Specific heat and $\mu^+\text{SR}$ measurements in Gd(hfac)$_3$NITiPr molecular magnetic chains: indications for a chiral phase without long range helical order

A. Lascialfari$^1$, R. Ullu$^1$, M. Affronte$^2$, F. Cinti$^2$, A. Caneschi$^3$, D. Gatteschi$^3$, D. Rovai$^3$, M.G. Pini$^4$, and A. Rettori$^5$

$^1$ I.N.F.M. and Dipartimento di Fisica “A. Volta”, Università di Pavia, Via Bassi 6, I-27100 Pavia, Italy
$^2$ I.N.F.M. - S$^5$ National Research Center and Dipartimento di Fisica, Università di Modena e Reggio Emilia, Via G. Campi 213/A, I-41100 Modena, Italy
$^3$ I.N.S.T.M. and Dipartimento di Chimica, Università di Firenze, Via della Lastruccia 3, I-50019 Sesto Fiorentino (FI), Italy
$^4$Istituto di Fisica Applicata “Nello Carrara”, Consiglio Nazionale delle Ricerche, Via Pansini 36/30, I-50127 Firenze, Italy
$^5$I.N.F.M. and Dipartimento di Fisica, Università di Firenze, Via G. Sansone 1, I-50019 Sesto Fiorentino (FI), Italy

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Low temperature specific heat $C(T)$ and zero-field muon spin resonance ($\mu^+\text{SR}$) measurements were performed in Gd(hfac)$_3$NITiPr, a quasi one-dimensional molecular magnet with competing nearest neighbor and next-nearest neighbor intrachain exchange interactions. The specific heat data exhibit a $\lambda$-peak at $T_0=2.08\pm0.01$K that disappears upon the application of a 5 Tesla magnetic field. Conversely, the $\mu^+\text{SR}$ data do not present any anomaly at $T\approx 2$ K, proving the lack of divergence of the two-spin correlation function as required for usual three-dimensional (3D) long range helical order. Moreover, no muon spin precession can be evinced from the $\mu^+\text{SR}$ asymmetry curves, thus excluding the presence of a long range ordered magnetic lattice. These results provide indications for a low $T$ phase where chiral order is established in absence of long range helical order.

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I. INTRODUCTION

For three-dimensional (3D) $XY$ helimagnets, Kawamura$^1$ proposed a new universality class as a consequence of frustration. In addition to the SO(2) symmetry of the spin variable $S_i$, there is a further degree of freedom, the spin chirality $\kappa_i$ defined as $\kappa_i = |S_{i_1} \times S_{i_2}|^2/|\sin(Qa)|$ (Q is the pitch of the helical ground state, $S_{i_1}$ and $S_{i_2}$ are spins on nearest neighbor planes perpendicular to Q). For $T=0$, the order parameter $\kappa_0 = \pm 1$ describes the clockwise or anti-clockwise degeneracy $Z_2$ of the helical structure. If chiral order and spin order occur simultaneously, the order parameter space becomes $Z_2 \times$ SO(2), leading to a new universality class.

For quasi one-dimensional (1D) helimagnets, a different behavior was predicted by Villain$^2$. In addition to the low temperature ($T < T_N$) 3D long range helical phase and to the high temperature ($T > T_0$) paramagnetic one, Villain proposed that a chiral phase is stable for $T_N < T < T_0$. The chirality order parameter associated to a nearest neighbor spin pair is $\kappa_n = [S_n \times S_{n+1}]^2/|\sin(Qa)|$. The chiral phase can be described as a collection of corkscrews that turn all clockwise or all anti-clockwise, whereas their phases are random$^3$. Due to the Ising nature of chirality, $T_0$ results greater than $T_N$ because the chirality-chirality correlation function is stronger than the usual spin-spin correlation. In fact the chiral correlation length $\xi_c$, defined via the chirality-chirality correlation function $\langle \kappa_i \kappa_{i+n} \rangle \approx A \exp(-na/\xi_c)$, diverges exponentially as temperature is decreased $\xi_c \approx \exp(|J|/T)$ (where $J$ is the exchange constant), while the spin correlation length $\xi_s$, defined via the spin-spin correlation function $\langle S_1 \cdot S_{n+1} \rangle \approx A' \exp(-na/\xi_s)$, diverges as a power law $\xi_s \approx |J|/T$. As a consequence, an anomaly is expected at $T_0$ for the physical properties related to $\langle \kappa_i \kappa_{i+n} \rangle$, such as the magnetic specific heat, while the quantities related to $\langle S_1 \cdot S_{n+1} \rangle$, such as the magnetic susceptibility, are expected to behave critically only at $T_N$. At $T_0$, a continuous phase transition or a first-order one can be present.$^4$

