Magnetic structure and properties of a vanthoffite mineral $Na_6Mn(SO_4)_4$

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A detailed analysis of the magnetic properties of a vanthoffite type mineral $Na_6Mn(SO_4)_4$, based on dc magnetization, low temperature neutron powder diffraction and theoretical calculations is reported. The mineral crystallizes in a monoclinic system with space group $P2_1/c$, where $MnO_6$ octahedra are linked via $SO_4$ tetrahedra. This gives rise to super-exchange interaction between two $Mn^{2+}$ ions mediated by two nonmagnetic bridging anions and leads to an antiferromagnetic ordering below 3 K. The magnetic structure derived from neutron powder diffraction at 1.7 K depicts an antiferromagnetic spin arrangement in the $bc$ plane of the crystal. The magnetic properties are modelled by numerical calculations using exact diagonalization technique, which fits the experimental results and provides antiferromagnetic ground state of $Na_6Mn(SO_4)_4$.

INTRODUCTION

Over the last two decades, design of polyanionic materials $[(XO)_n$ with $X = S, P, As, V, Si, Mo or W]$, has attracted significant attention due to their adaptability towards various potential applications. For example, the discovery and commercialization of $LiFePO_4$ [1, 2] significantly shed light on the use of insertion materials in battery research with other polyanionic units [3, 4]. In this context, it may be noted that many naturally occurring minerals with a variety of polyanionic units offer a treasure trove of materials with associated tunable properties. Moreover, the presence of 3d transition metals in the chemical composition of such materials will open up the possibility of synthesizing solids with interesting magnetic behaviour. Several electrode materials inspired by the naturally occurring minerals have been investigated leading to the discovery of interesting magnetic properties in these materials [7, 8]. The coupling between magnetic and electrical properties in 3d metal based polyanionic compounds results in magneto-electric effect [8, 11, 13–22], which has been successfully utilized to design various multiferroic materials [23, 24]. Specifically, the compound $TbPO_4$ [25, 27] displays intrinsic bulk magneto-electric effect. A series of polyanionic phosphates $LiMPO_4$ ($M = Mn, Co, Ni or Fe$) have aroused special interest to evaluate the associated magnetic behaviour in these minerals [19, 28–32].

The origin of magnetic interactions in these transition metal oxides, sulfates, phosphates and arsenates are governed by the overlap between 3d orbitals of the transition metal and 2p orbitals of the oxygen atom. Usually, in super exchange interactions, two magnetic metal centers are bridged via a single electronegative anion, like oxygen (M-O-M). However, in this material two metal centers interact via two oxygen atoms (M-O-O-M) and the magnetic interactions are hence weaker. A set of semi-empirical rules referred to as Goodenough-Kanamori-Anderson rules which these systems follow, are well described in the literature [33, 35].

Many polyanionic compounds have been largely studied for their structural diversity where both types of interactions (M-O-M or M-O-O-M) are possible when changing the 3d transition metal as well as polyanions (e.g. $PO_4$, $SO_4$, $AsO_4$, $VO_4$ etc). For example, the magnetic structure of anhydrous $FeSO_4$ and $NiSO_4$ have antiferromagnetic sheets with ferromagnetic coupling between the sheets whereas in the case of $CoSO_4$, only antiferromagnetic ordering exists within each sheet. But the magnetic structure of $CrVO_4$ has ferromagnetically ordered sheets that stack antiferromagnetically. However, in each case, magnetic coupling involves a long super exchange pathway between magnetic centers via nonmagnetic sulfate or vanadate tetrahedron [39]. Beside these class of materials, other families of electrode materials such as fluorosulfates [40–42], phosphates [19, 28, 29, 33, 43, 44] and borates [45] have been studied and these materials also exhibit magnetic ordering at low temperatures. In fluorosulfates magnetic exchange interaction between nearest-neighbour ions is mediated either through M-F-M link or through M-O-M interaction via the oxygen anions at the sulfate tetrahedral edge.

