Magneto-elastic coupling and symmetry breaking in the frustrated antiferromagnet $\alpha$-NaMnO$_2$

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Introduction

The potential applications of the AMnO$_3$ (A = Li, Na, Mn) 3d transition metal compounds as intermediate electrodes in rechargeable Li batteries 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. NaMnO$_3$ 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.

Deviation from paramagnetic Curie-Weiss behaviour up to 400K

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

At about 45K a small anomaly in the $\chi'(T)/T$ is observed. The same anomaly is observed in the $\xi(T)/T$ curve (not shown).

A full degenerated magnetic ground state is expected

What is the mechanism that lifts the ground state degeneracy?

Octahedral crystal field

JT $d_{xy}$ $d_{yz}$ $d_{zx}$

$\downarrow$ $\downarrow$ $\downarrow$

Mn$^{3+}$ 3d$^7$ HS

JT = Jahn Teller distortion

$5\sigma^3$ 3d$^7$ LS

$\theta$ $\theta$ $\theta$

Magnetic ordering

Below 200K, broad asymmetric features are observed around 4N/2, K(O$_2$), Bragg positions, the strongest being at $(\frac{1}{2}, \frac{1}{2}, 0)$. The asymmetry of the signal with a tail at 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.

Crystal distortions

$D_{ij} = \frac{a_i - b_i}{2}$

$D_{ij} = \frac{2a_i}{2} + b_i$

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 2m → 11) involving the $\alpha_2$ and $\alpha_3$ components of the strain tensor, consistent with the anisotropic broadening of the peak profiles observed in the 2D regime.

Concentration

Our neutron diffraction data demonstrate that $\alpha$-NaMnO$_3$ is the experimental realisation of a triangular antiferromagnet with anisotropic exchange interactions ($J_1$, $J_2$) in the weakly coupled chain limit (3J, 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 cause 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

References