

## Spin liquid versus spin solid in A-site spinels

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### Abstract

Spinel compounds of stoichiometry  $AB_2X_4$  with magnetic A-site cations exhibit strong frustration effects. Frustration leads to strongly enhanced spin fluctuations that can easily suppress long range magnetic order (corresponding to a spin solid state) resulting in a dynamic spin liquid ground state. The same argument holds true for the orbital sector if an orbital moment is present. Neutron scattering is ideally suited to investigate the corresponding correlation functions. Here we present neutron diffraction studies on the A-site spinels  $MAI_2O_4$  ( $M = Co, Fe, Mn$ ). Whereas the Mn compound representing a spin-only system shows long range magnetic order below 42 K, the diffraction patterns of the Fe and Co spinel reveal a characteristic liquid structure factor of the magnetic scattering. This contrasting behavior can be related to the absence/presence of an orbital moment.

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PACS: 75.25.+z; 71.55.Jv; 61.12.-q

Keywords: Spin liquids; Frustration; Neutron scattering

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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  $MAI_2O_4$  ( $M = Fe, Co, Mn$ ) 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  $MAI_2O_4$  ( $M = Fe, Mn, Co$ ) 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  $1.6 \leq T \leq 300$  K. The data have been analyzed by standard Rietveld refinements. Excellent agreement between observed and calculated intensities with corresponding residuals of  $1.8\% \leq R_{Bragg} \leq 3.8\%$  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  $M = Fe$ ,  $x = 0.2653(3)$  for  $M = Mn$  and  $x = 0.2635(5)$  for  $M = Co$ , respectively. These values are close to  $x = 0.25$  of the ideal spinel structure. The cation distribution was

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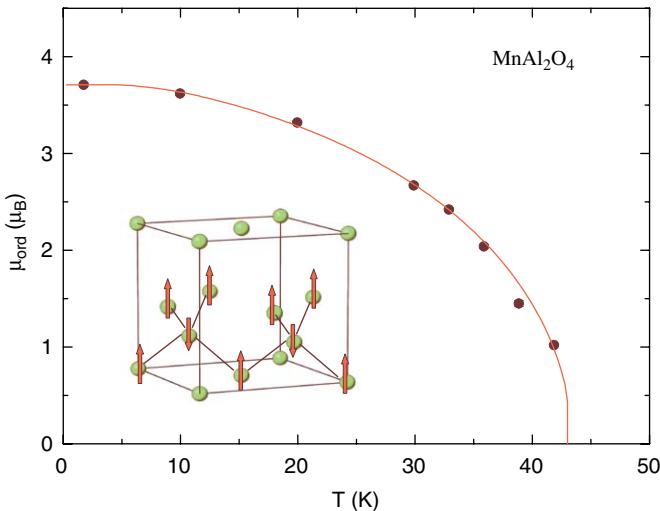


Fig. 1. Temperature dependence of the ordered magnetic moment of  $\text{MnAl}_2\text{O}_4$  fitted by a Brillouin function (solid line). The inset shows the corresponding magnetic structure.

found to exhibit a minor degree of inversion between 6% and 8% for the compounds investigated. Overall, the refined crystal structures of  $\text{MAl}_2\text{O}_4$  ( $\text{M} = \text{Fe}, \text{Mn}, \text{Co}$ ) are in satisfying agreement with previously published structural data [11–14].

For  $\text{MnAl}_2\text{O}_4$ , 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  $\text{MnAl}_2\text{O}_4$  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  $\text{FeAl}_2\text{O}_4$  nor  $\text{CoAl}_2\text{O}_4$  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  $\text{CoAl}_2\text{O}_4$ . 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-nearest neighbor shell of a liquid.

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

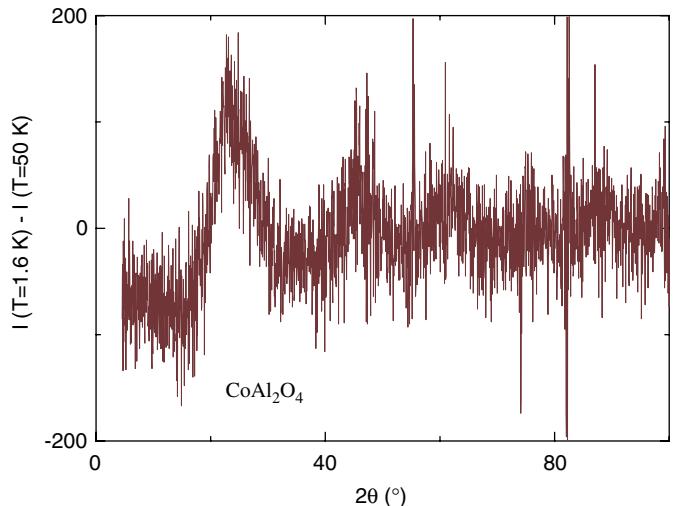


Fig. 2. Magnetic liquid-like structure factor  $S(Q)$  of  $\text{CoAl}_2\text{O}_4$  as obtained by subtracting the intensities at  $T = 50 \text{ K}$  from the diffraction pattern at  $T = 1.6 \text{ K}$ .

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].  $\text{Co}^{2+}, S = \frac{3}{2}$  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  $\text{CoAl}_2\text{O}_4$ , in turn leads to a distinct liquid-like structure factor as shown in Fig. 2.

This work was supported by the BMBF under contract no. 13N6917-A by the DFG via SFB484/Augsburg and by the European Union via the framework program “Transnational Access to Research Infrastructures”.

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