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μSR study of frustrated $S = \frac{1}{2}$ Delafossites $YCuO_{2+\delta}$

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Abstract

Over-oxidized Delafossites $MCuO_{2+\delta}$ are frustrated antiferromagnets formed by a stacking of alternating M^{3+} and $Cu^{(1+2\delta)+}$ planes. Frustration arises from the geometry of the magnetic lattice, which is based on corner sharing triangles. We present here a study of $YCuO_{2.5}$ and $YCuO_{2.66}$, both with $S = \frac{1}{2}$ spin magnetic atoms. μSR data of $YCuO_{2.5}$, a one-dimensional Δ-chain compound, show dynamical behaviour with no transition to a frozen state down to 100 mK. $YCuO_{2.66}$, which possesses a 2D kagomé-like magnetic lattice, orders at 100 K, with an internal magnetic field of about 700 G at 5 K. Further hole doping is achievable in this compound through Ca^{2+}/Y^{3+} substitution. We show that only 1% Ca doping strongly reduces the transition temperature to 80 K.

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Keywords: Frustration; Low dimensionality; Antiferromagnetism; Copper oxides

1. Introduction

The Delafossite structure is formed by a stacking of alternating M^{3+} and $Cu^{(1+2\delta)+}$ planes. The copper-based lattice is frustrated with a triangular corner-sharing geometry. The Cu electronic spin state as well as the details of the structure depend on the oxygen doping ($\delta = 0$, $S = 0$ for Cu^{+}; $\delta = 0.5$, $S = \frac{1}{2}$ for Cu^{2+}; $\delta = 0.66$, $S = \frac{1}{2}$ for Cu^{2+} ions and 33% holes). Cava et al. showed [1] that for M = Y it is possible to insert oxygen up to $\delta = 0.5$ to obtain frustrated triangular-based chains with $S = \frac{1}{2}$ and for M = Y, La, Nd, Sc, In it is possible to go up to $\delta = 0.66$ to get a kagomé-like frustrated quantum magnet ($S = \frac{1}{2}$). Recently, it was possible to obtain high-quality samples which allowed accurate experimental study [2]. We present here our μSR results on $YCuO_{2.5}$ and $YCuO_{2.66}$.

The $YCuO_{2.5}$ compound has an orthorhombic 2H structure with the Cu^{2+} first-neighbour interactions forming a one-dimensional Δ-chain (Fig. 1). The extra-oxygen ions are located at the centre of Cu triangles and create super-exchange interactions between the Cu ions. Two Cu sites exist depending on whether the Cu^{2+} ions are bound to one (Cu2) or two (Cu1) oxygen atoms within the Cu plane. This implies two possibly different super-exchange constants, J_1 for the Cu1–O–Cu1 path and J_2 for the Cu1–O–Cu2 path. Depending on the ratio of these exchange constants, the existence or the absence of a gap in the excitation energy, with a maximum gap for $J_1/J_2 = 1$, has been predicted [3]. Recently, the existence of two non-negligible intra-chain ferromagnetic interactions has been proposed, in addition to the nearest-neighbour interactions [4]. The effect of these ferromagnetic interactions on the gap value is currently being studied.

The $YCuO_{2.66}$ structure is hexagonal 2H with two-dimensional interactions. Considering only first-neighbour interactions the Cu-network is topologically equivalent to the kagomé lattice (Fig. 2). The average valence of Cu is 2.33, which can be interpreted as a 33% hole doping of the

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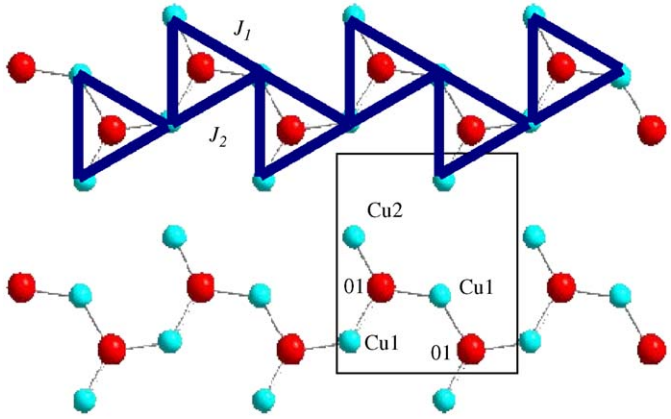

Fig. 1. CuO planes in $YCuO_{2.5}$. The Cu-network is supposed to form a Δ-chain (figure reproduced from Ref. [7]).

