Dynamic correlated Cu(2) magnetic moments in superconducting \( \text{YBa}_2(\text{Cu}_{0.96}\text{Co}_{0.04})_3\text{O}_y \) \( (y \sim 7) \)

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We have examined the magnetic properties of superconducting \( \text{YBa}_2(\text{Cu}_{0.96}\text{Co}_{0.04})_3\text{O}_y \) \( (y \sim 7, T_{\text{ce}}=65\,\text{K}) \) using elastic neutron scattering and muon spin relaxation (\( \mu\text{SR} \)) on single crystal samples. The elastic neutron scattering measurements evidence magnetic reflections which correspond to a commensurate antiferromagnetic Cu(2) magnetic structure with an associated Néel temperature \( T_N \sim 400\,\text{K} \). This magnetically correlated state is not evidenced by the \( \mu\text{SR} \) measurements. We suggest this apparent anomaly arises because the magnetically correlated state is dynamic in nature. It fluctuates with rates that are low enough for it to appear static on the time scale of the elastic neutron scattering measurements, whereas on the time scale of the \( \mu\text{SR} \) measurements, at least down to \( \sim 50\,\text{K} \), it fluctuates too fast to be detected. The different results confirm the conclusions reached from work on equivalent polycrystalline compounds: the evidenced fluctuating, correlated Cu(2) moments coexist at an atomic level with superconductivity.

PACS numbers: 74.72.Bk,74.25.Ha,76.75.+i,78.70.Nx

I. INTRODUCTION

For the cuprates showing high temperature superconductivity, there is much interest in how the superconducting properties of the Cu(2)-O planes and the Cu(2) based magnetic order evolve as function of the doping level. At the present time, the general consensus is that the ground state involves magnetically ordered Cu(2) for low dopings (typically for a doping level, \( p < \sim 0.05 \)), it involves d-wave superconductivity (for \( p \sim 0.05/0.10 \) to \( \sim 0.25 \)) and it involves a metallic state for higher dopings. The intermediate regions notably the underdoped pseudogap regime, where both superconductivity and Cu(2) magnetic order may be present, are not yet fully understood. In the underdoped region, it is problematic to experimentally determine whether or not superconductivity and Cu(2) magnetic order are mutually exclusive at an atomic level. However, since it is well established that at one end of the phase diagram there is region with magnetically ordered Cu(2) and no superconductivity and that around optimum doping there is a region with superconductivity and no magnetically ordered Cu(2), the two phenomena are usually considered to be mutually exclusive at an atomic level. Previously however,\(^3\) we have shown that this view is not always valid.

In Ref.\(^3\) (preceding paper), we reported that when Ni is substituted into fully oxidised \( \text{YBa}_2\text{Cu}_3\text{O}_y \) \( (y \sim 7) \), the Cu(2) in the neighbourhood of each Ni carry magnetic moments which are short range magnetically correlated. For the examined Ni concentration of 4\%, essentially all the Cu(2) of the sample were found to carry correlated magnetic moments. These moments undergo temperature dependent fluctuations with rates up to the GHz range.

We have also observed that when Co (rather than Ni) is substituted into fully oxidised \( \text{YBa}_2\text{Cu}_3\text{O}_y \) \( (y \sim 7) \), correlated magnetic Cu(2) moments are again clearly visible. These results related to elastic neutron scattering measurements on a single crystal of \( \text{YBa}_2\text{Cu}_3\text{O}_y \) \( (y \sim 7) \) substituted with 1.3\% of Co\(^2\) and \( ^{170}\text{Yb} \) Mössbauer\(^2\) and \( \mu\text{SR} \) probe measurements on polycrystalline samples of \( \text{YBa}_2\text{Cu}_3\text{O}_y \) \( (y \sim 7) \) substituted with from 1.0 to 4.0\% of Co. Here, we report additional results, obtained from elastic neutron scattering and \( \mu\text{SR} \) measurements, on superconducting single crystal samples of \( \text{YBa}_2\text{Cu}_3\text{O}_y \) \( (y \sim 7) \) substituted with 4.0\% Co.

