Universal superconducting and magnetic properties of the 
(Ca$_x$La$_{1-x}$)(Ba$_{1.75-x}$La$_{0.25+x}$)Cu$_3$O$_y$ system: a μSR investigation

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(November 1, 2018)

The Uemura relation is a milestone in the research of high temperature superconductors [HTSC] and a key ingredient in most modern theories of HTSC. This relation states that in underdoped HTSC the superconductivity transition temperature $T_c$ is proportional to the muon spin rotation [$\mu$SR] line width $\sigma$, and that the proportionality constant is universal for all HTSC materials. Since $\sigma$ is proportional to $\lambda_{ab}^{-2}$, where $\lambda_{ab}$ is the in-plane penetration depth [see Sec. [3]], there is a one to one relation between $T_c$ and $\lambda_{ab}^{-2}$ for all underdoped HTSC. However, this relation seems to break in the optimally and over doped regions. To date, the origin of this breakdown is not clear. Is strong magnetic background beneficial or detrimental to superconductivity?

Another key ingredient in the modern theories of HTSC is that at low temperatures (T), cuprates phase separate into regions that are hole “poor” and hole “rich”. While hole rich regions become superconducting below $T_c$, the behavior of hole poor regions at these temperatures is not quite clear. Some data support the existence of magnetic moments in these regions, but there are still many open questions regarding these moments and the spontaneous magnetic fields associated with them. For example: Is there a true phase transition at $T_g$? What is the field profile and how is it different from, or similar to, a canonical spin glass? Is the field confined solely to the hole poor regions or does it penetrate the hole rich regions? Also, the interplay between magnetism and superconductivity is not clear. Is strong magnetic background beneficial or detrimental to superconductivity?

We address these questions by investigating the (Ca$_x$La$_{1-x}$)(Ba$_{1.75-x}$La$_{0.25+x}$)Cu$_3$O$_y$ (CLBLCO) family of superconductors. These superconductors belong to the 1:2:3 family and has several properties that make it ideal for our purpose. It is tetragonal throughout its range of existence $0 \leq x < 0.5$, so there is no ordering of CuO chains. Simple valence sum rules more sophisticated bond-valance calculations and thermoelectric power measurements show that the hole concentration is $x$ independent. As shown in Fig. by changing $y$, for a constant value of $x$, the full superconductivity curve, from the underdoped to the overdoped, can be obtained. Finally, for different Ca contents, parallel curves of $T_c$ vs $y$ are generated. Therefore, with CLBLCO one can move continuously, and with minimal structural changes, from a superconductor resembling YBCO to one similar to LSCO. We study the superconducting and magnetic properties of CLBLCO by performing, zero, longitudinal, and transverse field $\mu$SR investigations.

The report on the zero and longitudinal field measurements is an extension of our recent letter.

![Phase diagram of (Ca$_x$La$_{1-x}$)(Ba$_{1.75-x}$La$_{0.25+x}$)Cu$_3$O$_y$. The dashed lines indicate samples with equal $T_g$.](image.png)

**FIG. 1.**

**TABLE 1.**

**I. EXPERIMENTAL ASPECTS**

The preparation of the samples is described elsewhere. Oxygen content was determined using iodometric titration. All the samples were characterized using X-ray diffraction and were found to be single phase. $T_c$ presented in the phase diagram is obtained from resistivity measurements.
Our \( \mu \)SR experiments were done at two facilities. When a good determination of the base line was needed we used the ISIS pulsed muon facility at Rutherford Appleton Laboratory, UK. When high timing resolution was required we worked at the Paul Scherrer Institute, Switzerland (PSI). In \( \mu \)SR experiments we inject polarized muons into the sample and applies a magnetic field. Decay positrons are emitted preferentially in the direction parallel to the muon spin and are detected by positron counters. We used two types of setups, the transverse field [TF] and the longitudinal field [LF], which also includes zero field, as shown in Fig. 2. The LF configuration works as in panel (a) in both facilities. The TF configurations work in ISIS as in panel (b) and at PSI as in panel (c). From the counters an histogram is generated of positrons counts as a function of time, where the time is measured from the moment the muons enter the sample. The asymmetries \( A_{FB}(t) \), \( A_{UD}(t) \) and \( A_{LR}(t) \) are than generated by \( A_{FB}(t) = [F(t) - B(t)]/[F(t) + B(t)] \) and similarly with \( U, D \) instead of \( F, B \), where \( F, B, U, D \) are the forward, backward, up, and down counters. \( A_{LR}(t) \) is generated only from the left counter in Fig. 2(c). Most of the data were taken with a \( ^4 \)He cryostat. However, in order to study the internal field profile we had to avoid dynamical fluctuations by freezing the moments completely.

