Anomalous doping dependence of the fluctuation-induced diamagnetism in superconductors of YBCO family.

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Abstract

SQUID magnetization measurements in oriented powders of Y_{1-x}Ca_{x}Ba_{2}Cu_{3}O_{y}, with \(x\) ranging from 0 to 0.2, for \(y \approx 6.1\) and \(y \approx 6.97\), have been performed in order to study the doping dependence of the fluctuating diamagnetism above the superconducting transition temperature \(T_c\). While for optimally doped compounds the diamagnetic susceptibility and the magnetization curves \(-M_{fl}(T = \text{const})\) vs. \(H\) are rather well justified on the basis of an anisotropic Ginzburg-Landau (GL) functional, in underdoped and overdoped regimes an anomalous diamagnetism is observed, with a large enhancement with respect to the GL scenario. Furthermore the shape of magnetization curves differs strongly from the one derived in that scheme. The anomalies are discussed in terms of phase fluctuations of the order parameter in a layered system of vortices and in the assumption of...
charge inhomogeneities inducing local, non percolating, superconducting regions with $T_c^{(loc)}$ higher than the resistive transition temperature $T_c$. The susceptibility displays activated temperature behavior, a mark characteristic of the vortex-antivortex description, while history dependent magnetization, with relaxation after zero-field cooling, is consistent with the hypothesis of superconducting droplets in the normal state. Thus the theoretical picture consistently accounts for most experimental findings.

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I. INTRODUCTION

A variety of experiments\(^1\) points out that the small coherence length, reduced carrier density, high transition temperature \(T_c\) and marked anisotropy of cuprate superconductors cause strong enhancement of superconducting fluctuations (SF). In contrast to conventional superconductors, in cuprates the transition region is considerably smeared by SF which can be detected in a wide temperature range, up to 10-15 K. The formation of the fluctuation Cooper pairs above \(T_c\) results in the appearance of a Langevin-type diamagnetic contribution to the magnetization \(-M_{fl}(T,H)\), existing side by side to the paramagnetic contribution from fermionic carriers.

Since the size of fluctuating pairs \(\xi(T)\) grows when \(T\) approaches the transition temperature \(T_c\), \(M_{fl}(T,H)\) should diverge near the transition for any small fixed magnetic field, being equal zero for \(H = 0\). On the other hand it is evident that very strong magnetic fields, comparable to \(H_{c2}(0)\), must suppress SF. Therefore the isothermal magnetization curve \(M_{fl}(T = const, H)\) has to exhibit an upturn. This upturn can be quantitatively described in the framework of the exactly solvable, for any magnetic field, zero-dimensional model\(^2\) (superconducting granula with the size \(\ll \xi(T)\)) or by means of cumbersome microscopic treatment accounting for the short-wavelength fluctuation contribution in the 3D case.\(^3\)

The experiments on conventional BCS superconductors show that the magnetization is quenched for fields as low as \(\sim 10^{-2}H_{c2}(0)\) (see Ref.\(^2\)). The value of the upturn field \(H_{up}\) in the magnetization curves can be considered inversely proportional to the coherence length.\(^2,4\) This explains why in optimally doped high-temperature superconductors, the Ginzburg-Landau (GL) picture works pretty well. Here the coherence length is so short that the quenching of fluctuating magnetization on increasing the magnetic field has not yet been observed.

The fluctuating magnetization of layered superconductors in the vicinity of the transition temperature and for \(H \ll H_{c2}(0)\), when the contribution of short-wavelength fluctuations\(^3\) is negligible, can be theoretically described\(^5-7\) in the framework of the GL scheme with the
Lawrence-Doniach Hamiltonian. The fluctuating diamagnetism (FD) turns out to be a complicated nonlinear function of temperature and magnetic field and cannot be factorized on these variables. An important role in FD is played by the degree of anisotropy of the electronic spectrum. All these aspects of FD have been found to occur in optimally doped YBCO. Also scaling arguments were found rather well obeyed in this compound.

In underdoped YBCO, instead, marked deviations from the behaviour expected in the framework of GL approaches have been detected. A first qualitative claim in this regard goes back to Kanoda et al., who noticed that in oxygen deficient YBCO the FD in small fields was enhanced. Later on, novel features of FD in underdoped compounds have been reported. In particular, in underdoped YBCO at \( T_c \approx 63 \, K \) marked enhancement of the susceptibility for fixed \( T - T_c \) in a field of 0.02 Tesla was detected above \( T_c(0) \), with magnetization curves strongly different from the ones in optimally doped YBCO. Magnetization curves have been subsequently reported in underdoped \( La_{1.9}Sr_{0.1}CuO_4 \) (LASCO). For the moment we only mention that the magnetization curves reported by Carballeira et al. in underdoped LASCO, although indicating field-affected fluctuation-induced diamagnetism, do not exhibit the upturn with the magnetic field as the ones in underdoped YBCO that we will discuss later on. Finally, recent magnetization data as a function of temperature in \( YBa_2Cu_3O_6.5 \) single crystal (with transition temperature in zero field \( T_c(0) = 45K \)) indicate SF obeying to 2D scaling conditions for \( H \gtrsim 1 \) Tesla and turning to 3D scaling for smaller fields.