Materials designed for potential battery electrode applications are also recognized as model compounds for their intriguing magnetic property; examples are marine phases $Li_2M(SO_4)_2$ ($M = Mn, Fe or Co$) and $LiFe(SO_4)_2$ [7]. At low temperatures, these compounds show antiferromagnetic ordering due to a specific arrangement of transition metal octahedra ($MO_6$) and sulfate tetrahedra ($SO_4$). This particular structural arrangement solely enables the M-O-O-M exchange path-
way between transition metal ions. Another interesting example in this series is the orthorhombic \( \text{Li}_2\text{Ni}(\text{SO}_4)_2 \) reported by Reynaud et al [8]. It has a particular arrangement of isolated \( \text{NiO}_6 \) octahedra which are interconnected via \( \text{SO}_4 \) tetrahedral units. As a result of exchange interaction between the 3\( \text{d} \) transition metal cations via two bridging ions, this phase is antiferromagnetic with a \( T_N = 28 \text{ K} \). Similar long-range antiferromagnetic ordering is also observed with isostructural orthorhombic \( \text{Li}_2\text{M}(\text{SO}_4)_2 \) (\( \text{M} = \text{Mn}, \text{Fe} \text{ or } \text{Co} \)) phase [11].

It is of interest to note that, Vanthoffite minerals occur in nature as oceanic salt deposits [46-47]. We have shown earlier that the crystal structure of \( \text{Na}_6\text{Mn}(\text{SO}_4)_4 \) (a Vanthoffite mineral) is built from an alternating corner-sharing of \( \text{SO}_4 \) tetrahedra and transition metal octahedra \( \text{MnO}_6 \) resulting in an infinite two-dimensional framework in the \( bc \) plane [48]. Such specific connectivity suggests the possibility of long exchange pathway between two \( \text{Mn}^{2+} \) centers via two oxygen atoms (\( \text{Mn-O-O-Mn} \)), which might lead to magnetic interaction akin to several other examples reported in the literature [7, 8, 11]. In this article, we investigate the magnetic structure of \( \text{Na}_6\text{Mn}(\text{SO}_4)_4 \) using variable temperature neutron diffraction. Besides, we have carried out exact diagonalization calculations of the model Hamiltonian to shed light on the magnetic properties and magnetic structure.

**EXPERIMENTAL METHOD**

Single crystals of \( \text{Na}_6\text{Mn}(\text{SO}_4)_4 \) were grown by slow evaporation at \( 80^\circ \text{C} \) from an aqueous solution containing 3:1 stoichiometric molar ratio of \( \text{Na}_2\text{SO}_4 \) (Sigma-Aldrich, 99.99%) and \( \text{MnSO}_4 \cdot \text{H}_2\text{O} \) (Sigma-Aldrich, 99.99%) as described in the earlier publication [48]. Colourless block-shaped crystals were obtained after 15 days. The single crystal x-ray diffraction of the as grown crystal was carried out on an Oxford Xcalibur(Mova) diffractometer equipped with an EOS CCD detector and a microfocus sealed tube using MoK\( \alpha \) X-radiation \( (\lambda = 0.71073 \text{ Å}; 50 \text{ kV and } 0.8 \text{ mA}) \) and the structural parameters agree with the earlier report [48]. Single crystals were crushed to form bulk polycrystalline powder for further characterization. Room temperature PXRD data was recorded on a PANalytical X'Pert PRO diffractometer using Cu K\( \alpha \) range of 8-60\( ^\circ \) using a step size of 0.013\( ^\circ \). X'Pert High Score Plus (version 4.8) [49] was used to analyze the pattern and profile fitting refinements were carried out using the room temperature unit cell parameters of \( \text{Na}_6\text{Mn}(\text{SO}_4)_4 \) [48] in JANA2006 [50]. Profile parameters such as \( \text{GU}, \text{GV}, \text{GW}, \text{LX}, \text{and } \text{LY} \) were refined using Pseudo-Voigt function. Neutron diffraction patterns over a wide \( Q \)-range \( (4\pi \sin \theta/\lambda = 0.3 - 9.5 \text{ Å}^{-1} \) where \( 2\theta \) and \( \lambda \) are the scattering angle and wavelength of the incident neutron beam, respectively) were recorded over 1.7-300 K by using the powder diffractometer PD-
RESULTS AND DISCUSSION

$Na_6Mn(SO_4)_4$ belongs to a monoclinic system, space group $P2_1/c$ with $Z = 2$ as determined from single crystal X-ray diffraction for the present work and agrees well with the earlier report by our group [48]. The fractional coordinates of all atoms and the bond lengths and angles for $MnO_6$ octahedra are given in Table I and II. The asymmetric unit contains half the formula unit, where Mn atom is in a special position (Wyckoff position 2a, local site symmetry -1) along with three sodium atoms and two sulfate units in general position (Wyckoff position 4e, local site symmetry 1) [Table I]. Mn atom forms $MnO_6$ octahedra with symmetrically related oxygen atoms and connected to $SO_4$ tetrahedra in a “pinwheel pattern” (Figure 1b) [57].

