# Magnetic Aging in $Bi_2Sr_2CaCu_2O_8$ Displaying the Paramagnetic Meissner Effect

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Magnetic relaxation measurements have been performed on a bulk, melt-cast sample of $Bi_2Sr_2CaCu_2O_8$, displaying the paramagnetic Meissner effect (PME), revealing zero external field magnetic aging in a superconducting system. The aging effect, being a cooperative phenomenon, points out that the spontaneous orbital currents existing in PME samples behave collectively. The results can be understood by modeling of the polydomain microstructure of the superconducting grains as Josephson junction networks with randomly distributed $\pi$ junctions. [S0031-9007(98)08121-6]

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Certain ceramic high temperature, superconductors exhibit a positive magnetization when cooled in sufficiently low magnetic fields [1,2]. This unusual phenomenon has been called paramagnetic Meissner effect (PME). Originally, PME was observed in the $Bi_2Sr_2CaCu_2O_8$ (Bi-2212) system, which is the most extensively studied system. It has been shown that PME samples also display other peculiar properties besides the positive field cooled (fc) magnetization. In ac susceptibility experiments, the modulus of the second harmonic reveals the existence of internal fields in zero field cooled PME samples [3]. In microwave absorption PME samples display a maximum in the absorption in zero external field, instead of the minimum seen in non-PME samples [2].

A positive fc magnetization has also been observed in measurements on Nb disks [4–6], a conventional superconductor. The fact, though, that none of the other peculiar properties have been seen in this system differentiates it from the case of the Bi-2212 system [7]. It has been suggested [8] that the positive magnetization in this case is due to a Bean state with compressed flux.

Several theoretical models have been proposed in order to explain PME. These models are based on the appearance of spontaneous orbital currents developing below $T_c$. The spontaneous orbital currents, appearing even in zero applied field, are due to superconducting loops containing odd numbers of $\pi$ junctions [9]. A $\pi$ junction is a Josephson junction in which the Cooper pairs acquire a phase shift of $\pi$ across it. Sigrist and Rice [10] proposed that such $\pi$ junctions could arise naturally as a consequence of $d$-wave pairing of the superconducting order parameter. The most discussed candidate for this pairing is the $d_{x^2-y^2}$ state. This conjecture was supported by phase sensitive tests of the symmetry of the pairing state in high-$T_c$ superconductors [11,12]. These tests were done using a scanning SQUID microscope [11] and showed that spontaneous orbital currents were generated in $YBa_2Cu_3O_7$ rings containing three grain-boundary junctions, consisting of two ordinary Josephson junctions (0 junctions) and one $\pi$ junction, generating half a magnetic flux quantum, while no spontaneous currents were created in rings which contained two junctions.

In this Letter we report zero magnetic field aging as revealed by measurements of the magnetic relaxation of a Bi-2212 PME sample, which implies that the spontaneous magnetic moments behave collectively. In order to understand this collective behavior, we investigate two possibilities: the dipole-dipole interaction between the spontaneous magnetic moments associated with different $\pi$ loops and the existence of a Josephson junction network containing a random mixture of $\pi$ junctions and 0 junctions. The latter explanation also implies the possible occurrence of a novel equilibrium thermodynamic phase, occurring in zero external magnetic field, characterized by the random freezing of local vortex (superconducting current) degrees of freedom.

The sample used in this experiment was a granular $Bi_2Sr_2CaCu_2O_x$ sample, with $x \approx 8.18$, manufactured by a melt-cast process [13]. The sample is single phase apart from a minor fraction of Bi-2223 phase, which is nondetectable in x-ray diffraction, but is revealed from a faint anomaly in the $M$ vs $T$ curves at about 105 K. The onset of superconductivity is at $T_c \approx 87$ K and the transition width, as is defined by the low field magnetization, is approximately 5 K. A comparison with typical sintered samples shows that the grains are significantly larger and more densely packed in melt-cast samples. Recent studies using high resolution transmission electron microscopy (TEM) showed that our sample, as well as other Bi-2212 samples displaying the PME, have an extremely polydomain microstructure on a $\mu$m length scale [14]. These domains are preferably $c$ axis oriented with atomically sharp interfaces (width $\leq 1$ nm), parallel to the $c$ axis. The interface plane can freely rotate around the $c$ axis, resulting in a rather broad distribution of the interface orientations separating

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domains in the *ab* plane. The experimental setup used to study the magnetic properties of the PME sample was a low field superconducting quantum interference device magnetometer [15]. In this setup, the magnetic field is generated by a small solenoid working in a persistent mode during measurements and only at fields below $H_{c1}$ of its superconducting wire, thus the remanent field of the magnet was virtually zero. The sample space is shielded by $\mu$ metal and niobium cans, resulting in a residual field at the position of the sample of less than 0.5 mG. The longitudinal component of this field was further reduced by applying a compensating field yielding a longitudinal residual field of less than 0.1 mG. During all measurements, the sample was kept stationary in one of the coils of a third order gradiometer.