Villain's prediction was tested in the molecular-based quasi-1D magnet Gd(hfac)$_3$NITiPr$^{5,6}$ [hfac is hexafluoro-acetylacetonate and NITiPr is 2-isoPropyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl 3-oxide]; iPr are isoPropyl organic radicals (with spin $s=1/2$) that alternate with rare-earth Gd$^{3+}$ magnetic ions (with spin $S=7/2$) along the chain direction, z. The spins interact through competing nearest-neighbor ($J_1 > 0$) and next-nearest-neighbor ($J_2 < 0$ and $J_2' < 0$) exchange constants along the chain

$$\mathcal{H}_{i,\text{intra}} = \sum_{n=1}^{N/2} \left\{ -J_1(S_{i,2n-1} \cdot S_{i,2n} + s_{i,2n} \cdot S_{i,2n+1}) - J_2(S_{i,2n-1} \cdot S_{i,2n+1}) + D(S_{i,2n-1})^2 - g\mu_B H \cdot S_{i,2n-1} - J_2'(S_{i,2n} \cdot S_{i,2n+2}) - g'\mu_B H \cdot s_{i,2n} \right\}$$

(1)

where the index $n$ refers to the spin position along the $i$-th chain. $D > 0$ is an effective anisotropy favouring the
spins to lie in the $xy$ plane (perpendicular to the chain axis, $z$). $H$ is an external magnetic field and $g, g'$ are the gyromagnetic factors of the spins $S$ and $s$, respectively. The next-nearest neighbor antiferromagnetic exchange is dominant, leading to a helical ground state with pitch \( \pm Qa = \pm \cos^{-1} \left( \frac{1}{2Qa} \right) \), where $\delta = (|J_2|S^2)/(J_1 s S)$, $\delta' = (|J_2'|s^2)/(J_1 s S)$ and $2(\delta + \delta') > 1$. Different chains interact through a weak ferromagnetic interchain exchange ($0 < J_\perp << J_1$)

\[
H_{\text{inter}} = \sum_{(i \neq j)} \sum_{n=1}^{N} [-J_\perp (s_{i,n} \cdot s_{j,n})]
\]

so that the total Hamiltonian of a collection of $M$ weakly interacting chains is $H = H_{\text{inter}} + \sum_{i=1}^{M} (H_{i,\text{intra}})$. Magnetic susceptibility and zero field specific heat measurements\( \Delta \) were systematically performed on Gd(hfac)$_3$NITiPr\( \Delta \); while no anomaly was found in the magnetic susceptibility, a $\lambda$-type peak, like a second order phase transition, was clearly observed in the specific heat for $T \approx 2K$. Moreover, a linear $T$-dependence was found for $C(T)$ at very low temperatures, inconsistently with helical 3D long range order (which would give $T^3 \Delta $). This overall behavior was interpreted\( \Delta \) in terms of a chiral phase transition for $T_0 \approx 2K$ although the phase transition at $T_N$ to helical long range order, predicted by Villain\( \Delta \) was not observed down to the lowest investigated temperature ($T_{\min} = 0.175K$ for Gd(hfac)$_3$NITiPr). This was tentatively explained\( \Delta \) taking into account aging effects due to the moderate lability of the organic radicals: even in very good and fresh samples, chains are reduced to segments of finite length and this has the effect of destroying the phase coherence necessary for the onset of 3D helical long range order. On the contrary, chiral order is compatible with the presence of finite segments since, for its onset, it is only required that the chirality of the segments is the same, a much less strict condition to be fulfilled. In fact, while the $\lambda$-type anomaly in the specific heat is very intense and robust and its position does not change even in degraded samples, aging effects strongly influence the magnetic susceptibility\( \Delta \).