For this purpose we used the \( ^3 \)He cryostat at ISIS with a base temperature of 350 mK. All \( \mu \)SR measurements were done on sintered pellets.

### II. TF-\( \mu \)SR

These experiments are done by field cooling (FC) the sample to 1.8 K at an external field of 3 kOe in PSI and 400 Oe in ISIS. As explained above we apply the field perpendicular to their spin direction, and every muon then precesses according to the local field in its environment. When field cooling the sample, a vortex lattice is formed, and the field from these vortices decay on a length scale of \( \lambda \). This leads to a inhomogeneous field distribution in the sample. Since the magnetic length scale is much larger than the atomic one, the muons probe the magnetic field distribution randomly, which, in turn, leads to a damping of the muons average spin polarization. This situation is demonstrated in Fig. 3 where we present an image of the field profile, and the corresponding the real and imaginary part of the muon asymmetry. At temperatures above \( T_c \) the field is homogeneous and all muons experience the same field, and therefore no relaxation is observed. Well below \( T_c \) there are strong field variations and therefore different muon precess with different frequencies, and the average polarization quickly decays to zero. In intermediate temperatures the field variation are not severe and the relaxation is moderate.

It was shown that in powder samples of HTSC the muon asymmetry \( A(t) \) is well described by

\[
A(t) = \exp(-\sigma^2 t^2/2) \cos(\omega t + \varphi)
\]

where \( \omega = \gamma \mu H \) is the precession frequency of the muon, \( \sigma \) is the relaxation rate, and \( \varphi \) is a phase which depends on the counters used to generate the asymmetry. Our analysis for both ISIS and PSI data is done in a reference frame rotating at \( \omega_{rff} \) and the real and imag-
nary components of the signal are fitted simultaneously. Therefore, the frequency in Fig. 3 is $\gamma \mu H - \omega_{\text{rf}}$ where $\omega_{\text{rf}}$ is chosen arbitrarily for presentation purpose. The solid line in this figure is the fit result. The fact that the whole asymmetry relaxes indicates that CLBLCO is a bulk superconductor.

The fit results for $\sigma$ are shown in Fig. 4. As can be seen, the dependence of $T_c$ on $\sigma$ is linear in the underdoped region and universal for all CLBLCO families, as expected from the Uemura relations. However, there is a new aspect in this plot. There is no "boomerang" effect, namely, overdoped and underdoped samples with equal $T_c$ have the same $\sigma$, with only slight deviations for the $x = 0.1$ sample as demonstrated by the arrows in Fig. 4. Therefore, in CLBLCO there is one to one correspondence between $T_c$ and $\sigma$, and therefore $\lambda_{\text{ab}}^2$, over the whole doping range. This is our first important finding.

III. ZF-$\mu$SR

Typical muon asymmetry depolarization curves are shown in Fig. 5 (a) for different temperatures in the $x = 0.1$ and $y = 7.012$ ($T_c = 33.1K$) sample. The change of the polarization shape with temperature indicates a freezing process, and the data can be divided into three temperature regions. In region (I), given by $T \gtrsim 8 K$, the muon relaxes according to the well known Kubo-Toyabe (KT) function given by

$$KT(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta t^2) \exp(-\frac{1}{2}\Delta t^2),$$

(2)

(see Eq. 3) typical of the case where only frozen nuclear moments are present. In region (II), bounded by $8 K \gtrsim T \gtrsim 3 K$, part of the polarization relaxes fast and the rest relaxes as in the first region. As the temperature is lowered the fast portion increases at the expense of the slow one. Moreover, the relaxation rate in the fast portion seems independent of temperature. Finally, at long time the asymmetry relaxes to zero. In region (III), where $3 K \gtrsim T$, the asymmetry at long times no longer relaxes to zero, but instead recovers to a finite value. This value is $\simeq 1/3$ of the initial asymmetry $A_z(0)$.

