Anomalous doping dependence of fluctuation-induced diamagnetism in $Y_{1-x}Ca_xBa_2Cu_3O_y$ superconductors

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(Received 26 September 2001; revised manuscript received 21 December 2001; published 4 April 2002)

Superconduting quantum interference device magnetization measurements in oriented powders of $Y_{1-x}Ca_xBa_2Cu_3O_y$, with x ranging from 0 to 0.2, for $y \approx 6.1$ and 6.97, are 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 with 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 an activated temperature behavior, a marked characteristic of the vortex-antivortex description, while the 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.

DOI: 10.1103/PhysRevB.65.144523 PACS number(s): 74.40.+k, 74.25.Ha

I. INTRODUCTION

A variety of experiments[1] pointed 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's). In contrast to conventional superconductors, in cuprates the transition region is considerably smeared by SF's which can be detected in a wide temperature range, up to 10–15 K above T_c. The formation of 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 with 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 to zero for $H=0$. On the other hand it is evident that very strong magnetic fields, comparable to $H_{c2}(0)$, must suppress SF's. Therefore the isothermal magnetization curve $M_{fl}(T=\text{const},H)$ has to exhibit an upturn. This upturn can be described quantitatively within the framework of the exactly solvable, for any magnetic field, zero-dimensional model[2] [superconducting granules with a size $\ll \xi(T)$] or by means of a cumbersome microscopic treatment accounting for the short-wavelength fluctuation contribution in the three-dimensional (3D) case.[3]

Experiments on conventional BCS superconductors showed 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 rather 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.[8–10] 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 $Y_{1-x}Ca_xBa_2Cu_3O_y$ (YBCO).[7–11] Scaling arguments[12] were found[13,14] to be rather well obeyed in this compound.

In underdoped YBCO, marked deviations from the behavior expected in the framework of GL approaches have been detected. A first qualitative claim in this regard goes back to Kanoda *et al.*,[15] who noted that in oxygen-deficient YBCO the FD in small fields was enhanced. Later on, interesting features of FD in underdoped compounds were reported.[8,16–20] In particular, in underdoped YBCO at $T_c \simeq 63$ K, a marked enhancement of the susceptibility for fixed $(T-T_c)$ in a field of 0.02 was detected above $T_c(0)$, with magnetization curves strongly different from the ones in optimally doped YBCO.[16,18] Magnetization curves were subsequently reported[19] 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.*[19] in underdoped LASCO, although indicating field-affected fluctuation-induced diamagnetism, do not exhibit the upturn with magnetic field like the ones in underdoped YBCO that we will discuss later. Finally, recent magnetization data[20] as a function of temperature in $YBa_2Cu_3O_{6.5}$ single crystal [with a transition temperature in zero field $T_c(0)=45$ K] indicate SF's obeying 2D scaling conditions for $H \gtrsim 1T$, and turning to 3D scaling for smaller fields.

Qualitative justifications of the anomalous diamagnetism in underdoped YBCO have been tried,[18,21] essentially based on the idea of charge inhomogeneities leading to nonpercolating superconducting "drops" or on the extension of the theory of Ovchinnikov *et al.*,[22] where the anomalous diamagnetism was 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.[23] In the framework of the Lawrence-Doniach model, these authors justified 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 fluctuating diamagnetism in the $Y_{1-x}Ca_xBa_2Cu_3O_y$ family and of its dependence from the number of holes, by reporting superconducting quantum interference device (SQUID) magnetization measurements in a series of samples. Preliminary results on overdoped compounds were presented to a meeting and published elsewhere.[24] Since some differences in the magnetic behavior of chain-ordered and chain-disordered YBCO were noted,[18] 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 Sec. II experimental details and the majority of the experimental results are reported. The analysis of the data (Sec. 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 nonoptimally 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.[23] In particular, nonreversibility and relaxation effects of the magnetization are argued to support the picture of nonpercolating, locally superconducting droplets above the resistive transition temperature, that we interpret as phase fluctuations of a nonzero 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 summarized in Sec. 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 h. 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 h, or deoxygenated as much as possible close to $y=6$, for about 100 h in vacuum. The final oxygen content turned out $y=6.97\pm0.02$ for overdoped YBCO and $y=6.10\pm0.05$ for the underdoped samples, estimated with loss of mass measures. Before the measurements, the samples stayed at room temperature for about one 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 T). 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 were carried out in the oriented powders by means of a Quantum Design MPMS-XL7 SQUID magnetometer. Measurements were also performed 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 Sec. III we will recall a few results of studies of optimally doped compounds, when it is required for the comparison of our data in strongly underdoped or overdoped YBCO:Ca.

The transition temperatures $T_c(H=0)=T_c(0)$ were estimated from the magnetization curves vs T at small fields (20 Oersted), by extrapolating at $M=0$ the linear behavior of χ 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 $(T_c/T_c^{max})=1-82.6(n_h-0.16)$,[2] giving the parabolic behavior[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 below about the anomalous diamagnetism, which is detected in a temperature region well above $T_c(0)$.

