Magnetism of frustrated A-site spinels $(Mn, Fe, Co)Al_2O_4$

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1. Introduction

Currently, there is great interest in frustrated magnetic systems since they often exhibit a large variety of complex short-range ordered (SRO) magnetic states [1]. Frustration in the magnetic spin system tends to suppress long-range magnetic order (LRO) and enhances spin fluctuations. The ratio f of the Curie–Weiss temperature (reflecting the energy scale of the leading magnetic exchange) to the ordering temperature is commonly taken as a measure of frustration.

A prime example of frustrated magnets are AB_2O_4 compounds crystallizing in the cubic spinel structure. Mostly studied are the B-site spinels where the magnetic ions occupy the octahedral B-site, forming a spin–lattice of the frustrated pyrochlore type. Much less is known of A-site spinels where the magnetic ions are located at the tetrahedral A-site that forms a diamond lattice which also suffers from frustration, affecting both spin and orbital degrees of freedom [2,3].

The three compounds of the present study show Curie–Weiss behavior at high temperatures. $MnAl_2O_4$ orders, according to neutron data, below $T_N = 40\,K$ into a simple collinear AFM structure [3] coexisting with a paramagnetic component. The temperature dependence of the ordered Mn moment is Brillouin like with $\mu_{ord} = 3.7\mu_B$ which is reduced compared to the effective moment $\mu_{eff} = 5.75\mu_B$. In $CoAl_2O_4$ and $FeAl_2O_4$ magnetic Bragg peaks were not found. A cusp was observed in their susceptibilities at 5 K (Co) and 12 K (Fe). Differences in the field-cooled and zero-field cooled branches below T_{cusp} suggested spin-glass like freezing [2]. A liquid-like magnetic structure factor, detected by neutrons, is indicative of pure short-range correlations. Heat capacity shows below T_{cusp} a T^2-temperature dependence as seen in other frustrated magnets, instead of the linear dependence expected for a spin glass. In $FeAl_2O_4$ heat capacity reveals additional orbital freezing below ~10 K [2] analogous to $FeSc_2S_4$, an A-site sulfur spinel which we studied previously by μSR [4]. Mössbauer spectroscopy on $FeAl_2O_4$ [5] showed the majority of Fe ions to be 2^+, as expected. In addition a weak signal from Fe^{3+}-ions was present, yet an assignment of this portion was not possible. Below 13 K a poorly resolved Zeeman pattern was interpreted as the signature of a spin-glass like state.

In short, the A-site spinels are located at the border between LRO and SRO magnetism driven by magnetic frustration. Using T_N for $MnAl_2O_4$ and T_{cusp} for $CoAl_2O_4$ and $FeAl_2O_4$ leads to frustration parameters $f = 3.6$(Mn), 22(Co), and 11(Fe). Consistently, only $MnAl_2O_4$ is capable of forming a LRO magnetic ground state. μSR spectroscopy is particularly suited to characteristic properties of frustrated magnetism like local spin disorder and persistent spin fluctuations.

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2. Experimental

Polycrystalline samples were prepared by solid state reaction from high purity (99.99% and better) binary oxides. Sample purity was checked by powder X-ray and neutron diffraction. Less than 8% inversion and no foreign compounds were found. Data were taken at the DOLLY instrument of PSI. The VETO method was enabled to suppress the signal from muons stopped outside the sample. TF data confirmed the absence of such a signal.

3. Results

Spectra were recorded in low transverse field (TF = 3 mT), in zero field (ZF) and in longitudinal field (LF = 5 mT) between 2 and ~200 K. The small value of TF was chosen to ensure the same beam geometry as in ZF/LF. The compounds contain Al with a sizable nuclear dipole moment. In the Mn and Co samples nuclear moments exist on the magnetic ions as well. Data taken in longitudinal geometry were analyzed by combined ZF and LF least squares fits employing electronic and nuclear double relaxation. The nuclear contribution is described by a static Gaussian Kubo–Toyabe response. It was found to be weak ($0.1 \leqslant \Delta \leqslant 0.2\,\mu s^{-1}$), influencing the spectral shape only at elevated temperatures where the electronically induced relaxation rate is low. Thus, spectral parameters measured in low TF and in ZF/LF were quite comparable and could be used together. Similarly, no difference existed between TF and ZF for the baseline parameter α.