In this paper, we report new specific heat measurements in magnetic field that demonstrate the magnetic nature of the phase transition at $T \approx 2K$. In order to obtain further information about the behavior of the two-spin correlation function, muon spin resonance ($\mu^+\text{SR}$) experiments in zero-field were also performed. Such a technique is particularly useful since it does not require the application of an external magnetic field, which in a sample with helical long range order is expected to cause the onset of complicated spin arrangements (“fan” phase)\( \Delta \). To our knowledge, no $\mu^+\text{SR}$ work on insulating helimagnets has been reported in the literature to date.

The paper is organized as follows. In Section II the new specific heat data are reported, while in Section III the results of $\mu^+\text{SR}$ experiments are shown. Finally, the conclusions are drawn in Section IV.

**FIG. 1**: The specific heat (normalized to the gas constant $R$) versus temperature of Gd(hfac)$_3$NITiPr, measured in zero field (filled circles), in a field of 0.5T (T=Tesla)(open circles), and 5T (open squares).

**II. SPECIFIC HEAT MEASUREMENTS**

Details about the preparation of samples can be found in Ref.\( \Delta \). The heat capacity of different pellets of pressed Gd(hfac)$_3$NITiPr micro-crystals was measured by using three different calorimeters and techniques: the adiabatic, the $ac-$ and the relaxation method. The heat signal was minimized in order to reduce the temperature ($T$) variation with respect to the equilibrium state. The best results, on which we concentrate in the following, were obtained by using the relaxation method for which the $T$-modulation was less than 0.5% of the base temperature. This implies an experimental resolution of $\log_{10} t \approx -2.5$ in terms of the reduced temperature $t = |T/T_0 - 1|$. Measurements in magnetic field were performed by using a Quantum Design PPM-7T System with a $^3$He insert and we begin presenting the new results of these experiments.

Fig. 1 shows the specific heat $C$, normalized to the gas constant $R = 8.314 \text{J mol}^{-1} \text{K}^{-1}$, as a function of temperature. In zero field a $\lambda$-anomaly is clearly visible at 2.08±0.01K while, at lower temperatures, $C/R$ scales to zero with a quasi linear $T$-law. Note that the value of the transition temperature is reproducibly found in different samples (compare also data in Ref.\( \Delta \)) in spite of their different quality and of the height of the $\lambda$-anomaly. The latter gets smoother in a magnetic field of 0.5T (T=Tesla) and is completely removed by the application of a 5T magnetic field. This definitively proves the magnetic origin of the transition, a fact that could not be surely deduced from results of previous experiments\( \Delta \).

Concerning the order of the phase transition, an important feature is the absence of latent heat: we evaluated an upper limit of $7 \times 10^{-3} \text{J mol}^{-1}$. This fact seems to indicate that the phase transition is of the second order in zero field, although the roundness of the peak, which can be due to the polycrystalline nature of the sample, prevents from determining the value of the critical expo-
incident α. It is worth noticing that the rounded peak at 2K and the absence of a latent heat might be justified even in the case of a first-order chiral transition by the effect of microscopic random quenched impurities that are surely present in the magnetic chain.

In order to gain information about the magnetic order, we determined the magnetic entropy removed in the low temperature region $T < T_0$, and in particular that below the anomaly. (The magnetic entropy for $T > T_0$ was not evaluated since for Gd(hfac)$_3$NITiPr the lattice contribution cannot be estimated in a reliable way owing to the complexity of the crystal structure and to the absence of a non-magnetic isomorph.) Such a calculation was performed using the specific heat data relative to sample C1 in Fig. 2 of Ref. 6, since it is considered the best sample hereto obtained, owing to its sensibly higher values of $C/\gamma$.