Qualitative justifications of the anomalous diamagnetism in underdoped YBCO have been tried, essentially based on the idea of charge inhomogeneities leading to non-percolating superconducting "drops" or on the extension of the theory by Ovchinnikov et al., where the anomalous diamagnetism is related to regions having local \( T_c \)'s higher than the resistive transition temperature. The first theoretical study specifically aimed at the description of FD in underdoped YBCO was undertaken by Sewer and Beck. In the framework of the Lawrence-Doniach model, these authors justify the temperature and field dependences of the magnetic susceptibility by taking into account the phase fluctuations of
the order parameter, thus arriving to a layered XY-model for a liquid of vortices.

In this paper we address the problem of the fluctuating diamagnetism in the $Y_{1-x}Ca_xBa_2Cu_3O_y$ family and of its dependence from the number of holes, by reporting SQUID magnetization measurements in a series of samples. Preliminary results on overdoped compounds have been presented to a meeting and published elsewhere. Since some differences in the magnetic behaviour of chain-ordered and chain-disordered YBCO have been noticed, we also attained the underdoped regime by means of $Ca^{2+}$ for $Y^{3+}$ substitution in ideally chain-empty $YBa_2Cu_3O_6$, while for the overdoped regime the same heterovalent substitution was performed in chain-full $YBa_2Cu_3O_7$.

The paper is organized as follows. In Sect.II experimental details and the majority of the experimental results are reported. The analysis of the data (Sect.III) is first tentatively carried out on the basis of an anisotropic free energy GL functional, within the Gaussian approximation. The inapplicability of such an approach for non-optimally doped compounds is stressed. Then the theory for phase fluctuations of the order parameter in layered liquid of vortices is revised, to properly take into account terms neglected in the previous formulation. In particular non-reversibility and relaxation effects of the magnetization are argued to support the picture of non-percolating, locally superconducting droplets above the resistive transition temperature, that we interpret as phase fluctuations of a non-zero order parameter below the local irreversibility temperature. Thus a comprehensive description of FD in the $Y_{1-x}Ca_xBa_2Cu_3O_y$ family is obtained, as it is summarized in Sect. IV.

### II. EXPERIMENTAL DETAILS AND RESULTS

The samples of chemical composition $Y_{1-x}Ca_xBa_2Cu_3O_y$ were prepared by solid state reactions of oxides and carbonates in flowing oxygen at 1000 K for about 100 hours. X-Ray diffractometry was used to check the presence of a single phase. The oxygen stoichiometry was first estimated by thermogravimetry and energy dispersive spectrometry. The samples were then oxygenated close to $y = 7$ by annealing in oxygen atmosphere (25 Atm) at 450 K
for about 100 hours or deoxygenated as much as possible close to $y = 6$, for about 100 hours in vacuum. The final oxygen content turned out $y = 6.97 \pm 0.02$ for overdoped YBCO and $y = 6.10 \pm 0.05$ for the underdoped samples, estimated with loss of mass measures. Before the measurements, the samples stay at room temperature for about 1 week. The resistive transition in samples of the same batch appeared very sharp, with moderate evidence of paraconductivity in a temperature range of 5-10 K above the transition. After mixing the samples with epoxy resin, they were oriented by hardening in a strong magnetic field (9 Tesla). The orientation was tested by comparing the diamagnetic susceptibility for $H//c$ with the one for $H$ in the ab plane, where practically no enhancement of $M_{fl}$ was noted to occur. For samples used in previous works $^{18,24}$, the orientation was also tested by means of the $^{63}$Cu NMR line (see ref. 18).

Magnetization measurements have been carried out in the oriented powders by means of a Quantum Design MPMS-XL7 SQUID magnetometer. Measurements were performed also in optimally doped YBCO in order to prove that the results in oriented powders do not significantly differ from the ones in single crystals. The data already obtained by other authors $^{8,9,13,25−27}$ were confirmed. In the following Section we will recall a few results of the studies in optimally doped compounds, when it is required for the comparison of our data in strongly underdoped or overdoped YBCO:Ca.

The transition temperatures $T_c(H = 0) = T_c(0)$ have been estimated from the magnetization curves vs. $T$ at small fields (20 Oersted), by extrapolating at $M=0$ the linear behavior of $\chi$ occurring below $T_c$, as shown in the insets in Fig.1. The values of $T_c(0)$ are collected in Table I, where the numbers of holes $n_h$, as evaluated from the expression $(\frac{T_c}{T_{c,max}}) = 1 - 82.6(n_h - 0.16)^2$, giving the parabolic behaviour $^{28}$ of the phase diagram $T - x$, are also reported. It is noted that because of the enhanced fluctuating diamagnetism some uncertainty in the estimate of $T_c(0)$ is present, particularly in strongly underdoped samples. This uncertainty does not affect the discussion given later on about the anomalous diamagnetism, which is detected in a temperature region well above $T_c(0)$.

Magnetization measurements at constant field $H$ have been performed as a function
of temperature, with $H \parallel c$. In general two contributions to the magnetization $M$ were observed: a Pauli-like, positive term $M_P$, almost $T$-independent or only slightly increasing with decreasing temperature in the range $\Delta T$ from 200K down to about 100 K and a negative diamagnetic contribution $-M_{fl}$ arising on approaching $T_c$. This latter contribution was extracted by subtracting from $M$ the value obtained by extrapolating for $T \to T_c^+$ the curve $M_P$ vs. $T$ in $\Delta T$, where $M_{fl}$ is practically zero. Thus the possible slight temperature dependence of $M_P$ around $T_c$ was neglected in comparison to the much stronger diamagnetic term.

