between these peaks  $\Delta \sim 2.75 \text{ eV}$  confirming the pentavalent oxidation state of Nb [19]. The deconvolution of *Mn-2p* core level spectrum (figure 3(b)) required minimum of five peaks; four main peaks at  $640.41\text{eV}(\text{M}_1)$ ,  $642.0\text{eV}(\text{M}_2)$ ,  $652.15 \text{ eV}(\text{M}_3)$ , and  $653.48 \text{ eV}(\text{M}_4)$  and one broad satellite peak at  $645.2\text{eV}(\text{S}_1)$ . For the deconvolution, we applied a fitting constraint on the FWHM of the peak profile *i.e.* the FWHM should range within  $0.2 \text{ eV}$ . This constraint is relaxed during the final iteration. The observed values of spin orbit splitting  $\Delta(\text{M}_3- \text{M}_1) \sim 11.74 \text{ eV}$  and  $\Delta(\text{M}_4- \text{M}_2) \sim 11.4 \text{ eV}$  suggests the divalent oxidation state of 'Mn' [20]. Moreover, the *O-1s* spectrum (figure 3(c)) exhibits a sharp peak centred at  $529.8 \text{ eV}$  along with a low intensity broad hump at  $531.9 \text{ eV}$  associated with the metal-oxygen (M-O) bonding and surface oxygen, respectively [21], present in the system. Overall, the XPS analysis confirms the presence of  $\text{Mn}^{2+}$  and  $\text{Nb}^{5+}$  ions in the polycrystalline  $\text{MnNb}_2\text{O}_6$  sample.

### 3. Temperature and magnetic field dependence of magnetization:

Measurements of magnetization ( $M$ ) of the  $\text{MnNb}_2\text{O}_6$  sample were done using a vibrating sample magnetometer (VSM) based Physical Property Measurement System (PPMS) from Quantum Design (PPMS DynaCool) capable of magnetic fields up to  $\pm 90$  kOe in the temperature range of 1.9 K to 400 K. For these measurements, the sample was cooled to 1.9 K in zero field, followed by applying a measuring non-zero  $H$  and acquiring the data with increasing  $T$  (step size = 0.02K) after stabilizing the temperature at each  $T$ . For isothermal  $M$  vs.  $H$  measurements, the step size was 50 Oe for  $H < 1500$  Oe and 300 Oe for  $H > 1500$  Oe.

#### 3.1. Néel temperature and its magnetic field dependence:

The temperature dependence of magnetic susceptibility  $\chi = M/H$  ( $H = 100$  Oe) of the polycrystalline  $\text{MnNb}_2\text{O}_6$  sample is shown in figure 4(a) covering the temperature range of 1.9K to 15K. There is a peak in  $\chi$  near  $T_P \sim 5.7$  K. However as theoretically established by Fisher [22], in antiferromagnets  $T_P > T_N$ , the Néel temperature. Instead,  $T_N$  is accurately given by the peak in  $\partial(\chi T)/\partial T$  vs.  $T$  plots since  $\chi T$  is proportional to magnetic energy. Experimentally, this has been established in several antiferromagnets such as  $\text{MnF}_2$  [23] and  $\text{Er}_2\text{O}_3$  [24]. In figure 4(b), the plot of computed  $\partial(\chi T)/\partial T$  vs.  $T$  using the  $\chi$  vs.  $T$  data yields peak at  $T_N = 4.33$  K, a value in general agreement with  $T_N = (4.40 \pm 0.05)$  K reported previously by Nielson *et al* [1, 2] and Holmes *et al* [3].

The  $H$ -dependence of  $T_N$  was measured next for  $H$  up to 90 kOe following the same procedure of determining the peak in the computed  $\partial(\chi T)/\partial T$  vs.  $T$  plots. This was done to map out the  $H$ - $T$  phase boundary analogous to that reported in the uniaxial antiferromagnet  $\text{MnF}_2$  with  $T_N \simeq 67.3\text{K}$  [23, 25, 26, 27]. For lower  $H$ , this  $T_N$  vs.  $H$  variation follows the equation:

$$T_N(H) = T_N(0) - D_I H^2 \quad \text{----- (2)}$$

as shown theoretically and experimentally in  $\text{MnF}_2$  [25, 26]. This plot of  $T_N(H)$  vs.  $H^2$  is shown in figure 5 with  $D_I = 0.9 \times 10^{-9}$  K/Oe<sup>2</sup> determined from the slope and  $T_N(0) = 4.36$  K. These results are compared with  $D_I = 1.59 \times 10^{-10}$  K/Oe<sup>2</sup> for  $\text{MnF}_2$  [25,26] and  $D_I = 7.3 \times 10^{-9}$  K/Oe<sup>2</sup> for  $\text{Er}_2\text{O}_3$  [24]. Theoretically, the molecular field theory (MFT) for  $H$  parallel to the easy axis yields [25,26]:

$$D_1 = \frac{g^2 \mu_B^2 (2S^2 + 2S + 1)}{40 k_B^2 T_N} \quad \text{----- (3)}$$