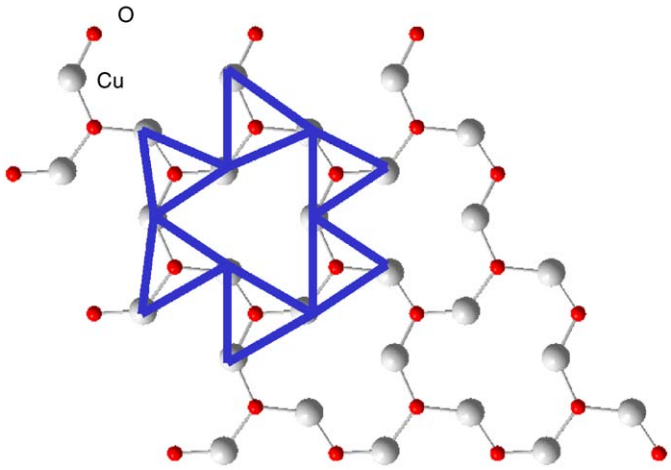

Fig. 2. CuO planes in $YCuO_{2.66}$. The Cu-network is supposed to be topologically equivalent to a kagomé lattice with 33% holes (figure reproduced from Ref. [7]).

Cu^{2+} ($S = \frac{1}{2}$) kagomé-like planes. For this system, it is possible to study the effect of doping by Y^{3+}/Ca^{2+} substitution. We present here the study of a 1% Ca^{2+}-doped compound. This system, characterized by low dimensionality, frustrated interactions, quantum $\frac{1}{2}$ spin and hole doping could be a first attempt towards the experimental realization of the initial RVB state of Anderson.

2. $YCuO_{2.5}$

Zero field (ZF) measurements appear as the sum of two different contributions coming from two different muon sites. As one can see on the ZF curve of Fig. 3, one of them is easily decoupled with a 50 G longitudinal field. It comes from a weakly coupled muon site, dominated by the static copper nuclear field which yields a Kubo–Toyabe-type relaxation. About 50% of the muons stop in this weakly coupled sites.

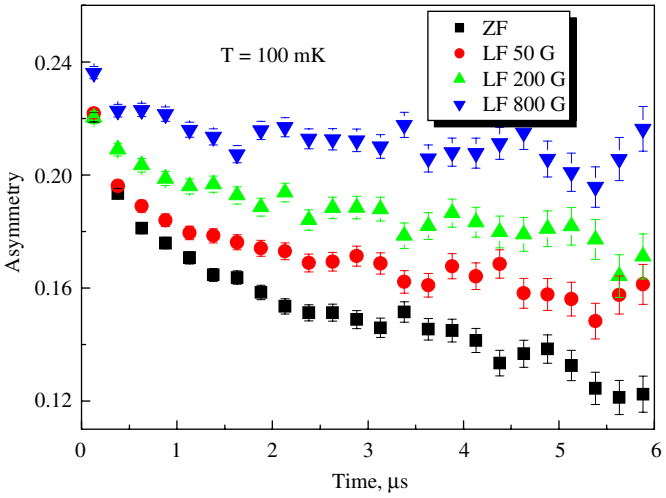

Fig. 3. Decoupling experiment at 100 mK : applying a much higher longitudinal field than the supposed static internal field does not restore the initial asymmetry, which proves that behaviour is dynamical.