Typical magnetization curves $M(H = \text{const}, T)$ for overdoped and underdoped samples are reported in Fig.2. The enhancement of FD, in both regimes, is evidenced.

In Fig.3 some isothermal magnetization curves $-M_{fl}(T = \text{const})$ vs H, obtained by cooling in zero magnetic field (ZFC) down to a certain temperature above $T_c(0)$, are shown. In Fig 3c also a few data for field cooled (FC) magnetization, to be discussed later on, are reported.

III. ANALYSIS OF THE DATA, FURTHER RESULTS AND THE THEORETICAL PICTURE

A. GL anisotropic free energy functional

The generalization of the GL functional for layered superconductors [Lawrence-Doniach (LD) functional $^9,^{11}$] in a perpendicular magnetic field can be written

$$F_{LD} [\Psi] = \sum_l \int d^2r \left( \alpha |\Psi_l|^2 + \frac{\beta}{2} |\Psi_l|^4 + \frac{\hbar^2}{16\pi^2 m} \left| \left( \nabla_n - \frac{2ie}{c\hbar} A_z \right) \Psi_l \right|^2 \right) + J |\Psi_{l+1} - \Psi_l|^2, \quad (1)$$

where $\Psi_l$ is the order parameter of the $l$–th superconducting layer and the phenomenological constant $J$ is proportional to the Josephson coupling between adjacent planes and $\alpha = \alpha_0 \left( \frac{T - T_c}{T_c} \right) \equiv \alpha_0 \varepsilon$. The gauge $A_z = 0$ is chosen in Eq.(1). In the vicinity of $T_c$ the LD
functional is reduced to the GL one with the effective mass $M = (4J s^2)^{-1}$ along $c$-direction, where $s$ is the inter-layer spacing. In the GL region the fourth order term in (1) is omitted and the standard procedure\textsuperscript{2,4} to derive the fluctuation part of the free energy yields

$$F(\epsilon, H) - F(\epsilon, 0) =$$

$$= -\frac{TV k_B}{4\pi^2 s \xi_{ab}^2} h \int_{-\pi}^{\pi} dz \sum_{n=0}^{1/2} \int_{-1/2}^{1/2} dx \ln \frac{(2n + 1 + 2x) h + r/2(1 - \cos z) + \epsilon}{(2n + 1) h + r/2(1 - \cos z) + \epsilon}.$$

where $c$-axis is along the $z$ direction, $r = \frac{4 \xi^2}{s^2}$ and $h = \frac{H}{H_{c2}(0)}$.

By means of numerical derivation of Eq.2 with respect to the field one obtains the fluctuating magnetization $M_{fl}$ vs. $H$. As shown in the inset of Fig.4, the magnetization curves in optimally doped YBCO are satisfactorily fitted by $M_{fl}$ derived in this way and evidence how the 3D scenario of SF is obeyed on approaching $T_c$, with a crossover from linear to non-linear field dependence occurring a few degrees above the transition. Correspondingly, the scaling arguments for 3D anisotropic systems hold and $M_{fl}/H^{1/2}$ vs. $T$ cross at $T_c(0) \approx 92K$, as already observed\textsuperscript{13}.

In contrast to optimally doped YBCO, the magnetization curves for underdoped and overdoped compounds depart in a dramatic way from the ones expected on the basis of Eq.2. In particular (see Fig.2a-3b-3c), even relatively far from $T_c$, while for small fields ($H(Hlinear in H$, upon increasing the field the magnetization shows an upturn and then $| - M_{fl}|$ decreases. Let us remind that in the GL weak fluctuation regime the saturation of the magnetization at high field has to be expected\textsuperscript{10,11}, the superconducting coherence being broken for fields larger than $\sqrt{\varepsilon H_{c2}}$. An estimate of the order of magnitude of the upturn field $H_{up}$ can be done from the analysis of the '0D' case\textsuperscript{2,4}, namely for superconducting granules of radius $d$ smaller than the coherence length $\xi(T)$. In this case the order parameter is spatially homogeneous and the exact solution of the GL model can be found and yields

$$M_{fl} = -\frac{k_B T^2 \frac{\pi^2 \xi^2}{5\phi_0^2} d^2 H}{(\epsilon + \frac{\pi^2 \xi^2}{5\phi_0^2} H^2)}.$$

It can be noticed that the most sizeable contribution to the magnetization comes from the fluctuations-induced SC droplets of radius of the order of $\xi(T)$, which imply most efficient
screening. By assuming the condition of zero dimension for these droplets, from Eq.3 with \( d = \xi(T) \) one derives an upturn field given by \( H_{up} \approx \frac{\varepsilon \Phi_0}{\xi^2} \). For \( \xi \approx 10\,\text{Å} \) and \( \varepsilon \) in the range \( 10^{-1} - 10^{-2} \), \( H_{up} \) is expected to be in the range of ten Tesla.

Thus the magnetization curves in Fig.s 3 can hardly be ascribed to the breakdown of the GL approach of the type commonly observed in BCS superconductors. In other words, a description of FD based on the GL functional in principle should be suitable in YBCO compounds for fields smaller than several Tesla, particularly not too close to \( T_c \), as in fact it is observed in optimally doped YBCO.

