

Spin liquid versus spin solid in A-site spinels

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Geometrically frustrated magnets are compounds in which all pairwise interactions cannot be satisfied simultaneously due to the geometry of the crystal lattice. The frustration parameter defined as the ratio of the Curie–Weiss temperature to the ordering (or spin glass freezing) temperature is usually taken as a measure of frustration. Additional interactions other than the leading exchange enter in a non-perturbative way and result in a variety of fascinating complex ground states [1–6]. Concerning spinel compounds of stoichiometry AB_2X_4 , it is well known that the B-site sublattice forms a pyrochlore lattice which exhibits strong geometric frustration (GF) effects [7]. However, it has been shown only recently that spinels with magnetic ions located solely at the A-site also exhibit strong GF effects, both in the spin and orbital sector, respectively [6,8,9]. Orbital frustration may be inferred from the observation that a lattice of Jahn–Teller (JT) active ions does not undergo a cooperative JT distortion. In this case an orbital liquid or orbital glassy ground state

is expected [10]. Here we report on neutron diffraction experiments of the A-site spinels MA_2O_4 ($M = \text{Fe, Co, Mn}$) that provide further evidence for frustration resulting in a dynamic spin liquid ground state as opposed to a conventional long range ordered spin solid ground state.

Polycrystalline samples of MA_2O_4 ($M = \text{Fe, Mn, Co}$) were prepared by conventional solid state reactions from high purity binary oxides in evacuated quartz ampoules at 1000°C . Neutron powder diffraction experiments have been performed on the high resolution diffractometer HRPT at the PSI, Switzerland, in a temperature range $1.6 \leq T \leq 300 \text{ K}$. The data have been analyzed by standard Rietveld refinements. Excellent agreement between observed and calculated intensities with corresponding residuals of $1.8\% \leq R_{\text{Bragg}} \leq 3.8\%$ could be achieved for the cubic spinel type structure (space group $Fd\bar{3}m$) where the A-site ions are located at the tetrahedrally coordinated Wyckoff position (8a) $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$, octahedrally coordinated B-sites at the Wyckoff position (16d) $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and oxygen ions at the Wyckoff site (32e)(x, x, x) with $x = 0.2640(5)$ for $M = \text{Fe}$, $x = 0.2653(3)$ for $M = \text{Mn}$ and $x = 0.2635(5)$ for $M = \text{Co}$, respectively. These values are close to $x = 0.25$ of the ideal spinel structure. The cation distribution was

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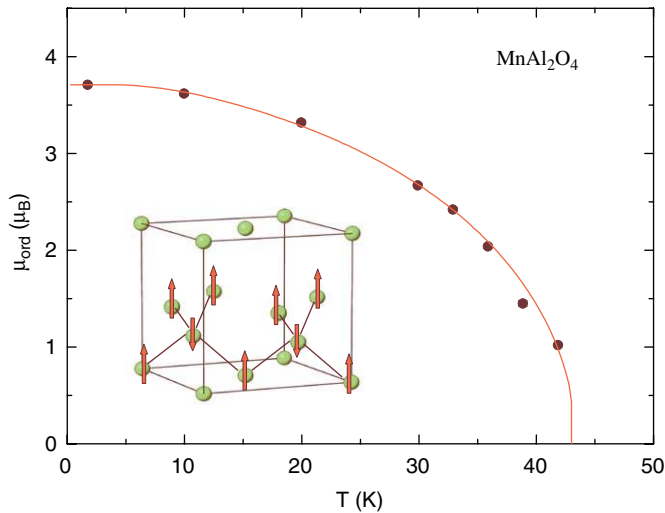


Fig. 1. Temperature dependence of the ordered magnetic moment of MnAl_2O_4 fitted by a Brillouin function (solid line). The inset shows the corresponding magnetic structure.

found to exhibit a minor degree of inversion between 6% and 8% for the compounds investigated. Overall, the refined crystal structures of MAl_2O_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}$) are in satisfying agreement with previously published structural data [11–14].

For MnAl_2O_4 , additional sharp resolution limited magnetic Bragg reflections show up at low temperatures indicating long range magnetic order. The diffraction pattern could be fitted by assuming a simple co-linear antiferromagnetic structure as shown in Fig. 1. The temperature dependence of the ordered magnetic moment of MnAl_2O_4 reveals conventional mean field behavior that can be described by a Brillouin function. A Néel temperature of $T_N = 42 \pm 0.5 \text{ K}$ and an ordered magnetic moment of $\mu_{\text{ord}} = 3.71(2)\mu_B$ at $T = 1.6 \text{ K}$ can be determined.

In contrast, neither FeAl_2O_4 nor CoAl_2O_4 shows any indications of long range magnetic order, in agreement with recent ESR, magnetization and specific heat measurements [14]. Instead, the magnetic intensities reveal the typical behavior of a liquid structure factor $S(Q)$ as shown in Fig. 2 for CoAl_2O_4 . By taking the difference of the intensities at low (1.6 K) and high (50 K) temperatures the nuclear scattering contributions cancel, leaving the intensities of magnetic origin only. Strongly broadened maxima of the intensity indicate the nearest, next nearest and next-next nearest neighbor shell of a liquid.

An explanation of this contrasting magnetic behavior can be given in terms of frustration. We note that Mn^{2+} , $S = \frac{5}{2}$ is a spin only ion and consequently, frustration effects are limited to the spin sector. Fe^{2+} , $S = 2$ has an orbital moment and, additionally, is JT active. However, based on specific heat measurements [14] no indica-

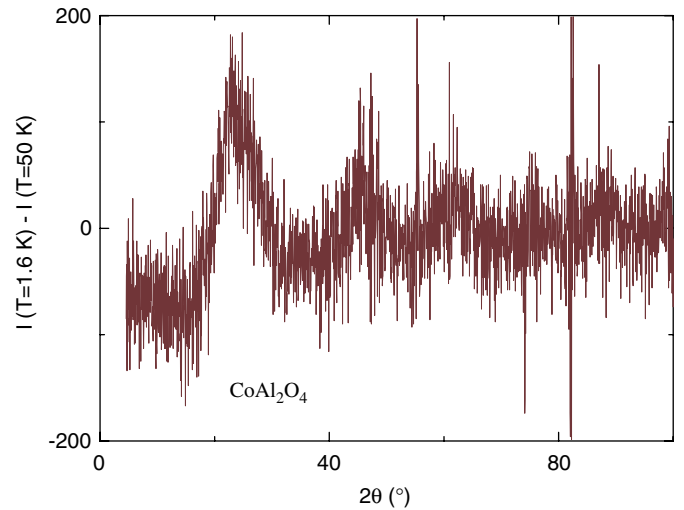


Fig. 2. Magnetic liquid-like structure factor $S(Q)$ of CoAl_2O_4 as obtained by subtracting the intensities at $T = 50 \text{ K}$ from the diffraction pattern at $T = 1.6 \text{ K}$.

tions of a cooperative JT transition could be detected. Additional orbital frustration effects are therefore expected. Previous neutron powder diffraction experiments observed significant diffuse magnetic scattering due to short ranged spin–spin correlations indicative of a spin-glass state [12]. Co^{2+} , $S = \frac{3}{2}$ has a lower spin value and therefore the magnetic interactions are expected to be weaker. Susceptibility measurements revealed frustration parameters of 22, 11 and 3.6 for the Co, Fe and Mn compound, respectively [14]. Such a strong GF, most pronounced for CoAl_2O_4 , in turn leads to a distinct liquid-like structure factor as shown in Fig. 2.

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