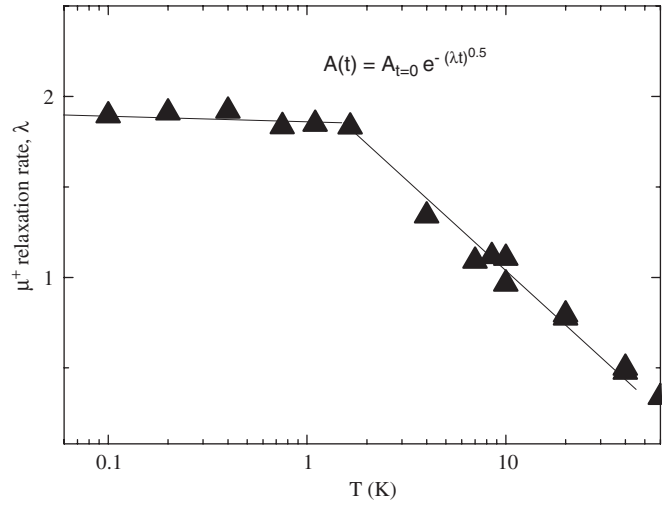

Fig. 4. Variation of the relaxation rate with temperature for $YCuO_{2.5}$, showing slowing down of dynamics with a plateau below 1.6 K.

To figure out whether the behaviour at 100 mK is static or dynamical, we performed a decoupling experiment (Fig. 3). Assuming that relaxation is of static origin, it would be due to an internal field of less than 50 G at 100 mK. Application of a much higher longitudinal field should align the local field along the z-axis and this would restore the initial asymmetry. As shown in Fig. 3 the relaxation rate does not change much when applying a longitudinal field of 200 G. The ground state is thus dynamical.

In order to decouple the weakly coupled component, the temperature evolution of the relaxation rate shown in Fig. 4 was recorded in a small 20 G longitudinal field. The data could be very well fitted with a stretched exponential function with the stretched exponent fixed at 0.5 for all temperatures. The obtained relaxation rate slowly increases when the temperature is lowered and reaches a dynamical

plateau below 1.6 K. This fluctuating low temperature behaviour suggests a spin liquid ground state.

The presence of a dynamical plateau below 1.6 K is rather surprising for a system with exchange constant values of about 400 K, as estimated from ab-initio calculations [4]. Also macroscopic susceptibility measurements show a very broad maximum at about the same temperature [5] and NMR measurements show an increase in the relaxation time T_1 also below a high temperature of about 100 K. The low-energy scale found in our μSR data is certainly a trademark of the frustration of the interactions at play in this compound.

This low-temperature change of the dynamics could be associated with a phase transition. Indeed, other frustrated systems, like the kagomé bilayers [6], were found to present a spin–glass transition concurrently with a dynamical plateau in μSR experiments. SQUID and NMR measurements at low temperature are planned to further investigate the nature of this ground state.

3. $YCuO_{2.66}$

ZF μSR data on the pure compound have been recorded from room temperature down to 1.6 K. Below 100 K, clear oscillations of the muon decay asymmetry are observed and reveal an antiferromagnetic long-range order with a well-developed internal magnetic field. A representative asymmetry measured in the frozen phase at 5 K is presented in Fig. 5.

Low-temperature data were well fitted with a two-component function of the form

$$A(t) = A_1\left(\frac{2}{3}e^{-\lambda_1 t}\cos(2\pi\nu t + \varphi) + \frac{1}{3}\right)e^{-\lambda_2 t} + (A_{tot} - A_1)e^{-\lambda_3 t}.$$

The first term of the fit function comes from muons sitting next to frozen Cu. The value of the internal magnetic field, extracted from the frequency ν of the oscillation is about 700 G at 5 K. λ_1 represents the damping of the oscillation coming from the internal magnetic field distribution and is about 14 μs^{-1} at 5 K. We account for a slight dynamical behaviour of this component through a small λ_2 relaxation rate, about 4 ms^{-1} at 5 K. The occurrence of a second exponential component in the fitting function could be the signature of a second muon site, but further investigation has to be done in order to elucidate its nature, as there is no evidence of a second crystallographic Cu site. Also X-ray data excludes the possibility of a sizeable impurity phase [2].

We followed the temperature evolution of the order parameter, i.e. the magnitude of the internal field, as shown on Fig. 6. The transition temperature at 100 K is in good agreement with the macroscopic susceptibility data, showing a kink at about the same temperature [7].

The most important difference with a true kagomé lattice is the presence of 33% holes. Hole-doping effect is not severe here in comparison to the high-T_c superconductors case, where only 5% holes completely destroy magnetism. This result probably demands more investigations on the structure of this compound and the role of oxygen doping.

