

THE NATURE OF SUPERCONDUCTING FLUCTUATIONS AND NEW ASPECTS IN HIGH T_c SUPERCONDUCTORS

ALESSANDRO LASCIALFARI (*,**) e ATTILIO RIGAMONTI (**)

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SUNTO. – Dopo una breve introduzione sulle fluttuazioni superconduttive, si presentano tipici risultati sperimentali in diversi sistemi. Le fluttuazioni superconduttive sono note esistere sin dagli anni '60 e sono state evidenziate dapprima in nanoparticelle di superconduttori convenzionali. Nelle ultime decadi, attraverso misure di diamagnetismo precursore al di sopra della temperatura critica T_c , sono stati messi in evidenza particolari aspetti delle fluttuazioni nei superconduttori ad alta T_c , particolarmente in quelli definiti “sotto-drogati”. I risultati ottenuti, qui riassunti, sono stati interpretati in termini di fluttuazioni della fase del parametro d'ordine superconduttivo, una funzione complessa. Un modello teorico, già sviluppato per condizioni rigorose di dimensionalità nulla (quindi in sistemi di nanoparticelle) è stato da noi esteso a includere approssimativamente anche sistemi a dimensioni finite, dell'ordine della distanza di coerenza tra isole locali di superconduttività fluttuante. Sono così stati descritti e giustificati i risultati di diamagnetismo fluttuante in cuprati, pnictidi e anche in superconduttori a base Fe. Oltre a questi risultati, qui riassunti, vengono anche presentati risultati preliminari ottenuti in superconduttori a base Ca. Si mostra come un particolare parametro (il campo di upturn) ove la magnetizzazione diamagnetica inizia a diminuire al crescere del campo, consente di discriminare con sicurezza gli effetti di natura squisitamente superconduttiva da simili effetti di natura più convenzionale, legati a una distribuzione di T_c per disomogeneità di carattere chimico.

(*) Dipartimento di Fisica & INSTM, Università degli Studi di Pavia, Italy.
E-mail: alessandro.lascialfari@unipv.it

(**) Dipartimento di Fisica “A. Volta”, Università degli Studi di Pavia, Italy.
E-mail: attilio.rigamonti@unipv.it

ABSTRACT. – After a brief introduction to thermodynamical superconducting fluctuations, some experimental results in different systems are presented. Superconducting fluctuations were predicted and revealed in nanoparticles of conventional superconductors since late 60s. However, just in the last two decades phenomena related to an anomalous diamagnetism have been discovered in high- T_c underdoped compounds, mainly by collecting the isothermal magnetization curves above the critical temperature T_c . These experimental data can be interpreted in terms of fluctuations of the phase of the order parameter and a related theoretical model can explain the results in cuprates, pnictides and Fe-based materials. Such results, here presented together with preliminary data on a Ca-based high- T_c system, allow one to extract a fundamental parameter, the upturn magnetic field above which the diamagnetic magnetization initiates to decrease on increasing the field. Its temperature dependence distinguishes among diamagnetic effects related to superconducting phase fluctuations and to analogous effects due to chemical inhomogeneities.

1. FLUCTUATIONS, SUPERCONDUCTING FLUCTUATIONS AND RELATED DIAMAGNETISM

The concept of fluctuations of a specific quantity, is spreaded across different disciplines, ranging from *e.g.* economy, finance, health sciences, mathematics, chemistry and physics. In physics, one of well known experimental evidences of fluctuations (of thermodynamical type), is the density fluctuations in liquids, generating the critical opalescence effect, observed since centuries ago, that can be described by means of the Ginzburg-Landau (GL) theory. As a translation of the GL theory of fluctuations in correspondence of the transition critical temperature in different systems (magnetic, superconducting, superfluid, etc), superconducting fluctuations (SF) of the order parameter (the Cooper pair wave-function [1,2]) were evidenced by measurements mainly of the resistivity, the magnetization and the susceptibility just above T_c [3]. After the discovery of high- T_c systems [4], through STM microscope it was possible to observe directly superconducting fluctuations in the system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

From the quantitative point of view, the order parameter of superconductors is represented by the wave-function of the Cooper pairs: $\Psi = |\Psi| e^{i\vartheta}$, where $|\Psi|$ is the modulus and ϑ is the phase [5]. The square modulus of this parameter can be locally different from zero for $T \geq T_c$, where Cooper pairs start to form in metastable states: the system is preparing for the transition to the superconducting phase (*Fig. 1*).

