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Oxygen doped $S = 1/2$ Cu delafossites: a muon spin rotation/relaxation study

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Abstract

We present a μSR study of oxygen-doped delafossites $RCuO_{2+\delta}$ ($\delta = 0.5, 0.66$; $R^{3+} = La^{3+}, Y^{3+}$) which present triangular based lattices of Cu^{2+}, $S = 1/2$ spins. A slowing down of the spin dynamics without onset of a magnetic static freezing down to 1.6 K is found for $YCuO_{2.5}$, which is believed to be an example of a Δ-chain. In contrast, $YCuO_{2.66}$ and $LaCuO_{2.66}$ clearly order, probably into an antiferromagnetic state, which was rather unexpected.

1. Introduction

Although pointed out soon after the high T_c superconductors as an alternative way to realize hole doped Cu^{2+} layered compounds [1], the delafossite family has been very little investigated since then, partly because the synthesis of perfectly stacked compounds turned out to be quite difficult. New chemical routes were explored recently and they yielded pure delafossite oxygenated phases $RCuO_{2+\delta}$ with few stacking faults [2, 3]. For $\delta = 0.5$, one gets a triangular $S = 1/2$ based structure which leads to the interesting case of a frustrated $S = 1/2$ quantum spin lattice. Further oxygenation ($\delta = 0.66$) could even be achieved, which opens the possibility of hole doping in a case where a resonating valence bond state might be stabilized.

Motivated by these potential physical openings, we have undertaken a systematic study of the magnetic properties of $R^{3+} = Y^{3+}, La^{3+}$ compounds with $\delta = 0.5$ or 0.66 using muon spin rotation/relaxation (μSR) techniques. This gives insight into the possible ground states for oxygenated delafossites.

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Only for the Y compound can the $\delta = 0.5$ phase be stabilized. In this case, Cu^{2+} ions bind either to one or two oxygens within the Cu plane and form chains of corner sharing triangles, the so-called 'sawtooth chain'. A singlet ground state is predicted and, depending upon the value of the Cu–Cu exchange interactions, a gap in the excitation energy could exist or simply vanish [4].

For $\delta = 0.66$, a 2D layered magnetic lattice is inferred where double oxygen coordinated Cu arrange into corner sharing triangles, even forming a Kagomé lattice in the case of La [5]. For the Y compound, in the case of first neighbour interactions only, the lattice is topologically equivalent to Kagomé. The formal valency of Cu is 2.33, which suggests that either the Kagomé lattice is $1/3$ depleted or homogeneous doping of the Kagomé lattice occurs. In the Fe-jarosite Kagomé, long range order is observed, whereas in Cr-jarosite and in the Kagomé bilayer compounds $SrCr_{9p}Ga_{12-9p}O_{19}$ and $Ba_2Sn_2ZnGa_{10-7p}Cr_{7p}O_{22}$, a spin-glass phase is observed at very low-T as compared to the Néel temperature, with only a partial freezing of the spins at $T = 0$ [6].

2. Experimental details

All our samples were synthesized in Laboratoire de Cristallographie, Grenoble (France) and come from the same batches as the ones used for various x-ray, susceptibility and neutron refined measurements presented at this conference [7, 8]. The μSR data were taken at the ISIS and PSI facilities, depending on the best time window suited for these experiments.

In oxides, one can expect the muon to form a 1 Å long O^{2-}–μ^+ bond and therefore at least one muon site belonging to the La/Y layer will be weakly sensitive to the Cu^{2+} magnetism, which is indeed what we observe. Weak transverse field, zero field and longitudinal field (LF) experiments were performed, in order to characterize respectively the transition temperatures, if any, and the magnetic ground state of our samples. In the case of a dynamical state, we applied a small longitudinal field, typically 20 G, which is enough to overcome the dominant nuclear contribution on the weakly coupled sites and make the contribution to relaxation from those sites negligible. This allows us to single out the contribution to the relaxation coming from electronic spins on the most coupled site(s).

Our paper is next divided into two sections, one for each δ, where we report and discuss our experimental results, followed by concluding remarks.

