Flux pinning and phase separation in oxygen-rich $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4+y$

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We have studied the magnetic characteristics of a series of superoxygenated $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples. As shown in previous work, these samples spontaneously phase separate into an oxygen-rich superconducting phase with a $T_C$ near 40 K and an oxygen poor magnetic phase that also orders near 40 K. The oxygenated samples studied are highly magnetically reversible even to low temperatures. Although the internal magnetic regions of these samples might be expected to act as pinning sites, our present study shows that they do not favor flux pinning. Flux pinning requires a matching condition between the defect size and the superconducting coherence length. Thus, our results imply that the magnetic regions are too large to act as pinning centers. This also implies that the much greater flux pinning in typical $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ materials is the result of nanoscale inhomogeneities that grow to become the large magnetic regions in the superoxygenated materials. The superconducting regions of the phase separated materials are in that sense cleaner and more homogenous than in the typical cuprate superconductor.

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I. INTRODUCTION

$\text{La}_2\text{CuO}_4$ holds an important place in studies of high-temperature superconductors (HTSC). It is the parent compound of the first cuprate superconductor discovered by Bednorz and Muller.1 Among the most intensively studied cuprate compounds, doped $\text{La}_2\text{CuO}_4$ has the simplest structure. The system can be hole doped to produce a superconductor either by cation substitution ($\text{La}_{2-x}\text{M}_x\text{CuO}_4$) or intercalation of excess oxygen ($\text{La}_2\text{CuO}_4+y$), or both.2–5 The standard phase diagram for the cuprates is based upon $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. It is also in doped versions of $\text{La}_2\text{CuO}_4$ that the well-known $1/8$ anomaly occurs: Superconductivity is at least partially suppressed and an incommensurate ordered magnetic phase appears, often described as a stripe phase.7 Previous studies have shown that doped holes in the system do not necessarily have a uniform density but may phase separate into hole rich phase and hole poor phase. There is evidence for such phases existing with a disordered, very short-range nature in cation doped $\text{La}_2\text{CuO}_4$ but may form much larger domains in systems doped via interstitial oxygen.8–10 Our recent studies on codoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ identified the coexistence of separate phases consisting of a $T_C=40$ K optimally doped superconductor ($n_h=0.16$) and a spin-density wave, or stripe phase, that also orders near 40 K ($n_h=1/8$).10 These phases occur at a given hole density regardless of the specific amount of Sr (x) or O (y), thus indicating that the phase separation is driven by the physics of the doped holes themselves.

Much research has focused on the complex interplay between the Cu moments and superconducting properties of cuprate superconductors.11–13 One consequence of this interplay is the field-dependent magnetic response of the superconducting properties, such as hysteretic diamagnetic response, flux trapping, and irreversibility. A primary motivation for such studies is the desire to improve the current carrying capabilities of superconducting cables by increasing flux pinning. For the purest materials that can be made, such pinning is generally rather large in the cuprates compared to traditional, elemental superconductors. Although it is not a primary candidate for cables, some such experiments have been performed on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.14,15 Very few such studies have been reported for superoxygenated $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4+y$. In this study, we report the magnetic response of the superconducting state of several samples of superoxygenated $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ in large fields. Other studies have shown that the trapped flux and thus the critical current density can be increased by introducing artificial pinning sites through the use of either substitutional defects or radiation damage.16–19 Since the superoxygenated compounds have nonsuperconducting regions it might be expected that these would act as pinning centers as well. However, we have found that in fact flux pinning in the superoxygenated materials is substantially reduced compared to purely cation doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. We argue that this is evidence that the typical cation doped lanthanum cuprate may contain nanoscale inhomogeneities that are effective in trapping flux while in the superoxygenated material such separate domains grow to a length scale on the order of microns and are thus ineffective at pinning flux.

II. SAMPLE PREPARATION

In this work, we investigated a series of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples by varying the Sr content ($x=0, 0.04$ and $0.09$). The samples consisted of both crucible grown and float-zone-grown single crystals. $\text{La}_2\text{CuO}_4$ ($x=0$) was prepared by slow cooling from the melt in a Pt crucible.20 The remaining two samples were traveling solvent float-zone-grown single crystals and were synthesized as discussed in Ref. 21. We chose to use samples from very different synthesis techniques in order to test the magnitude of general sample to sample variations in the magnetization compared to those between regular cation doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and our superoxygenated...
samples. Initially, neither the $x=0$ nor the $x=0.04$ sample was superconducting, the former was antiferromagnetic and the latter apparently was in the intermediate spin-glass regime.\cite{22} The $x=0.09$ sample was superconducting with a $T_C$ that is consistent with the well-known phase diagram for La$_{2-x}$Sr$_x$CuO$_4$.\cite{23} We intercalated excess oxygen into all of our samples using wet chemical techniques as discussed in Ref. 3. The process took weeks to months to produce well-oxygenated homogeneous samples. As we reported in our earlier work, after oxidation all of the samples are phase separated between a stripelike magnetic phase with $n_h=0.125$ and an optimally doped superconductor with $n_h=0.16$.\cite{10} The $x=0$ sample was 66% magnetic, the $x=0.04$ sample was 42% magnetic, and the $x=0.09$ sample was 51% magnetic as measured using muon spin rotation ($\mu$ SR). The rest of the sample is the superconducting phase. More details are given below.

