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NMR and μSR study of magnetic dilution in the triangular Heisenberg antiferromagnet $NaCrO_2$

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Abstract. $NaCrO_2$ has been shown to be a very good model compound for the study of triangular Heisenberg antiferromagnets with isotropic interactions [1]. We examine by NMR and μSR the effect of substitution of non magnetic Ga^{3+} ions at the Cr^{3+} sites ($S = 3/2$). The presence of non-magnetic defects is found to impact both the dynamics and the static properties of the triangular network.

1. Introduction

Although from a theoretical point of view, there is a consensus that the Heisenberg triangular antiferromagnet with nearest-neighbour coupling presents at $T = 0$ an ordered state of spins in a configuration at 120° [2], on the experimental side, the field of triangular antiferromagnets was revived quite recently by the discovery of systems that present a fluctuating behaviour down to very low temperature [3, 4, 5]. Most of the studied compounds are however far from the ideal case, and present either a large anisotropy of the interactions or a single-ion anisotropy, as well as next-nearest-neighbour coupling, that seem to destabilize the Néel ground state [6].

$NaCrO_2$, a compound whose structure consists of hexagonal planes of edge-sharing CrO_6 octahedra separated by Na^+, was shown to be a unique example of 2D isotropic triangular Heisenberg antiferromagnet. The magnetic structure is built out from the stacking of well separated triangular planes of Cr^{3+}, with spin $S = 3/2$, in an $ABCABC$ sequence. This system is characterized by an isotropy of the in-plane interactions, a negligible single-ion anisotropy, a magnetic coupling that is limited to nearest neighbours, and a very strong 2D character [1]. At high temperatures, the macroscopic susceptibility displays a Curie-Weiss character with $\theta_{CW} \sim 290$ K, which yields an exchange constant $J \sim 40$ K. In Ref. [1], we evidenced an exotic fluctuating regime which extends well below the specific heat peak at $T_N \sim 41$ K, and characterized by a peak of the relaxation rate that appears at $\sim 0.75T_N$. This behaviour is

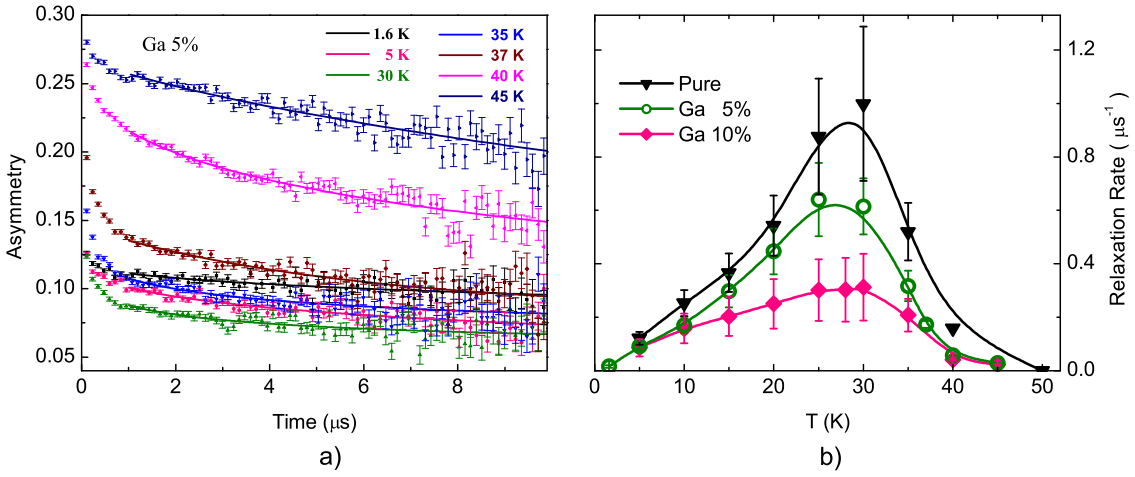

Figure 1. a) μSR asymmetry spectra for the Ga 5 % sample. Lines are for fits, as described in the text. b) Temperature dependance of the relaxation rate for the pure, Ga 5 % and Ga 10 % samples.

likely a landmark of excitations characteristic of triangular systems. No clear theoretical model has been yet reproducing in detail our data.

In the aim of obtaining more insight in this fluctuating regime, we performed a NMR and μSR study of dilution with non magnetic defects. Our measurements were performed on powder samples that have 5 % and 10 % non magnetic Ga^{3+} substituted for Cr^{3+}. Samples were prepared as described in Ref. [1], with the partial substitution of dried Ga_2O_3 for part of the Cr_2O_3 in the initial mixtures. Macroscopic susceptibility indicated a scaling of the Curie-Weiss constant with the concentration of magnetic sites, as expected.

