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Precursor diamagnetism above the superconducting transition in $La_{1.9}Sr_{0.1}CuO_4$

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High-resolution isothermal magnetization curves above the transition temperature T_c in a single crystal of superconducting underdoped cuprate $La_{1.9}Sr_{0.1}CuO_4$ ($T_c = 26$ K) are reported. For magnetic field $H \geqslant 1$ kOe the diamagnetic magnetization is rather well described by the Ginzburg-Landau theory in finite fields, as observed in previous works. On the contrary, in the low-field range and for T within $T_c + 2$ K, evidence is given for precursor diamagnetism of different character, with magnetization curves displaying an upturn in the field dependence and magnetic-history dependent effects below $T \simeq 27$ K. These findings are the magnetic counterpart of the observation by scanning superconducting quantum interference device microscopy of regions precursor of bulk superconductivity. The interpretation of the experimental data in terms of phase fluctuations of local order parameter is shown to account for most of the aspects of the precursor diamagnetism, which appears to be a general phenomenon in cuprates.

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On approaching the transition temperature T_c from above, superconducting fluctuations occur, with an average order parameter $\sqrt{\langle|\psi|^2\rangle}$ different from zero, related to local concentration of fluctuating Cooper pairs. The formation of fluctuating pairs causes[1] the appearance, above T_c, of a Langevin-type diamagnetic contribution $-M_{fl}(T,H)$ to the total magnetization, which also includes the paramagnetic contribution M_P from carriers. This *fluctuating diamagnetism* is enhanced in cuprate superconductors (SC) because of their small coherence length, reduced carrier density, strong anisotropy, and high transition temperature T_c.[2] Since the size of fluctuating pairs $\xi(T)$ grows when the temperature approaches T_c, $-M_{fl}$ is expected to show a progressive increase on cooling from above. On the other hand very high magnetic fields, comparable to the critical field $H_{c2}(0)$, must evidently suppress the superconducting fluctuations. Thus the isothermal magnetization curves $-M_{fl}$ ($T = \text{const}, H$) have to exhibit an upturn. The value of the upturn field H_{up} for layered superconductors in the framework of the Ginzburg-Landau (GL) phenomenology is inversely proportional to the square of the coherence length $\xi(T)$.[1,3] Therefore, while in conventional BCS superconductors the values of H_{up} are rather small[1,4] (typically around 50–100 Oe), in high T_c SC's, due to the extremely small coherence length the upturn in $-M_{fl}$ versus H could be detected, in principle, only in very high fields, even for temperatures close enough to T_c. Correspondingly, in $YBa_2Cu_3O_7$ (YBCO optimally doped) the magnetization curves, in the vicinity of the transition temperature and for $H \ll H_{c2}$ (when the contribution from short-wavelength fluctuations is negligible[1]), are rather well justified in the framework of the GL theory with an anisotropic free-energy functional.[5–7] For $T \approx T_c$ one has $-M_{fl} \propto \sqrt{H}$ (Prange regime[1]) and, by increasing the field, saturation of $-M_{fl}$ is expected.[5] The data for $M_{fl}/\sqrt{H}$ as a function of temperature cross at $T_c(0)$. Furthermore, scaling arguments[8,9] can be used and the features characteristic of anisotropic three-dimensional (3D) systems have been found to occur in optimally doped YBCO.[6,7,9–11]

On the contrary, in underdoped and in overdoped YBCO's, with $T_c < T_c^{max}$, dramatic deviations from the conventional GL behavior have been detected. Marked enhancement of the reduced magnetization $m(T_c) = -M_{fl}/\sqrt{H}T_c$ has been observed with magnetization curves showing an upturn around $H_{up} \approx 200$ Oe. Furthermore, in some cases, magnetic-history dependent effects[12] were also detected. These features could be justified by the hypothesis of nonpercolating superconducting "islands" having local T_c^{loc} higher than the bulk transition temperature T_c.[13] Then the theoretical description of phase fluctuations of non-zero-order parameter in layered liquid of vortices,[14] extended[12,13] in order to include irreversibility effects, seemed to account for the experimental findings.