3. δ = 2.5 : $YCuO_{2.5}$

Our μSR data were taken between 300 and 1.5 K. We found that around 50% of the total number of muons stop in weakly coupled sites which gives rise to a persistent Kubo–Toyabe Gaussian-like contribution even at low-T. In figure 1 (left-hand panel), where a 20 G longitudinal field has been applied to suppress the latter contribution, as explained above, one can notice a progressive increase of the muon spin relaxation rate, for the most relevant site(s), which is therefore linked to a slowing down of the spin dynamics.

Whether the low-T state is static or still dynamical on the μSR time window can be probed by applying a longitudinal field along the muon initial polarization. Taking the case of the lowest temperature (1.65 K), in the static scenario, one would attribute the relaxation to a broad distribution of static fields whose amplitude is of the order of $H_{\text{int}} < 50$ G. One would therefore observe a complete decoupling for applied fields of the order of $5H_{\text{int}}$, which could be ruled out by such LF experiments performed at 1.65 K (figure 1, right-hand panel). We therefore first analysed our data using a dynamical model with a stretched exponential to model the dynamical relaxation. Although there is no clear support for such a choice of

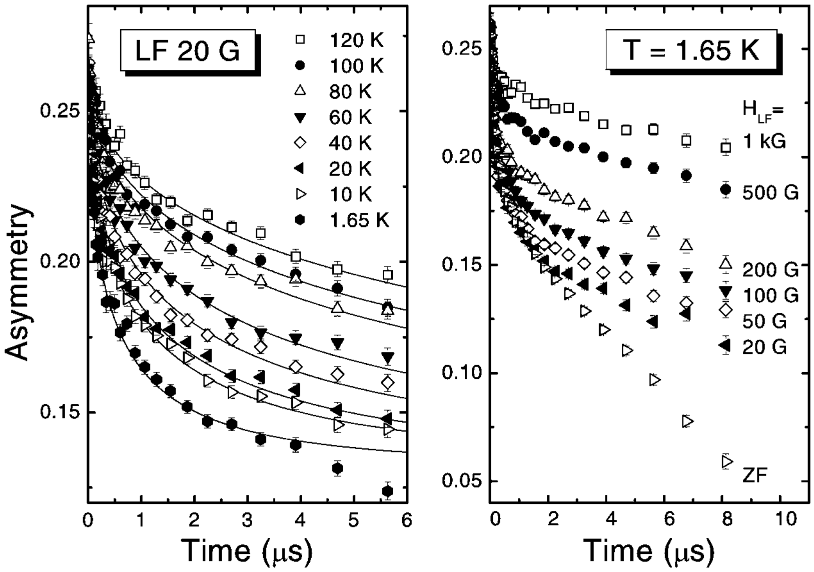

Figure 1. Left-hand panel: muon-decay asymmetry versus time for T ranging from 1.65 to 120 K in $YCuO_{2.5}$. A small longitudinal field is applied to decouple the nuclear contribution from weakly coupled muon sites, as explained in the text. Right-hand panel: decoupling experiments at base temperature, $T = 1.65$ K. The long-time Gaussian tail in zero field is associated with the weakly coupled site(s). Except for the latter tail, the effect of a longitudinal field H_{LF} is much weaker than expected for a static distribution of field which could have given rise to the LF = 20 G relaxation.

relaxation function, this allows us to determine conveniently the $1/e$ point and also to show the change of shape of the relaxation with T. Below 100 K, we found a stretched exponent of the order of 0.5 and fixed it to this value to minimize the interplay between the relaxation rate and the exponent. The quite satisfactory fits obtained are displayed in figure 1.

Our values of the relaxation rate are reported in figure 2 and clearly indicate a very progressive slowing down of the Cu^{2+} spin dynamics, which agrees quite well with the susceptibility data of $YCuO_{2.5}$, known to exhibit a broad maximum around 400 K [7]. Moreover, the square root exponential which seems to correspond to the best exponent fit in the 1.65–140 K T-range is an indication in favour of a large distribution of relaxation times in a dynamic magnetic state [9]. Such a dynamical state at temperatures much below the susceptibility maximum found in macroscopic susceptibility is a strong indication of original dynamics in $YCuO_{2.5}$. Whether the dynamics directly reflects the existence of a dimerized singlet ground state, as could be observed in the case of $S = 1/2$ spin ladders [10], or is more specific of the triangles corner-sharing geometry has to be investigated in further detail. Also, the persistence of dynamics or the onset of a frozen phase should be further checked at lower T.