Using  $g = 2.001$  and  $S = 5/2$  for  $\text{MnNb}_2\text{O}_6$  as shown later yields calculated  $D_I = 1.92 \times 10^{-9}$  K/Oe<sup>2</sup> compared to the experimental  $D_I = 0.9 \times 10^{-9}$  K/Oe<sup>2</sup>. As in  $\text{MnF}_2$  [25,26] and  $\text{Er}_2\text{O}_3$  [24], the difference in the calculated and measured  $D_I$  is likely related to the inadequacy of the MFT near  $T_N$ .

### 3.2. Temperature dependence of specific heat:

The temperature dependence of specific heat  $C_P(T)$  measurements from 1.9 K to 8 K were performed using a Physical Property Measurement System (PPMS) of Quantum Design using the standard heat-pulse calorimetry [28]. Near the phase transition, a dual-slope analysis was applied to precisely study the effect of the magnetic field on the phase transition. In this method, at any temperature the specific heat is estimated by direct comparison of the heating and cooling rates of the sample temperature without explicit use of the thermal conductance between sample and bath [29]. The plots of the  $C_P$  vs.  $T$  data so obtained for  $H = 0$  and  $H = 90$  kOe are shown in figure 6 yielding peaks at  $T_N = 4.36$  K for  $H = 0$ , in good agreement with  $T_N = 4.33$  K obtained earlier from the peak in  $\partial(\chi T)/\partial T$  vs.  $T$  plot of figure 4(b). For  $H = 90$  kOe, the peak shifts to  $T_N = 3.52$  K, a result discussed later in connection with the  $H$ - $T$  phase diagram.

The temperature variation of  $C_P$  near a second order phase transition is expected to vary as:  $C_P = A(T-T_N)^{-\alpha}$  where  $\alpha$  is the critical exponent [30] and  $A$  is a constant. Using log-log plot, the plots of  $C_P$  vs.  $|T-T_N|$  for both above and below  $T_N$  are shown in figure 7. As observed in other systems [30], the linear fit is sensitive to the choice of  $T_N$  and so we varied  $T_N$  between 4.32 K and 4.36 K in 0.01K steps and determined that  $T_N = 4.36$  K gives the best overall linear fit yielding  $\alpha = 0.12$  (0.15) for  $T > T_N$  ( $T < T_N$ ). For comparison, similar magnitudes of  $\alpha = 0.16$  (0.18) for  $T > T_N$  ( $T < T_N$ ) have been reported in the uniaxial antiferromagnet  $\text{MnF}_2$  with  $T_N = 67.3$  K [30].

### 3.3. Spin-flop field and its temperature dependence:

The variation of  $M$  vs.  $H$  in  $\text{MnNb}_2\text{O}_6$  was measured in the temperature range of 1.9 K to  $T_N$  with a typical variation shown in the inset of figure 8. There is a clear change in the slope of the  $M$  vs.  $H$  curve near 18 kOe which becomes distinctly evident in the computed  $\partial M/\partial H$  vs.  $H$  curves shown in figure 8 for different temperatures. The position of the peak near  $H = 18$  kOe is identical to the results reported by Nielsen *et al* [1, 2] at a few temperatures  $T < T_N$  for  $H // a$ -axis in a single crystal of  $\text{MnNb}_2\text{O}_6$ . In a polycrystalline sample, only a fraction of the grains has  $H // a$ -axis and so the anomaly is understandably weaker than reported by Nielsen *et al* [1, 2] in a single crystal. This peak in  $\partial M/\partial H$  vs.  $H$  is associated with the spin-flop transition since  $a$ -axis is the easy axis. The magnitude of  $H_{sf}$  increases slightly with increase in  $T$  towards  $T_N$  hinting at the presence of triple point, like that reported in  $\text{MnF}_2$  [25-27]. The magnitudes of  $H_{sf}$  determined here in the polycrystalline sample of  $\text{MnNb}_2\text{O}_6$  at different  $T < T_N$  are in excellent agreement with those reported by Nielsen *et al* [1, 2] at a few temperatures in a single crystal with  $H // a$ -axis.