II. SAMPLES, METHODOLOGY

The single crystal samples of \( \text{YBa}_2(\text{Cu}_{0.96}\text{Co}_{0.04})_3\text{O}_y \) \( (y \sim 7) \) were prepared by the top seeding, melt texturing method and they were subsequently annealed in oxygen. Because of the growth technique used, the samples necessarily contain \( \text{Y}_2\text{BaCuO}_5 \) as a second phase (\( \sim 40\% \) by weight) as well as small amounts of some other impuri-
ties. \( T_{\text{sc}} \), the superconducting transition temperature, is 65 K which is typical for a 4% Co substitution level. The elastic neutron scattering measurements were carried out at the Laboratoire Léon Brillouin, Saclay, France and the muon probe measurements were made at the ISIS facility of the Rutherford-Appleton Laboratory, Chilton, UK.

The Co enters only the Cu(1) or chain sites and it pulls in additional oxygen atoms\(^{6,7,8}\). The Co tend to form dimers\(^{5,8}\) or even short chains along the (110) directions which introduce microtwinning and trigger the change to the tetragonal phase that occurs for Co levels \( \sim 0.025 \). The introduction of Co reduces the carrier density\(^{12}\) and the resulting underdoped samples evidence a pseudogap which is seen, for example, in local spin susceptibility measurements\(^{12}\). Nuclear quadrupole resonance measurements have shown that the substitution of Co into \( \text{YBa}_2\text{Cu}_3\text{O}_y \) introduces magnetic moments at both the chain, Cu(1) and plane, Cu(2) sites\(^{12}\).

### III. EXPERIMENTAL RESULTS

Before presenting the results for the single crystal samples, we briefly recall the results that have been obtained on the corresponding polycrystalline samples. Both \(^{170}\text{Yb}\) M\"ossbauer\(^{2}\) and \( \mu\text{SR}\)\(^{2}\) local probe measurements on superconducting samples of \( \text{YBa}_2\text{Cu}_3\text{O}_y \) \( (y \sim 7) \) substituted with Co have shown that the samples contain correlated magnetic Cu(2) moments. These moments are introduced over a distance of approximately 3 to 4 \( a/b \) lattice spacings around the Co. This length scale is similar to that of the staggered Cu(2) moments which are introduced around Ni atoms substituted in \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) as obtained from NMR measurements\(^{13,14}\). The Cu(2) magnetic correlations in superconducting \( \text{YBa}_2\text{Cu}_3\text{O}_y \) \( (y \sim 7) \) substituted with Co are short range since the magnetic reflections are too broad to be seen by neutron diffraction measurements\(^{14}\). The correlated Cu(2) moments are dynamic with temperature dependent rates. The rates increase as the temperature increases and they extend up to the GHz range. At each particular temperature, the local fluctuation rates show a distribution.

These characteristics are quite similar to those evidenced by polycrystalline superconducting \( \text{YBa}_2\text{Cu}_3\text{O}_y \) \( (y \sim 7) \) substituted with Ni\(^{14}\), with however one difference: at a given temperature, the average fluctuation rate of the correlated Cu(2) moments in samples containing Co\(^{25}\) is considerably lower than that in samples containing an equivalent amount of Ni\(^{14}\).