![FIG. 4. A Uemura plot showing $T_c$ vs. the muon relaxation rate $\sigma$ in Eq. 3 for the CLBLCO family of superconductors.](image)

![FIG. 5. (a) ZF-$\mu$SR spectra obtained in a $x = 0.1$, $y = 7.012$ sample with $T_c = 33.1K$. The solid lines are fit to the data using Eq. 3, the dashed line is a fit using the simulation as described in the text. (b) $\mu$SR spectra obtained in longitudinal fields from the $x = 0.4$, $y = 6.984$ sample at 350 mK. (c) Polarization curves generated by the simulation program as described in the text.](image)
internal field is smaller than the external one due to the Meissner effect, this recovery indicates that the internal field is static and of the order of tens of Gauss. Next we perform quantitative data analysis in two parts: high temperatures (region II), and base temperature.

### A. High T Data Analysis

First we discuss region II. Here we focus on the determination of $T_g$. For that purpose we fit a combination of a fast relaxing function and a KT function to the data\[3\]

$$A_z(t) = A_m \exp\left(-\sqrt{T(t)}\right) + A_n KT(t), \tag{3}$$

where $A_m$ denotes the amplitude of the magnetic part, $\lambda$ is the relaxation rate of the magnetic part, and $A_n$ is the amplitude of the nuclear part. The relaxation rate of the KT part was determined at high temperatures and is assumed to be temperature independent. The sum $A_m + A_n$ is constrained to be equal to the total initial asymmetry at high temperatures. The relaxation rate $\lambda$ is common to all temperatures. The solid lines in Fig. 5(a) are the fits to the data using Eq. 3.

![Fig. 6. Magnetic amplitude as function of temperature for different samples. The solid lines are guides to the eye.](image)

The success of this fit indicates the simultaneous presence of two phases in the sample; part of the muons probe the magnetic phase while others probe only nuclear moments. As the temperature decreases $A_m$, which is presented in Fig. 6, for three samples, grows at the expense of $A_n$. At low temperatures $A_m$ saturates to the full muon asymmetry. A similar temperature dependence of $A_m$ is found in all samples. The origin of the magnetic phase is electronic moments that slow down and freeze in a random orientation. The fact that $\lambda$ is temperature independent means that in the magnetic phase $\gamma \langle B^2 \rangle^{1/2}$, where $\gamma$ is the muon gyromagnetic ratio, is temperature independent. In other words, as the temperature is lowered, more and more parts of the sample become magnetic, but the moments in these parts saturate upon freezing.

![Graph showing magnetic amplitude vs. temperature](image)

Our criterion for $T_g$ is the temperature at which $A_m$ is half of the total muon polarization as demonstrated by the vertical lines in Fig. 6 for the three different samples. The phase diagram that is shown in Fig. 7 represents $T_g$ for various samples differing in Ca and O contents. This diagram is systematic and rather smooth suggesting good control of sample preparation. As expected, for constant $x$, higher doping gives lower $T_g$.

We have singled out three groups of samples with a common $T_g = 11, 8$ and $5$ K as shown in Fig. 7 by the horizontal solid lines. These samples are represented in the phase diagram in Fig. 1 by the dotted lines. The phase diagram, containing both $T_g$ and $T_c$, is the second main finding of this work. It provides clear evidence of the important role of the magnetic interactions in high temperature superconductivity as discussed in Sec. V.

### B. Low T Data Analysis

We now turn to discuss the muon depolarization at base temperature. In this case all the muons experience only a static magnetic field, as proven above. This allows one to reconstruct the internal field distribution out of the polarization curve. The polarization of a muon spin experiencing a unique field $B$ is given by $P_z(t) = \cos^2(\theta) + \sin^2(\theta) \cos(\gamma B t)$, where $\theta$ is the angle between the field and the initial spin direction. When there is an isotropic distribution of fields, a 3D powder averaging leads to

$$P_z(t) = \frac{1}{3} + \frac{2}{3} \int_0^\infty \rho(|B|) \cos(\gamma |B| t) B^2 dB \tag{4}$$

where $\rho(|B|)$ is the distribution of $|B|$. Therefore, the polarization is given by the Fourier transform of $\rho(|B|) B^2$ and has a $1/3$ base line. When the distribution of $B$ is centered around zero field, $\rho(|B|) B^2$ is a function with a peak at $\langle B \rangle$ and a width $\Delta$, and both these numbers are of the same order of magnitude [e.g. Fig. 8(b)]. Therefore we expect the polarization to have a damped oscillation and to recover to $1/3$, a phenomenon known as the dip.