4. $\delta = 2.66$: $(Y, La)CuO_{2.66}$

μSR data which are typical of the low-T ground state are presented in figure 3. Our major result lies in the presence of oscillations in zero applied field experiments. One can then firmly conclude that a well defined static internal field exists for muons stopping on one site, which is clear-cut evidence for an ordered state. The estimated value from the precession frequency measured at the lowest T is $H_{int} = 700$ G in the case of $YCuO_{2.66}$ and 550 G in the case

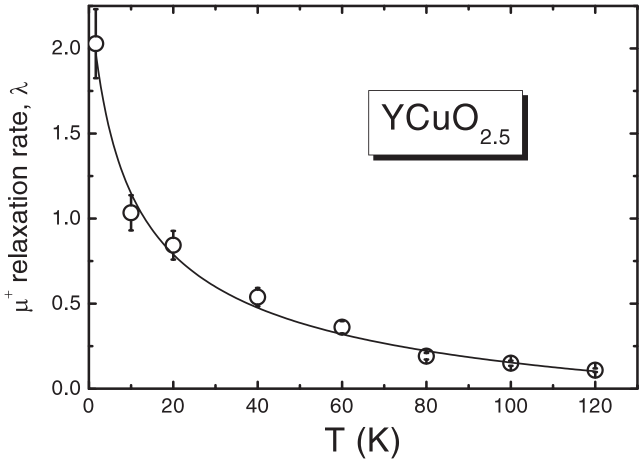

Figure 2. Muon relaxation rate, λ, versus T in $YCuO_{2.5}$. λ is extracted from a square root fit of the asymmetry $A(t) = A(0)\exp(-\sqrt{\lambda t})$ under $H_{LF} = 20$ G versus time. Notice the progressive increase without any sharp feature, which also supports the absence of any phase transition.

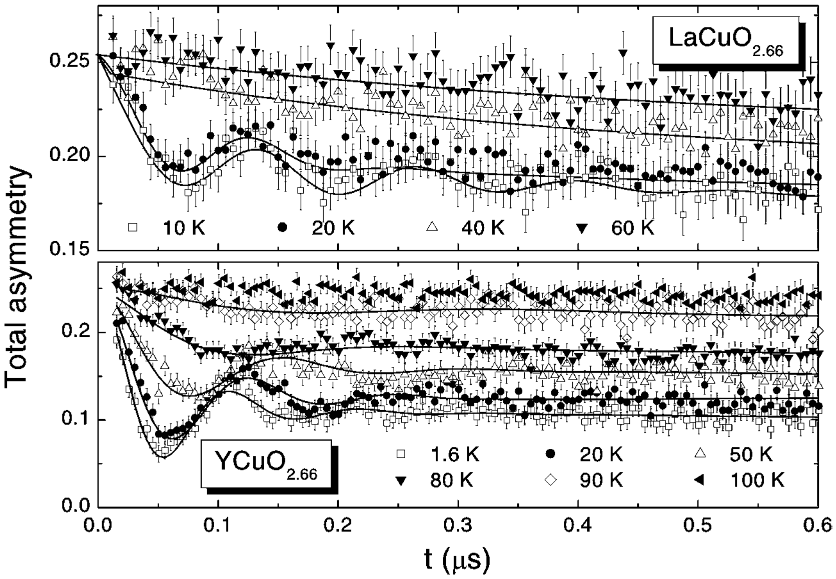

Figure 3. Asymmetry under zero external field obtained for various T. Notice the presence of oscillations and the different vertical scales for $YCuO_{2.66}$ and $LaCuO_{2.66}$.

of $LaCuO_{2.66}$. As for the other site(s) a clear Kubo–Toyabe Gaussian-like shape was found, indicating that there is little coupling between this site and the Cu moments (see section 2). The amount of muon sites weakly coupled to the electronic spins is found to vary from 80% for La to 20–50% for Y compounds, which might not be surprising since the crystallographic structures differ.