**B. Phase fluctuations and superconducting droplets above \( T_c \) : a theoretical picture**

Then one has to look for other explanations. As already mentioned, a recent theory has been developed by Sewer and Beck at the aim to justify the unusual magnetization curves detected in underdoped YBCO. The theory assumes a frozen amplitude of the order parameter while phase fluctuations are taken into account. As a consequence one has to deal both with thermally activated vortex loops and field induced vortex lines. Two major conclusions of general character can be outlined. For small field the temperature dependence of the susceptibility is controlled by the vortex loops density \( n_v \), for which

\[
 n_v = n_0 \exp[-E_0/kT]
\]

according to the XY model. For strong fields, instead, the vortex line elements dominate, the vortex correlations between different layers become relevant and \( M_{fl} \) only slightly increases with \( H \) and finally it flattens. No upturn field is predicted, at least for \( H << H_c \).

In Fig.5 the data for \( \chi \), defined as \((-M_{fl}/H)\), are shown to obey rather well to Eq.4, in correspondence to \( E_0 \approx 940K \), in agreement with calculations yielding for the activation energy values around \( 10 \, T_c \) (see Ref. and references therein). \( E_0 \) turns out to depend only little from doping, being slightly field dependent. It is necessary to mention that the temperature dependence of the susceptibility above \( T_c(0) \) differs from that one measured below \( T_c \), as shown in Fig.5.
However the magnetization curves, as the ones reported in Figs. 3 and 4, cannot be accounted for by a theory which does not include an upturn with the field. Furthermore similar effects are found also in overdoped samples (see Figs.2a and 3a).

Thus we are going to consider the second aspect possibly leading to an anomalous diamagnetism, the one related to charge inhomogeneities causing regions where the hole density is different from the average. Evidences of inhomogeneous structure of cuprates have been found by means of neutron and electron diffraction, as related to stripes and lattice effects or to local variation in the oxygen concentration, particularly near grain boundaries. Intrinsic inhomogeneities, with spatially dependent critical temperature have been considered as possible cause of pseudogap phenomena. A theory for high temperature superconductivity and of the pseudogap temperature dependence based on inhomogeneous charge distribution with site-dependent transition temperature has been recently formulated. In particular, Ovchinnikov et al. have considered the anomalous diamagnetism above $T_c$ induced by non-uniform distribution of magnetic impurities, depressing $T_c$ but leaving ”islands” which become superconductors above the resistive transition temperature. An anomalous large diamagnetic moment results above $T_c$ and in this way the strong diamagnetic susceptibility observed in overdoped Tl-based cuprates could be explained. It should be stressed, however, that in this description the magnetization is linear in the field, since the condition of small field is implicitly assumed. Direct evidence of inhomogeneous magnetic domains showing diamagnetic activity above $T_c$ has been obtained by Iguchi et al. by scanning SQUID microscopy in underdoped LASCO. Regions of few tens of $\mu m$, precursors of bulk superconductivity have been imaged in this remarkable work.

In the light of the experimental findings and of the theoretical supports outlined above we consider now as a source of diamagnetism above $T_c$ the presence of locally superconducting droplets. From the volume susceptibility, let us say at $T_c-5K$ (see Fig.1), one deduces that a few percents of the total material being superconductor above the resistive transition, could actually justify the screening effects observed as FD. A test of this hypothesis is obtained from the search of magnetic-history dependent effects. It is known, in fact, that in YBCO
the irreversibility temperature is not far from $T_c$ and therefore if the anomalous FD has to be attributed to locally SC droplets then one should detect differences between ZFC and field-cooled (FC) magnetization. In Fig. 6 magnetization curves after zero field cooling and the correspondent values of $M_{fl}$ obtained at the same temperature after cooling in the presence of a given magnetic field, are compared. Furthermore relaxation effects have been observed. In Fig.7 it is shown how the negative magnetization depends on time, displaying a progressive decrease from the ZFC value towards the one measured in FC condition. The time constant for this relaxation process is close to the one measured in the critical state\textsuperscript{37}. It can be remarked than in underdoped chain-disordered YBCO (Fig.3c) no upturn is observed and the ZFC and FC magnetization curves almost coincide. The explanation that will be supported from our theoretical picture is that the magnetization curves without hysteretic effects refer to superconducting droplets which are above the irreversibility temperature.

One could suspect that the occurrence of superconducting droplets results from trivial chemical inhomogeneities of the samples. As described in the Section on experimental details many experimental checks allow us to rule out this hypothesis. Furthermore, samples grown with different procedures and already used by other authors, have been studied. Thus it is believed that the inhomogeneity does not mean the presence of macroscopic parts of the samples at different oxygen and/or calcium content, but it is rather intrinsic, as the ones evidenced in the experiments recalled above. Furthermore it should be remarked that the temperature dependence of the susceptibility above the bulk transition temperature is different from the one occurring in the superconducting state (see Fig.5).

In the following we are going to modify the theoretical description of Sewer and Beck\textsuperscript{23}, still keeping their basic idea of phase fluctuations but taking into account the presence of mesoscopic ”islands” with non-zero average order parameter amplitude that can be below or above the local irreversibility temperature.

Let us start, as in Ref.\textsuperscript{23}, from Eq.1 by evidencing the order parameter phase contribution

$$\mathcal{F}_{LD} [\theta] = \frac{1}{s} \sum_{l} \int d^2r \left\{ J_\parallel \left( \nabla_\parallel \theta - \frac{2ie}{ch} A_\parallel \right)^2 + J_\perp \left[ 1 - \cos(\theta_{l+1} - \theta_l) \right] \right\}$$

(5)
where \( J_u = \frac{\pi \hbar^2 n_h}{4 m_e} \) and \( J_\perp = 2\pi J n_h \) are the order parameter phase coupling constants on the plane and between planes respectively.