On the other hand, doping the pure compound by 1% Ca^{2+} has a dramatic effect. The asymmetry and order parameter are qualitatively unchanged and have been analysed in the same way as the pure compound. However, the transition temperature is lowered by 20% ($T_c = 80$ K). At this point, one can only conjecture that either $YCuO_{2.66}$ has to be considered as a bulk antiferromagnet and in this case, Ca doping destroys very rapidly any magnetic order as in the cuprate case, or that $YCuO_{2.66}$ is already very close to the percolation threshold of the kagomé lattice (0.65) due to oxygen doping. In this latter case, one hole would roughly be responsible for one non-magnetic Cu through some mechanism that is still to be understood. Ca^{2+} substitution could then be considered as further

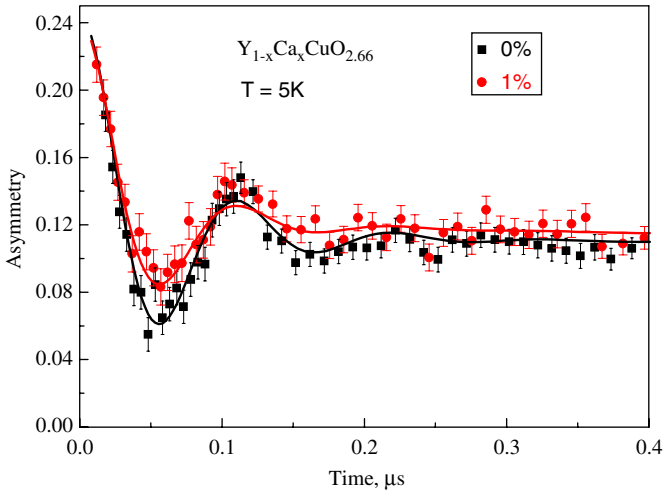

Fig. 5. Asymmetry of disintegration of the μ^+ for $YCuO_{2.66}$ and the 1% Ca^{2+}-doped compound at 5 K. Oscillations are the signature of a well-developed internal magnetic field.

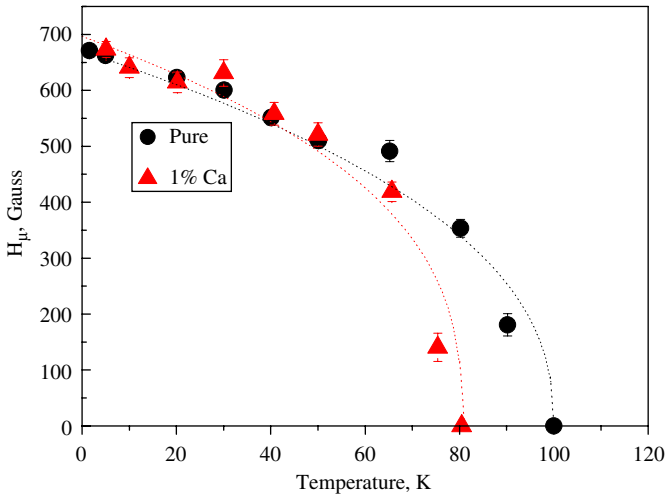

Fig. 6. Variation of the internal magnetic field, the order parameter, versus temperature in $YCuO_{2.66}$ and $Y_{0.99}Ca_{0.01}CuO_{2.66}$.

doping and would bring the system even closer to its percolation limit.

4. Conclusions

μSR technique allowed us to study two low-dimension frustrated systems with corner-sharing geometry and quantum $\frac{1}{2}$ spin: over-oxidized Delafossites $YCuO_{2.5}$ and $YCuO_{2.66}$. The $YCuO_{2.5}$ compound was shown to have a spin liquid behaviour with a dynamical plateau below 1.6 K. $YCuO_{2.66}$ presents an unexpected transition to an antiferromagnetic order at 100 K, which calls for further understanding of the exchange coupling in this sample and the role of oxygen doping. This latter compound opens the route to study the effect of doping in a frustrated magnet. First results in a 1% calcium-doped compound encouragingly point to a strong influence on the magnetic properties.

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