A support to the hypothesis of superconducting droplets above the bulk T_c was offered by the observation, by means of scanning superconducting quantum interference device (SQUID) microscopy,[15] of inhomogeneous magnetic domains with diamagnetic activity in underdoped $La_{1.9}Sr_{0.1}CuO_4$ (LASCO). The isothermal ($T = 27.9$ K) magnetization curves $-M_{fl}$ versus H in grain-aligned $La_{1.9}Sr_{0.1}CuO_4$ with $T_c(0) = 27.1$ K, up to 50 kOe,[16] apparently did not show any upturn with the field and were essentially explained in terms of GL fluctuations. The apparent lack of precursor diamagnetism in underdoped LASCO was a puzzling issue, which could rule out the idea of precursor diamagnetism of general character in nonoptimally doped cuprates.

In the present paper we solve the apparent contrast between SQUID microscopy and magnetization curves. By means of high-resolution magnetization measurements in a single crystal of underdoped $La_{1.9}Sr_{0.1}CuO_4$, we show that the nonconventional precursor diamagnetism does occur in underdoped LASCO, with isothermal magnetization curves exhibiting the upturn with the field and the effects characteristic of precursor SC droplets. Insights on the properties of the precursor SC droplets are obtained by resorting to a the-

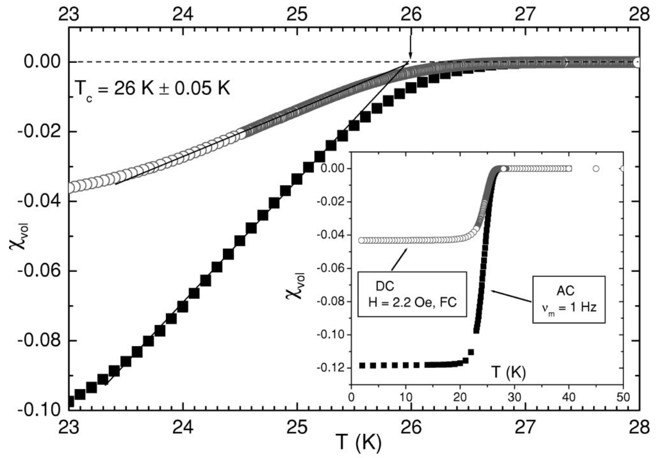

FIG. 1. Temperature dependence of the magnetic susceptibility in the single crystal of $La_{1.9}Sr_{0.1}CuO_4$ for DC field $H=2.2$ Oe or AC field amplitude $\Delta H\sim 1$ Oe and estimate of the transition temperature. In the inset the behavior in a wide temperature range is reported.

oretical description of phase fluctuations of local order parameter and the generality of the precursor diamagnetism in nonoptimally doped cuprates is pointed out.

The sample (kindly lent by M. H. Julien, Grenoble) has been grown by Revcolevschi (Paris Sud) by the traveling solvent floating-zone method. The single crystal has a thickness of about 0. 2 mm and the largest face is semicircle shaped with a diameter $\sim$3 mm. Neutron scattering and x-ray diffraction confirmed that the sample is constituted by a very high quality single crystal (see Refs. 17,18).

Magnetization measurements have been carried out by means of the Quantum Design MPMS-XL7 SQUID magnetometer. The magnetization curve up to magnetic field $H=70$ kOe, at $T\simeq 300$ K, evidences the Pauli-like linear behavior M_P versus H. A certain amount of ferromagnetic impurities causes a very small contribution to the magnetization, M_{imp}, saturating at $H\simeq 2$ kOe. (M_P+M_{imp}) were found to be only lightly temperature dependent in the normal state. Thus the diamagnetic contribution $-M_{fl}$ due to the fluctuating Cooper pairs on approaching T_c was obtained by subtracting from the raw data the magnetization (M_P+M_{imp}) measured at $T\simeq 40$ K, where $-M_{fl}$ was practically zero.

The transition temperature was estimated by applying a field of 2. 2 Oe along the c axis and extrapolating at zero the linear behavior of $-M_{fl}$ on cooling below T_c (Fig. 1). One has $T_c(0)=26\pm 0.05$ K. In the inset of Fig. 1, DC and low-frequency AC susceptibilities are reported. The high quality of the sample is indicated by the sharpness of the transition and by the equivalence of the DC and AC data for $T\rightarrow T_c^-$ while the expected difference between field cooled (FC) and zero-field-cooled (ZFC) behaviors occurs for $T\ll T_c$.