Magnetization measurements at a constant field H have been performed as a function of temperature, with $\mathbf{H}\|\mathbf{c}$. 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 ΔT from 200 K 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 $T\rightarrow T_c^+$ the curve M_P vs T in ΔT, where M_{fl} is practically zero. Thus the possible slight temperature dependence of M_P around T_c was ne-

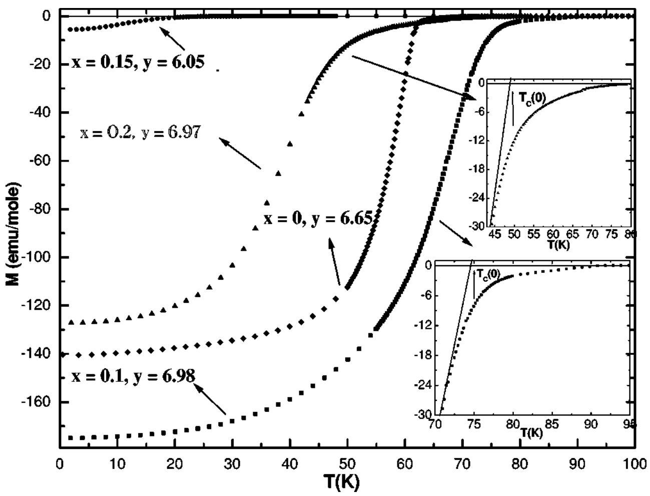

FIG. 1. Some magnetization data in low field, parallel to the c axis, as a function of temperature in oriented powders of $Y_{1-x}Ca_xBa_2Cu_3O_y$. The values of the magnetization measured from 250 K down to 90 K, with a positive Pauli-like temperature-independent term, are not reported in the figure.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

glected 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 3(c) a few data for field-cooled (FC) magnetization, to be discussed below, 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 [the Lawrence-Doniach (LD) functional[9,11]] in a perpendicular magnetic field can be written

TABLE I. Superconducting transition temperature in overdoped and underdoped $Y_{1-x}Ca_xBa_2Cu_3O_y$, and the 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	34.0±1	0.07
≈0.15	6.05	20.0±2	0.06
0.1	6.10	14.0±2	0.06

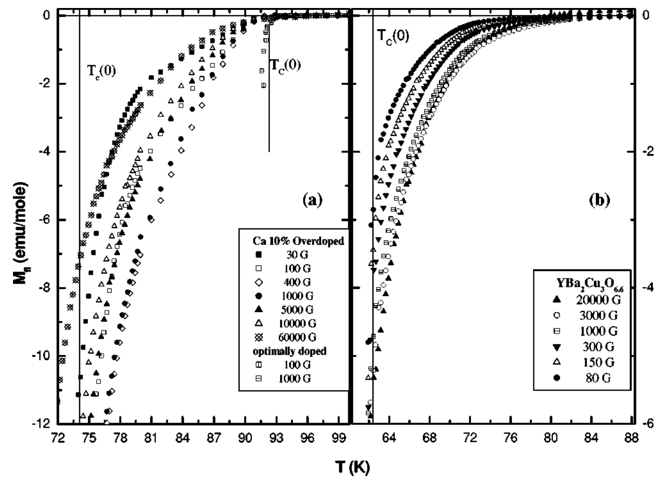

FIG. 2. Constant field ($\mathbf{H}\|\mathbf{c}$) magnetization vs temperature in overdoped ($x=0.1$ and $y=6.96$) (a) and underdoped ($x=0$ and $y=6.65$) (b) YBCO compounds. For comparison, in (a) of the figure the behavior of M_{fl} in optimally doped YBCO is shown.

$$\mathcal{F}_{LD}[\Psi]=\sum_l \int d^2r\Bigg(\alpha|\Psi_l|^2+\frac{\beta}{2}|\Psi_l|^4+\frac{h^2}{16\pi^2 m}\times\left|\left(\boldsymbol{\nabla}_{\|}-\frac{2ie}{c\hbar}\mathbf{A}_{\|}\right)\Psi_l\right|^2+\mathcal{J}|\Psi_{l+1}-\Psi_l|^2\Bigg), \quad (1)$$

where Ψ_l is the order parameter of the lth superconducting layer and the phenomenological constant $\mathcal{J}$ is proportional to the Josephson coupling between adjacent planes and $\alpha=\alpha_0[(T-T_c)/T_c]\equiv\alpha_0\varepsilon$. 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 $M=(4\mathcal{J}s^2)^{-1}$ along the c direction, where s is the interlayer spacing. In the GL region the fourth-order term in Eq. (1) is omitted, and the standard procedure[2,4] to derive the fluctuation part of the free energy yields

$$F(\epsilon,H)-F(\epsilon,0)=-\frac{TVk_B}{2\pi s\xi_{ab}^2}h\int_{-\pi}^{\pi}dz\sum_{n=0}\int_{-1/2}^{1/2}dx\,\ln\times\frac{(2n+1+2x)h+r/2(1-\cos z)+\epsilon}{(2n+1)h+r/2(1-\cos z)+\epsilon}. \quad (2)$$

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

By means of a 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 show how the 3D scenario of SF is obeyed on approaching T_c, with a crossover from a linear to a nonlinear 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 $T_c(0)\simeq 92$ K, as already observed.[13]