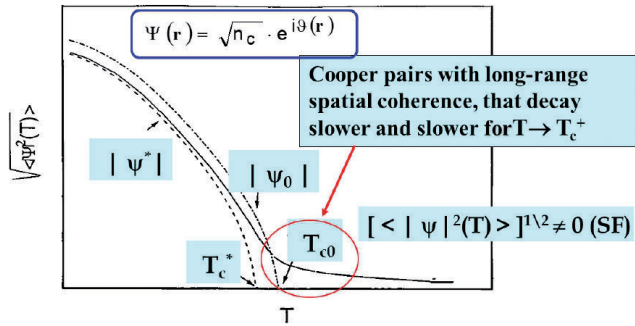


Fig. 1 – The order parameter is renormalized by the fluctuations. Dashed line: curve deduced from the Bardeen-Cooper-Schrieffer theory, with T_c^* renormalized by fluctuations. Continuous line: T -dependence of $|\Psi|$ renormalized by fluctuations.

The occurrence of superconducting fluctuations has relevant consequences: the “fluctuating” Cooper pairs above T_c imply the presence of (fluctuating) diamagnetism and of excess conductivity (Fig. 2). A qualitative understanding of the fluctuating diamagnetism (FD) can be achieved by considering the two electrons (of the Cooper pairs) at an average distance of the order of $\xi_{GL}(T)$ (the Ginzburg-Landau coherence length).

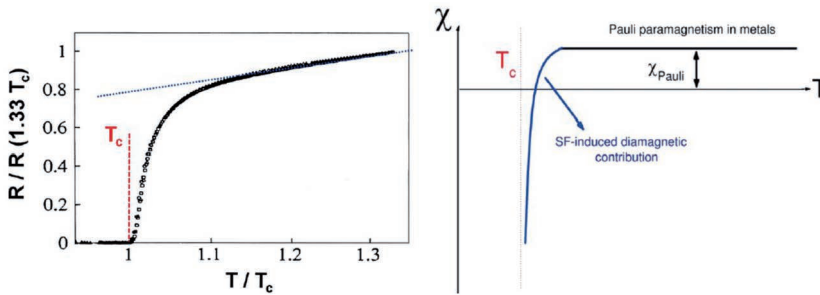


Fig. 2 – Left: renormalized electrical resistance as a function of reduced temperature. Above T_c where the SF set in, the resistance is decreased with respect to metallic behaviour (blue line). Right: effect of magnetic susceptibility “smoothing” just above T_c , as consequence of the fluctuating diamagnetism.

The theory of FD in conventional superconductors (SC) in the limit of zero field has an exact solution, proposed by Prange [2,5,6], but no field quenching of fluctuating pairs is taken into account. In the

1960s, Gollub, Tinkham et al [7,8], demonstrated experimentally in metals the breakdown of a description which neglects the effect of the field in suppressing the fluctuating pairs. Further developments of the GL theory of SF in the gaussian approximation, allowed to extract the H-dependence of the magnetization (Fig. 3).