### 3.4. H-T phase diagram:

The  $H$ - $T$  phase diagram determined here from the variation in  $T_N$  with  $H$  using the peaks in  $\partial(\chi T)/\partial T$  vs.  $T$  and  $H_{sf}$  vs.  $T$  from the peaks in  $\partial M/\partial H$  vs.  $H$  at different  $T$  is shown in figure 9. We have

included the data of  $H_{sf}$  vs.  $T$  reported by Nielsen *et al* [1, 2] who also reported that for  $\vec{H} \parallel \vec{a}$ ,  $M$  saturates for  $H > 190$  kOe and this point is also included in the plot. The phase diagram in figure 9 with triple point  $T_{TP}(H, T) = (18 \text{ kOe}, 4.06 \text{ K})$  is qualitatively similar to that reported in the uniaxial antiferromagnet  $\text{MnF}_2$  [25-27]. This is an important result of this work because of its resemblance to the  $H$ - $T$  phase diagram in  $\text{MnF}_2$  and drastic differences from the  $H$ - $T$  phase diagram of  $\text{CoNb}_2\text{O}_6$  [14].

For  $\text{MnNb}_2\text{O}_6$ , two critical fields are evident in figure 9: (i) the spin flop field  $H_{sf} = 18$  kOe at 1.9 K and  $H_{C2} \sim 200$  kOe at 1.6 K determined by Nielsen *et al* [1, 2] above which the spins are forced to align along the applied field thus overcoming the exchange field  $H_E$  and yielding the saturation magnetization  $M_S \simeq 27 \times 10^3$  emu/mol. Using the well-known relation:  $M_S = \chi_{\perp} H_E$  [31] yields  $\chi_{\perp} = 0.135$  emu/mol-Oe as the susceptibility perpendicular to the easy axis which is near equal to the peak value of  $\chi$  just above  $T_N$  near 5.7 K shown in figure 4(a). This is like the observation in the antiferromagnet  $\text{MnF}_2$ , for which  $\chi_{\perp}$  below  $T_N$  is nearly temperature independent [25] and equal to the peak value of  $\chi$  just above  $T_N$ . For  $\text{MnNb}_2\text{O}_6$ , the calculated  $M_S = N_A g \mu_B S_Z = 27.9 \times 10^3$  emu/mol at absolute zero is quite close to  $M_S \simeq 27 \times 10^3$  emu/mol measured at 1.6 K by Nielsen *et al* [1, 2]. Using the equation  $H_{sf} = (2H_A H_E)^{1/2}$  [24,26],  $H_E \simeq 200$  kOe and  $H_{sf} = 18$  kOe yields  $H_A = 0.8$  kOe as the anisotropy field in  $\text{MnNb}_2\text{O}_6$  between the easy  $a$ -axis and the hard  $c$ -axis. This estimated magnitude of  $H_A$  is close to the magnitude of  $H_A$  calculated by Nielsen *et al* [1, 2] assuming dipole-dipole interaction as the source of anisotropy.

### 3.5. Temperature dependence of the paramagnetic susceptibility:

The temperature dependence of the magnetic susceptibility  $\chi = M/H$  ( $H = 300$  Oe) for the temperature range of 1.9 K to 400 K. is shown in figure 10. The larger  $H = 300$  Oe (rather than  $H = 100$  Oe) was used for these measurements to improve the accuracy of the data for  $T > 300$  K where  $M$  with  $H = 100$  Oe is comparatively smaller and noisier. However, since  $M$  vs.  $H$  is linear for  $T > T_N$ , the paramagnetic susceptibility ( $\chi$ ) is independent of  $H$ .

Following the procedure outlined in our analysis of  $\chi$  vs.  $T$  data for isostructural  $\text{CoNb}_2\text{O}_6$  [14], we first fitted the data to the modified Curie-Weiss (MCW) law:

$$\chi = \chi_0 + \frac{C}{(T-\theta)} \quad \text{----- (4)}$$

Here  $\chi_0 = -1.85 \times 10^{-4}$  emu.mol<sup>-1</sup>Oe<sup>-1</sup> is determined in the limit of  $1/T = 0$  from the plot of our data of  $\chi$  vs.  $1/T$  with a focus on the high- $T$  data (see inset of figure 11). This value of  $\chi_0$  is in excellent agreement with the theoretical estimate of diamagnetic susceptibility [32] of  $\text{MnNb}_2\text{O}_6$  based on adding the diamagnetic contributions of the constituent atoms. The plot of  $(\chi - \chi_0)^{-1}$  vs.  $T$  for both  $\chi_0 = 0$  and  $\chi_0 = -1.85 \times 10^{-4}$  emu.mol<sup>-1</sup>Oe<sup>-1</sup> are shown in figure 11, both yielding  $\Theta = (-17 \pm 2)$  K from the linear fit for  $T > 100$  K but different magnitudes of  $C = 4.385$  (4.297) emu.K.mol<sup>-1</sup>Oe<sup>-1</sup> for  $\chi_0 = -1.85 \times 10^{-4}$  (0)