The spectra of all three samples consisted of two signals, one much faster relaxing than the other. On several occasions the rate of the fast relaxing portion became so large at low temperatures that the muon spins depolarized within the initial dead time of the spectrometer (~7 ns). The strength of the hidden signal was inferred from the missing signal amplitude taking the constant value of $A_{tot} = A_{fast} + A_{slow}$ from high temperature (>100 K) data.

$MnAl_2O_4$: For the Mn spinel the existence of a magnetic transition is well established. The μSR data fully confirmed this by a distinct change in spectral shape between 38 and 40 K, i.e. putting T_N at 39 K (see Fig. 1). At 38 K and below only a fast signal of substantially reduced intensity can be made out. At 40 K and above a fast plus a slowly relaxing pattern exist. The slowly relaxing fraction shows in TF the muon spin rotation due to the applied field. In the fast relaxing fraction the muon spin depolarizes too rapidly to develop the oscillatory pattern. In ZF/LF the signals for $T > T_N$ are well described by pure exponential decay. The relative intensity of the two signals ($A_{slow}/A_{fast} = 0.25/0.75$) is independent of temperature. Fig. 2 shows a typical ZF spectrum for $T < T_N$. The data were fitted with a dynamic Lorentzian Kubo–Toyabe (DLKT) function. The signal intensity (A_{KT}) is equal to A_{slow}.

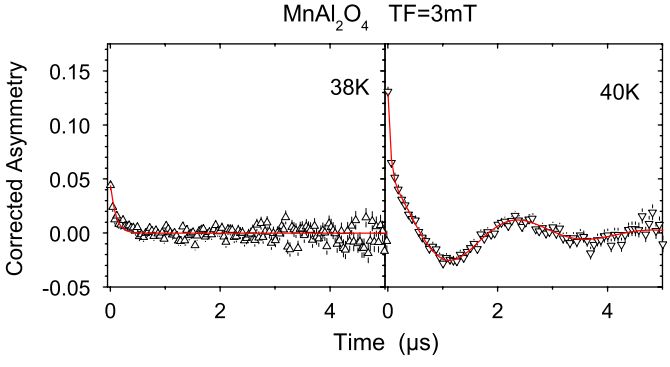

Fig. 1. μSR spectra of $MnAl_2O_4$ in TF = 3 mT just below and above T_N.

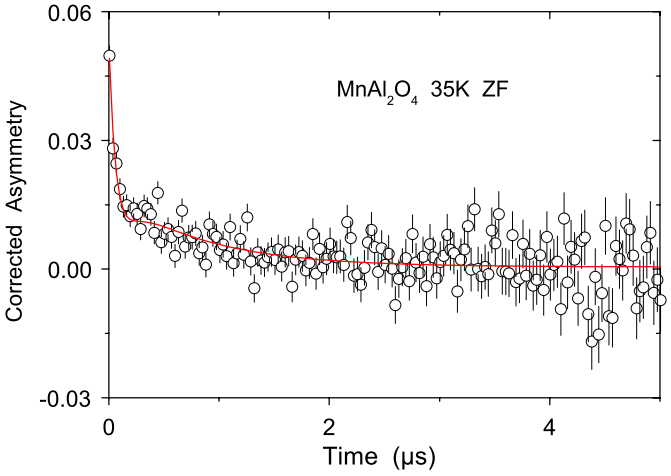

Fig. 2. Characteristic ZF spectrum of $MnAl_2O_4$ below T_N. The fit is dynamic Lorentzian Kubo–Toyabe function.

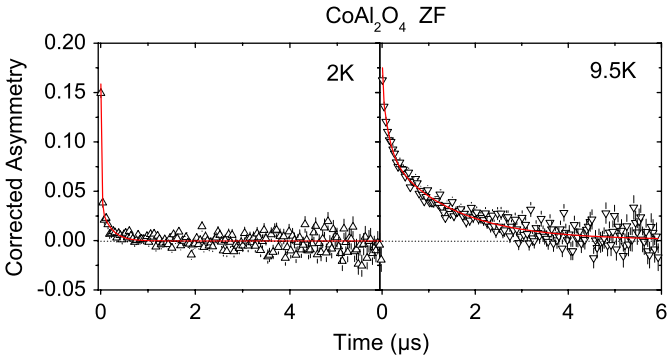

Fig. 3. Characteristic ZF spectra of $CoAl_2O_4$ below and above T_{cusp}. The fit is in both cases the sum of a fast and a slower exponentially relaxing pattern.