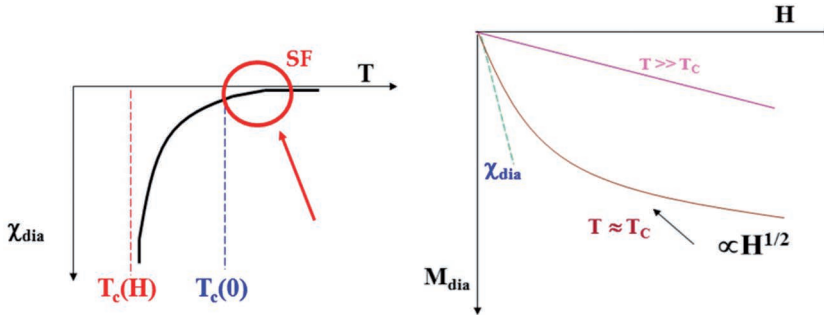


Fig. 3 – Sketchy T-behaviour of magnetic susceptibility (after subtraction of the Pauli term) and H-behaviour of the isothermal magnetization curves in the presence of SF. The curves on the right of the figure report the behaviour according to the GL theory in the gaussian approximation.

2. SUPERCONDUCTING FLUCTUATIONS IN Pb NANOPARTICLES: THE ZERO-DIMENSIONAL CASE

A case where the theory of superconducting fluctuations has been directly verified, is the zero-D (0D) case for Pb nanoparticles [2,5]. In Fig. 4 the diamagnetic magnetization M_{dia} is reported as a function of H for 3 distinct temperatures just above T_c ($T_c(0) = 7.09$ K), in the sample with average diameter $d=750$ Å. The solid lines represent the best fit obtained by using the 0D equations [5], derived from complete GL theory in 0D (*i.e.* by including the $|\Psi_0|^4$ term in the free energy expression [2,5]). It is noted the presence of an experimental “upturn field” H_{up} that shifts toward lower fields as the temperature is decreased: $H_{\text{up}} = 110, 67, 60$ Oe. The zero-dimensional condition is applied to the evanescent SC droplets of size which causes the maximum diamagnetic screening. The magnetic susceptibility data present clearly the diamagnetic effect, reported in Fig. 5 for two different particles dimensions. In the 0D-case it could be noted that, by means of GL theory, a direct eval-

uation of the thermodynamical free energy can be made and the effect of H can be exactly taken into account [9].

Interestingly the data in MgB_2 are qualitatively explained for $\xi(T \rightarrow 0) \approx 100 \text{ \AA}$ and $10^{-3} < \varepsilon < 10^{-2}$ ($\varepsilon = (T - T_c) / T_c$); in this case one obtains $H_{up} \approx 100 \div 1000 \text{ Oe}$ by using the expression of diamagnetic magnetization in the 0D case [10]:

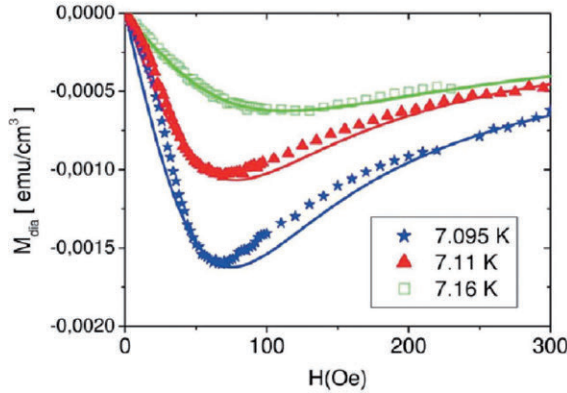


Fig. 4 – Pb nanoparticles with average diameter $d=750 \text{ \AA}$: magnetization curves for T just above $T_c(0)=7.09\text{K}$. The “upturn” field, clearly evidenced by experimental data, shifts toward higher values as the temperature is increased.

