Magnetic order in the normal state of the archetypal high-$T_c$ superconductor $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

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We report detailed bulk magnetization measurements of the normal state in the high transition temperature (high-$T_c$) superconductor $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. A magnetic order in the form of hysteresis in the low field magnetization was observed at temperatures well above $T_c$ but below the pseudogap temperature. The order arises from the interaction of magnetic domains, and the doping ($x$) dependence of its onset and strength broadly follows that of $T_c(x)$.

High temperature superconductivity arises by adding charge carriers to certain copper-oxide insulators, such as the prototype $\text{La}_2\text{CuO}_4$. Resolving the high-$T_c$ mechanism basically depends on understanding the evolution of the material with charge doping and identifying the putative charge or spin order in the non-superconducting (normal) state possibly associated with the presence of a pseudogap below a characteristic temperature.
Doping the parent insulator causes intrinsic electronic heterogeneity which governs some of the unconventional physical properties of high-$T_c$ materials\(^1\text{-}^3,^7\). On the other hand, there is no evidence of a bulk ordered state above $T_c$ and although various scenarios involving charge, spin, orbital currents and stripes, which either compete or cooperate with superconductivity, have been proposed\(^1\text{-}^3,^8\text{-}^10\), it is unclear if this state exists at all. Although a signature of the order is the formation of domains\(^2,^3,^8\text{-}^10\), properties arising due to a domain structure are weak and consequently experimentally very difficult to detect. So far these are probably reflected as electronic phase separation in atomic resolution experiments in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$\(^1\text{-}^3,^11\text{-}^13\) and as telegraph-like fluctuations in fabricated YBa$_2$Cu$_3$O$_{7-\delta}$ nanowires\(^14\). Here we report detailed magnetization measurements of the high-$T_c$ superconductor La$_{2-x}$Sr$_x$CuO$_4$. We show evidence for a well developed bulk order due to the presence of magnetic domains, in the form of a magnetic hysteresis over a wide range of doping ($x$) and temperatures in the normal state.

The materials studied were La$_{2-x}$Sr$_x$CuO$_4$ with $x=0.03\text{-}0.24$ (among these the $x=0.03$ and 0.15 samples were both poly- and single-crystals). The La$_{2-x}$Sr$_x$CuO$_4$ powders and single crystals were prepared using solid-state reaction procedures and the travelling solvent floating zone technique, respectively. Electron probe microanalysis, x-ray diffraction and muon spin relaxation showed all our samples to be phase pure and stoichiometric. High field magnetization studies indicate no evidence for extrinsic magnetic impurities. Magnetic penetration depth measurements performed by the low field ac-susceptibility technique show a linear low temperature dependence for the in-plane penetration depth, indicative of the high quality of our samples\(^15,^16\). Except the magnetic noise tests (see
below), the measurements reported here were carried out using a Quantum Design (MPMS-XL) SQUID magnetometer at 3 cm scan length after we first applied a zero field procedure to suppress the remnant field of its superconducting magnet. A key to the present study has been the special care that was taken to minimize external noise to the system, the absence of extra material to hold the sample and the use of a non-magnetic sample holder with no discontinuity so there is no background due to the sample holder. The temperature regions the measurements were performed were monitored and controlled, the apparatus performance was optimum and the data reproducible. To confirm the absence of any magnetic signal arising from the apparatus itself, measurements were also made using an empty sample holder and without the presence of a sample-holder/sample. Unless indicated otherwise, all our $M-H$ measurements were performed by cooling the samples from 320 K to 5 K in zero-field and then warming in zero-field to the respective temperature at which the $M-H$ run commenced. To establish that the magnetic behaviors for all samples reported here are a uniform bulk property we performed several measurements on polished and unpolished pieces cut from larger samples. The results for the smaller pieces were the essentially the same as for the original uncut samples.