In Fig. 2(a) the magnetization curves up to 7 T are reported. Neglecting the effects for small magnetic fields (H $\leqslant 0.1$ T), which will be discussed later on, the analysis can be carried out on the basis of the well-known free-energy functional of GL character:

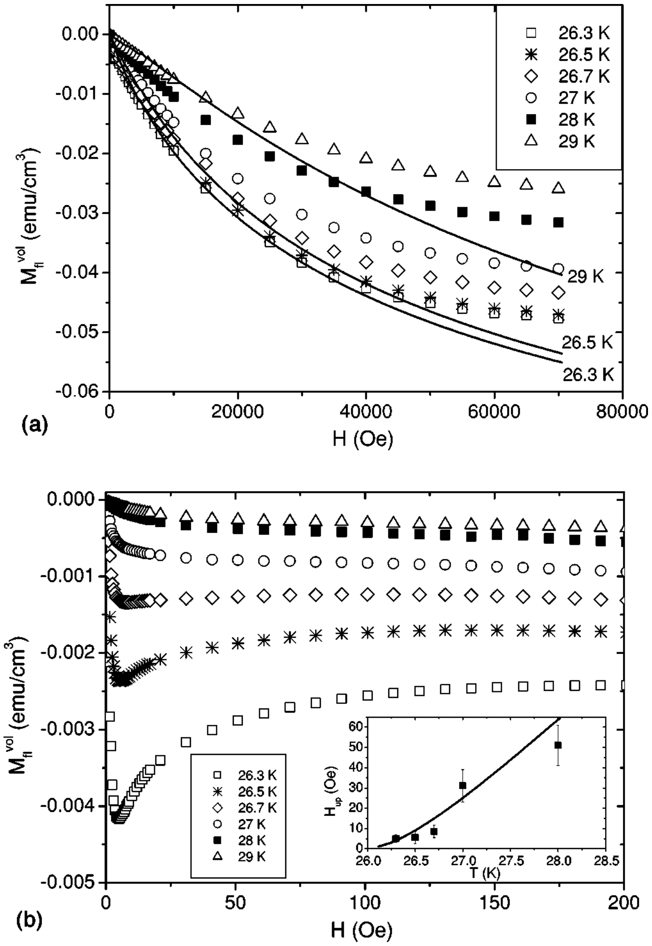

FIG. 2. Magnetization curves $-M_{fl}$ vs H at different temperatures; (a) in the whole explored range of magnetic field H and (b) in the range 1 Oe$\leqslant H\leqslant$200 Oe. The solid lines in (a) are the theoretical behaviors in correspondence to the Gaussian approximation for anisotropic GL functional [see Eq. (2) in the text], for reduced temperature $\epsilon=(T-T_c)/T_c=1.1\times 10^{-1}$, $\epsilon=1.9\times 10^{-2}$, and $\epsilon=1.1\times 10^{-2}$, for the anisotropy parameter $r=2\xi_c^2/s^2=0.1$ (s interlayer spacing, see Ref. 3) and critical field $H_{c2}=300$ kOe. In the inset in (b), the temperature behavior of the upturn field H_{up} is evidenced. The solid line is a guide to the eye.

$$F(\psi)=\sum_n \int d^2\vec{r}\left[a|\psi|^2+\frac{b}{4m_\parallel}|\psi|^4 + \left|\left(\nabla_\parallel-\frac{2ie}{c\hbar}\vec{A}\right)\psi_n\right|^2+t|\psi_{n+1}-\psi_n|^2\right], \qquad (1)$$

where t is the tunneling coupling between the nth and $(n+1)$th layer. The magnetization can be obtained by numerical derivation of the free energy (as in Refs. 12,19) or by analytical derivation[10] using the Hurwitz functions.

As shown by the solid lines in Fig. 2(a), on approaching the transition temperature the 3D nonlinear behavior $M_{fl}\propto\sqrt{H}$ is attained. The conclusions that can be extracted about the field and temperature dependences of the ordinary GL contribution to the fluctuating magnetization are similar to the ones already reported in previous works[6,7,9,16,20] and we do not discuss them in detail here.