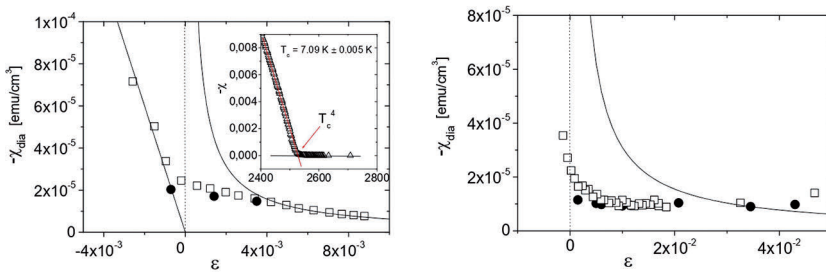


Fig. 5 – Temperature behavior of the magnetic susceptibility for Pb nanoparticles of average diameter 750 \AA (left) and 160 \AA (right) (figure from [9]). Solid circles: data from the isothermal magnetization curves; empty squares: data from the isofield measurements as a function of T . The solid lines report the behavior of M_{dia} obtained by neglecting nonlinear fluctuations. In the inset the curve from which the transition temperature has been determined is shown (ε =reduced temperature).

3. HIGH- T_c SUPERCONDUCTORS: ANOMALOUS FLUCTUATING DIAMAGNETISM

Since 1986, a new class of high- T_c SC (HTSC) compounds has been developed. A particular ensemble of such systems is constituted by the so-called high- T_c cuprates, the first example being the one of Bednorz and Muller [4], the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ oxide. These systems do not follow the Bardeen-Cooper-Schrieffer (BCS) theory [3], the main coupling mechanism still being substantially unknown. The main family of high- T_c compounds other than cuprates, are the Fe-based one [11].

In HTSC, the diamagnetic effects above T_c depend on the charge carriers concentration n_h [12-14]. One has to distinguish between optimally doped materials (highest T_c , optimal concentration n_h^{opt}), underdoped compounds ($n_h < n_h^{\text{opt}}$) and overdoped ones ($n_h > n_h^{\text{opt}}$). The behaviour of T_c vs n_h is plotted in *Fig. 6* in order to clarify the different dependence of T_c from the carrier concentration in the two branches.

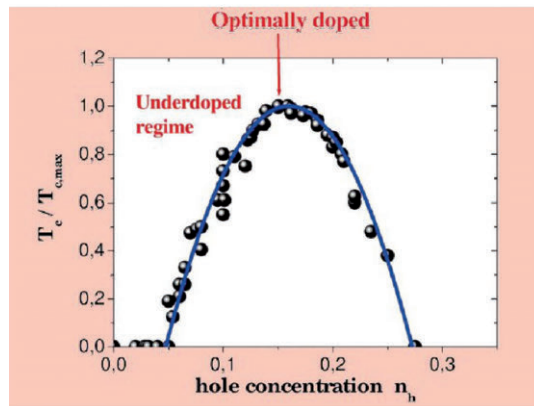


Fig. 6 – Renormalized superconducting transition temperature T_c vs charge carriers concentration n_h . The curve is universal, for a variety of HTSC.

In the underdoped HTSC, the SF has an anomalous diamagnetic behaviour above T_c . The main characteristics are (see *Fig. 7* for the system $\text{SmBa}_2\text{Cu}_{3-y}\text{Al}_y\text{O}_{6+d}$ [15]): (i) the absolute value of the diamagnetic magnetization is particularly high, presumably due to high T_c and to the short coherence length; (ii) there exists an upturn field H_{up} that assumes low values (with respect *e.g.* to the critical field ones), increases with T (for $T > T_c$) and depends on the magneto-thermal history. The origin of

this anomalous behaviour relies in the phase (ϑ) fluctuations of the order parameter, as evidenced by the model presented *e.g.* in Ref.s [14,16]. The model predicts the presence of vortices and anti-vortices above T_c , giving rise to mesoscopic superconducting droplets (and phase fluctuations). The irreversibility effect and the effect of the magnetic field on the thermally-activate vortices has been predicted correctly as well. As a consequence of the existence of such phenomenon, the predicted M vs H behavior is sketched in Fig. 8, where the curves are not in scale. As seen, in addition to the observed “low” upturn field, there is a second “high” upturn field ($> 2,5 \times 10^4$ Oe) corresponding to the Cooper pairs breaking and related to the superconducting critical field.