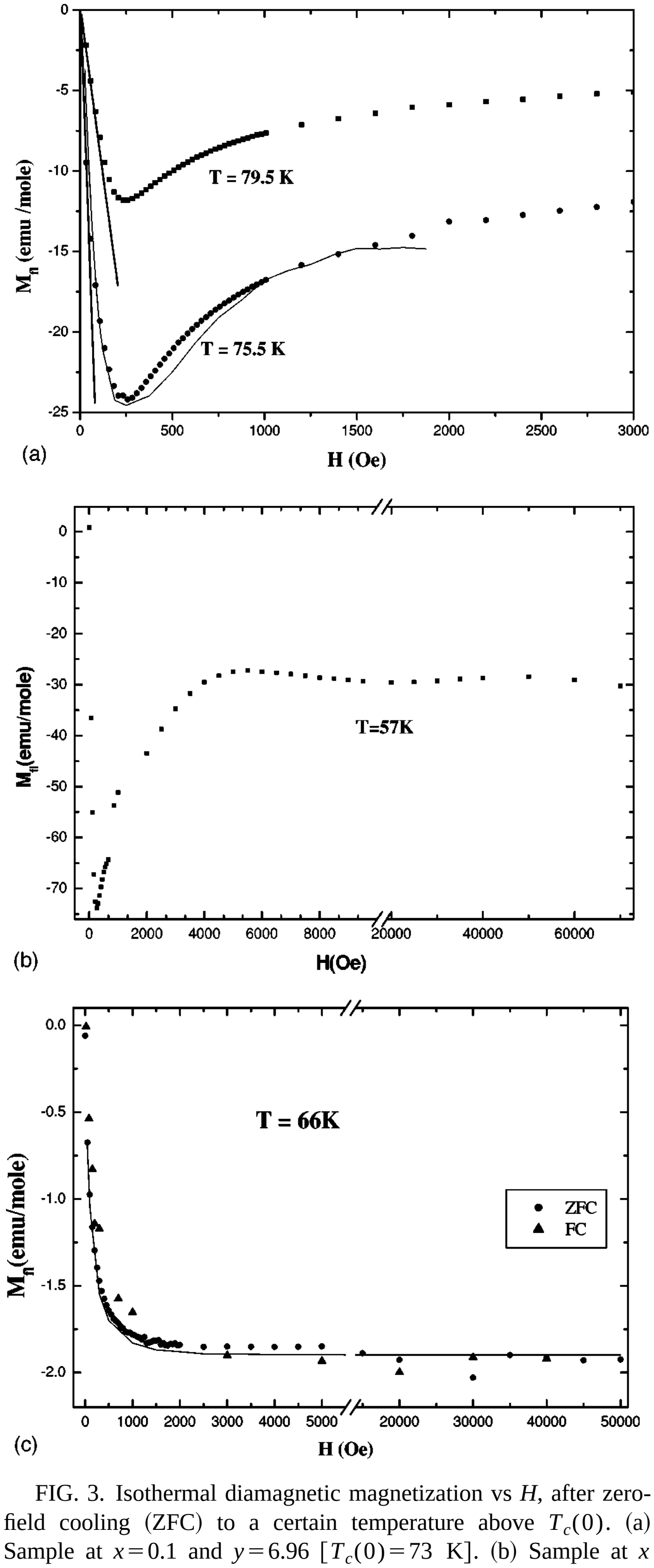

FIG. 3. Isothermal diamagnetic magnetization vs H, after zero-field cooling (ZFC) to a certain temperature above $T_c(0)$. (a) Sample at $x=0.1$ and $y=6.96$ [$T_c(0)=73$ K]. (b) Sample at $x=0.2$ and $y=6.98$ [$T_c(0)=49.5$ K]. (c) Chain-disordered underdoped YBCO at $y=6.65$ and $x=0$ [$T_c(0)=62.5$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

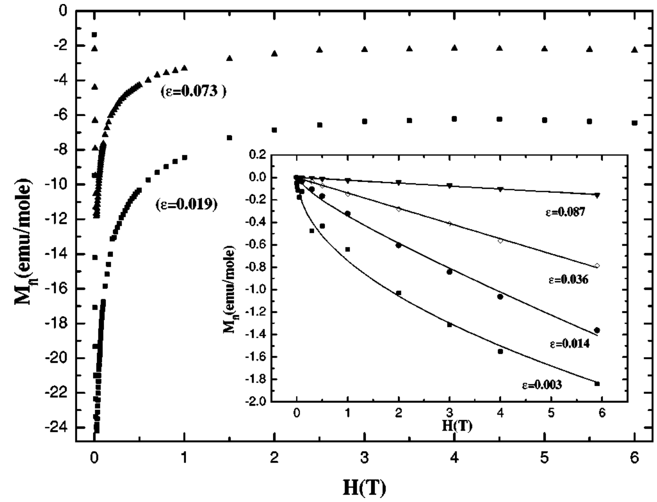

FIG. 4. Comparison of the magnetization curves M_{fl} vs H (after ZFC) in overdoped YBCO:Ca ($x=0.1$ and $y=6.96$) with the ones in optimally doped YBCO (inset), for similar reduced temperature ε. The solid lines fitting the data in optimally doped YBCO are derived from Eq. (2) in the text by means of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

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 Figs. 3(a), 3(b), and 3(c)], even relatively far from T_c, while for small fields (H$\lesssim$200 G) M_{fl} is linear in H, upon increasing the field the magnetization shows an upturn and then $|-M_{fl}|$ decreases. Let us remind the reader that in the GL weak fluctuation regime the saturation of the magnetization at high field has to be expected,[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 ‘‘zero-dimensional’’ case,[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

$$M_{fl}=-\frac{k_BT\frac{2}{5}\,\frac{\pi^2\xi^2}{\Phi_0^2}d^2H}{\left(\varepsilon+\dfrac{\pi^2\xi^2}{5\Phi_0^2}H^2d^2\right)}. \tag{3}$$

It can be noted 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 the most efficient screening.[29] By assuming the condition of zero dimension for these droplets, from Eq. (3) with $d=\xi(T)$, one derives an upturn field given by $H_{up}\simeq\varepsilon\Phi_0/\xi^2$. For $\xi\simeq 10$ Å and ε in the range 10^{-1}–10^{-2}, H_{up} is expected to be in the range of 10 T.