III. MAGNETIZATION EXPERIMENTS

In order to obtain information concerning the superconducting transition and flux penetration in the superconducting state, a variety of magnetization experiments were carried out. After intercalating excess oxygen into the samples, the magnetization was measured using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. Magnetization versus temperature scans were obtained with both zero-field cooling (ZFC) and field cooling (FC) conditions using a small external magnetic field (10 Oe) along the $c$ axis of the single crystals. Figure 1 shows the FC magnetization versus temperature, with the signal normalized by the maximum ZFC response for that crystal. This normalization accounts for demagnetization effects and follows the approach of Kodama et al.,\cite{14} a source used extensively for comparisons below. After oxidation, all samples developed a Meissner response with a superconducting transition temperature near $T_C=40$ K. The superconducting transition temperature is similar for all samples, but the superconducting volume fraction differs from sample to sample. The maximum Meissner signal reflects the variation in superconducting phase fraction but is not an exact measurement of superconducting volume. We do find that the $x=0.04$ sample has the largest Meissner signal and the $x=0$ sample the smallest. This is consistent with our previous result that the $x=0.04$ sample had the smallest magnetic phase fraction and the $x=0$ sample the largest.\cite{10} The superconducting volume should vary in the opposite manner.

The key measurements obtained in this work are the magnetization versus applied field scans at a variety of temperatures in the superconducting state. These experiments were carried out in order to investigate the flux pinning in our samples. For these measurements, the samples were aligned with the magnetic field either parallel or perpendicular to the crystalline $c$ axis. The samples were $ZF$ cooled to the desired temperature and then the field was swept from 0 to 50 kOe and back to 0. In some cases we performed a full hysteresis loop by sweeping the applied field from 0 to 50 kOe, then −50 kOe, and finally back to 0.

Typical magnetization results for our samples are reported in Fig. 2 and Fig. 3. In Fig. 2 the magnetization curves are shown for the case where the magnetic field is applied parallel to the $c$ axis for the samples with Sr content $x=0$, 0.04 and 0.09. In Fig. 3, similar results are shown for the case where the field is applied perpendicular to the $c$ axis for the samples with $x=0$, 0.04 and 0.09. These curves can be characterized by two parameters. The first is the openness of the curves, $\Delta M=M(H^+)-M(H^-)$, with $M(H^+)$ being the value of $M$ at a given $H$ for increasing field and $M(H^-)$ being the value of $M$ at a given $H$ for decreasing the field in the hysteresis loop. The value of $\Delta M$ is determined by the amount of flux trapped in the sample upon reversal of the applied
field and, according to Bean’s critical model calculations, it is related to the critical current density, \( J_C \). The absolute value of \( J_C \) depends on the sample type and shape; however, in general \( J_C \) is directly proportional to \( \Delta M \). As can be seen in Fig. 2, at 10 K and \( H \parallel c \), the three samples have an average \( \Delta M_{\text{max}} \) of about 15 emu/g. As shown in Fig. 3 when the field is applied perpendicular to the crystallographic \( c \) axis the average \( \Delta M_{\text{max}} \) reduces to about 10 emu/g. These values are about an order of magnitude smaller than the previously reported values for other high-temperature superconductors. Since \( J_C \) is directly proportional to \( \Delta M \), we can conclude that the current density for our samples is about an order of magnitude smaller than that of the reported values for other high \( T_C \) materials.\(^{14,25,26}\)

The second parameter derived from the magnetization data is the irreversibility field, \( H_{\text{irr}} \), which is the field at which the magnetization upon decreasing the applied field separates from the magnetization upon increasing the field. This number is related to the pinning energy for flux vortices. The sample to sample variation we observe for \( H_{\text{irr}} \) is somewhat larger than that for \( \Delta M_{\text{max}} \). None of these variations are obviously correlated with materials parameters such as \( \text{Sr} \) content, so we assume they are related to the overall crystal defect levels. However, this variation is small compared to the results from similar high-temperature superconductors with other dopant ions.\(^{27}\) Thus we can make meaningful comparisons of the average values we find for \( H_{\text{irr}} \) with other high-temperature superconductor results from the literature. At 10 K, our samples have an average value of \( H_{\text{irr}} \) near 22 kOe for the case of the field applied along the \( c \) axis as read off from the data of Fig. 2. From Fig. 3, it can be seen that there is a substantially larger \( H_{\text{irr}} \) when the field is applied perpendicular to the \( c \) axis, although the total amount of trapped flux, \( \Delta M_{\text{max}} \), is not larger. The average number for \( H_{\text{irr}} \) in this case at \( T=10 \) K is near 50 kOe. Our results, most notable strongly reversible magnetic response, are in good agreement with a previously reported study of a crucible grown, superoxygenated crystal of \( \text{La}_3\text{CuO}_4\text{y} \) that was most likely phase separated in the same manner as our samples.\(^{27}\)