2. μSR measurements on $NaCrO_2$ doped with 5 % and 10 % Ga

The μSR technique is particularly well-suited for the study of magnetism at a microscopic scale in this system. Positive muons have a spin 1/2 that is initially 100 % polarized, and a very large gyromagnetic factor $\gamma/2\pi = 135.5$ MHz/Tesla. Muons are implanted into the sample, where their spin sense the dipolar magnetic field created by the magnetic environment.

Examples of asymmetry spectra are presented in Figure 1, a) for the Ga 5 % sample between 1.2 and 45 K. In order to get rid of the depolarization of the muon due to the small random fields produced by the static nuclear dipoles, all measurements were performed under a longitudinal field of 30 Gauss applied along the initial polarization of the muon spin. Note that the field value is weak enough that it neither impacts the dynamics of the system nor decouples any static behaviour characterized by fields of the order of 1 kG, see ref. [1]. In our measurements, performed at the ISIS facility (UK), early time oscillations due to well defined internal fields cannot be detected, hence we mainly focus on the long-time tail, for which the muon depolarization relates to dynamical relaxation. We fitted the asymmetry as a function of time according to the ansatz:

$$A = \begin{cases} (A_0 - B)e^{-(t/T_1)^\alpha} + B, \text{ for } T \geq 40 \text{ K (paramagnetic regime)} \\ \\ (A_0 - B')\frac{1}{3}e^{-(t/T_1)^\alpha} + B', \text{ for } T < 40 \text{ K} \end{cases}$$

Here, the constant $A_0 = 0.27$ stands for the initial asymmetry of the muon at $t = 0$ and the term $B = 0.045$ corresponds to the background, given by muons not stopping into the sample.

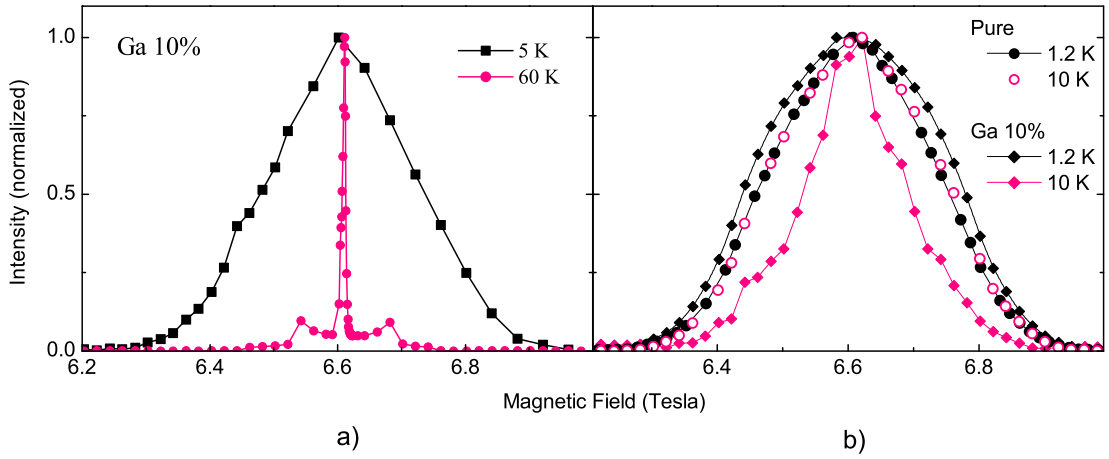

Figure 2. a) Comparison between spectra taken at low and high temperature. b) Comparison between spectra taken at 1.2 and 10 K on the pure and the Ga 10 % sample.

The use of a stretched exponential with exponent α less than 1 is purely empiric, but it usually indicates a distribution of sites with different relaxation rates.

Below 40 K, a static component develops at the expense of the paramagnetic one, as evidenced from the presence of the so-called 'one-third tail' at long times. Indeed, in the case of a complete freezing $T_1^{-1} \rightarrow 0$, and $A \rightarrow \frac{A_0-B}{3} + B$, which is the case here. At intermediate temperatures, we were forced to allow a base asymmetry B', which slightly differs from B. This is related to the existence of a small paramagnetic component which survives below T_N. For simplicity, we crudely neglected the relaxation corresponding to these sites. Certainly the values of T_1 extracted from our fits are significant enough to give a clear picture of the physics at work in the substituted samples.

As already clear from the mere inspection of the slope of the tail in Figure 1, a), a maximum of T_1^{-1} is found at the same temperature, 25±5 K, for pure $NaCrO_2$ and the substituted samples, but is less pronounced for the latter (figure 1, b). In the case of pure local modes, a simple counting argument of the unperturbed Cr triangles would yield a decrease of $1 - c^3 = 27$ % of the value of the relaxation rate, much less than what we observe for a Ga concentration $c = 10\%$. This argues in favor of attributing the exotic relaxation behaviour observed in pure $NaCrO_2$ to collective modes.