Thus the magnetization curves in Fig. 3 can hardly be ascribed to the breakdown of the GL approach of the type commonly observed in BCS superconductors.[2] In other

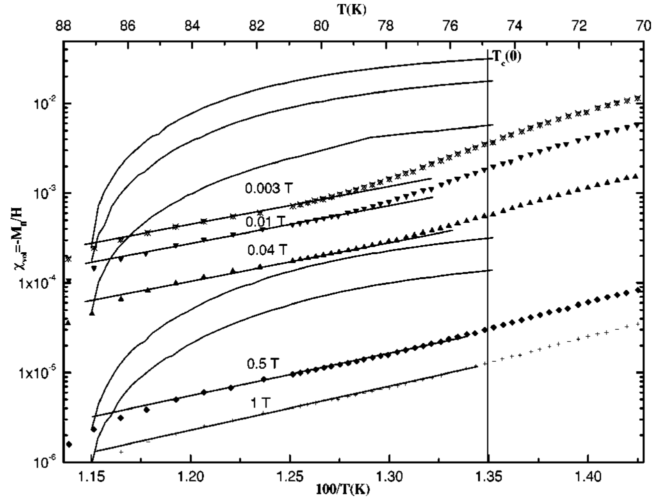

FIG. 5. Susceptibility as a function of the inverse temperature showing the activated temperature behavior (straight lines) in the sample at $y=6.96$ and $x=0.1$. Analogous temperature dependence has been observed in underdoped YBCO compounds. The lines bending are obtained by transferring above $T_c(0)$ the temperature behavior of the bulk susceptibility measured below T_c, and by normalizing the data at $T\simeq 88$ K.

words, a description of FD based on the GL functional in principle should be suitable in YBCO compounds for fields smaller than several T, particularly not too close to T_c, as in fact it is observed in optimally doped YBCO.[8,9,13,26,27]

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 was developed by Sewer and Beck[23] with the aim of justifying the unusual magnetization curves detected in underdoped YBCO.[18] The theory assumes a frozen amplitude of the order parameter while phase fluctuations are taken into account. As a consequence one has to deal with both thermally activated vortex loops and field-induced vortex lines. Two major conclusions of a general character can be outlined. For small fields the temperature dependence of the susceptibility is controlled by the vortex loops density n_v, for which

$$n_v = n_0 \exp[-E_0/kT] \tag{4}$$

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} increases only slightly with H and finally flattens. No upturn field is predicted, at least for $H \ll H_{c2}$.

In Fig. 5 the data for χ, defined as $(-M_{fl}/H)$, are shown to obey Eq. (4), rather well in correspondence to $E_0 \simeq 940$ K, in agreement with calculations yielding values for the activation energy around $10T_c$ (see Ref. 23, and references therein). E_0 turns out to depend only little on doping, being slightly field dependent. It is necessary to mention that the temperature dependence of the susceptibility above $T_c(0)$ differs from that measured below T_c, as shown in Fig. 5.

However, magnetization curves, such 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 also found in overdoped samples [see Figs. 2(a) and 3(a)].

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. Evidence of the inhomogeneous structure of cuprates has been found by means of neutron and electron diffraction,[30–32] as related to stripes and lattice effects or to local variations in the oxygen concentration, particularly near grain boundaries. Intrinsic inhomogeneities, with spatially dependent critical temperatures have been considered as possible causes of pseudogap phenomena.[33] A theory for high-temperature superconductivity and for the pseudogap temperature dependence based on an inhomogeneous charge distribution with a site-dependent transition temperature, were recently formulated.[34] In particular, Ovchinnikov *et al.*[22] considered the anomalous diamagnetism above T_c, induced by a nonuniform 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[35] could be explained. It should be stressed, however, that in this description[22] the magnetization is linear in the field, since the condition of a small field is implicitly assumed. Direct evidence of inhomogeneous magnetic domains showing diamagnetic activity above T_c was obtained by Iguchi *et al.*[36] by scanning SQUID microscopy in underdoped LASCO. Regions of a few tens of μm, precursors of bulk superconductivity, were imaged in this remarkable work.[36]

In light of the experimental findings and of the theoretical supports outlined above, we now consider, as a source of diamagnetism above T_c, the presence of locally superconducting droplets. From the volume susceptibility, let us say at T_c-5 K (see Fig. 1), one deduces that a few percent of the total material being a superconductor above the resistive transition, could actually justify the screening effects observed as FD. A test of this hypothesis is obtained from a search of the 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 is attributed locally to SC droplets, then one should detect differences between ZFC and 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 are observed. In Fig. 7 it is shown how the negative magnetization depends on time, displaying a progressive decrease from the ZFC value toward the one measured in the FC condition. The time constant for this relaxation process is close to the one measured in the critical state.[37] It can be remarked than in underdoped