The Mn-O bond lengths in $MnO_6$ octahedra varies between 2.1597 (12) to 2.1901(13) Å (Table II) where the bond length distortion parameters and bond angle variance are calculated using formulas $\Delta d = \frac{1}{n} \sum \left| d_i - d_{av} \right|$ and $\sigma_{oct}^2 = \frac{1}{3} \sum (\alpha_i - 90)^2$, ($d_n$ and $d_{av}$ are the individual and average Mn-O bond length and $\alpha_i$ are the individual O-Mn-O bond angles) [58–60]. It is to be noted that, $\Delta d$ and $\sigma_{oct}^2$ values for an ideal octahedron should be exactly zero. The bond length distortion parameter obtained ($\Delta d = 3.35 \times 10^{-5}$) though indicates a quite symmetrical $MnO_6$ octahedra, the calculated bond angle variance of 18.32 show a distorted $MnO_6$ octahedra. The bond valence sum for Mn atom is calculated to be around 1.927 using the Zachariasen formula $V_i = \sum_j s_{ij} = \sum_j e^{d_{ij} - d_{ij}}$ and it is in good agreement with the expected valance of +2 [61]. These are isolated $MnO_6$ octahedra (pink) and are connected to $SO_4$ tetrahedra (yellow) via their oxygen vertices (Figure 1). Thus the structure presents an exchange pathway via two bridged oxygen atoms viz., Mn-O-O-Mn magnetic interaction where Mn-O-O-Mn dihedral angle is about 148° (Figure 1b). A similar long exchange pathway (M-O-O-M) is found in $Li_2M(SO_4)_2$, ($M = Ni$, Co, Fe, Mn), where magnetism in the materials are explained based on this interaction [7,8,11]. The single crystals grown are further crushed to form the powder sample and the phase purity was checked using PXRD measurement. The PXRD profile refinement ($R_p = 3.43$, $R_{wp} = 4.50$ and $\chi^2 = 1.01$) at room temperature was carried out using the cell parameter and space group obtained from the single crystal XRD, where the close similarity between the observed and the calculated patterns suggests the purity of the desired compound, $Na_6Mn(SO_4)_4$ (Figure 2).

Magnetic Measurements

The zero-field-cooled susceptibility curve of $Na_6Mn(SO_4)_4$ measured under magnetic field of 50 Oe (Figure 3a) shows a peak revealing a transition to antiferromagnetic (AFM) state below $T_N \sim 3$ K. The AFM ordering is confirmed by our zero field neutron...
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stant value expected in the paramagnetic region. The
increases slightly with temperature, contrary to the con-
value in the high temperature (paramagnetic) region
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interactions in

20 K. This corroborates the existing antiferromagnetic

1000 Oe [inset of Figure 3b] yields a downturn below
Figure 3a. It is to be noted that ZFC
χT vs T plot under
observation made under a weak applied field of 50 Oe in
any distinct magnetic transition in contrast to the
vs T curve in Figure 3b, however does not exhibit
χ under 1000 Oe over the temperature range 2-300 K. The
temperature dependent susceptibility curve measured
diffraction study presented later. Figure 3b shows the
temperature dependent susceptibility curve measured
under 1000 Oe over the temperature range 2-300 K. The
χ vs T curve in Figure 3b, however does not exhibit any
distinct magnetic transition in contrast to the
observation made under a weak applied field of 50 Oe in
Figure 3b. It is to be noted that ZFC χT vs T plot under
1000 Oe [inset of Figure 3b] yields a downturn below
20 K. This corroborates the existing antiferromagnetic
interactions in Na₆Mn(SO₄)₄. We also notice that χT value in
the high temperature (paramagnetic) region increases slightly with temperature, contrary to the constant
value expected in the paramagnetic region. The
reason for the same could be attributed to additional
correction arising from the van Vleck paramagnetism
(χVV) which is discussed in the theoretical section.