The conventional wisdom in high-$T_c$ superconductors (HTS) is that in the normal state the susceptibility ($\chi=M/H$) is paramagnetic and $\chi$ increases or decreases with temperature ($T$) at low or high doping, $x$, respectively$^{17,18}$. Although our magnetization results [Fig. 1 (a), (b)] are in agreement with the $x$, $T$ dependence of $\chi$, in the low field region we observe a clear departure from the expected paramagnetic behavior (circled region in Fig. 1 (a,b)): $M$ does not grow linearly with $H$ across the whole field range but instead
deviates at low fields and over a wide range of \( x, T \). To examine the nature of this deviation at low fields and how generic it is we first obtained detailed low-field \( M(H) \) data (Fig. 1 (c,d)) for a single crystal with the non-superconducting concentration \( x=0.03 \) at \( T=5K \) (similar results have been observed at \( T=25K \)). We find non-linear field dependence with a \textit{magnetic hysteresis below \( \approx 1kG \)}. Furthermore, the size of the hysteresis, \textit{i.e.}, the magnitude of the remnant magnetization \( \Delta M \), defined as the difference in the value of \( M \) at \( H=0 \) between increasing (virgin curve) and decreasing \( H \), is smaller for \( H//c \). That is \( \Delta M=1x10^{-5} \) emu/g for \( H//c \) compared to \( 1.8x10^{-5} \) emu/g for \( H//ab \). This difference, is reproducible and within our experimental resolution and indicates the \textit{magnetism responsible for the hysteresis is preferentially aligned along the CuO\textsubscript{2} planes}.

There are a number of other characteristic features in the data: The field dependence of the magnetization tells us that the hysteresis cannot be due to mere weak ferromagnetism but instead due to a \textit{hysteretic mechanism coupled to the paramagnetic background}. If it was conventional weak ferromagnetism the magnetization would saturate at fields higher than the value the magnetic hysteresis collapses\textsuperscript{19}. The data in Fig. 1(c,d) for example show a continuous rise in \( M \) with \( H \). This behavior is not unique to the \( x=0.03 \) crystals. Let us take another example, the polycrystalline sample with \( x=0.07 \) shown in Fig. 1(a). At low fields, \( H<1kG \), (Fig. 1(a), inset) we observe a magnetic hysteresis (better shown in the zoom-in plot in Fig. 1(c)) yet no saturation at higher fields. Instead, once the hysteresis is suppressed at \( H>1kG \) the magnetization continues to rise with applied field and joins smoothly the paramagnetic state (Fig. 1(a)).
Low field magnetization measurements for several values of $x$ at $T>T_c$ indicate a systematic departure from paramagnetism with doping (Fig. 1(e-h)). This deviation is reflected qualitatively in the change of the magnetization curvature $M(H)$ at low $H$ (Fig. 1(e-h)) and quantitatively in the magnitude of $\Delta M$ (Fig. 1(i)). The values of $\Delta M$ shown in Fig. 1(i) were obtained by taking into account also the errors that may arise from the fluctuation of the data with decreasing field. The noise level in the two typical sets of data, for single and polycrystalline samples in Fig. 1(c,d) and Fig. 1(e) for $x=0.03$ and 0.07, respectively, is 2-3 orders of magnitude above the experimental resolution. The data reveal another important piece of information: For all dopings displaying magnetic hysteresis, the virgin curves at $H<1kG$, are always smooth (see e.g. Fig. 1(c-h)) whereas all other curves of the magnetic loop are noisy, displaying switching fluctuations (see Fig. 1(c-e) and Fig. 2). This indicates that once the magnetic structure causing the hysteresis is “de-stabilized”, at $H>1kG$, it never returns to an equilibrium state, i.e. as in the virgin state. We have checked the reproducibility of our observations over the twenty eight months course of these measurements. We obtain essentially the same results for as long as we follow the same experimental procedure. Also the results are the same when obtained in different apparatuses.