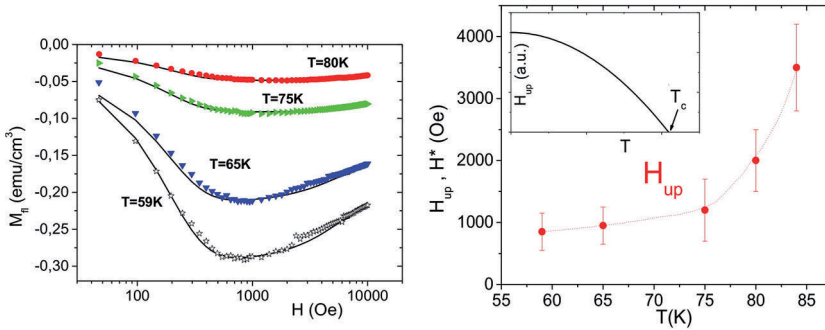


Fig. 7 – Fluctuating magnetization curves in $\text{SmBa}_2\text{Cu}_{3-y}\text{Al}_y\text{O}_{6+\delta}$ (left). The temperature behaviour of the upturn field H_{up} is reported on the right (for details on this aspect see Ref. [15]). It is noted the increase of H_{up} with T , typical of underdoped HTSC compounds.

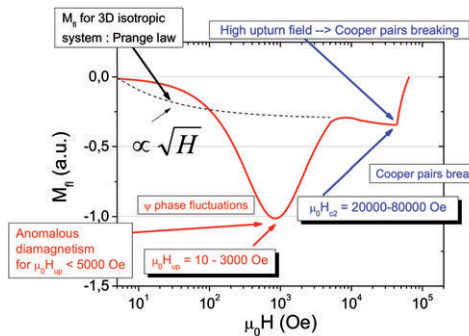


Fig. 8 – Sketchy view of the fluctuating magnetization behaviour as a function of the external field, above T_c in a system where anomalous diamagnetism occurs. At low fields, the presence of an upturn field due to phase fluctuations of the order parameter is evidenced. At high field the conventional critical field upturn due to the Cooper pairs break is shown.

4. SUPERCONDUCTING FLUCTUATION DIAMAGNETISM IN PNICTIDES, FE-BASED SYSTEMS AND IN CALABALACUO

The presence of an anomalous diamagnetism of sizeable strength and of an upturn field in the isothermal fluctuating magnetization curves, has been revealed also in pnictide SC systems [17] and in Fe-based superconductors [18]. The fluctuating magnetization curves are shown in *Fig. 9*, left and right side, respectively.

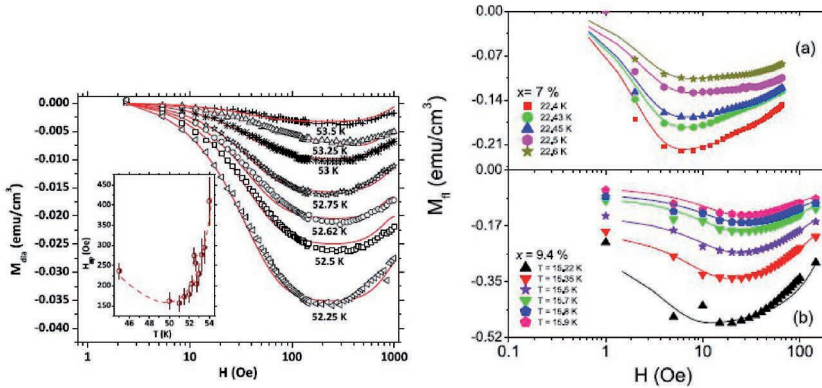


Fig. 9 – Left: isothermal fluctuating magnetization in $\text{SmFeAsO}_{0.8}\text{F}_{0.2}$. The upturn fields (ranging from 200 to 400 Oe) at different temperatures above T_c ($T_c=52.3\text{K}$) are displayed. The fitting red curves have been obtained by means of an early model reported in [14] and [15]. In the inset H_{up} behaviour, increasing by increasing T , is reported (dashed line is a guide to the eye). Right: isothermal fluctuating magnetization in $\text{Ba}(\text{Fe}_{1-x}\text{Rh}_x)_2\text{As}_2$ iron-based SC, for $x=7\%$ and $x=9\%$. The solid lines are fits obtained using the model in Ref. [15].