$CoAl_2O_4$: Although the Co spinel does not possess a transition into a LRO magnetic state, it features still a characteristic temperature, the susceptibility cusp $T_{cusp} = 5$ K, which is well reflected in its μSR data. Fig. 3 depicts ZF spectra a few Kelvins below and above T_{cusp}, demonstrating a distinct change in shape caused by a marked increase of relaxation rates for both signals. Rising the temperature well above T_{cusp} the fast relaxing fraction diminishes, but never vanishes completely.

$FeAl_2O_4$: The situation is quite comparable to $CoAl_2O_4$ with $T_{cusp} = 12$ K being the temperature for the sudden change in spectral shape. The main difference is that the fast relaxation rate is about an order of magnitude larger than in the Co spinel. Its signal intensity also gets smaller with rising temperature and at high temperatures a residual fast relaxing fraction remains as well.

4. Discussions

The contribution to muon spin relaxation from nuclear fields is essentially independent of temperature showing that no change in crystal structure occurs over the temperature region covered. Also, at all temperatures we deal with a static interaction, confirming that the implanted muons are fixed at their interstitial stopping sites.

The temperature dependencies of the various muon spin depolarization rates for the two μSR signals in $MnAl_2O_4$ are plotted in Fig. 4. Their relative intensities ($A_{slow} = 1/3A_{fast}$) show no change with temperature. In the paramagnetic regime

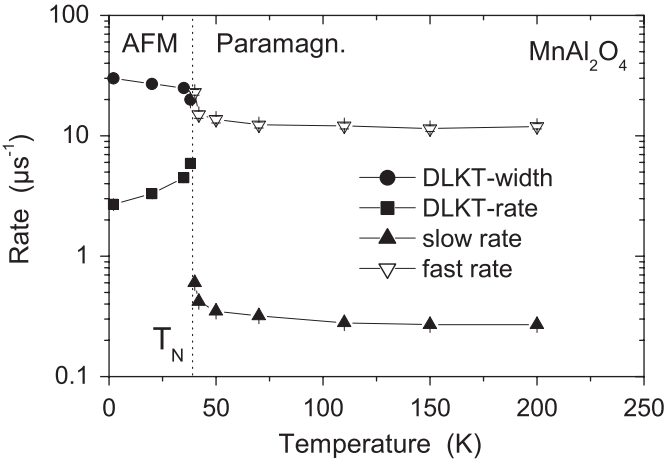

Fig. 4. Temperature dependencies of different spectral parameters in the AFM and paramagnetic regime of $MnAl_2O_4$. The lines are guides to the eye.

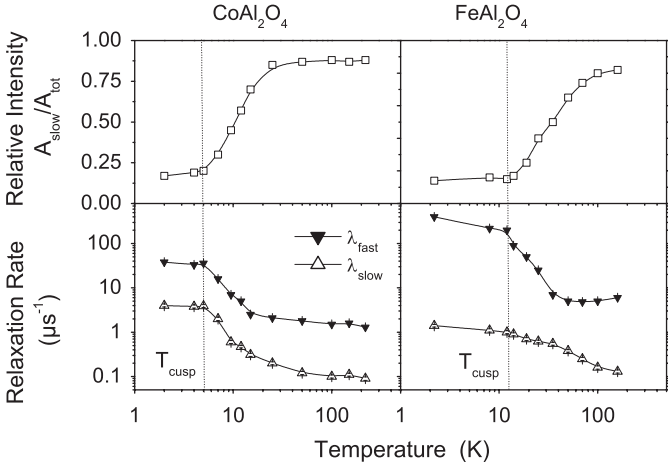

Fig. 5. Temperature dependencies of different spectral parameters of $CoAl_2O_4$ and $FeAl_2O_4$. The lines are guides to the eye.