So far, our experiments indicate the following: The presence of a magnetic hysteresis at low fields joining smoothly the high field paramagnetic state. The strength of the hysteresis is larger for $H//ab$ and develops with doping in a manner similar to $T_c$ - although unlike $T_c$ and the superfluid density$^{16}$ it does not survive up to $x=0.27$ but vanishes at $x=0.24$ (Fig. 1(i)). To investigate further the actual cause of the observed deviation from paramagnetism and the presence of a magnetic hysteresis at low fields, we
performed $M(H)$ measurements at various temperatures and field histories. To
demonstrate our essential findings we show a typical $M-H$ loop for $x=0.10$ obtained at
$T=45K (>T_c)$ (Fig. 2). We have obtained similar data for other values of $x$ and samples.
The magnetization loop in Fig. 2 displays clearly the presence of a bulk magnetic order at
$T> T_c$, but below $T^*_{2,3,8-10}$ with a remnant moment which for $x=0.10$ is $6 \times 10^{-5}$ $\mu_B$/Cu-
atom. This result constitutes the essence of this work: The identification of a well
developed bulk order in the pseudogap state of the archetypal high-$T_c$ cuprate. The
magnitude and structure of the magnetic hysteresis loop in Fig. 2 resembles that of pinned
magnetic domains$^{19}$. Henceforth we adopt the term “domain” to name the moments
responsible for the magnetic effects we observe, in the sense that domains represent local
moments which reverse with field polarity and are distributed throughout the bulk of the
sample. The domain walls are responsible for the remnant magnetization. Their de-
stabilization above a critical field ($\sim 1kG$) causes the presence of discrete jumps$^{19}$. This is
the behavior also observed in the samples discussed in Fig. 1. To determine the frequency
of the domain wall motion we used a separate experimental set up where a pick up coil
was wrapped around the $x=0.10$ sample while a counter wound air core coil connected in
series with the pick up coil offsets the induced voltage from the applied magnetic field.
When the set up is placed in a superconducting solenoid magnet and a field (1.5 kG)
applied along the length of the sample, the domain wall motion in the region of the pick
up coil induces a voltage whose spectrum we fast Fourier transformed and obtained a
frequency of $10^8$ Hz.

Let us note that a magnetic hysteresis loop similar to that shown in Fig. 2 has been
reported for some spin glasses$^{20}$. However, we believe our observations cannot be due to
a conventional spin glass for the following reasons. First we observe the same effect at
temperatures both below and above the glass transition temperature (e.g., the glass
transition temperatures for \(x=0.03\) and \(x=0.10\) are \(\sim 7\)K and \(2\)K, whereas as mentioned
above we observe magnetic hysteresis even at \(T=25\)K and \(45\)K, respectively). Second,
unlike the doping dependence of the magnetic hysteresis and associated remnant
magnetization (Fig. 1(i)), the spin glass temperature, which is of the order of only a few
degrees Kelvin, for \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\) in particular has been shown to set in at \(x<0.19\) and to
gradually increase with decreasing doping all the way down to at least \(x=0.02^{6,7}\). These
trends are very different to the doping dependence of the magnetic order observed here
(Fig. 1(i)). Third in traditional spin glasses the magnetic loop does not display the
discrete jumps observed here (Fig. 2 – black and blue curves). One possibility however,
might be that the spins along the domain walls freeze at low temperatures to a distinct
order whose end point (doping) transition might be below that of the higher temperature
order observed here.

The cause of the doping dependent magnetic order at \(T>T_c\) is most likely to be due to a
domain structure which at \(H<1\)kG is pinned and at higher fields displays instabilities
arising from domain wall motion. It is important to clarify whether the domains causing
the observed magnetic order act independently or interact and collective effects take
place. Hysteretic systems are described in terms of domains each of which can be
oriented at particular values of the applied field\(^{19,21}\). A real system consists of a number
of such domains and as the applied field is increased while on the virgin curve various
domains orient, in the direction of the applied field. With reducing field a subset of these
domains is no longer oriented and subsequent increase in the applied field to the original
value restores the original set of non-oriented domains, thus demonstrating return point memory\textsuperscript{19,21,22}. In other words, the system is able to restore memory of its past states and is able to return back to those states under appropriate conditions. This is the \textit{return point memory effect}. It has been observed and well-studied in a variety of systems containing domains: ranging from magnetic materials\textsuperscript{19} to even systems displaying hysteretic capillary condensation of helium – here the domains are pores and the tuning parameter is not field but the time of flight of third sound\textsuperscript{22}. Our subloop tests performed on the virgin curve (Fig. 3(a), red subloop) clearly show this effect occurs also in the normal state of the HTS, and it is the very same domain structure displaying return point memory which is responsible for the magnetic order at $T>T_c$.