We found that the residual magnetic entropy below $T_0$ is rather large: 59% of the total magnetic entropy, which is given by $R[\ln(2s+1) + \ln(2S+1)] = 4R\ln 2$. Such a large value of the residual magnetic entropy below $T_0$ is probably due to a high concentration of defects that prevents the onset of a strong short range order in the paramagnetic phase, as it usually happens in quasi one-dimensional systems. For the sake of comparison, we remind that in the quasi one-dimensional anti-ferromagnet TMMC, the residual magnetic entropy below the Néel transition temperature $T_N$ was estimated to be nearly 1% of the total magnetic entropy. To obtain the entropy removed below the anomaly at $T_0$, one has to subtract the spin wave contribution (responsible for the linear $T$-dependence of $C$ observed well below $T_0$) from the total specific heat. In this way one obtains the residual magnetic entropy $\Delta S = 0.59R$ for the magnetic entropy related to the anomaly, in fair agreement with the value expected for an Ising system $\Delta S_{Ising} = R\ln 2 \approx 0.69R$. Such a result may be interpreted as a further indication for the onset, at $T_0 = 2.08K$, of a chiral transition which removes the $Z_2$ degeneracy between clockwise and anticlockwise chirality.

### III. $\mu^+$SR MEASUREMENTS

The $\mu^+$SR data were collected in pellets of pressed Gd(hfac)$_3$NITiPr micro-crystals at the ISIS facility (Rutherford Appleton Laboratory, UK), in the temperature range 0.3-300 K, in zero magnetic field (for data in longitudinal applied field, see Ref. [14]). After a proper background (titanium sample holder) subtraction, the muon asymmetry $A$ (whose total value is $A \sim 0.21$, close to 0.23, the expected value on the EMU beamline at RAL), can be analyzed by means of a single "stretched" exponential decay $e^{-(t/\lambda)^{0.5}}$ in the whole $T$-range (see Fig. 2).

This fact implies, in the whole investigated $T$-range:

(i) a distribution of relaxation rates $\lambda$, witnessed by the stretched behavior;
(ii) the absence of a local field due to long-range magnetic order at the muon site (in presence of long-range magnetic order, one should observe an oscillation in the asymmetry $A$, caused by the precession of the muon spin around the local field itself, or a loss of asymmetry);
(iii) as in the case of short-range magnetic order the muon asymmetry should display a Kubo-Toyabe-like behavior, one guesses a wide distribution of local fields values at the muon site, further broadened by powders average.

Further support for the absence of long-range order comes from the analysis of the temperature behavior of the muon longitudinal relaxation rate $\lambda$ (see Fig. 3).

The parameter $\lambda$ represents the muon relaxation rate as a result of the muon-lattice interaction. The general formula for $\lambda$ in a weak collision approach for fluctuations faster than the muon resonance frequency, $\omega_R$, is:

$$\lambda \propto \gamma^2 [J_+(\omega_R) + J_-(\omega_R)]$$

where

$$J_\pm = \int dt e^{-i\omega_R t} \langle h_\pm(t) \cdot h_\pm(0) \rangle$$

are the spectral densities, at the resonance frequency $\omega_R$, of the correlation functions for the local hyperfine (dipolar and contact) field components $h_\pm$. Let us now assume that the electronic spin components $S_\alpha$ (coming from the Gd ion) and $s_\alpha$ (coming from the iPr organic radical) have isotropic fluctuations.

To analyze the muon relaxation rate behavior in terms of scaling laws, we consider the three types of correlation functions that involve two spins. Thus, Eq. (3) can be
rewritten in terms of the collective spin components $S_q$ and $s_q$ as

$$
\lambda \propto \gamma^2 \frac{1}{N} \sum_{i,j=1,2} \sum_q |h_q|^2 \int dt \left< \sigma_i^+ (0) \sigma_j^- (t) \right>
$$

$$
= \gamma^2 \frac{1}{N} \sum_{i,j=1,2} \sum_q |\sigma_{iq}|^2 |J_{iq}^1| \frac{1}{\Gamma_q} \left< \sigma_i^+ \sigma_j^- \right> \tag{5}
$$

where $\sigma_1 = S$ and $\sigma_2 = s$; $\Gamma_q$ is the decay rate of the collective spin fluctuations, while $h_q$ is the Fourier transform of the lattice functions that couple the muons to the spins of the magnetic ions. Now, we will show that, in the event that long range order sets in below a transition temperature $T_{tr}$, then a divergence in the muon longitudinal relaxation rate $\lambda$ is expected (at least for $H = 0$) upon approaching $T_{tr}$ from higher temperatures. In fact, by expanding the $h_q$ vector around the value corresponding to the critical wave vector $Q$ (which characterizes the long range order below the transition temperature $T_{tr}$), and by using conventional scaling arguments for the $q$-dependence of the correlated fluctuations,\textsuperscript{16} Eq. (5) takes the form