emu.mol<sup>-1</sup>Oe<sup>-1</sup>. Using  $C = N_A \mu^2 / 3k_B$  ( $N_A$  = Avogadro's number,  $k_B$  = Boltzmann constant) yields  $\mu = 5.920 \mu_B$  for  $\chi_0 = -1.85 \times 10^{-4}$  emu.mol<sup>-1</sup>Oe<sup>-1</sup>. and  $\mu = 5.862 \mu_B$  for  $\chi_0 = 0$ . Since  $\mu^2 = g^2 S(S+1) \mu_B^2$ , the expected value of  $\mu$  for  $S = 5/2$  and  $g = 2$  is  $\mu = 5.916 \mu_B$ , in good agreement with  $\mu = 5.920 \mu_B$  and  $g = 2.001$  obtained for  $\chi_0 = -1.85 \times 10^{-4}$  emu.mol<sup>-1</sup>Oe<sup>-1</sup>. For  $\mu = 5.862 \mu_B$  obtained for  $\chi_0 = 0$  yields  $g = 1.982 < 2$  which is not physical for the  $S$ -state of  $Mn^{2+}$ . This shows the importance of including the correct non-zero  $\chi_0$  in the analysis using the MCW law, as also emphasized for the case of  $Co_3O_4$  [33].

### 3.6. Determination of the exchange constants:

The effective spin  $S = 5/2$  of  $Mn^{2+}$  in  $MnNb_2O_6$  is large enough to be classical like, unlike  $S = 1/2$  for  $CoNb_2O_6$  in which quantum effects were dominant [14]. Therefore, molecular field theory (MFT) should provide good estimates of the exchange constants in  $MnNb_2O_6$ . Using the Hamiltonian:

$$H = -\sum J_{ij} \vec{S}_i \cdot \vec{S}_j - g\mu_B H \cdot \sum \vec{S}_i \quad \text{----- (5)}$$

the following equation for  $\Theta$  and  $T_N$  using MFT are obtained [31]:

$$3k_B\Theta = S(S+1)[J_0Z_0 + (J_1Z_1 + J_2Z_2)] \quad \text{----- (6)}$$

$$3k_B T_N = S(S+1)[J_0Z_0 - (J_1Z_1 + J_2Z_2)] \quad \text{----- (7)}$$

Following the Hamiltonian defined in equation (1),  $J_0$  is the exchange constant between  $Mn^{2+}$  ions along the  $c$ -axis with nearest neighbours  $Z_0 = 2$ . In addition,  $J_1$  and  $J_2$  are respectively the exchange interaction along the  $b$ -axis with  $Z_1 = 2$  and along the body-diagonal of the  $ab$  plane with  $Z_2 = 4$ . Having only two experimental constants  $\Theta$  and  $T_N$ , only two exchange constants can be determined. Since there are three exchange constants in equations (6) and (7), we assume  $J_1 = J_2 = J_\perp$  as found to be nearly valid in  $CoNb_2O_6$  [14]. These assumptions, and  $S = 5/2$  leads to the following equations for  $J_0$  and  $J_\perp$ :

$$J_0/k_B = 3(\Theta + T_N)/35 \quad \text{----- (8)}$$

$$J_\perp/k_B = (\Theta - T_N)/35 \quad \text{----- (9)}$$

Using experimental magnitudes of  $\Theta = (-17 \pm 2)$  K, and  $T_N = 4.36$  K yields  $J_0/k_B = (-1.08 \pm 0.17)$  K and  $J_\perp = (-0.61 \pm 0.06)$  K. The sum of the three exchange constants  $J/k_B = (J_0 + 2J_\perp)/k_B = -2.3$  K. This magnitude of  $J/k_B \simeq -2.3$  K is further discussed in the next section.