In $YCuO_{2.66}$, one can easily follow the precession frequency versus T in order to determine the variation of the order parameter (figure 4, bottom panel). This sets the transition temperature to the value $T_N = 98(2)$ K, which explains quite well the kink observed in the macroscopic susceptibility around 100 K [5]. In order to check whether the zero-internal field site is also

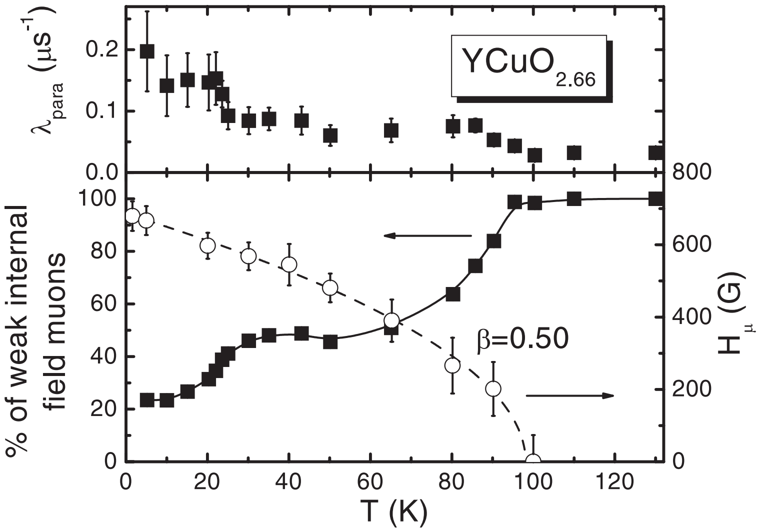

Figure 4. Bottom panel. Right: variation of the internal field H_μ in $YCuO_{2.66}$ at the well coupled muon site versus T, as extracted from the oscillating frequency. The dashed curve is a $(1 - T/T_N)^\beta$ fit. Left: variation of the fraction of weak internal field sites. The dip at 100 K corresponds to the magnetic transition observed in ZF data. Top panel. The relaxation rate of the 'paramagnetic' muons. The kinks at T_N and 30 K indicate that this site also feels the same physics.

slightly sensitive to the magnetic transition, we performed weak transverse field measurements (figure 4). For $T > T_N$, the muon behaves for both sites as in a simple paramagnet and feels the external field only. Below T_N, the fraction of those muons decreases as the internal field on the 'strongly' coupled site develops due to the onset of magnetic order. At low enough temperature, only the muons stopping in the weakly coupled sites can give a paramagnetic response, i.e. oscillate with a Larmor frequency corresponding to the external field. The slight change observed in the relaxation rate λ_{para} associated with the paramagnetic response is an indication that all muons feel the same physics, which confirms the single-phase scenario which could be inferred from x-ray measurements. In addition, the paramagnetic fraction varies around 30 K, which certainly indicates the occurrence of a new magnetic transition which remains still unclear to us since we could not find any signature in the ZF oscillating frequency.

For $LaCuO_{2.66}$, the weak amplitude of the oscillations corresponding to 20% of the muon sites does not allow us to make as accurate a study as in the previous compound. An estimate for the transition temperature of 40–50 K can be extracted from our data. Here, no signature was found in the susceptibility, but it could be masked by the substantial low-T Curie tail [5]. In any case, the sizeable fraction of muon sites allows one to rule out an impurity phase since no signature is found in the x-ray data [3].

The occurrence of spin freezing into an antiferromagnetic state is quite surprising since one would not expect this to occur for frustrated magnets in the presence of holes. Indeed, if one refers to high T_c cuprates, a small percentage of holes is enough to destroy the antiferromagnetic phase completely. One can therefore wonder whether a simple Cu^{2+} layers picture can apply or whether sizeable transverse couplings do exist in this compound. This calls for a more detailed study of the exchange couplings in the $\delta = 0.66$ delafossites.

5. Concluding remarks

Our μSR studies bring new information on the magnetism of oxidized delafossites. They clearly establish the existence of original dynamics down to 1.65 K in $\mathrm{YCuO_{2.5}}$, which could provide, to our knowledge, the first experimental realization of the sawtooth chain Hamiltonian, which features a fashionable lattice with $S = 1/2$ and frustration in a corner-sharing geometry.

The counterintuitive result of an ordered ground state in $\mathrm{(Y, La)CuO_{2.66}}$, which should rather combine a Kagomé lattice and hole-doping, is quite surprising and calls for further study of transverse couplings of the Kagomé layers in these systems.

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