A final example concerns a particular Ca-doped compound, $\text{Ca}_x\text{La}_{1-x}\text{Ba}_{1.75-x}\text{La}_{1.25+x}\text{Cu}_3\text{O}_{6+y}$ (in brief CALABALACUO, first synthesized in 1993), whose peculiarity is to have the possibility of double doping (both Ba/Ca and/or oxygen content). The crystal structure of the system is reported in *Fig. 10a*, while *Fig. 10b* reports the M vs H fluctuating curves typical of an underdoped compound ($x=0.4$, $y=1.15$) for $T>T_c$.

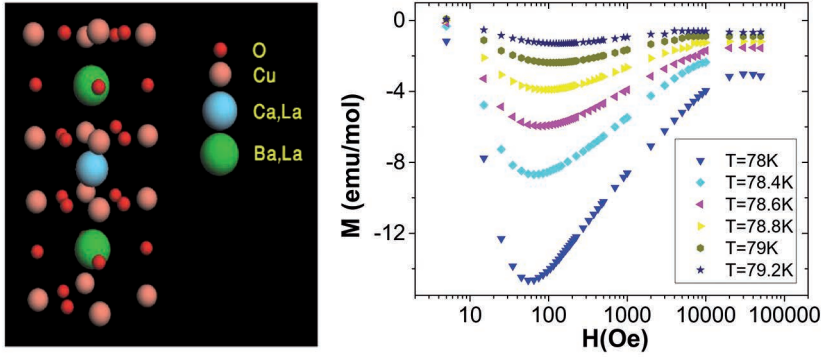


Fig. 10 – Left: Crystal structure of $\text{Ca}_x\text{La}_{1-x}\text{Ba}_{1.75-x}\text{La}_{1.25+x}\text{Cu}_3\text{O}_{6+y}$; Right: diamagnetic magnetization for the compound with $x=0.4$, $y=1.15$ (near to optimal doping but still underdoped). Even for this compounds, an upturn field is displayed for $T > T_c$ ($T_c = 78.4\text{K}$).

5. CONCLUSIONS

It has been recalled how in underdoped HTSC compounds an anomalous diamagnetism was revealed by the experimental M vs H curves collected at constant temperature just above T_c (once corrected by Pauli paramagnetism and paramagnetic impurities contribution, thus giving M_{dia} , the diamagnetism fluctuating magnetization). The anomalous diamagnetism is accompanied by irreversibility effects (field-cooled, FC, and zero-field-cooled, ZFC, curves different also above T_c) and can be explained in terms of mesoscopic charge inhomogeneities and of the simultaneous presence of an XY anisotropic liquid of vortexes, giving rise to phase fluctuations of the order parameter. An upturn field H_{up} that increases with T above T_c is the signature of such fluctuating diamagnetism, whereas for chemical inhomogeneities the T -behaviour of the upturn is demonstrated to have the opposite T -behaviour. The effect of the field is qualitatively described by the 0-D model derived from the classical GL theory: above T_c evanescent droplets set in and an upturn field increasing with T is singled out. On the other hand, in optimal SC M_{dia} follows the conventional GL theory thus giving M_{dia} linear in H for $T \gg T_c$, and $M_{\text{dia}} \propto H^{1/2}$ around T_c .

Finally one should note that the diamagnetic behaviour could be linked to the superconducting mechanism and eventually to the pseudo-gap formation, a strongly debated issue [see *e.g.* 19-21].

From the nature of SF, the origin of the SC mechanism could be ideally deduced and it is currently under further theoretical investigation.

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