#### A. Elastic neutron scattering measurements

The details concerning the measurement procedure are given in ref. \(^{22}\) which reported well defined magnetic reflections in superconducting, single crystal \( \text{YBa}_2\text{Cu}_3\text{O}_y \) \( (y \sim 7) \) substituted with 1.3% Co. The reflections corresponded to commensurate antiferromagnetically corre-

lated Cu(2) magnetic moments with correlation lengths typically \( > \sim 20 \text{nm} \). For the superconducting single crystal of \( \text{YBa}_2\text{Cu}_3\text{O}_y \) \( (y \sim 7) \) substituted with 4% Co considered here, similar well defined magnetic reflections are observed and they again evidence commensurate antiferromagnetically correlated Cu(2) magnetic moments. As is discussed below, this magnetically correlated state possesses some, but not all, of the characteristics generally associated with conventional (static) long range magnetic order. To distinguish the presently reported state from that of conventional long range magnetic order, we refer to it as an extended range, magnetically correlated state.

The temperature dependence of the neutron scattering intensities at \( Q = (0.5,0.5,-1.5) \) and \( (0.5,0.5,-2) \) are shown in Fig. \(^{21}\). As the temperature is reduced below \( \sim 300 \text{K} \), the intensity at \( Q = (0.5,0.5,-2) \) initially increases progressively and then below \( \sim 90 \text{K} \) it decreases. Near 90 K, an intensity appears at \( (0.5,0.5,-1.5) \) which progressively increases as the temperature is lowered. This behaviour indicates that near 90 K, the system undergoes an AF1 - AFII transition characterised by a doubling of the AF unit cell along the c-axis. A similar doubling of the AF unit cell also occurred in the superconducting sample containing 1.3%Co but at a lower temperature \( (\sim 12 \text{K}) \). It also occurs in non-superconducting \( \text{YBa}_2\text{Cu}_3\text{O}_8+\delta \) when substituted at the Cu(1) site\(^{15}\). In the non-superconducting samples, the temperature of the AF1 - AFII transition also increases as the concentration of the substituted cation increases.

Although the measurements were made at room temperature and below, this range is sufficiently wide to provide a reasonable estimate of the Néel temperature \( (T_N) \) which lies above room temperature. The extrapolation was made assuming that the thermal dependence of the scattering intensity, normalised to \( T_N \) is the same as in the sample with 1.3%Co\(^{15}\). The obtained value, \( T_N \sim 400 \text{K} \), is higher than that for the sample with 1.3%Co \( (T_N \sim 330 \text{K}) \). The maximum size of the correlated Cu(2) magnetic moment \( (\sim 0.3 \mu_B) \), is approximately twice that \( (\sim 0.14 \mu_B) \) observed in the part of the sample containing 1.3% Co where the moments are extended range correlated\(^{12}\).

Using elastic neutron scattering, a total of six separately prepared superconducting samples of \( \text{YBa}_2(\text{Cu}_{1-x}\text{Co}_x)_3\text{O}_y \) \( (y \sim 7) \) have been examined. Each of them evidences well defined magnetic reflections corresponding to antiferromagnetically correlated Cu(2) magnetic moments. This characteristic is thus very robust. However, in samples having the same concentration of Co, the size of the Cu(2) magnetic moment obtained assuming all the Cu(2) in the sample contribute to the magnetic reflections, is found to vary from sample to sample. It was generally lower (by up to 40%) than the value \( \sim 0.3 \mu_B \) reported for the sample above.

The origin of this sample dependent behaviour may be considered in terms of two limiting cases. It could be due to a variation in the size of the extended range corre-
related moments (assuming all the Cu(2) contribute to the magnetic reflections in each sample) or it could be due to a variation in the volume fraction over which the Cu(2) are extended range correlated. In this context we recall that our local probe measurements on a number of separately prepared single phase, polycrystalline samples of YBa$_2$Cu$_3$O$_y$ (y~7) substituted with 4% Co show that in each sample essentially all the Cu(2) carry (short range) correlated magnetic moments$^2$ and that the average size of the moment remains essentially the same. We thus anticipate that in the single crystal samples, all the Cu(2) also carry correlated magnetic moments having a common average size. We then attribute the variation of the neutron measured Cu(2) magnetic moment from sample to sample to variations in the relative volumes where the correlations are respectively extended range (which contribute to the narrow magnetic reflections) and where they are short range (which do not contribute to the narrow magnetic reflections).