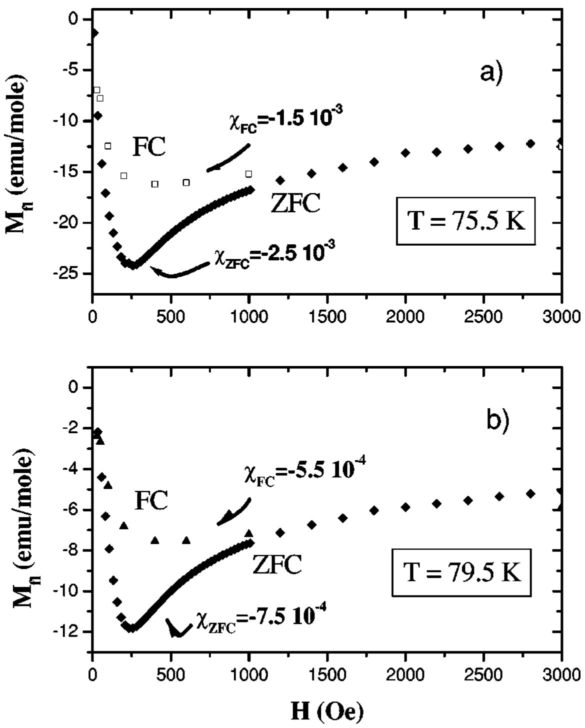

FIG. 6. Magnetization curves in YBCO:Ca at $x=0.1$ and $y=6.96$ obtained by cooling in zero field to a given temperature [(a) $T=75.5$ K and (b) $T=79.5$ K] above the resistive transition temperature and then applying the field (ZFC), and after the application of the field at room temperature, cooling at the same temperature, and measuring the correspondent magnetization (FC). The volume susceptibility in the limit $H\rightarrow 0$ is reported.

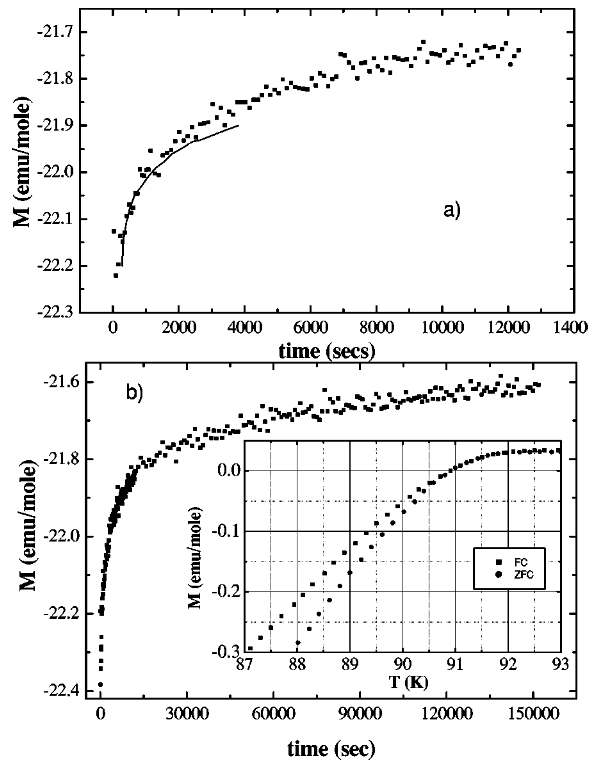

FIG. 7. Relaxation of the raw magnetization after ZFC and then a sudden application of a magnetic field of 260 G, in YBCO:Ca at $x=0.1$ and $y=6.96$, at $T=75.5$ K (a) Short-term relaxation. (b) Long-term relaxation. From the comparison of the ZFC and FC magnetizations in $H=20$ G (see the inset), an irreversibility temperature of the locally superconducting droplets at the 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 in Ref. 33 in the critical state, in optimally doped YBCO.

chain-disordered YBCO [Fig. 3(c)] no upturn is observed, and the ZFC and FC magnetization curves almost coincide. The explanation that will be supported by our theoretical picture is that 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 Sec. II many experimental checks allow us to rule out this hypothesis. Furthermore, samples grown with different procedures, already used by other authors, have been studied. Thus it is believed that an inhomogeneity does not mean the presence of macroscopic parts of the samples at different oxygen and/or calcium content, but is rather intrinsic, as like 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,[23] still keeping their basic idea of phase fluctuations but taking into account the presence of mesoscopic "islands" with nonzero average order parameter amplitudes that can be below or above the local irreversibility temperature.

Let us start, as in Ref. 23, from Eq. (1), by showing the order-parameter phase contribution

$$\mathcal{F}_{LD}[\theta]=\frac{1}{s}\sum_{l}\int d^2r\left\{J_{\parallel}\left(\nabla_{\parallel}\theta-\frac{2ie}{c\hbar}\mathbf{A}_{\parallel}\right)^2+J_{\perp}[1-\cos(\theta_{l+1}-\theta_l)]\right\},\qquad(5)$$

where $J_{\parallel}=\pi\hbar^2 n_h/4m_e$ and $J_{\perp}=2\pi\mathcal{J}n_h$ 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 two dimensions and vortex loops in the anisotropic model). The potential vector $\mathbf{A}_{\parallel}$ 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 $q_v=\sqrt{2\pi J_{\parallel}}$ and a vortex-antivortex pair has an energy $E_0=q_v^2\ln(r/\xi_{ab})$, 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 ns, and a correction to q_v was found self-consistently.