![Graph showing $T_g$ vs. $y$. The horizontal solid lines are the equal $T_g$ lines appearing in Fig. 6.](image)
Gaussian, Lorentzian and even exponential random field distribution, and, more importantly, all known canonical spin glasses, produce polarization curves that have a dip before the 1/3 recovery. This is demonstrated in Fig. 9. For a Gaussian distribution of width $\Delta$ we obtain Eq. 4 which is demonstrated in panel (a). The cases of a canonical spin glass $Fe_{0.05}TiS_2$, and an extremely underdoped CLBLCO are presented in panels (b) and (c). Furthermore, a dipless polarization curve that saturates to 1/3 cannot be explained using dynamical arguments. Therefore, the most outstanding feature of the muon polarization curve at base temperature is the fact that no dip is present, although there is a 1/3 tail. This behavior was found in all of our samples with $T_c > 7$ K, and also in Ca doped YBCO\(^{13}\) and Li doped YBCO\(^{14}\).

\[ \langle B \rangle \ll \Delta \]

The lack of the dip in $P_z(t)$ can tell much about the internal field distribution. It means that $\langle B \rangle$ is much smaller than $\Delta$. In that case the oscillations will be over-damped and the polarization dipless! In Fig. 8(b) we show, in addition to the $\langle B \rangle \approx \Delta$ case described above [panel (a)], a field distribution that peaks around zero [panel (b)]. Here $\langle B \rangle$ is smaller than $\Delta$, and, indeed, the associated polarization in the inset is dipless. Thus in order to fit the base temperature polarization curve we should look for $\rho(|B|)B^2$ with most of its weight around zero field. This means that $\rho(|B|)$ diverges like $1/B^2$ at $|B| \to 0$, namely, there is abnormally high number of low field sites.

It also means that the phase separation is not a macroscopic one. If it were, all muons in the field free part would probe only nuclear moment and their polarization curve should have a dip or at least its beginning as in the high temperature data. The same would apply for the total polarization curve, in contrast to observation. Thus, the superconducting and magnetic regions are intercalated on a microscopic scale ($\sim 20\AA$). This is the third main finding of this work.

**FIG. 8.** (a) The internal field distribution extracted from the simulations for the case of correlation length $\xi = 3$ lattice constants, maximum moment size of $0.6\mu_B$ and magnetic moment concentration $p = 15\%$. Inset: The muon spin polarization for that distribution. (b) The same as above for the case of $p = 35\%$.

The special internal field distribution, and the nature of the gradual freezing of the spins, can be explained by the intrinsic inhomogeneity of hole concentration. The part of the sample that is hole poor, and for that reason is "more" antiferromagnetic, will freeze, while the part which is hole rich will not freeze at all. The variation in the freezing temperature of different parts of the sample...
can be explained by the distribution of sizes and hole concentration in these antiferromagnetic islands. The large number of low field sites is a result of the fact that the magnetic field generated in the magnetic regions will penetrate into the hole rich regions but not completely.

IV. NUMERICAL SIMULATION

To improve our understanding of the muon polarization, we performed simulations of a toy model aimed at reproducing the results described above. A 2D \( 100 \times 100 \) square lattice is filled with two kinds of moments, nuclear and electronic. All the nuclear moments are of the same size, they are frozen and they point in random directions. Of the electronic moments only a small fraction \( p \) is assumed to be frozen; they represent magnetic regions with uncompensated antiferromagnetic interactions. Since these regions may vary in size, the moments representing them are random, up to a maximum size. The frozen electronic moments induce spin polarization in the other electronic moments surrounding them. Following the work of others, we use decaying staggered spin susceptibility which we take to be exponential, namely,

\[
\chi'(\mathbf{r}) = (-1)^{n_x + n_y} \exp(-r/\xi)
\]

where \( \mathbf{r} = n_x a\hat{x} + n_y a\hat{y} \) represents the position of the neighbor Cu sites, \( a \) is the lattice vector, and \( \xi \) is the characteristic length scale. Because of this decay, at low frozen spin concentration, large parts of the lattice are practically field free (expect for nuclear moments). However, the important point is that no clear distinction between magnetic and field free (superconducting) regions exists. This situation is demonstrated in Fig. 10.