($T > 39$ K) the rate of the slowly relaxing signal is typical for a normal paramagnet, i.e. an assembly of randomly oriented, independently and fast fluctuating spins. It shows the characteristic rise on approaching T_N, reflecting critical slowing down. The rate in the fast relaxing majority fraction is two orders of magnitude larger, meaning that substantial spin–spin couplings must exist, reducing the fluctuation rate of the paramagnetic spins accordingly. Critical slowing down is also present. The fast relaxing signal is the signature of a strongly correlated paramagnet. Below T_N this fraction forms the established AFM state. Yet, both relaxation rates of the μSR response function for an ordered magnet (λ_{trans} and λ_{long}) must be so big that the signal is lost in the instrument dead time. A large λ_{trans} means that, independent of LRO, the spin system possesses substantial local disorder on the scale of a few lattice constants. The large λ_{long} tells that, despite LRO, the spin fluctuation remain fast, even for $T \to 0$. The still observable μSR spectrum of the minority fraction indicates, by its dynamic Kubo–Toyabe shape, that incomplete spin freezing takes place at T_N leading to a weakly dynamic spin-glass like state. In this state we also find strong spin disorder (large value of the DLKT-width) and persisting spin fluctuations (leveling off of the DLKT-rate at a sizable magnitude). That confirms the coexistence of LRO with a disordered spin state. Basically, the properties of the two coexisting spin systems are similar but for the absence of LRO in the minority fraction.

Fig. 5 depicts the spectral parameters for $CoAl_2O_4$ and $FeAl_2O_4$ as a function of temperature, clearly demonstrating the central role of T_{cusp} as the characteristic temperature for their magnetic properties. Like in $MnAl_2O_4$ the two signals show the coexistence of free and highly correlated paramagnetic spins. Approaching T_{cusp}, the rates of both fractions increase, which means that their spin fluctuations slow down marking the onset of spin freezing. Below T_{cusp} the rates level off, albeit at a very high value for the dominating fraction. Since the spectral shape remains exponential, a fully spin frozen state, which would have a static Kubo–Toyabe pattern as its μSR signature, is not formed. In agreement with heat capacity data the ground state is not a spin glass but must be considered a SRO state with sizable spin dynamics persisting down to $T \to 0$. The residual free paramagnetic fraction develops more pronounced spin correlations but has still to be considered paramagnetic for $T < T_{cusp}$.

The main difference between the data of $FeAl_2O_4$ and $CoAl_2O_4$, is a much larger fast relaxation rate in the former, indicating more pronounced spin–spin interactions. The increased slowing down of spin fluctuation causes the spin freezing to take place at higher temperatures, fully in keeping with the weaker frustration. The further increase of relaxation rates when cooling below T_{cusp} might be due to the presence of additional orbital freezing in $FeAl_2O_4$.

The μSR data demonstrate well the fundamental role of frustration in forming the magnetic ground states of the MAl_2O_4 spinels. The increasing frustration from M = Mn to M = Fe, Co suppresses long-range order and also increases the spin dynamical properties. For example, while in $MnAl_2O_4$ the paramagnetic fraction forms, below T_N, a spin-glass like state (albeit not fully frozen), it only increases its spin–spin correlations but remains essentially paramagnetic in the other two compounds. The characteristic properties of frustrated magnets, strong local spin disorder and persistent spin fluctuations are present in all three spinels.

The origin of the two signals remains enigmatic. The usual explanation is the existence of two interstitial muon stopping sites. This is not very likely the case here due to the different behavior of $MnAl_2O_4$ on the one side and $CoAl_2O_4$ and $FeAl_2O_4$ on the other, both having the same crystal structure. The temperature dependence of the relative intensities in the latter two compounds is clearly connected to their magnetic properties. Furthermore, it requires muon hopping from one site to the other which should be visible in a dynamic response of the nuclear relaxation pattern. As said, this is not the case. It is interesting that a two signal response has been seen by us in related highly frustrated magnets such as the A-site sulfur spinel $FeSc_2S_4$ [4] and the B-site spinel $ZnFe_2O_4$ [6]. It is suspected that the origin lies in the disorder of the frustrated spin–lattices, but clarification of this phenomenon requires future studies which are in part under way.

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