$$
\lambda \propto \sum_{i=1}^{3} \left< \gamma h_{i,eff}^2 \right> \frac{1}{N} \sum_q \xi^2 \sum_{\xi_i} \frac{1}{\omega_{\xi_i}^d \omega_{\xi_i}^2} f(q_i \xi_i) \tag{6}
$$

where $h_{i,eff}^2$ are the static fields at the muon sites, resulting from the ordered configuration of the Gd and radical spins, while $q_i$ are the wavevectors measured with respect to the critical ones; $\xi_i$ are the correlation lengths; $\omega_{\xi_i}^d$ are the Heisenberg exchange frequencies. The decay rate of two-spin fluctuations is given by $\Gamma_q = (\omega_{\xi_i}^d \xi_i) g(q_i \xi_i)$, where $g(q_i \xi_i)$ and $f(q_i \xi_i)$ are homogeneous functions of the product $x = q_i \xi_i$. By transforming the $q$-summation into an integral, and noting that the latter converge to a number of the order of unity, one finally obtains

$$
\lambda \propto \sum_{i=1}^{3} \left( \gamma h_{i,eff}^2 \right)^2 \frac{1}{\omega_{\xi_i}^d} \xi_i^{-d+2-\eta_i} \tag{7}
$$

By setting $\xi_i \propto (T - T_{tr})^{-n_i}$, a divergence of the form

$$
\lambda \propto \sum_{i=1}^{3} (T - T_{tr})^{-n_i} \tag{8}
$$

with $n_i = \nu_i(z_i - 1 - \eta_i)$, is expected. As can be easily seen from Fig. 3, the muon longitudinal relaxation rate $\lambda$ does not present any divergence at $T \approx 2$ K for Gd(hfac)$_3$NITiPr, thus indicating that this temperature does not mark any transition $T_{tr}$ to a long range order for the two-spin correlation function.

Finally we observe that one of the main motivations of the present $\mu^+$SR measurements was that of investigating the behavior of the muon longitudinal relaxation rate $\lambda$ around the temperature for which the specific heat presents a peak and that the main result of the $\mu^+$SR investigation presented in this paper is the absence of any anomaly in $\lambda$ at $T_0 \approx 2$ K. The strong increase of $\lambda$ observed below 1 K may have different possible explanations: e.g., a progressive increase of the coherence lengths $\xi_i$’s or a resonance with a spin-wave mode. Further measurements of $\lambda$ for temperatures lower than 1K should be necessary in order to ascertain the origin of such a feature, but this goes beyond the scope of the present work.

IV. CONCLUSIONS

In conclusion, we have performed specific heat and $\mu^+$SR experiments in the molecular magnetic chain Gd(hfac)$_3$NITiPr. While the four-spin correlation function (probed by the magnetic specific heat) showed a seemingly continuous magnetic phase transition at $T \approx 2$K, the two-spin correlation function (probed by $\mu^+$SR) did not show any anomaly related to a transition to conventional long range helical order (similar to that present in the 3D helimagnets Tb, Yb, Dy, for instance).\textsuperscript{19} Moreover, below $T \approx 2$K no precession of the muon spin or loss of muon asymmetry similar to what happens in the case of long-range magnetic order, was observed. Taking also into account that at very low temperatures (0.175-0.8 K) a linear $T$-dependence of the magnetic specific heat was observed in Gd(hfac)$_3$NITiPr (a clear indication for isotropic 1D magnetic behavior),\textsuperscript{16} and relying upon an estimation of the residual magnetic entropy below the anomaly, we are led to conclude that,
below $T_0 = 2.08$ K, an ordered chiral phase without 3D long range helical order sets in.

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*Electronic address: lascialfari@fisicavolta.unipv.it
†Electronic address: affronte@unimo.it

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\[ \lambda (\mu s^{-1}) \]

\[ T (K) \]

ZF - \( \mu^+ \)SR

\[ \lambda = \mu^+ SR \]

\[ \lambda = ZF - \mu^+ SR \]

\[ \lambda = T (K) \]

\[ \lambda = \mu^+ SR \]