By considering, as usual, the partition function $Z=\int D\theta\exp(-\beta\mathcal{F}_{LD}[\theta])$ with $\beta=1/k_BT$, the susceptibility $\chi=\partial M_{fl}/\partial H$, where $M_{fl}=\partial F/\partial H$, is obtained as the sum of three contributions:

$$\chi=\left\langle\frac{\partial^2\mathcal{F}_{LD}}{\partial^2 H}\right\rangle^2-\beta\left\langle\left(\frac{\partial\mathcal{F}_{LD}}{\partial H}\right)^2\right\rangle+\beta\left(\left\langle\frac{\partial\mathcal{F}_{LD}}{\partial H}\right\rangle\right)^2 \qquad (6)$$

where $\langle\,\rangle$ is the thermal average.

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

$$\chi=\lim_{q\to 0}\frac{K(q)}{q^2}, \qquad (7)$$

where

$$K(q)=\frac{J_\|}{d}\left(\frac{2\pi}{\Phi_0}\right)^2\left[\frac{J_\|}{kT}[P(q)-Q(q)]-1\right]. \qquad (8)$$

In Eq. (8), $P(q)$ derives from the term $\langle(\partial\mathcal{F}_{LD}/\partial H)^2\rangle$ of Eq. (6), and it involves the current-current correlation function, as in Ref. 23,

$$P(\mathbf{q})=\frac{1}{NL^2}\sum_{l,l'}\int d^2\rho\int d^2\rho'\exp[i\mathbf{q}(\mathbf{r}-\mathbf{r}')]\left\langle\left(\nabla_x\theta_l(\rho)-\frac{2\pi}{\Phi_0}A_{\|,x}(\mathbf{r})\right)\left(\nabla_x\theta_{l'}(\rho')-\frac{2\pi}{\Phi_0}A_{\|,x}(\mathbf{r}')\right)\right\rangle, \qquad (9)$$

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

$$\nabla_x\theta_n(\rho)=d\sum_{s_1,l_1}\frac{y-R_y(m_1,l_1)}{|[\rho-\mathbf{R}(m_1,l_1)]^2+d^2(l-l_1)^2|^{3/2}}t(m_1,l_1),$$

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 $A_{\|,x}$ give the same contribution of $P_{\theta A}(q)=P_{A\theta}(q)=P_{\theta A}(-q)$]. 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 also be used to describe the vortex system in the glassy phase, below the irreversibility line temperature; 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

$$P_{AA}(q)=\frac{\pi^2}{36}\left(\frac{HL^2}{\Phi_0}\right)L^2q^2. \qquad (10)$$

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

$$P_{\theta A}(q)+P_{\theta A}(-q)=2\frac{Hd}{L}\frac{(2\pi)^2}{\Phi_0}\frac{Lq\cos\frac{Lq}{2}-2\sin\frac{Lq}{2}}{q^2}\sum_{l,l'}\exp(-dq|l-l_1|)\left\langle\sum_{m_1,l_1}t(m_1,l_1)\cos[iqlR_y(m_1,l_1)]\right\rangle.$$

The thermal average is performed under the assumption that the vortices are uniformly distributed in the planes; the calculations are reported in the Appendix. The expansion of $P_{\theta A}(q)$ in powers of qL gives

$$P_{\theta A}=-\frac{2\pi^2}{3}\left(\frac{HL^2}{\Phi_0}\right)^2+\frac{2L^2}{45}\pi^2\left(\frac{HL^2}{\Phi_0}\right)q^2. \qquad (11)$$

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

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

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), and (12) and Eq. (6) of Ref. 23, from Eq. (8) one finally obtains

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

where $\delta=\pi^2(J_\|/kT)$, and $H^*=\Phi_0/\pi R^2$ is an effective "critical" field depending on the island size (for $T\geqslant T_{\mathrm{irr}}$ the numerical factor is $\pi^2/3$).

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:

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

In view of the field-dependent vortex charge, the pair energy (in the limit $H < H^*$) becomes

$$E = \frac{E_0}{\left[1+\delta\left(\frac{H}{H^*}\right)^2\right]}.$$

According to Eq. (4), the thermally excited vortex pair density turns out to be 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

$$\chi = -\frac{kT}{s\Phi_0^2}\frac{1}{1+2n}\frac{\left(1+\delta\left(\frac{H}{H^*}\right)^2\right)^2}{n_v} - \frac{s^2\gamma^2(1+n)}{1+2n} \times\left[1+\delta\left(\frac{H}{H^*}\right)^2\right] + \frac{47\pi R^2}{540}\frac{J_\parallel}{s}\left(\frac{2\pi}{\Phi_0}\right)^2\delta\left(\frac{H}{H^*}\right)^2. \tag{15}$$

In the limit $H \to 0$ a good agreement between 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 of the presence of the factor $(H/H^*)^2$ and of a 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 is a critical parameter depending on some characteristics of the material. By choosing $\gamma = 6$, the interlayer distance $s = 12$ Å, $n = 2$, and $J_\parallel/kT = 2.5$, which are typical values for YBCO, for $T = 75.5$ K one estimates $R_0 \simeq 50$ Å. In this case the solution of the equation $\chi = 0$ is $H_{up}/H^* \simeq 0.06$ and, by considering the experimental value $H_{up} \simeq 250$ G, the effective critical field turns out to be $H^* \simeq 0.4$ T.