In this way the occurrence of superconducting droplets below the critical temperature is assumed, where the order parameter phase can fluctuate producing thermal excitations (vortex and antivortex pairs in 2D, vortex loops in anisotropic model). The potential vector \( \mathbf{A}_u \) in Eq.5 describes both the magnetic field applied parallel to the \( c \)-axis and the one induced by thermal fluctuations.

By following the 2D Coulomb gas theory, at each vortex is associated an effective charge \( q_v = \sqrt{2\pi J} \) and a vortex-antivortex pair has an energy \( E_0 = q_v^2 \ln\left(\frac{r}{\xi_{ab}}\right) \), playing the role of an activation energy and thus yielding Eq.4. In order to refer to the anisotropic 3D model the vortex lines (or the vertical elements of the vortex loops) are correlated along the \( c \)-axis for a length \( n s \) and a correction to \( q_v \) was found selfconsistently.

By considering, as usual, the partition function \( Z = \int D\theta \exp\left(-\beta F_{LD}[\theta]\right) \) with \( \beta = \frac{1}{k_B T} \), the susceptibility \( \chi = \frac{\partial M_{fl}}{\partial H} \), where \( M_{fl} = \frac{\partial F}{\partial H} \), is obtained as the sum of three contributions:

\[
\chi = \left\langle \frac{\partial^2 F_{LD}}{\partial^2 H} \right\rangle^2 - \beta \left\langle \left( \frac{\partial F_{LD}}{\partial H} \right)^2 \right\rangle + \beta \left( \left\langle \frac{\partial F_{LD}}{\partial H} \right\rangle \right)^2
\]

(6)

where \( \langle \rangle \) means the thermal average.

In the gauge \( A = -yH \), \( z \) being the \( c \)-axis direction, the homogeneous susceptibility is given by

\[
\chi = \lim_{q \to 0} \frac{K(q)}{q^2},
\]

(7)

where

\[
K(q) = \frac{J_u}{d} \left(\frac{2\pi}{\Phi_0}\right)^2 \left[ \frac{J_u}{kT} (P(q) - Q(q)) - 1 \right].
\]

(8)

In Eq.(8) \( P(q) \) derives from the term \( \left\langle \left( \frac{\partial F_{LD}}{\partial H} \right)^2 \right\rangle \) of Eq.(6) and it involves the current-current correlation function, as in Ref.23:
\[
P(q) = \frac{1}{NL^2} \sum_{l,l'} \int d^2 \rho \int d^2 \rho' \exp [i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')] \\
\left\langle \left( \nabla_x \theta_l (\rho) - \frac{2\pi}{\Phi_0} A_{u,x}(\mathbf{r}) \right) \left( \nabla_x \theta_{l'} (\rho') - \frac{2\pi}{\Phi_0} A_{u,x}(\mathbf{r}') \right) \right\rangle
\]

with \( N \) the number of layers and \( L^2 = \pi R^2 \), \( R \) being the average radius of the superconducting islands.

The x-component of the phase gradient is

\[
\nabla_x \theta_n (\rho) = d \sum_{s_1, l_1} \frac{y - R_y (m_1, l_1)}{\left( \rho - \mathbf{R} (m_1, l_1) \right)^2 + d^2 \left( l - l_1 \right)^2} t(m_1, l_1),
\]

where \( t(m_1, l_1) = \pm 1 \) and \( \mathbf{R}(m_1, l_1) \) labels the position of each "pancake" \( m_1 \) on the layer \( l_1 \).

Three terms are obtained by the evaluation of Eq.(9): \( P_{\theta\theta}(q) \), \( P_{AA}(q) \) and \( P_{\theta A}(q) \) (the two terms due to the correlation between \( \nabla_x \theta \) and \( A_{u,x} \) give the same contribution being \( P_{\theta A}(q) = P_{AA}(q) = P_{\theta A}(-q) \)). The first one involves the positional correlation function of the vortex line elements. In order to calculate it, Sewer and Beck\(^{23} \) introduced the static structure factor of a disordered vortex liquid. Because of the weak interlayer coupling harmonic deviations of the vortex lines (or loops) along the \( z \) direction are taken into account. This model can be used to describe also the vortex system in the glassy phase, below the irreversibility line temperature and therefore the same expression for \( P_{\theta\theta}(q) \) is used here.

The evaluation of the term \( P_{AA}(q) \) is straightforward and one has

\[
P_{AA}(q) = \frac{\pi^2}{36} \left( \frac{HL^2}{\Phi_0} \right) L^2 q^2
\]

The further contribution \( P_{\theta A}(q) \), appearing due to the cross correlation between \( \nabla_x \theta \) and \( A_{u,x} \) and disregarded in Ref.\(^{23} \), cannot be neglected below the vortex lattice melting temperature, where irreversibility effects occur. In this case one obtains

\[
P_{\theta A}(q) + P_{\theta A}(-q) = 2 \frac{Hd}{L} \left( 2\pi \right)^2 \frac{Lq \cos \frac{Lq}{2} - 2 \sin \frac{Lq}{2}}{q^2} \sum_{l,l'} \exp \left( -dq |l - l_1| \right) \\
\left\langle \sum_{m_1,l_1} t(m_1, l_1) \cos [iqR_y (m_1, l_1)] \right\rangle.
\]
The thermal average is performed in the assumption that the vortices are uniformly distributed in the planes and the calculations are reported in Appendix. The expansion of \( P_{\theta A}(q) \) in powers of \( qL \) gives

\[
P_{\theta A} = -\frac{2\pi^2}{3} \left( \frac{HL^2}{\Phi_0} \right)^2 + \frac{2L^2}{45\pi^2} \left( \frac{HL^2}{\Phi_0} \right) \tag{11}
\]