The inverse ZFC susceptibility plot under 1000 Oe is
shown in Figure 3c. The linear fit to the inverse
susceptibility curve yields the Curie-Weiss temperature ΘCW
= -6.0 K and the effective paramagnetic moment μeff
= 5.8 μB/f.u. The observed value of the effective
moment 5.8 μB/f.u is in good agreement with the theo-
retically expected μeff (where μeff(s) = g√s(s+1)
with g=2 (Lande g-factor)) value of 5.92 μB/Mn²,
considering only spin moment. This result confir-
m+2 oxidation state of the magnetic Mn ion (s=5/2) in
Na₆Mn(SO₄)₄. The isothermal field dependent mag-
netization curve (Figure 4) measured at 2 K, shows a
linear increase in the low field regime and then tends to
show a change in slope above 35 kOe and a saturation
above 65 kOe. However, we do not observe any open-
ing of the hysteresis loop (inset in Figure 4) under field
sweeping. The observation of negative Curie-Weiss tem-
perature, downturn of χT vs T, linear magnetization be-
haviour in the low field region and the absence of hystere-
sis altogether suggest an antiferromagnetic ground state
of Na₆Mn(SO₄)₄.

Neutron Diffraction

In order to further investigate the magnetic ground
state of the material, neutron diffraction data were col-

| Atom Wickoff position | Occupancy | x/a | y/b | z/c | uiso(A²) | BVS |
|-----------------------|-----------|-----|-----|-----|---------|-----|
| Mn1 2a | 0.5 | 0.000000 | 0.000000 | 0.000000 | 0.01093(11) | 1.927 |
| Na1 4e | 1 | 0.11489(9) | 0.36352(8) | 0.18562(11) | 0.02590(19) | 1.079 |
| Na2 4e | 1 | 0.31418(8) | -0.01160(7) | 0.46824(9) | 0.01645(17) | 1.105 |
| Na3 4e | 1 | 0.43369(9) | -0.15142(8) | 0.07766(10) | 0.02486(19) | 1.060 |
| S1 4e | 1 | 0.34511(4) | 0.15332(4) | 0.16518(5) | 0.01101(12) | 6.028 |
| S2 4e | 1 | 0.14234(4) | -0.30579(4) | 0.21800(5) | 0.01055(12) | 2.061 |
| O1 4e | 1 | 0.20375(13) | -0.23682(14) | 0.30234(18) | 0.0218(3) | 1.979 |
| O2 4e | 1 | 0.02432(14) | -0.19349(13) | 0.15358(17) | 0.0176(3) | 2.046 |
| O3 4e | 1 | 0.36223(15) | 0.08889(14) | 0.0135(17) | 0.0222(3) | 2.043 |
| O4 4e | 1 | 0.46806(13) | 0.11001(14) | 0.32974(17) | 0.0201(3) | 2.110 |
| O5 4e | 1 | 0.02432(14) | -0.19349(13) | 0.15358(17) | 0.0176(3) | 2.046 |
| O6 4e | 1 | 0.28843(14) | -0.23682(14) | 0.30234(18) | 0.0218(3) | 1.979 |
| O7 4e | 1 | 0.13626(14) | -0.39575(13) | 0.06987(16) | 0.0196(3) | 2.061 |
| O8 4e | 1 | 0.11064(16) | -0.39682(14) | 0.34471(18) | 0.0229(3) | 1.983 |

| Bond | Length (Å) | Bond | Angle (°) | Bond | Angle (°) |
|------|------------|------|----------|------|----------|
| Mn1-O5x2 | 2.1597(12) | O5-Mn1-O1x2 | 96.08(5) | O5-Mn1-O8x2 | 90.78(5) |
| Mn1-O1x2 | 2.1706(12) | O5-Mn1-O1x2 | 83.92(5) | O1-Mn1-O8x2 | 86.42(5) |
| Mn1-O8x2 | 2.1901(13) | O5-Mn1-O8x2 | 89.22(5) | O1-Mn1-O8x2 | 93.58(5) |
FIG. 5. Rietveld refinement of Neutron diffraction patterns for Na$_6$Mn(SO$_4$)$_4$ measured at (top) 300 K and (bottom) 10 K.

