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Magneto-elastic coupling and symmetry breaking in the frustrated antiferromagnet α-$NaMnO_2$

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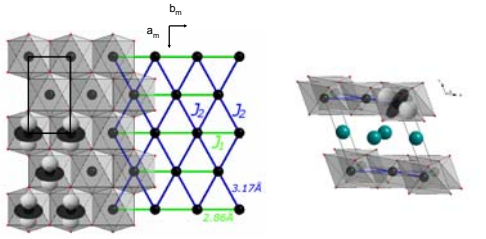
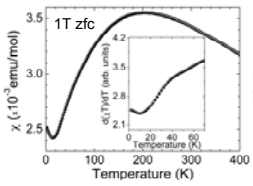
Introduction

The potential applications of the AMO_2 (A=H,Li,Na;*M*=3d transition metal) compounds as intermediate electrodes in rechargeable Li batteries[1] have motivated many investigations in the last 20 years. Recently, these systems, in particular the ones where *M* is magnetic, have attracted considerable interest from experimentalists and theorists because of the two-dimensional (2D) triangular lattice arrangement of the transition metal ions[2]. $NaMnO_2$ is particularly interesting because the $3d^4$ electronic state of Mn^{3+} in an octahedral oxygen environment induces a Jahn-Teller distortion and ferro-orbital ordering of the Mn^{3+}-dz^2 orbitals above room temperature. Unusually, the in-plane interactions in $NaMnO_2$ are *antiferromagnetic*, so the strong lattice anisotropy does not completely relieve the geometrical frustration. Our system is therefore an experimental realization of a frustrated triangular spin lattice with anisotropic interactions, which is widely studied for the various exotic ground state predicted for this type of system[3].

[1] M. Winter et al., Adv. Mater. 10, 725 (1998).
[2] M. V. Mostovoy and D. I. Khomskii, Phys. Rev. Lett. 89, 227203 (2002);
C. A. Marianetti et al., Phys. Rev. B 63, 224304 (2001); K. Takada et al., Nature 422, 53 (2003).
[3] G. Wannier, Phys. Rev. 79, 357 (1950); T. P. Eggarter, Phys. Rev. B 12, 1933 (1975); Y. Takana and N. Uryu, J. Phys. Soc. Jpn. 44, 109, (1978); Z. Weihong et al., Phys. Rev. B 59, 14367 (1999); C. N. Likos, Phys. Rev. E 55, 2001 (1997).



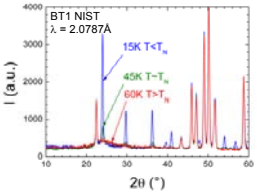
A full degenerated magnetic ground state is expected



Deviation from paramagnetic Curie-Weiss behaviour up to 400K

Broad magnetic peak typical of a low dimensional magnetic ordering centred around 200K

At about 45K a small anomaly in the d(χT)/dT is observed. The same anomaly is observed in the Cp curves (not shown).

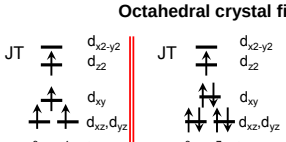


Below 200K broad magnetic features appear in the data

Below 50K sharp magnetic peaks grow

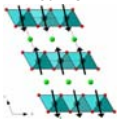
α-$NaMnO_2$ has a magnetically ordered AFM ground state.
What is the mechanism that lifts the ground state degeneracy?

Octahedral crystal field



Mn^{3+} $3d^4$ HS Ni^{3+} $3d^7$ LS Fe^{3+} $3d^5$ HS

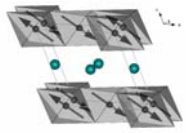
JT = Jahn Teller distortion



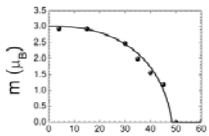
[4] **C. Darie**, *et al.* Eur. Phys. J. B 43, 159–162 (2005) Magnetic structure of the spin-1/2 layer compound $NaNiO_2$
[5] **F. Habbal**, G.E. Watson and P.R. Elliston Physics Letters 46 (4), 31 (1973) Magnetic Susceptibility of α-$NaFeO_2$

Magnetic ordering

3D

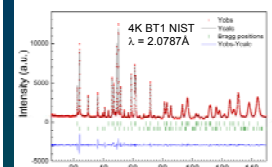


k = ½ , ½ , 0



Evolution of the Mn magnetic moment in the 3D magnetic ordered phase.

A unique magnetic structure model is refined from the neutron powder diffraction data. The moments are align in the d_{z2} orbitals direction and are antiferromagnetically order within the Mn-triangular lattice. No reorientation of the moment is observed on cooling.

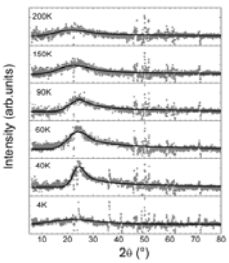


a_m = 5.6706(1)Å
b_m = 2.85547(3)Å
c_m = 5.80453(8)Å
β_m = 113.234(1)°

k=(½,½,0)$_m$, m=2.92(2)μ_B, m_x=-1.79(6)μ_B, m_z=1.71(6)μ_B
χ^2=3.82, R+=1.56%, R(F^2)=1.19%, R_{magn}=5.63%

Weak shifts of the Bragg peaks are observed, in particular the magnetic one.