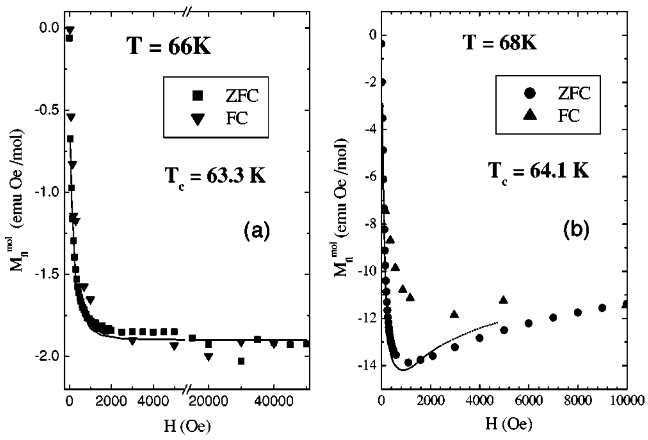

FIG. 3. Typical isothermal magnetization curves measured in two samples of underdoped YBCO for FC and ZFC conditions (see text).

The novelty to be remarked is represented by the contribution to $-M_{fl}$ detected in the low field range [Fig. 2(b)]. An analogous "anomalous" diamagnetism has been observed also in underdoped YBCO's (Fig. 3). It is believed that this precursor diamagnetism in underdoped LASCO and YBCO originates from *intrinsic charge inhomogeneities typical of cuprates*, causing nonpercolating regions with T_c^{loc} higher than the bulk transition temperature, as evidenced in LASCO by SQUID microscopy.[15] These islands are characterized by non-zero-order parameter with frozen amplitude.[21,22] The intrinsic character of such anomalous diamagnetism is confirmed by the temperature behavior of the upturn field H_{up}, reported in the inset of Fig. 2(b). As can be noted, H_{up} *increases* with temperature, and this will be shown to be a characteristic mark of phase fluctuations. On the contrary, if one could simply have in the sample a distribution of local T_c's as related, for instance, to impurities, then the upturn field would practically coincide with H_{c1} and therefore would *decrease* with temperature.

The solid lines in Fig. 3 are the theoretical behaviors according to the mechanism of phase fluctuations for locally superconducting droplets above [Fig. 3(a)] and below [Fig. 3(b)] the local irreversibility temperature.[12,13] In ZFC measurements one cools the sample in zero field to a given temperature (above T_c) and then the field is applied. In FC measurements a given magnetic field is applied at room temperature, the crystal is cooled at the same ZFC temperature and the corresponding magnetization is measured.

By resorting to the theory developed for phase fluctuations,[12,13] information on the precursor diamagnetism in underdoped LASCO can be derived, as outlined in the following.

The non-GL diamagnetism appearing in the low-field range [Fig. 2(b)] is related to vortices generated, in principle, both by the external field H and by the phase fluctuations of the local order parameter. A field-dependent diamagnetic susceptibility $\chi(H)$ can be derived from the second derivative of the free energy $F(\theta)$ obtained through Eq. (1), keeping $|\psi|^2$ constant and by taking into account the dependence from the phase θ:

$$F(\theta)=\frac{1}{s}\sum_n \int d^2\mathbf{r}\left[J_\parallel\left(\nabla_\parallel\theta_n-\frac{2ie}{c\hbar}A_\parallel\right)^2 + J_\perp\{1-\cos(\theta_{n+1}-\theta_n)\}\right], \qquad (2)$$

where $J_\parallel$ and $J_\perp$ are the order-parameter phase coupling constants on the plane and between the planes, respectively. The susceptibility depends on the current-current correlation function

$$\langle j(r)j(r')\rangle, \qquad (3)$$

where $j=\nabla\theta_n(\rho)-(2\pi/\Phi_0)A_\parallel(\mathbf{r})$, $r=(\rho,ns)$ being the vortex position with n being an integer and s the distance between layers. The irreversible behavior is due to the cross term in Eq. (2), describing the correlation between vortices in different positions. According to the Kosterlitz-Thouless model, the thermally excited vortices are correlated only below a certain temperature T_k. Above T_k a liquid vortex configuration is achieved and the cross terms in Eq. (2) go to zero.