The function \( Q(q) \) in Eq.8, related to the third term of Eq.6, has been neglected in Ref.23. It can be calculated as described in Appendix, yielding

\[
Q = (2\pi)^2 \left( \frac{HL^2}{\Phi_0} \right)^2 \left[ \frac{1}{q^2L^2} + \frac{1}{144} \times 4q^2L^2 + \frac{1}{12} \right]. \tag{12}
\]

It should be noted that the first term in \( Q \), diverging for \( q \to 0 \), exactly cancels out the \( q^{-2} \) term in the expansion of \( P(q) \) which appears from the structure factor.

By using Eqs. (10), (11), (12) and Eq.(6) of Ref.23, from Eq.(8) one finally obtains

\[
K(q) = \frac{J_v}{s} \left( \frac{2\pi}{\Phi_0} \right)^2 \left[ \frac{2\pi J_v}{q_v^2} (1+2n) - \delta \left( \frac{H}{H^*} \right)^2 - 1 \right] + \\
\left[ \frac{-kT}{s\Phi_0^2} \frac{1}{1+2n} \frac{1+\delta \left( \frac{H}{H^*} \right)^2}{n_v} - \frac{s^2\gamma^2(1+n)}{1+2n} (1+\delta \left( \frac{H}{H^*} \right)^2) + \\
\frac{47\pi R^2 J_v}{540} \frac{2\pi}{\Phi_0} \delta \left( \frac{H}{H^*} \right)^2 \right] q^2 \tag{13}
\]

with \( \delta = \frac{3\pi^2 J_v}{4kT} \) and \( H^* = \frac{\Phi_0}{\pi R^2} \) is an effective "critical" field depending on the island size.

To avoid unphysical divergences in the calculation of the susceptibility from Eq.(7), the first term in square brackets of Eq.(13) has to be zero, giving a renormalization of \( q_v \) due to both the anisotropy of the system and the presence of applied magnetic field:

\[
q_v^2(H) = \frac{q_v^2(1+2n)}{(1+\delta \left( \frac{H}{H^*} \right)^2)}. \tag{14}
\]

In view of the field-dependent vortex charge, the pair energy (in the limit \( H < H^* \)) becomes \( E = \frac{E_0}{(1+\delta \left( \frac{H}{H^*} \right)^2)} \). According to Eq.(4) the thermally-excited vortex pair density turns out field dependent. This field dependence, formally derived in our description, is significantly different from the one assumed in Ref.23.
Finally the diamagnetic susceptibility is obtained in the form

\[
\chi = -\frac{kT}{s\Phi_0^2} \frac{1}{1 + 2n} \frac{(1 + \delta \left(\frac{H}{H^*}\right)^2)^2}{n_v} \left(1 + \frac{s^2\gamma^2(1 + n)}{1 + 2n} \right) \left(1 + \delta \left(\frac{H}{H^*}\right)^2\right) + \frac{47\pi R^2 J_u}{540 s} \left(\frac{2\pi}{\Phi_0}\right)^2 \delta \left(\frac{H}{H^*}\right)^2
\]

(15)

In the limit \( H \to 0 \) a good agreement of the susceptibility and its temperature dependence with the experimental findings is again achieved. The main differences between our susceptibility in Eq.(15) and the one given in Ref.23 consists in the presence of the factor \(||H/H^*||^2\) and of the third, positive term. This term can give an inversion in the sign of the susceptibility corresponding to an upturn in the magnetization curves. This phenomenon depends on the dimension of the islands and \( \chi = 0 \) (i.e. the occurrence of the upturn) requires \( R > R_0 \) where \( R_0 \) depends on some characteristics of the material. By choosing \( \gamma = 6 \), the interlayer distance \( s = 12\text{Å} \), \( n = 2 \), \( \frac{J_u}{kT} = 2.5 \), which are typical values for YBCO, for \( T = 75.5K \) one estimates \( R_0 \approx 50\text{Å} \). In this case the solutions of the Equation \( \chi = 0 \) is \( \frac{H_{up}}{H^*} \approx 0.06 \) and by considering the experimental value \( H_{up} \approx 250 \text{ G} \), the effective critical field turns out \( H^* \approx 0.4T \).

The isothermal curves can be obtained from Eq.(15) by means of numerical integration. The shape of the magnetization curve depends on the parameters in the susceptibility and by using the values quoted before, with \( R = 370\text{Å} \) one derives the behaviour sketched in Figs.3a for an island below the irreversibility line. The same parameters with \( T = 66K \), \( \frac{J_u}{kT} = 1.8 \) and \( R = 10\text{Å} \) lead to the curve shown in Fig.3c for the magnetization of the island above irreversibility.