The isothermal curves can be obtained from Eq. (15) by means of a numerical integration. The shape of the magnetization curve depends on the parameters in the susceptibility, and by using the values quoted before, with $R = 370$ Å one derives the behavior sketched in Fig. 3(a) for an island below the irreversibility line. The same parameters with $T = 66$ K, $J_\parallel/kT = 1.8$, and $R = 10$ Å lead to the curve shown in Fig. 3(c) 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 the magnetization curves $-M_{fl}$ vs H in underdoped LASCO [Sr content $x = 0.1$, and $T_c(0) = 27.1$ K] with no upturn field. A role of the chains in favoring the nucleation of local superconducting droplets above T_c is conceivable. In fact, in chain-ordered compounds the droplets appear to have an irreversibility temperature higher than those in chain-disordered compounds, as shown by the difference in the magnetization curves [see Figs. 3(a)–3(c)]. We recall 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 underdoping or overdoping is also involved, since a marked variation of T_c with n_h is evidently crucial. It is noted that in the measurements of Carballeira *et al.*[19] in LASCO at $T_c = 27.1$ K, the magnetization curves show only a weak tendency to saturate, while in LASCO at $T_c \simeq 18$ K (therefore more underdoped) a scanning SQUID microscopy study by Iguchi *et al.*[36] did show diamagnetic effects to associate with 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 present until now between LASCO and YBCO.

IV. CONCLUSIONS

By means of SQUID measurements in the $Y_{1-x}Ca_xBa_2Cu_3O_y$ family, a nonconventional fluctuating diamagnetism has been observed in overdoped and 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. A recent theory[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 nonoptimally doped YBCO, particularly the ''precritical'' temperature activated behavior 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, nonpercolating, superconducting ''droplets.'' On the basis of both types of experimental findings, we have extended the theory of phase fluctuations in the presence of a nonzero order parameter. The terms leading to relevant dependence of the fluctuating magnetization on 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.

ACKNOWLEDGMENTS

Thanks are due to F. Borsa, F. Licci, and S. Kramer for having provided some of the samples used in the present work and for useful discussions. F. Cordero is thanked for the deoxygenation of the underdoped samples, and S. Sanna for the resistivity measurements as a function of temperature. One of the authors (A.V.) thanks H. Beck and A. Sewer for interesting discussions during his visit to Neuchatel University. D.E. carried out the work in the framework of the stage program of the INFM National School (2000).

APPENDIX

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

$$\left\langle \sum_{m,l} t(m,l)\cos iqlR_y(m,l) \right\rangle$$

$$=\sum_m \langle t(m)\rangle - \frac{1}{2}q^2\sum_m \langle R^2(m)\rangle + o(q^3). \tag{A1}$$

Indicating the number of vortex line elements parallel (antiparallel) to the field by $N_+(N_-)$, 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:

$$\sum_m t(m)\langle R_y^2(m)\rangle = \sum_{m+} \langle R_y^2(m)\rangle - \sum_{m-} \langle R_y^2(m)\rangle,$$

One can assume that the vortices are uniformely distributed in the planes, and that the y components of their positions are distributed on a line, separated each other by a distance $\Delta L = L/N_+$. Then, the ith vortex is in the mean position $\langle R_i\rangle = \Delta L i = (\Delta L/N_+)i$, with $i = -N_+/2 \cdots N_+/2$:

$$\sum_{m_\pm} \langle R(m_\pm)^2\rangle = \sum_{i=-N_+/2}^{N_+/2} \frac{L^2}{N_\pm^2} i^2 = \frac{L^2}{12N_\pm}(N_\pm+2)(N_\pm+1).$$

By considering $N_\pm \gg 1$, one finally finds

$$\sum_m t(m)\langle R_y^2(m)\rangle \approx \frac{L^2}{12}(N_+ - N_-).$$

Then Eq. (A1) can be written

$$\sum_m t(m)\langle \cos qR(m)\rangle = \frac{HL^2}{\Phi_0} - q^2\frac{L^4H}{24\Phi_0} + o(q^3).$$