In  $CoNb_2O_6$ , the variation of the paramagnetic  $\chi$  vs.  $T$  was shown to fit nicely with the prediction of Ising linear chain (ILC) using the equation [14,34]:

$$\chi = \chi_0 + \frac{C}{T} \exp\left(\frac{2J_0 S^2}{k_B T}\right) \quad \text{----- (10)}$$



The fit with  $S = 1/2$  valid for  $\text{CoNb}_2\text{O}_6$  yielded  $J_0/k_B = (6.2 \pm 0.2)$  K as the ferromagnetic exchange coupling between  $\text{Co}^{2+}$  ions along the  $c$ -axis. For Heisenberg linear chain (HLC), the corresponding expression for the temperature variation of  $\chi$  is given by [34]:

$$\chi = \chi_0 + \frac{C}{T} \left( \frac{1+\Gamma}{1-\Gamma} \right) \quad \text{----- (11)}$$

In Eq. (11),  $\Gamma = \coth(y) - (1/y)$  with  $y = JS^2/k_B T$ . We tried fits of the data of  $\chi$  vs.  $T$  in  $\text{MnNb}_2\text{O}_6$  to both Eq. (10) for ILC and Eq.(11) for HLC using  $S = 5/2$ ,  $C = 4.385 \text{ emu.K.mol}^{-1}\text{Oe}^{-1}$  and  $\chi_0 = -1.85 \times 10^{-4} \text{ emu.mol}^{-1}\text{Oe}^{-1}$  determined from our analysis based on the MCW law. The fit to Eq.(10) for ILC using positive  $J_0$  is not possible since in this case there is no peak in  $\chi$  vs.  $T$ . For negative  $J_0/k_B = -1.1\text{K}$ , we show the fit to ILC in figure 10, the fit failing for  $T < 100$  K. For HLC, we show the fit for three different values of  $J/k_B = -1.7$  K,  $-1.9\text{K}$  and  $-2.1$  K. For  $J/k_B = -2.1$  K, the fit of the data to HLC is very good above 25 K. For  $T < 20$  K, the calculated curve falls below the experimental data, the peak position occurring near 15 K compared to about 6 K for the experimental data. This is likely due to neglect of anisotropy in the HLC model. So fits of the data to the HLC model for  $\chi$  vs.  $T$  is considered to be semiquantitative only since the position of the peak and magnitude of  $\chi$  for  $T < 20$  K do not match well with the HLC model. However, the magnitude of  $J/k_B = -2.1$  K determined from the fit to HLC is close to total  $J/k_B \approx -2.3$  K estimated from the MFT. For these reasons,  $J_0/k_B = -1.08$  K and  $J_{\perp}/k_B = -0.61$  K determined earlier are suggested to be reliable estimates of the intrachain and interchain exchange interactions in  $\text{MnNb}_2\text{O}_6$ . There have no other reported estimates of these exchange constants reported in  $\text{MnNb}_2\text{O}_6$  with which to compare these results. For comparison,  $J_0/k_B = 6.2$  K,  $J_1/k_B = -0.42$  K and  $J_2/k_B = -0.67$  K were determined for  $\text{CoNb}_2\text{O}_6$  [14]. Although the signs and magnitude of the interchain exchange constants for  $\text{CoNb}_2\text{O}_6$  and  $\text{MnNb}_2\text{O}_6$  are nearly same, theoretical reasons for  $J_0/k_B$  being negative in  $\text{MnNb}_2\text{O}_6$  and positive in  $\text{CoNb}_2\text{O}_6$  still need to be understood.

#### 4. Concluding Remarks

The results reported in this paper on  $\text{MnNb}_2\text{O}_6$  include the following: (i) The system orders antiferromagnetically below  $T_N = 4.36$  K, in agreement with previous reports; (ii) A complete  $H$ - $T$  phase diagram is presented with a triple point  $T_{TP}(H, T) = (18 \text{ kOe}, 4.06 \text{ K})$ , spin flop field  $H_{sf} \approx 18 \text{ kOe}$  and exchange field  $H_E \approx 200 \text{ kOe}$ ; (iii) Molecular field theory and fit to the Heisenberg linear chain model yields  $J_0 = -1.08$  K as the intrachain exchange and  $J_{\perp} \approx -0.61$  K as the interchain exchange coupling; (iv). The anisotropy field  $H_A \approx 0.8 \text{ kOe}$  is determined from the magnitude of the spin-flop field, in good agreement with the estimates based on the dipole-dipole interaction; and (v) Analysis of the specific heat data on approach to  $T_N$  yields the critical exponent  $\alpha = 0.12$  (0.15) for  $T > T_N$  ( $T < T_N$ ). Good theoretical understanding is still needed regarding the differences in the magnetic properties of the four-transition metal niobates  $\text{MNb}_2\text{O}_6$  ( $M = \text{Mn}, \text{Fe}, \text{Co}$  and  $\text{Ni}$ ) having the same columbite structure, along

the lines of our understanding of the magnetic properties of the transition metal oxides MO (M = Mn, Fe, Co and Ni) with the NaCl structure [35].

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