![FIG. 10. Demonstrating the numerical simulations. Two spins (long arrows) are placed on the lattice. They polarize the near by spins. The muon interacts with the spin by dipolar interaction. Nuclear moment (which participate in the simulation) are not shown.](image)

The muon polarization time evolution in this kind of field distribution is numerically simulated. The interaction between the muon and all the other moments is taken to be dipolar, and \( \xi \) is taken to be 3 lattice constants. The dashed line in Fig. 11 is a fit to the \( T = 350 \) mK data, which yield \( p = 15\% \) and maximum moment size \( \approx 0.06 \mu_B \). As can be seen, the line fits the data very well. However, as expected, the fit is sensitive to \( p\xi^2 \) only, namely the effective area of the magnetic islands, so longer \( \xi \) would have given smaller \( p \). The field distributions and the polarization curve shown in Fig. 10 were actually generated using the simulation. In (a) the spin density is 15\% while in (b) the density is 35\%. In panel (c) of Fig. 8 we show the spin polarization for different hole concentration, varying from 0\% to 35\% with the same \( \xi = 3 \). The resemblance between the simulation results as a function of \( p \) and the muon polarization as a function of temperature in panel (a) leads us to our fourth conclusion that the freezing process is mostly a growth in the total area of the frozen AF islands.

V. DISCUSSION

We now discuss the phase diagram presented in Fig. 1. This diagram is consistent with recent theories of hole pair boson motion in an antiferromagnetic background. Those theories conclude that

\[
T_c \propto Jn_s
\]

where \( n_s \) is the superconducting carrier density, and \( J \) is the antiferromagnetic coupling energy. Let us define \( \Delta phl = phl - p_0 \) where \( p_{hl} \) is the number of mobile holes and \( p_0 \) is the number of mobile holes at optimum. We assume that

\[
n_s(\Delta phl) = \frac{1}{2}(p_0 + \Delta phl)
\]

and write

\[
\Delta phl = K(x)\Delta y
\]

where \( \Delta y = y - 7.15 \) is chemical doping measured from optimum, and \( K \) is a scaling parameter which relates \( \Delta y \) to \( \Delta phl \). Since there is a linear dependence between \( T_g \) and chemical doping (Fig. 3) we predict that

\[
T_g \propto J(1 -cg n_s).
\]

From Eq. 6 \( T_c^{max} \propto Jn_s(0) \), therefore both \( T_c/T_c^{max} \) and \( T_g/T_g^{max} \) should be functions only of \( \Delta phl \). This is demonstrated in Fig. 1(b). We find \( K(x) \) by making all \( T_c/T_c^{max} \) collapse onto one curve resembling the curve of \( La_{2-x}Sr_xCuO_4 \), where the exact doping is known. Using these values of \( K(x) \) we also plot \( T_g/T_g^{max} \) as a function of \( \Delta phl \) in Fig. 1(b). Again all data sets collapse onto a single line described by \( T_g/T_g^{max} = -3.1(2)\Delta phl - 0.21(2) \), or
\[ T_g = 0.3 T_c^{\text{max}} (1 - c_g n_s) \]  

with \( c_g = 10.3 \) when converting back to Eq. A. This indicates that the same single energy scale \( J \) controls both the superconducting and magnetic transitions, and provides the exact \( n_s \) and \( T_c^{\text{max}} \) dependence of \( T_g \). Finally, and most importantly, the phase diagram containing both \( T_c \) and \( T_g \) leads us to believe that these temperatures are determined by the same energy scale.

VII. ACKNOWLEDGMENTS

We would like to thank the PSI and ISIS facilities for their kind hospitality and continuing support of this project. We acknowledge very helpful discussions with Assa Auerbach and Ehud Altman. This work was funded by the Israeli Science Foundation and the EU-TMR program.

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