FIG. 6. Low-temperature neutron diffraction patterns down to 1.7 K collected on bulk powder sample over the temperature range 1.7-300 K. Preparation of phase pure compound in sufficient quantity to perform neutron diffraction is rather challenging. However, almost 5 gm of single crystals were grown in different batches and these crystals were crushed to form polycrystalline powdered sample. Phase purity of bulk amount of powdered sample was checked via laboratory PXRD. The Rietveld refined neutron diffraction patterns measured at 300 K and 10 K are shown in Figure 5. The crystal structure for Na$_6$Mn(SO$_4$)$_4$ remains monoclinic with space group $P2_1/c$ over the entire temperature range 1.7-300 K.

In order to probe the long-range antiferromagnetic interaction in Na$_6$Mn(SO$_4$)$_4$, neutron diffraction data were collected down to 1.7 K (Figure 6). The appearance of additional magnetic Bragg peaks at $2\theta \sim 7.6^\circ$, 9.4$^\circ$, and 11$^\circ$ (Marked with asterisks in Figure 6) below 3 K confirms a long-range antiferromagnetic ordering of the material.

All magnetic reflections observed for Na$_6$Mn(SO$_4$)$_4$ could be indexed with a propagation vector $\mathbf{k} = (0,0,0)$ with respect to the same monoclinic unit cell as the nuclear structure. The symmetry-allowed magnetic structure is determined by a representation analysis, as applied for various kinds of spin systems [62–65], using the program BASIREPS available with the FULLPROF program suite [52]. The results of the symmetry analysis reveal that there are four irreducible representations (IRs). Among the four IRs, the IR(1) or $\Gamma_1$ and IR(3) or $\Gamma_3$ are non-zero for the magnetic site of the present compound. Therefore, there are two possible symmetry allowed magnetic structures for Na$_6$Mn(SO$_4$)$_4$. Both the IRs $\Gamma_1$ and $\Gamma_3$ are one-dimensional.

### Table III

| IRs  | Basis vectors |
|------|---------------|
| Site (2b) | Mn-1 | Mn-2 |
| $\Gamma_1$ | $\Psi_1$ | 100 | -100 |
| $\Psi_2$ | 010 | 010 |
| $\Psi_3$ | 001 | 00-1 |
| $\Gamma_2$ | $\Psi_1$ | 100 | 100 |
| $\Psi_2$ | 010 | 0-10 |
| $\Psi_3$ | 001 | 001 |

FIG. 7. Experimentally observed (circles) and calculated (solid lines through the data points) neutron diffraction patterns for Na$_6$Mn(SO$_4$)$_4$ at (top) 20 K (paramagnetic state) and (bottom) 1.7 K (magnetically ordered state), respectively. The solid lines at the bottom of each panel represent the difference between observed and calculated patterns. The vertical bars indicate the positions of allowed nuclear and magnetic [the bottom panel] Bragg peaks.
FIG. 8. The magnetic structure of Na₆Mn(SO₄)₄.

FIG. 9. The temperature-dependent lattice parameters and unit cell volume of Na₆Mn(SO₄)₄ over the temperature range 1.7-300 K.

The magnetic representation Γ_{mag} is composed as

Γ_{mag} = 3Γ₁ + 3Γ₃

(1)

The basis vectors (the Fourier components of the magnetization) for these two IRs Γ₁ and Γ₃ for the magnetic site are given in Table III. The basis vectors are calculated using the projection operator technique implemented in the BASIREPS program [52, 66]. Out of the Γ₁ and Γ₃, the best refinement of the magnetic diffraction pattern is obtained for the IR Γ₁. The refinement with the Γ₁ is shown in Figure 7. A good agreement is observed between observed and calculated pattern.