Then, introducing $h=H/H^*$, with $H^*=\Phi_o/L^2$ being a characteristic field depending on the island dimension L, one has

$$\chi(h)=-\frac{k_BT}{s\Phi_0^2}\frac{1}{1+2n}\left(\frac{[1+\delta(h)^2]^2}{n_v} + s^2\gamma^2(1+n)n(1+\delta(h)^2)\right) + \frac{47L^2}{540}\frac{J_\parallel}{s}\left(\frac{2\pi}{\Phi_0}\right)^2\delta(h)^2, \qquad (4)$$

where γ is the anisotropy parameter and $\delta=\pi^2(J_\parallel/k_BT)$. Two terms contribute to the vortex density n_v: the thermally excited vortices, with density $n_{th}(h)=n_o\exp(-E_0/[k_BT(1+\delta(h)^2)])$, and field induced vortices with $n_F=(H^*h)/\phi_o$. In Eq. (4), δ approaches zero above T_k, where the third term, responsible for the upturn in the magnetization curves can be neglected.

The solid lines in Figs. 4 and 3(b) correspond to the contribution to the magnetization obtained from numerical integration of $\chi(h)$, as given in Eq. (4), pertaining to an anisotropy parameter $\gamma=7$, while n runs from 6 to 20 (with increasing temperature). For LASCO (Fig. 4), $E_0=2100$ K and $n_0=1.4\times10^{18}$ cm^{-2} are obtained from the temperature dependence of the susceptibility in the limit of $H\rightarrow0$.

Table I reports the values of δ and of the characteristic field H^* (and therefore of the size of the SC islands) resulting from the best fit of the experimental data. As appears from Fig. 4, a remarkable agreement of the theoretical predictions with the experimental findings is observed. The reliability of the description is pointed out in particular by the occurrence of the upturn in the field dependence for $T\leqslant27$ K, just the temperature above which irreversibility effects are no longer detected. The absolute values of the size of the SC droplets and their temperature dependence are in agreement with the phenomenological observation by scan-

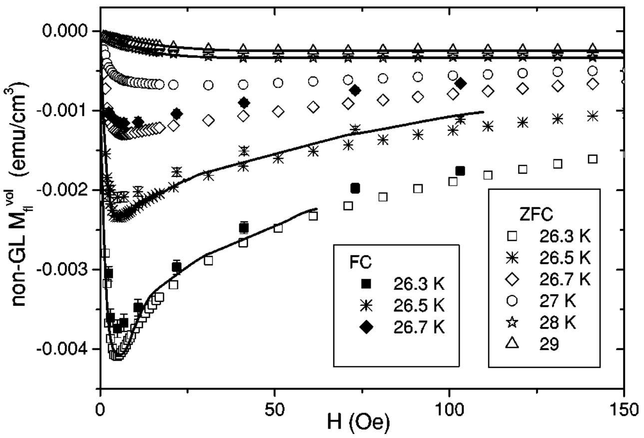

FIG. 4. Theoretical fits (solid lines), according to the picture of phase fluctuations of the order parameter in SC droplets above the bulk T_c, for the non-GL contribution to the diamagnetic magnetization in low field [see Fig. 2(b)]. Evidence of hysteretic effects is provided by the comparison of FC and ZFC magnetization curves (for $T \leqslant 26.7$ K). For $T \geqslant 27$ K FC and ZFC data practically coincide.

ning SQUID microscopy.[15] A percolative behavior of the SC islands on approaching the bulk transition temperature T_c is suggested from the data in Table I supporting the basic ideas of de Mello *et al.*[23]

Summarizing, from high-resolution magnetization measurements in a single crystal of underdoped superconductor LASCO we have shown that precursor diamagnetism occurs unrelated to conventional GL superconducting fluctuations. Our measurements allow one to achieve insights into the physical properties of the superconducting droplets having T_c^{loc} higher than the bulk transition temperature. The temperature dependence of the SC droplets on approaching T_c is deduced and it indicates a percolative character of the transition. The SC droplets are believed to be intrinsic consequence of the charge inhomogeneities at mesoscopic level occurring in all the superconducting cuprates.

TABLE I. Parameters δ and H^* as a function of the temperature T and estimate of the effective size L of the superconducting droplets above the bulk T_c (see text).

$T(K)$	δ	H^*(Oe)	$L(\mu\text{m})$
26. 3	39. 7	91. 74	0. 48
26. 5	29. 15	109. 68	0. 44
26. 7	23. 86	116. 07	0. 42
27	14. 8	227. 02	0. 30
28	5. 6	2737. 3	0. 09
29	0. 19	3750. 1	0. 07

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