Now, if the domains act independently, two subloops taken while on the virgin curve and between the same applied field end points must be congruent\textsuperscript{19,21}. Our data (Fig. 3(a)) show that we do not have congruence at $T=45$K; the subloops A and B are rotated relative to one another (Fig. 3(a), inset). Therefore, our material cannot consist of independent domains; \textit{the domains must interact}. The interaction is likely to be via the domain walls separating the domains. This subloop behavior (Fig. 3(a)) is not limited to $x=0.10$. We have observed a similar effect in other samples and dopings. In Fig. 3b we show the results for single crystals with $x=0.15$. We notice that although the effect here is smaller compared to that for $x=0.10$ the magnetic subloops are clearly not congruent at $T=70$K ($>T_c$) - the domains interact. On the other hand, at higher temperatures, $T \geq 300$K and $T \geq 270$K for $x=0.10$ and $x=0.15$, respectively, the subloops are congruent. This behavior is shown in Fig. 3(a) (upper inset) and Fig. 3(b) (inset) for the $x=0.10$ and $x=0.15$ samples, respectively. The result indicates that just as in other magnetic systems\textsuperscript{19}, our system too
reached an energy threshold above which the domain walls fluctuate randomly, the domains no longer interact and the magnetic order has almost collapsed. Broadly speaking this is the thermal equivalent of the field effect where the magnetic hysteresis collapses at $H>1\text{kG}$ and the measured magnetization turns noisy (Figs 1 and 2).

Following the tests depicted in Fig. 3 we have performed similar measurements across the phase diagram and determined the doping dependence of $T_{\text{onset}}$: the temperature below which for a given doping we first observe lack of congruence. Figure 4 summarizes the result: $T_{\text{onset}}$ has a strong doping dependence which broadly resembles $T_c(x)$ and $\Delta M(x)$ (Fig. 1(i)), and falls within the pseudogap temperature regime. In fact the values of $T_{\text{onset}}(x \geq 0.10)$ are in good agreement with $T^*(x \geq 0.10)^{2,3,10}$. The variation of $T_{\text{onset}}$ and $\Delta M$ with $x$ indicates the association of the domain structure with the key parameter tuning the properties of HTS: carrier concentration.

We would like to emphasize that it is impossible for our observations to be due to an undetected impurity. Although the size of the magnetic effects observed here could be speculatively attributed to undetectable Fe impurities, of the order of 10-30 ppm, such impurities cannot not cause the doping dependence of $\Delta M$ and $T_{\text{onset}}$, the lack of congruence below $T_{\text{onset}}$, or the dependence of the effect on the orientation of the applied magnetic field. Therefore, the observed magnetic order must be intrinsic to the system.

Several theories which involve some form of ordering have been proposed to account for the anomalous normal state of HTS$^{2,3,8-10}$. There is no prevailing view of the pseudogap physics and no experimental signatures which describe or favor consistently a particular
proposal. A key however to understanding the pseudogap state is the identification of the associated elusive order and as mentioned earlier the underlying signature of the latter is a domain structure. With this in mind we optimized our experiments to search for its presence and discovered that indeed there is a domain structure, one displaying typical return point memory and domain wall motion characteristics. Although, the question whether the magnetic order identified in the present study is indeed related to the physics of the pseudogap and superconductivity remains to be answered, we hope the systematic results reported here have at least provided compelling evidence to motivate further investigations into this direction.

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17. J.R. Waldram, Superconductivity of metals and cuprates (Institute of Physics, 1996).