With this description in terms of different relative volumes of the extended range correlated and short range correlated fractions, it also follows that it is possible that not all the Cu(2) are extended range correlated in any of the single crystals samples including that reported above (Fig. 1). In this case, the average size of the Cu(2) moment for this sample would be higher than the value of ~0.3 $\mu_B$ obtained assuming that all the Cu(2) in the sample are extended range correlated.

We do not know why the correlations are sufficiently extended range in the single crystals to give rise to magnetic reflections whereas in the equivalent polycrystalline samples they remain short range. It is possible that the ~40% of Y$_2$BaCuO$_5$ which is distributed throughout the single crystal sample volume could play a role. To test this, it would be of interest to examine if the extended range correlations are present in equivalent single crystal samples which do not contain any secondary phases.

The AFI and AFII type magnetic structures we observe in the superconducting samples are also present in non-superconducting YBa$_2$Cu$_3$O$_6$ (AFI)$^{14,15}$ and in non-superconducting YBa$_2$Cu$_3$O$_6$ substituted at the Cu(1) sites (AFI and AFII)$^{16,17}$. Comparing the results obtained here with those in non-superconducting YBa$_2$Cu$_3$O$_6$, we note that the Néel temperature in the superconducting sample (~400 K) is only marginally lower than that of the non-superconducting sample (~420 K) whereas the sample averaged size of the Cu(2) magnetic moment in the superconducting sample (~0.3 $\mu_B$) amounts to a considerable fraction of that in non-superconducting sample (0.61 $\mu_B$).

There are thus a number of similarities between the extended range magnetically correlated state observed in superconducting YBa$_2$(Cu$_{0.96}$Co$_{0.04}$)$_3$O$_y$ (y~7) and the conventional long range magnetically ordered state observed in non-superconducting YBa$_2$Cu$_3$O$_6$. There is however, one important difference. Whereas for YBa$_2$Cu$_3$O$_6$, the conventional (static) magnetic order observed by neutron measurements$^5$ is also strongly evidenced by $\mu$SR measurements$^{16}$ (in fact, the $\mu$SR measurements preceded the neutron measurements in identifying the existence of magnetic order), for single crystal YBa$_2$(Cu$_{0.96}$Co$_{0.04}$)$_3$O$_y$ (y~7), as is described in the following section, the extended range correlated state (both AFI and AFII structures) evidenced by the neutron scattering measurements is not evidenced by the $\mu$SR measurements.

B. $\mu$SR measurements

The $\mu$SR measurements were made on a sample where the value of the extended range correlated Cu(2) magnetic moment measured by neutron scattering was ~0.2 $\mu_B$. Since the sample contains ~40% of Y$_2$BaCuO$_5$ which orders magnetically near 15 K and since the muons are implanted over the whole sample volume, the $\mu$SR response will involve contributions from the two main constituents as well as from the muons which contribute to the background. It turns out that it is not possible to unambiguously define the contributions coming from each of the two main phases in the sample or to precisely define the contribution coming from the background. Because of this, it is not feasible to make a detailed quantitative analysis and this is especially the case at temperatures near and below the magnetic ordering temperature of Y$_2$BaCuO$_5$. Nevertheless, even limiting the analysis to the temperatures of 30 K and above, it is possible to obtain pertinent information.

Fig. 2 shows the $\mu$SR depolarisation at 100, 50 and 30 K with the incident muons propagating parallel to the c-axis of the single crystal. We first describe the simplified approach, in terms of sample averaged parame-
temperature, we obtain (sample averaged) values for a sample where the major part ($YBa_{2}$) at temperatures above the magnetic ordering temperature of $Y_{2}BaCuO_{5}$. Despite the fact that neutron scattering measurements on this sample show the Cu(2) in $YBa_{2}(Cu_{0.96} Co_{0.04})_{3}O_{7}$ give rise to magnetic reflections which correspond to a commensurate antiferromagnetic structure with an associated Néel temperature above room temperature, the presence of this correlated state does not markedly influence the depolarisation (there is no reduction in the initial asymmetry and there are no oscillations).