Finally we discuss the differences observed in the magnetization curves between chain-ordered and chain-disordered YBCO compounds and the relevant observation by Carballeira et al.19 of magnetization curves -M\(_{fi}\) vs H in underdoped LASCO (Sr content \( x=0.1 \), \( T_c(0)=27.1 \text{ K} \)) with no upturn field. A role of the chains on favouring the nucleation of local superconducting droplets above \( T_c \) is conceivable. In fact, in chain-ordered compounds the droplets appear to have the irreversibility temperature higher than the ones in chain-
disordered compounds, as it is evidenced by the difference in the magnetization curves (see Figs. 3a-b-c). We remind that the inversion in the sign of the susceptibility is related to the third term in Eq.15 and thus to the term $P_{\theta A}(q)$. The amount of impurities and/or imperfections acting as nucleation centers might also play a role. Furthermore the degree of under or over-doping is also involved since a marked variation of $T_c$ with $n_h$ is evidently crucial. It is noted that in the measurements by Carballeira et al.\textsuperscript{19} in LASCO at $T_c=27.1$ K the magnetization curves show only a weak tendency to saturation while in LASCO at $T_c \simeq 18$ K (therefore more underdoped) scanning SQUID microscopy by Iguchi et al\textsuperscript{36} does evidence diamagnetic effects to associate to locally superconducting droplets. These droplets should imply a contribution to the magnetization curves similar to the one detected by us in YBCO compounds. Future research work will have to explore these interesting aspects and the differences until now present between LASCO and YBCO.
By means of SQUID measurements in $Y_{1-x}Ca_xBa_2Cu_3O_y$ family a non conventional fluctuating diamagnetism has been observed in overdoped and in underdoped compounds. Compared to optimally doped YBCO, a large enhancement of the diamagnetic susceptibility occurs and no anisotropic GL functional or scaling arguments can justify the isothermal magnetization curves. The recent theory\textsuperscript{23} for phase fluctuations of the order parameter in a layered liquid of vortices has been revised and it appears to justify some aspects of the anomalous FD in non-optimally doped YBCO, particularly the ”precritical” temperature activated behaviour of the susceptibility in the limit of zero field. Other experimental observations, noticeably the upturn in the field dependence of the isothermal fluctuating magnetization and history-dependent effects, indicate the role of mesoscopic charge inhomogeneities in inducing local, non-percolating, superconducting ”droplets”. On the basis of both types of experimental findings we have extended the theory of phase fluctuations in the presence of non-zero order parameter. The terms leading to a novel and relevant dependence of the fluctuating magnetization from the magnetic field were included in the scheme. The field-related corrections are different when the superconducting droplets are below or above the local irreversibility temperature. In this way most of the experimental findings have been justified.

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To derive Eqs.(11) and (12) the following thermal average must be calculated:

$$
\left\langle \sum_{m,l} t(m,l) \cos iqlR_y(m,l) \right\rangle = \sum_m \langle t(m) \rangle - \frac{1}{2} q^2 \sum_m < R^2(m) > + o(q^3) \tag{A1}
$$

Indicating with $N_+$ ($N_-$) the number of vortex line elements parallel (antiparallel) to the field the first term gives

$$
N_+ - N_- = \frac{HL^2}{\phi_0}.
$$

The sum in the second term can be split in two parts which separately count the vortex line elements parallel and antiparallel to the field:

$$
\sum_m t(m) < R^2_y(m) > = \sum_{m+} < R^2_y(m) > - \sum_{m-} < R^2_y(m) > ,
$$

One can assume that the vortices are uniformly distributed in the planes and that the $y$ components of their positions are distributed on a line, separated each other by a distance $\Delta L = \frac{L}{N_+}$. Then, the $i$–th vortex is in the mean position $< R_i > = \Delta Li = \frac{\Delta L}{N_+}i$, with $i = -\frac{N_+}{2} \cdots \frac{N_+}{2}$.

$$
\sum_{m+} < R^2_{m+} > = \sum_{i=-\frac{N_+}{2}}^{\frac{N_+}{2}} \frac{L^2}{N_+^2} i^2 = \frac{L^2}{12N_+} (N_+ + 2) (N_+ + 1).
$$

By considering $N_+ >> 1$ one finally finds

$$
\sum_m t(m) < R^2_y(m) > \approx \frac{L^2}{12} (N_+ - N_-).
$$

Then (A1) can be written

$$
\sum_m t(m) < \cos qR(m) > = \frac{HL^2}{\phi_0} - q^2 \frac{L^4 H}{24\phi_0} + o(q^3)
$$
VIII. FIGURE CAPTIONS

Fig. 1 Some magnetization data in low field, parallel to the c-axis, as a function of temperature in oriented powders of $Y_{1-x}Ca_xBa_2Cu_3O_y$. The values of the magnetization measured from 250 K down to 90 K, with a positive Pauli-like temperature independent term, are not reported in the figure. In the insets the blow-up for the estimate of $T_c(0)$ is shown.

Fig. 2 Constant field ($H \parallel c$) magnetization vs. temperature in overdoped ($x = 0.1$ and $y = 6.96$) (a) and in underdoped ($x = 0$ and $y = 6.65$) (b) YBCO compounds. For comparison in the part a) of the figure the behaviour of $M_{fl}$ in optimally doped YBCO is shown.

Fig. 3 Isothermal diamagnetic magnetization vs. $H$, after zero-field cooling (ZFC) to a certain temperature above $T_c(0)$. a) sample at $x = 0.1$, $y = 6.96$ ($T_c(0) = 73K$); b) sample at $x = 0.2$, $y = 6.98$ ($T_c(0) = 49.5K$); c) chain disordered underdoped YBCO at $y = 6.65$ and $x = 0$ ($T_c(0) = 62.5K$) for ZFC (circle) and field-cooled (FC) (up-triangle) conditions. The solid lines in part a) of the Figure correspond to the diamagnetic susceptibility estimated in the limit of zero field. The solid lines in Figs. 3a and 3c are the theoretical behaviours according the mechanisms described in the text for droplets below and above the local irreversibility temperature.