IV. DISCUSSION

The most useful published data for comparison to our flux pinning data is a similar single crystal study of \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) performed by Kodama et al.\(^{14}\) In Fig. 3 of Kodama et al., magnetization versus field scans are shown for several single crystals, all with applied magnetic field parallel to the \( c \) axis. The most relevant samples for comparison is that for which \( x=0.14 \) and 0.15, roughly similar in total hole concentration to our samples. The Meissner fractions reported for these two samples can be seen from Fig. 1 of Kodama et al. to be about 10% or less. Those values are similar to our \( x=0.09 \) and \( x=0 \) samples and about a factor of 3 smaller than for our \( x=0.04 \) sample. From the magnetization versus field scans at 10 K, Kodama et al. find an irreversibility field, \( H_{\text{irr}} \), well above 50 kOe and a maximum separation, \( \Delta M \), of about 140 emu/g. Figure 4 shows the \( \Delta M \) values derived from Fig. 3 in Kodama et al. and the \( \Delta M \) values measured at 10 K for our samples. The superoxygenated samples have far less flux pinning. The \( \Delta M \) values for optimally doped \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) are approximately an order of magnitude larger than those we observe in the superoxygenated samples. \( H_{\text{irr}} \) is not well determined for the \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) samples but appears to be five times or greater than for the superoxygenated samples. We conclude that there is substantially less flux pinning in the superoxygenated samples as compared to most high-temperature superconductors with similar overall hole concentration.
In general, pinning sites in a superconductor are formed by regions with a suppressed superconducting order parameter. However, the site has to be approximately the same size as the superconducting correlation length. For 214-type superconductors, the in-plane correlation length is known to be about 10 Å. Regions much larger than this which have a suppressed superconducting order parameter will tend to form a separate nonsuperconducting phase, and thus, not strongly interact with the superconductor.

There are some excellent studies of flux trapping using well-controlled, artificially created defects that form regions with reduced superconductivity. These have typically involved either ion beam damage or impurity precipitates. For example, enhanced flux pinning was observed in Bi$_2$Sr$_2$CaCu$_2$O$_{8+}$ single crystals embedded with MgO particles by Zhao et al. In these experiments nanometer-sized particles of MgO were introduced into the superconductor crystals and the critical current density, $J_C$, was measured. $J_C$ is proportional to $\Delta M$ in our measurements. It was found that for MgO concentrations below 10%, $J_C$ at low temperatures were increased by over a factor of 3 compared with the samples without MgO. However, for concentrations of MgO above 10%, $J_C$ begins to decrease with further increase in impurities. Zhao et al. further found that when the defect concentration is large, particles assemble to form regions that have sizes greater than 10 μm. Apparently, these regions do not act as effective pinning sites.

Other experiments have reached similar conclusions. For example, Rudnev et al. report an enhancement of the critical current density in Bi$_2$Sr$_2$CaCu$_2$O$_{10+d}$ when nanodimensional inclusions of tantalum carbide, niobium carbide or niobium nitride are introduced. When the sizes of the introduced regions exceed 30 nm the critical current density decreases. The larger pinning sites not only do not favor flux pinning but in fact reduce the overall trapped flux in a material. Pu et al. also studied a series of Bi$_{1.8}$Pb$_{0.2}$Sr$_2$Ca$_{2-x}$Pr$_x$Cu$_4$O$_y$ samples with different amounts of Pr substitution. When the concentration of Pr is low they act as normal-like defects and enhance flux pinning. However when the Pr doping is increased up to a certain level, Pr or the defects induced by the Pr doping will congregate into large defect regions and reduce flux pinning. Based on the pinning force scaling analysis and microstructure observations this work concludes that only pointlike Pr defects significantly enhance flux trapping while large defect conglomerations reduce the total pinning. Thus there is a large amount of evidence that the total amount of pinning in a high $T_c$ superconducting sample depends on the number of point defects present only up to a value above which the defects are no longer small and isolated. When defects can conglomerate into larger structures that substantially exceed the size of the vortex cores then both the pinning strength and the total trapped flux decrease.