[1] See *Fluctuation Phenomena in High Temperature Superconductors*, edited by M. Ausloos and A.A. Varlamov (Kluwer, Dordrecht, 1997); also see A.A. Varlamov, G. Balestrino, E. Milani, and D.V. Livanov, Adv. Phys. **48**, 655 (1999).
[2] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1996), Chap. 8.
[3] J. Kurkijarvi, V. Ambegaokar, and G. Eilenberger, Phys. Rev. B **5**, 868 (1972).
[4] See A.I. Larkin and A.A. Varlamov, in *Physics of Conventional and Non-Conventional Superconductors*, edited by K.-H. Bennemann and J.B. Ketterson (Springer Verlag, Berlin, 2002).
[5] L.N. Bulaevskii, Int. J. Mod. Phys. B **4**, 1849 (1990).
[6] L.N. Bulaevskii, M. Ledvig, and V.G. Kogan, Phys. Rev. Lett. **68**, 3773 (1993).
[7] V.G. Kogan, M. Ledvij, A.Yu. Simonov, J.H. Cho, and D.C. Johnston, Phys. Rev. Lett. **70**, 1870 (1993).
[8] M.A. Hubbard, M.B. Salamon, and B.W. Veal, Physica C **259**, 309 (1995).
[9] C. Baraduc, A. Buzdin, J.Y. Henry, J.P. Brison, and L. Puech, Physica C **248**, 138 (1995).
[10] A.E. Koshelev, Phys. Rev. B **50**, 506 (1994).
[11] A. Budzin and V. Dorin, in *Fluctuation Phenomena in High Temperature Superconductors* (Ref. 1), p. 335. A detailed theoretical analysis of the field dependence of the Gaussian fluctuations in layered superconductors was given by T. Mishonov and E. Penev, Int. J. Mod. Phys. B **14**, 3831 (2000).
[12] T. Schneider and U. Keller, Int. J. Mod. Phys. B **8**, 487 (1993), and references therein; Physica C **207**, 336 (1993); also see T. Schneider and J.M. Singer, in *Phase Transition Approach to High Temperature Superconductivity* (Imperial College Press, London, 2000), Chap. 6.
[13] A. Junod, J-Y. Genoud, G. Triscone, and T. Schneider, Physica C **294**, 115 (1998).
[14] S. Salem-Sugui and E.Z. Dasilva, Physica C **235**, 1919 (1994).
[15] K. Kanoda, T. Kawagoe, M. Hasumi, T. Takahashi, S. Kagoshima, and T. Mizoguchi, J. Phys. Soc. Jpn. **57**, 1554 (1988).
[16] P. Carretta, A. Lascialfari, A. Rigamonti, A. Rosso, and A.A. Varlamov, Int. J. Mod. Phys. B **13**, 1123 (1999).
[17] D. Babic, J.R. Cooper, J.W. Hodby, and Chen ChangKang, Phys. Rev. B **60**, 698 (1999).
[18] P. Carretta, A. Lascialfari, A. Rigamonti, A. Rosso, and A.A. Varlamov, Phys. Rev. B **61**, 12 420 (2000).
[19] C. Carballeira, J. Mosqueria, A. Revcolevschi, and F. Vidal, Phys. Rev. Lett. **84**, 3157 (2000).
[20] B. Rosenstein, B.Y. Shapiro, R. Prozorov, A. Shaulov, and Y. Yeshurun, Phys. Rev. B **63**, 134501 (2001).
[21] A. Rigamonti and P. Tedesco, *Lecture Notes at the INFM National School in Structure of Matter* (Villa Gualino, Torino, September 2000); *Scientifica Acta* (University of Pavia, Pavia, 2000), Vol. XV, p. 49.
[22] Yu.N. Ovchinnikov, S.A. Wolf, and V.Z. Kresin, Phys. Rev. B **60**, 4329 (1999).
[23] A. Sewer and H. Beck, Phys. Rev. B **64**, 014510 (2001).
[24] P. Carretta, A. Lascialfari, A. Rigamonti, F. Tedoldi, F. Bolzoni, and F. Licci, Int. J. Mod. Phys. B **14**, 2815 (2000).
[25] U. Welp, S. Fleshler, W.K. Kwok, R.A. Klemm, V.M. Vinokur, J. Downey, B. Veal, and G.W. Crabtree, Phys. Rev. Lett. **67**, 3180 (1991).
[26] C. Torron, A. Diaz, A. Pomar, J.A. Veira, and F. Vidal, Phys. Rev. B **49**, 13 143 (1994)
[27] J. Mosqueira, C. Carballeira, M.V. Ramallo, C. Torron, J. Veira, and F. Vidal, Europhys. Lett. **53**, 632 (2001)
[28] J.L. Tallon, C. Bernhard, H. Shaked, R.L. Hitterman, and J.D. Jorgensen, Phys. Rev. B **51**, 12 911 (1995).
[29] J.P. Gollub, M.R. Beasley, R. Callarotti, and M. Tinkham, Phys. Rev. B **7**, 3039 (1973).

[30] M. Gutmann, S.J.L. Billinge, E.L. Brosha, and G.H. Kwei, Phys. Rev. B **61**, 11 762 (2000).
[31] E. Bozin, G. Kwei, H. Takagi, and S. Billinge, Phys. Rev. Lett. **84**, 5856 (2000).
[32] Z. Akase, Y. Tomokiyo, Y. Tanaka, and M. Watanabe, Physica C **339**, 1 (2000).
[33] Yu.N. Ovchinnikov, S.A. Wolf, and V.Z. Kresin, Phys. Rev. B **63**, 064524 (2001).
[34] E.V.L. De Mello, E.S. Caixeiro, and J.L. Gonzales, cond-mat/0110519 (unpublished); cond-mat/0110479 (unpublished).
[35] C. Bergemann, A.W. Tyler, A.P. Mackenzie, J.R. Cooper, S.R. Julian, and D.E. Farrell, Phys. Rev. B **57**, 14 387 (1998).
[36] I. Iguchi, T. Yamaguchi, and A. Sugimoto, Nature (London) **412**, 420 (2001).
[37] Y. Yeshurun, A.P. Malozemoff, and A. Shaulov, Rev. Mod. Phys. **68**, 911 (1996).