![FIG. 2: (color online) $\mu$SR spectra for single crystal $YBa_{2}(Cu_{0.96}Co_{0.04})_{3}O_{7}$ ($y \sim 7$) mixed with of $Y_{2}BaCuO_{5}$ at temperatures above the magnetic ordering temperature of $Y_{2}BaCuO_{5}$. Despite the fact that neutron scattering measurements on this sample show the Cu(2) in $YBa_{2}(Cu_{0.96}Co_{0.04})_{3}O_{7}$ give rise to magnetic reflections which correspond to a commensurate antiferromagnetic structure with an associated Néel temperature above room temperature, the presence of this correlated state does not markedly influence the depolarisation (there is no reduction in the initial asymmetry and there are no oscillations).](image)

We thus attribute the changes observed in the (sample averaged) muon relaxation rate in this temperature range to changes that occur in the dynamics of the extended range correlated moments in the $YBa_{2}(Cu_{0.96}Co_{0.04})_{3}O_{7}$ fraction. Thus, it is the slowing down of the fluctuation rate of the correlated Cu(2) moments in the superconducting fraction which gives rise to the appearance (near 50 K) and to the increase (below 50 K) of the muon spin relaxation rate. A quite similar appearance (near 50 K) and a quite similar increase (below 50 K) of the muon spin relaxation rate are also observed in the equivalent single phase superconducting polycrystalline samples where they are clearly related to the properties of the (short range) magnetically correlated Cu(2).

**IV. COMMENTS**

Although it is not commonplace to encounter a state involving fluctuating extended range correlated magnetic moments, in addition to the case of $YBa_{2}Cu_{3}O_{6.5}$ mentioned above, this state has been observed recently in the rare earth pyrochlores where frustration plays a role. In a manner analogous to that reported here, ref. reported both the observation of neu-
From measurements on polycrystalline samples, we predict that antiferromagnetically correlated moments exist. Important aspect is simply that these fluctuating moments are of interest, in the context of the present work, a more important aspect is that these fluctuating moments exist.

V. SUMMARY AND CONCLUSIONS

When Co is substituted (at the Cu(1) sites) into fully oxidised YBa$_2$Cu$_3$O$_y$ ($y \sim 7$), the Cu(2) in its neighbourhood carry antiferromagnetically correlated moments. From measurements on polycrystalline samples, we previously found a Co substitution level of $\sim 2\%$ was sufficient for essentially all the Cu(2) to carry magnetic moments (in such samples $T_{sc} = 84$ K). This indicates that the range around the Co with correlated Cu(2) moments is approximately three to four a or b lattice spacings.

A mechanism has been proposed to explain the magnetically correlated Cu(2) observed in underdoped cuprates, so that this mechanism could play a role here. It is possible however, that a different and so far undefined mechanism, is responsible for the correlated Cu(2) moments observed both in underdoped (YBa$_2$Cu$_3$O$_y$ + Co) cuprates and in optimally doped (YBa$_2$Cu$_3$O$_y$ + Ni) cuprates.

For reasons that remain to be established, the omnipresent fluctuating, short range magnetically correlated Cu(2) state observed in polycrystalline YBa$_2$(Cu$_{0.96}$Ni$_{0.04}$)$_3$O$_y$, ($y \sim 7$) is not conventional in that it possesses dynamic characteristics.

Finally, we note that although the details of the properties of the correlated Cu(2) magnetic moments are of interest, in the context of the present work, a more important aspect is simply that these fluctuating moments exist.

VI. ACKNOWLEDGEMENTS

J.A.H thanks Philippe Bourges and Yvan Sidis for the neutron scattering measurements.
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