3. ^{23}Na NMR measurements on $NaCrO_2$ doped with 10 % Ga

^{23}Na NMR measurements were performed in the range 1.2 - 60 K on powder samples. The ^{23}Na nucleus, with $I = 3/2$ and $\gamma = 11.2618$ MHz/Tesla, is located below and above the centre of Cr triangles from consecutive planes. Measurements were taken by sweeping the magnetic field in the 6 - 7 Tesla range, at a fixed frequency of 74.527 MHz. Two spectra taken at 5 and 60 K are shown in Figure 2, a). At high temperature, in the paramagnetic regime, the lineshape is typical of a powder pattern with quadrupolar singularities. At low temperature, in pure $NaCrO_2$, the lineshape and broadening were argued to reflect the multiplicity of Na sites, which certainly relates to the complexity of the magnetic structure. In the case of $LiCrO_2$, a 18 sublattices Néel state was indeed reported [7] and the T-evolution of their widths was found to mimic the variation of the order parameter. At 1.2 K, the lineshapes of the pure and substituted samples and the widths are fairly similar, the small excess found for Ga 10 % could simply be attributed to some extra disorder in the magnetic structure.

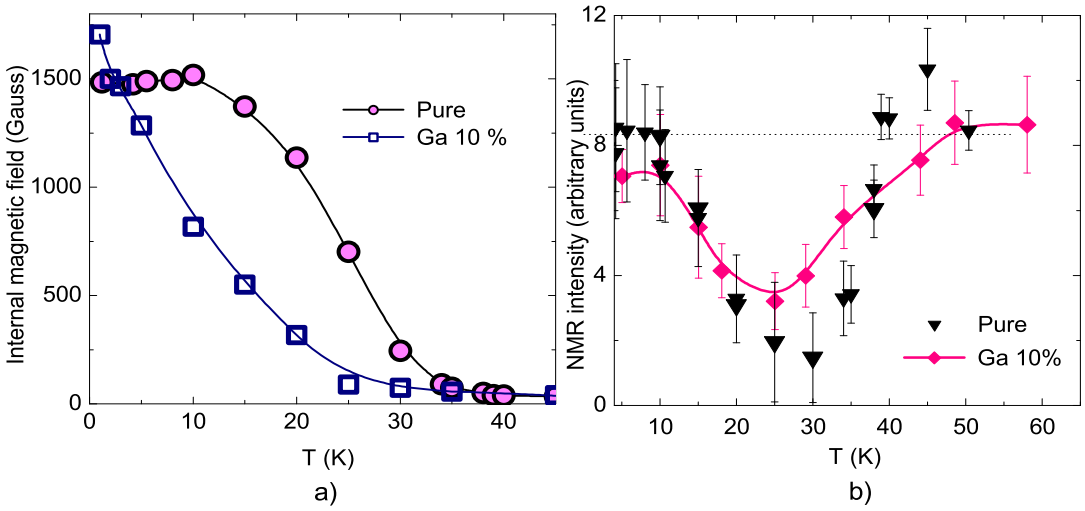

Figure 3. a) Temperature dependence of the half width at half maximum extracted from the NMR spectra for the pure and the Ga 10 % sample. b) The intensity of the NMR signal for both samples presents a minimum around 25 ±5 K.

Strikingly, the T-evolution markedly differs in pure and doped samples (Fig. 3, a). In the latter, it is found to drop quite sharply in a non-conventional manner at temperatures as low as 10 K. This is certainly related to the distribution of local environments due to the substitution of non-magnetic Ga, which makes the freezing quite inhomogeneous. In this respect, the interpretation of the μSR relaxation rate is certainly quite complex, as a distribution of relaxation times would be expected.

Another finding from the NMR measurements is the wipe-out of the NMR intensity. In the pure system, the intensity shows a minimum around 30 K [1], where only ~ 15 % of nuclei can be detected. The other 85 % probably have very fast relaxation times, shorter than the dead time of about 5 μs of NMR. The observed wipe-out of the NMR intensity corresponds to the maximum of the relaxation rate. We found that it is less pronounced for substituted sample, which might agree with the presence of non-frozen areas and the less pronounced maximum of the relaxation rate observed in μSR.

In conclusion, Ga substitution not only destabilizes the exotic excitations found in pure $NaCrO_2$, but also induces an inhomogeneous freezing. This study certainly calls for a more refined analysis of the local environment around substituted sites, as could be performed through NMR measurements over a series of well controlled and less diluted samples.

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