The corresponding magnetic structure is shown in Figure 8. The magnetic structure reveals antiferromagnetic chains of the Mn moments along the NN bond (red bonds) directions in the bc plane, and such chains are coupled ferromagnetically along the NNN bond (blue bonds) directions in the bc plane. Therefore, the magnetic structure within the bc plane is a Néel type AFM. Such antiferromagnetic planes are stacked ferromagnetically along the a-axis (grey bonds). The magnetic structure is purely antiferromagnetic in nature without having any net magnetization per unit cell. The magnetic moments are lying in the ac plane with moment components $m_a = 2.60(8)$ and $m_c = 1.35(28) \mu_B$ per magnetic site (Mn²⁺) along the a and c axes respectively. The net ordered site moment of Mn ions (considering all the components) is found to be $M_{total} = 2.42(3) \mu_B$/Mn²⁺ at 1.7 K. The magnetic moment is found to be strongly reduced from the theoretically expected value of $4 \mu_B$/Mn²⁺ (≈ 80% of the fully ordered moment of $5 \mu_B$/Mn²⁺) revealing the presence of a strong spin fluctuation at 1.7 K. The temperature variation of the lattice parameters and unit cell volume is shown in Figure 9. Change in slope at low temperature could be due to the interaction with magnetic spin and lattice.

Theoretical study of Na₆Mn(SO₄)₄

The refined X-ray diffraction data of Na₆Mn(SO₄)₄ (Figure 1) shows a primitive monoclinic crystal structure in which Mn²⁺ ions are placed at each corner of the unit cell and an additional Mn²⁺ ion is located at the face-center position in the bc plane. A careful analysis of the structural information reveals that any Mn²⁺ ion located at the corner of the unit cell is connected to four first nearest neighbours along the face diagonal in bc plane and two second neighbours along the c-axis. This arrangement repeats along the a-axis, as shown in the Figure 10a. Heisenberg Hamiltonian is solved on the minimum cluster which adequately represents the crystal. This involves fourteen Mn²⁺ ions at the vertices and at the centre of two hexagons parallel to each other, as shown in Figure 10a. The spin of each Mn²⁺ ion is 5/2 as the crystal field is weak. Exact diagonalization of the 14 site s = 5/2 spin Heisenberg system is computationally prohibitive as the number of spin orientations (dimensionality of the Fock space) is more than 78 billion. Hence we have replaced the s = 5/2 site spins by s = 1/2 site spins and have scaled the computed susceptibility by a factor of 11.67 which is the ratio of the square of the magnetic moments of a s = 5/2 ion and s = 1/2 ion. The Fock space dimension of the 14 spin-1/2 system is only 16,384. Furthermore, since z-component of the total spin, $S_z$ is conserved, we can factor the space into different $M_S$ sectors. Solving the eigen system for all the eigenvalues and eigenvectors is not compute in-
tensive and affords exploring the parameter space of the exchange constants in the Hamiltonian on a fine grid.

\[ \hat{H}_e = -J_1 \hat{s}_1 \cdot \hat{s}_3 + \hat{s}_1 \cdot \hat{s}_4 + \hat{s}_6 + \hat{s}_7 + \hat{s}_2 \cdot \hat{s}_3 + \hat{s}_4 \cdot \hat{s}_5 + \hat{s}_6 + \hat{s}_7 + \hat{s}_8 \cdot \hat{s}_{10} + \hat{s}_8 \cdot \hat{s}_{11} + \hat{s}_8 \cdot \hat{s}_{13} + \hat{s}_8 \cdot \hat{s}_{14} + \hat{s}_9 \cdot \hat{s}_{10} + \hat{s}_9 \cdot \hat{s}_{11} + \hat{s}_9 \cdot \hat{s}_{12} + \hat{s}_9 \cdot \hat{s}_{13} + \hat{s}_9 \cdot \hat{s}_{14} - J_2 (\hat{s}_1 \cdot \hat{s}_2 + \hat{s}_3 \cdot \hat{s}_4 + \hat{s}_5 \cdot \hat{s}_6 + \hat{s}_7 + \hat{s}_8 \cdot \hat{s}_{10} + \hat{s}_8 \cdot \hat{s}_{11} + \hat{s}_8 \cdot \hat{s}_{13} + \hat{s}_8 \cdot \hat{s}_{14} - J_3 (\hat{s}_1 \cdot \hat{s}_8 + \hat{s}_2 \cdot \hat{s}_9 + \hat{s}_3 \cdot \hat{s}_{10} + \hat{s}_4 \cdot \hat{s}_{11} + \hat{s}_5 \cdot \hat{s}_{12} + \hat{s}_6 \cdot \hat{s}_{13} + \hat{s}_7 + \hat{s}_{14}) \]