FIG. 1 Magnetization ($M$) and remnant magnetization ($\Delta M$) as a function of $dc$ field and doping ($x$), respectively, for La$_{2-x}$Sr$_x$CuO$_4$. (a, b) Data obtained with increasing $H$ on polycrystalline samples with $x=0.07$ ($T_c=14$K) and $x=0.22$ ($T_c=27.5$K), respectively, at 50K and 300K. The circled regions highlight the deviation from paramagnetism at low fields. The inset in (a) depicts low field data for $x=0.07$ at $T=50$K showing the continuous increase in magnetization even after the hysteresis (shown as the difference between the
black and red curves) has collapsed. The arrows indicate the trajectories followed in changing the applied field. (c, d) Low field data for a La$_{1.97}$Sr$_{0.03}$CuO$_4$ single crystal with $H//ab$ and $H//c$, respectively, showing the presence of a magnetic hysteresis at low fields. e-h) Low-field magnetization curves for polycrystalline La$_{2-x}$Sr$_x$CuO$_4$ ($x=0.07$-$0.24$) at $T>T_c$. Each panel depicts the field dependence of the magnetization for one value of doping at a given temperature. Panel (e) is a zoom-in plot of the inset in panel (a). Unlike panels (f-h), panel (e) includes data with decreasing field showing the magnetic hysteresis in the region where the data in panel (a) deviate from the paramagnetic behavior. i) Doping dependence of the remnant magnetization $\Delta M$ and superconducting transition temperature $T_c$. All results in this panel are for polycrystalline samples. The data for $x=0.03$ and 0.15 agree with the values obtained for single crystals with $H//ab$ and $H//c$ after accounting for the anisotropy. The data point of $\Delta M$ for $x=0.10$ has been divided by 10 for clarity.

FIG. 2  Magnetic hysteresis data for polycrystalline La$_{1.9}$Sr$_{0.10}$CuO$_4$ ($T_c=30$K) obtained at $T=45$K. Data in red show part of the virgin curve. The arrows indicate the trajectories followed in changing the applied field.

FIG. 3  Magnetic loops performed on the virgin curve for La$_{1.9}$Sr$_{0.10}$CuO$_4$ (polycrystal) and La$_{1.9}$Sr$_{0.15}$CuO$_4$ (single crystal). (a) The main plot shows a set of magnetic subloops for $x=0.10$ performed on the virgin curve at $T=45$K. The arrows denote the trajectories followed around the various loops. The lower inset compares the two subloops (A and B) shown on the main panel which were taken between the same applied field end points at $T=45$K. The upper inset shows subloops obtained the same way as in the lower inset but
at $T=300K$. The subloops in the insets have been shifted to zero for comparison. (b) Low-field magnetization data as a function of field for a La$_{1.85}$Sr$_{0.15}$CuO$_4$ single crystal ($T_c=37.5K$, $m=1.1mg$). Main panel: comparison of magnetic hysteresis subloops performed on the virgin curve at $T=70K$ by the same way as we did for $x=0.10$. The trajectories followed, as well as the colors and symbols are in accordance with those in panel (a). The inset depicts the magnetization subloops performed on the virgin curve at $T=275K$.

FIG. 4 Doping dependence of the onset temperature $T_{\text{onset}}$ (blue circles) of the normal state magnetic order. The blue colored region depicts the ($T, x$) regime where the measured magnetic order is present (i.e., $T<T_{\text{onset}}$) and the red colored region depicts the region of superconductivity (i.e., where $T_c>0$). The magnetic order data for $x=0.03$ and $0.15$ are for the single crystals with $H//ab$. 
Panagopoulos_Fig. 1
Panagopoulos_Fig. 2
Panagopoulos Fig. 3

a) $x=0.10$
$T=300K$

b) $x=0.15$
$H//ab$
$T=70K$

$M$ (emu)

$H$ (G)

$A$
$B$

$A$
$B$

$x=0.10$
$T=45K$

$x=0.15$
$T=275K$
Panagopoulos Fig. 4

![Graph showing the relationship between temperature and carrier concentration, with regions marked for magnetic order and superconductivity.]

- Temperature (K) on the y-axis
- Carrier concentration (x) on the x-axis
- Magnetic order
- (interacting domains)
- Superconductivity