In light of these comparisons, our data not only reveal information concerning the size of the phase separated magnetic regions in our superoxygenated samples, but also give an indication of how those regions evolve from the more well-controlled, artificially created defects that form regions with reduced superconductivity. These have typically involved either ion beam damage or impurity precipitates. For example, enhanced flux pinning was observed in Bi$_2$Sr$_2$CaCu$_2$O$_{8+}$ single crystals embedded with MgO particles by Zhao et al. In these experiments nanometer-sized particles of MgO were introduced into the superconductor crystals and the critical current density, $J_C$, was measured. $J_C$ is proportional to $\Delta M$ in our measurements. It was found that for MgO concentrations below 10%, $J_C$ at low temperatures were increased by over a factor of 3 compared with the samples without MgO. However, for concentrations of MgO above 10%, $J_C$ begins to decrease with further increase in impurities. Zhao et al. further found that when the defect concentration is large, particles assemble to form regions that have sizes greater than 10 μm. Apparently, these regions do not act as effective pinning sites.

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In light of these comparisons, our data not only reveal information concerning the size of the phase separated magnetic regions in our superoxygenated samples, but also give an indication of how those regions evolve from the more commonly studied cation doped La$_{2-x}$Sr$_x$CuO$_4$. There are a variety of experiments, notably scanning tunneling microscopy (STM) imaging, nuclear magnetic resonance (NMR) and muon spin rotation ($\mu$ SR) studies, that indicate the presence of inhomogeneity on a short, nanometer scale in most cuprate superconductors. On the other hand, there are several results which indicate that the separate magnetic and superconducting regions in the superoxygenated samples are quite large. Among these are the presence of a Meissner signal itself, requiring superconducting regions on the order of a penetration depth. We have carried out high-field $\mu$ SR that reflect the behavior of a muon in a vortex lattice state. The associated relaxation parameter matches that from optimally doped La$_{2-x}$Sr$_x$CuO$_4$ thus indicating that the penetration depth in both samples is about the same and that the superconducting regions in the superoxygenated samples are at least as large as a penetration depth. Neutron-scattering measurements of the magnetic phase by both our own group and Lee et al. show narrow peaks indicating an in-plane coherence of 400 Å or greater.

Thus it is natural to consider that the primary difference between the phase separated, superoxygenated compounds we report here and cation doped La$_{2-x}$Sr$_x$CuO$_4$ is the length scale associated with inhomogeneities, with the former having much larger phase separated regions. The nanoscale inhomogeneity reported for La$_{2-x}$Sr$_x$CuO$_4$ apparently provides many strong flux pinning centers. However, the much larger phase separated regions present in the super-oxygenated materials are not truly part of the superconducting matrix and not effective at pinning flux. A similar argument might also explain why there is substantial amount of flux pinning when the field is applied perpendicular to the c axis. In this case the flux is pinned between planes. Through an analysis of neutron peaks, Lee et al. have reported that the magnetic regions extend for only 13 Å in the c-direction. The shorter length scale perpendicular to the planes is more suitable for flux pinning and enhances the pinning energy. However, there are fewer pinning sites between the planes and as a result the overall flux trapping is small when compared to the c parallel case.

Taken together, the flux pinning results indicate that in some sense the separated superconducting regions in the superoxygenated compounds are more pure than typical superconducting La$_{2-x}$Sr$_x$CuO$_4$; within the superconducting regions there are fewer areas of weak superconductivity to trap flux. There is less charge inhomogeneity in the superconducting regions of the fully phase separated compound than in the usual La$_{2-x}$Sr$_x$CuO$_4$. This might also explain why the superoxygenated samples have critical temperatures above 40 K while the highest $T_c$ in cation doped La$_{2-x}$Sr$_x$CuO$_4$ is near 38 K. While charge inhomogeneity is beginning to appear ubiquitous in high-temperature superconductors, it may not be essential to the phenomenon.

V. CONCLUSION

The superconducting phase of superoxygenated and phase separated La$_{2-x}$Sr$_x$CuO$_{4+}$ traps little flux compared to most high-temperature superconducting samples. The lack of flux trapping appears to be due to the separated magnetic regions being too large to act as pinning centers. Furthermore, the presence of relatively strong trapping in optimally cation
doped La$_2$-$_x$Sr$_x$CuO$_4$ without excess oxygen may be due to nanoscale inhomogeneities that act as flux trappers. This view indicates that most high-temperature superconductors are inhomogeneous. Doping the structure with highly mobile interstitial oxygen allows for the inhomogeneous regions to grow to microlike length scales so that the separate regions are easily measured. The superconducting regions of these phase separated samples may provide a new materials system for exploring the superconducting properties of a more pure high $T_C$ superconductor.

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