where, \( J_1, J_2 \text{ and } J_3 \) are the strength of exchange interactions between first, second and third neighbours, respectively and \( \hat{s} \) are the site spin operators and the numbers in the subscript represent the site index as in Figure 10. A positive or negative value of \( J \) corresponds to a ferromagnetic or antiferromagnetic exchange interaction respectively. The three unique exchange parameters \( J_1, J_2 \text{ and } J_3 \) are all antiferromagnetic and have their strengths that are exponentially dependent on the distance between ions; hence \( |J_1| > |J_2| > |J_3| \). The exchange constants \( J_2 \) and \( J_3 \) are expressed as fractions of \( J_1 \), which is set to -1.0. We have taken the two exchange constants \( J_2 \) and \( J_3 \) as \( J_2 = -e^{-\frac{r_1}{14}} \) and \( J_3 = -e^{-\frac{r_2}{14}} \), where \( r_1, r_2 \) and \( r_3 \) are the first, second and third neighbour distances from the refined X-ray diffraction data. As the first neighbour Mn-O-O-Mn dihedral angle is about 148° (from X-ray structure), we take \( J_1 \) to be antiferromagnetic.

The matrix of the spin Hamiltonian (eq. 2) was constructed using a basis with constant total \( M_S \). The largest Hamiltonian matrix which is 3432 x 3432 corresponds to the \( M_S = 0 \) sector. We obtain the complete eigen spectrum in all the \( M_S \) sectors; this is used to compute the magnetic susceptibility of the system. As the magnetic measurements are carried out under an applied magnetic field, we include a Zeeman term in our calculation which contributes an energy \(-g\mu_B H_z M_S\) to the eigenstates in a given \( M_S \) sector; \( g \) is the gyromagnetic ratio, \( \mu_B \) is the Bohr magneton and \( H_z \) is the applied magnetic field. The magnetic susceptibility of the system is given by,

\[ \chi(T) = \frac{N_A g^2 \mu_B^2 F(J,T)}{k_B} \]

\[ F(J,T) = \frac{\sum_S \sum_{M_S} M_S^2 e^{\frac{-E_o(S,M_S)}{k_BT}}}{\sum_S \sum_{M_S} e^{\frac{-E_o(S,M_S)}{k_BT}}} \]

In the above expression \( N_A \) is the Avogadro number, \( k_B \) is the Boltzmann’s constant and \( E_o(S,M_S) \) are energies of the unperturbed Hamiltonian corresponding to the eigen state with z-component of total spin \( M_S \). We also add a Curie contribution \((C)\) to the total susceptibility to account for any unreacted residual spin moments left after the synthesis. Besides, our magnetic data shows that the high temperature susceptibility is larger than the 0.0076 emu K/(g Oe) expected for free spin-5/2 moments. The \( \chi(T) \) value also shows a small linear increase with temperature, contrary to the temperature independent behaviour expected in the paramagnetic region for a Curie paramagnet. This suggests that there is an additional temperature independent susceptibility term or the van Vleck paramagnetic \((\chiVV)\) contribution coming from the excited states. The total \( \chi(T) \) value is given by \( \chi(T) = \chi(T(ex)) + \chi(T(res)) + \chiVV(T) \).
The presence of antiferromagnetic interactions and singlet port the experimental results and unambiguously show numerical results from full diagonalization approach sup-

refinement at 1.7 K clearly shows an antiferromagnetic characteristics below 3 K. Neutron diffraction Na of a Vanthoffite mineral J fit parameters correspond to in the temperature range 2-300 K (Figure 10c) and best magnetic data. The experimental magnetic data is fitted obtained by turning off all the exchange interactions. The moments are anti-parallel along the parallel spin arrangement along the neutron diffraction measurement, which shows parallel spin arrangement along the a and c directions, while the moments are anti-parallel along the (011) direction.

CONCLUSIONS

In summary, the measurement of magnetic properties of a Vanthoffite mineral Na₆Mn(SO₄)₄ shows antiferro-
magnetic ground state in Na₆Mn(SO₄)₄.

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