2D



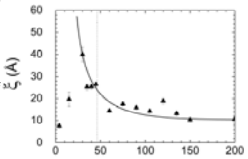
Warren function

$$I_{hk}(\theta) = CM_{hk}\left|F_m(Q)\right|^2 \frac{S(\theta)}{\sin\theta}$$

$$S(\theta) = \int_0^{\pi/2} \exp\left[-\frac{4\sin^2\theta}{\lambda^2}(\sin\theta\cos\varphi - \sin\theta_{hk})^2\right] d\varphi$$

$$F_m(Q) = \left\langle 1-(\hat{Q}.\hat{M})^2 \right\rangle \sum_{j=1}^{N} \left\langle \mu_j \right\rangle f_j(Q) \exp\left(i\,\hat{Q}\vec{r}_j\right)$$

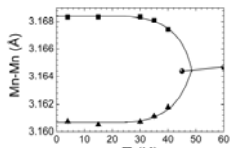
ξ magnetic correlation length along the c axis



Below 200K, broad asymmetric features are observed around the $(h/2,k/2,0)_m$ Bragg positions, the strongest being at $(½ ,½,0)_m$. The asymmetry of the signal with a tail on the high-Q side is typical of scattering from 2D lattices, as described initially by Warren. The evolution of the 2D scattering has been following by fitting the data with a Warren function.

Wu S. Y. *et al* Phys. Rev. B 54 (14), 10019-10026, (1996).
B. E. Warren, Phys. Rev. 59, 693 (1941).

Crystal distortions

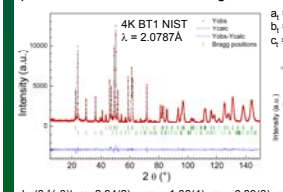


Mn-Mn interactomic distances along the a (●) and b-axis (■) in the triclinic cell; and the distances in the monoclinic phase(❶).

$$a_t = \frac{a_m - b_m}{2}$$

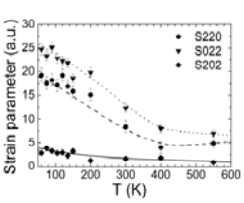
$$b_t = \frac{a_m + b_m}{2}$$

Below 48K the anisotropic strains are no longer sufficient to model the diffraction patterns. The structure is refined in a triclinic cell. The structural distortion (point groups 2/m → 1), involving the ε_{xy} and ε_{yz} components of the strain-tensor,consistent with the anisotropic broadening of the peak profiles observed in the 2D regime.

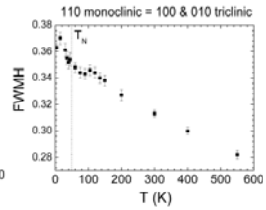


a_t = 3.16773(7)Å α_t = 110.465(2)°
b_t = 3.16046(7)Å β_t = 110.415(2)°
c_t = 5.78217(6)Å γ_t = 53.6173(8)°

k=(0,½,0)t, m=2.94(2)μ_B m_x=-1.06(4), m_y=-0.89(6), m_z=1.78(4)
χ^2=2.75, R_{Bragg}=2.10%, (F^2)=1.10%,R_{magn}=4.00%.



Evolution of selected micro-strain (Stephens) parameters with T.



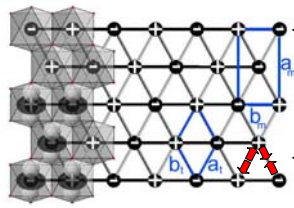
Evolution of the full width at half maximum of the 110 peak (in the monoclinic setting) with T.

To refine the crystal structure of the α-$NaMnO_2$ at room temperature and below, it has been necessary to introduce anisotropic strain model[6] as a certain hkl class of peaks show significant broadening. This peak broadening yields the same local strain as the triclinic distortion observed below 48K.

[6] P. W. Stephens, J. Appl. Cryst. 32, 281 (1999).

Conclusion

Our neutron diffraction data demonstrate that α-$NaMnO_2$ is the experimental realisation of a triangular antiferromagnet with anisotropic exchange interactions (J_1,J_2<0) in the weakly coupled chain limit (J_2/J_1 small). The inter-chain magnetic frustration is lifted by a magneto-elastic coupling that result in a small triclinic distortion of the cell.



Overlap of the half full t_{2g} orbitals
Strong AFM direct exchange in the chains

⬇

Formation of AFM chains along the b_m axis

Distortion of the cell that conduce to strains in the magnetic 2D regime and to a triclinic cell below 48K, in the magnetic 3D regime.

⬇

Lift the ground state degeneracy
Lead to a 2D AFM ordering under 200K
a 3D AFM ordering under 48K

FullProf_Suite, J. Rodríguez-Carvajal, Physica B 192, 55 (1993).