Fig. 4 Comparison of the magnetization curves $M_{fl}$ vs. $H$ (after ZFC) in overdoped YBCO:Ca ($x = 0.1$, $y = 6.96$) with the ones in optimally doped YBCO (inset), for similar reduced temperature $\varepsilon$. The solid lines fitting the data in optimally doped YBCO are derived from Eq. 2 in the text by means of numerical derivation, correspond to anisotropic parameter $r=0.1$ and evidence the 3D linear and 3D non-linear regimes.

Fig. 5 Susceptibility as a function of the inverse temperature showing the activated temperature behavior in the sample at $y = 6.96$ and $x = 0.1$. Analogous temperature dependence has been observed in underdoped YBCO compounds. The dashed lines are obtained by transferring above the superconducting temperature $T_c(0)$ the temperature behavior of the bulk susceptibility measured below $T_c$ and by normalizing the data at $T \simeq 88K$. 
Fig. 6 Magnetization curves in YBCO:Ca at $x = 0.1$ and $y = 6.96$ by cooling in zero field to a given temperature [a) $T = 75.5K$; b) $T = 79.5K$] above the resistive transition temperature and then applying the field (ZFC) and after the application of the field at room temperature, cooling at the same temperature and measuring the correspondent magnetization (FC). The volume susceptibility in the limit $H \to 0$ is reported.

Fig. 7 Relaxation of the raw magnetization after ZFC and then sudden application of a magnetic field of 260 G, in YBCO:Ca at $x = 0.1$ and $y = 6.96$, at $T = 75.5K$ a) short-term relaxation; b) long-term relaxation. From the comparison of the ZFC and FC magnetization in $H=20G$ (see inset) an irreversibility temperature of the locally superconducting droplets at highest $T_c$ can be estimated around 90 K. In part a) of the Figure the solid line is the sketchy behavior of the relaxation of the magnetization detected by Yeshurun et al. (Ref.33) in the critical state, in optimally doped YBCO.
**IX. TABLE CAPTION**

Table I: Superconducting transition temperature in overdoped and underdoped $Y_{1-x}Ca_xBa_2Cu_3O_y$ and estimated number of holes per CuO$_2$ unit

| $x$  | $y$  | $T_c$(K) | $n_h$ |
|------|------|----------|-------|
| 0    | 6.65 | 62.5     | 0.12  |
| 0.05 | 6.97 | 82.0     | 0.18  |
| 0.1  | 6.96 | 73.0     | 0.20  |
| 0.1  | 6.96 | 70.0     | 0.21  |
| 0.2  | 6.98 | 49.5     | 0.23  |
| 0.15 | 6.10 | 34.00 ± 1| 0.07  |
| ≈ 0.15 | 6.05 | 20.00 ± 2| 0.06  |
| 0.1  | 6.10 | 14.00 ± 2| 0.06  |
Fig. 1

- $x = 0.15, y = 6.05$
- $x / 0.2, y / 6.97$
- $x = 0, y = 6.65$
- $x = 0.1, y = 6.98$

$M$ (emu/mole) vs. $T$ (K)
Fig. 2

(a) $T_c(0)$ for Ca 10% Overdoped

(b) $T_c(0)$ for optimally doped YBa$_2$Cu$_3$O$_6.6$

M$_h$(emu/mole)

T(K)

Ca 10% Overdoped
- ■ 30 G
- □ 100 G
- □ 400 G
- ● 1000 G
- ▲ 5000 G
- △ 10000 G
- ◊ 60000 G
- optimally doped
- □ 100 G
- ◊ 1000 G

YBa$_2$Cu$_3$O$_6.6$
- ▲ 20000 G
- ○ 3000 G
- △ 150 G
- ▲ 300 G
- ▪ 80 G
Fig. 3a

$M_n$ (emu/mole)

$T = 79.5$ K

$T = 75.5$ K

$H$ (Oe)
Fig. 3b

$M_{\text{fl}}$ (emu/mole) vs. $H$ (Oe) at $T = 57$ K.
$T = 66K$

$M_{fl}$ (emu/mole) vs $H$ (Oe)

- ZFC
- FC

Fig. 3c
$\varepsilon = 0.014$
$\varepsilon = 0.036$
$\varepsilon = 0.087$

Fig. 4

$M_{\text{fl}}$ (emu/mole)

$H(T)$

$\varepsilon = 0.019$

$\varepsilon = 0.073$
\[ \chi = -\frac{M}{H} \]
Fig. 6

$a)$

$M_n$ (emu/mole)

$\chi_{ZFC} = -2.5 \times 10^{-3}$

$\chi_{FC} = -1.5 \times 10^{-3}$

$T = 75.5$ K

$b)$

$M_n$ (emu/mole)

$\chi_{ZFC} = -7.5 \times 10^{-4}$

$\chi_{FC} = -5.5 \times 10^{-4}$

$T = 79.5$ K

$H$ (Oe)
Fig. 7

(a) Variation of magnetization (M) with time (sec).

(b) Magnetization (M) vs. temperature (T) graph with FC and ZFC data points.

- a) M (emu/mole) vs. time (secs)
- b) M (emu/mole) vs. T (K)