The zero field cooled (zfc) and fc susceptibilities ($M/H_{\mathrm{dc}}$) are plotted versus temperature in Fig. 1, for dc magnetic fields between 0.001 and 1 G. At low magnetic fields $M_{\mathrm{fc}}/H_{\mathrm{dc}}$ becomes positive, displaying the largest magnitude at the lowest field. For fields larger than approximately 0.3 G, $M_{\mathrm{fc}}/H_{\mathrm{dc}}$ becomes negative, with an increasing magnitude with increasing field. $M_{\mathrm{zfc}}/H_{\mathrm{dc}}$ displays a sharp decrease with decreasing temperature, reaching a constant level of approximately $-1$ (in SI units) at low temperatures indicating a well screened sample. For temperatures just below $T_c$, $M_{\mathrm{zfc}}/H_{\mathrm{dc}}$ becomes more diamagnetic with increasing field. Furthermore, in a narrow temperature range and for fields for which $M_{\mathrm{fc}}/H_{\mathrm{dc}}$ is paramagnetic, $M_{\mathrm{zfc}}/H_{\mathrm{dc}}$ also becomes paramagnetic, displaying a positive maximum a few degrees below the transition temperature. A positive $M_{\mathrm{zfc}}/H_{\mathrm{dc}}$ in a narrow temperature region below $T_c$ has also been observed in numerical calculations on a system of independent $\pi$ loops [16].

The relaxation of the zfc magnetization has been measured by cooling the sample in zero field to the measuring temperature, allowing the sample to remain at that temperature for a certain time $t_w$ and then applying the probing field and recording the change of the magnetization with observation time as the temperature is kept constant. The relaxation is logarithmically slow in time and always towards a less diamagnetic magnetization. Also, at a temperature where $M_{\mathrm{zfc}}/H_{\mathrm{dc}}(T)$ is positive, the magnetization can be negative at short observation times while it becomes positive at longer observation times (Fig. 2c). In Fig. 2 $M_{\mathrm{zfc}}/H_{\mathrm{dc}}$ has been plotted against the observation time, at different temperatures, for $H_{\mathrm{dc}} = 0.02$ G. Two different wait times have been used in these experiments, $t_w = 300$ and 3000 s. The curves reveal a dependence of $M_{\mathrm{zfc}}/H_{\mathrm{dc}}$ on the wait time $t_w$. This phenomenon is called aging and has been observed for other magnetic systems such as spin glasses [17] and interacting magnetic nanoparticle systems

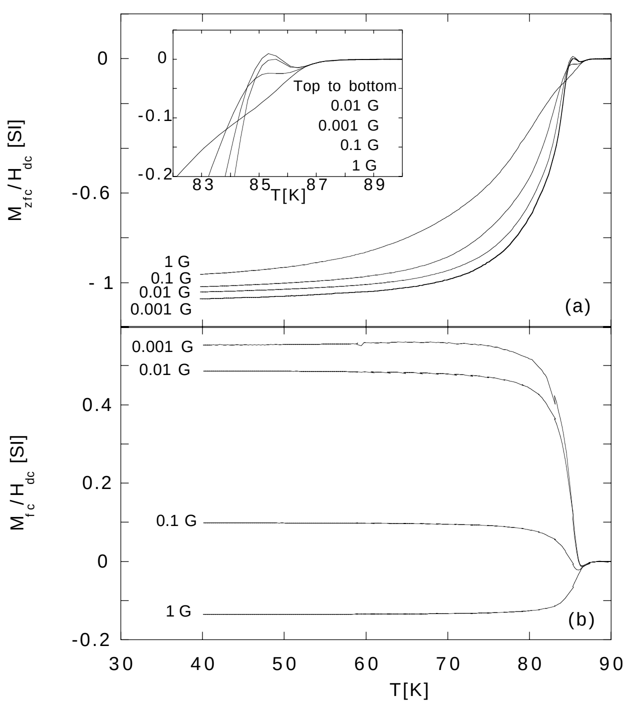


FIG. 1. $M_{\mathrm{zfc}}/H_{\mathrm{dc}}$ (a) and $M_{\mathrm{fc}}/H_{\mathrm{dc}}$ (b) vs temperature for different applied fields. The inset in (a) shows an enlargement of the region close to $T_c$, where the paramagnetic peak of $M_{\mathrm{zfc}}/H_{\mathrm{dc}}$ is displayed.

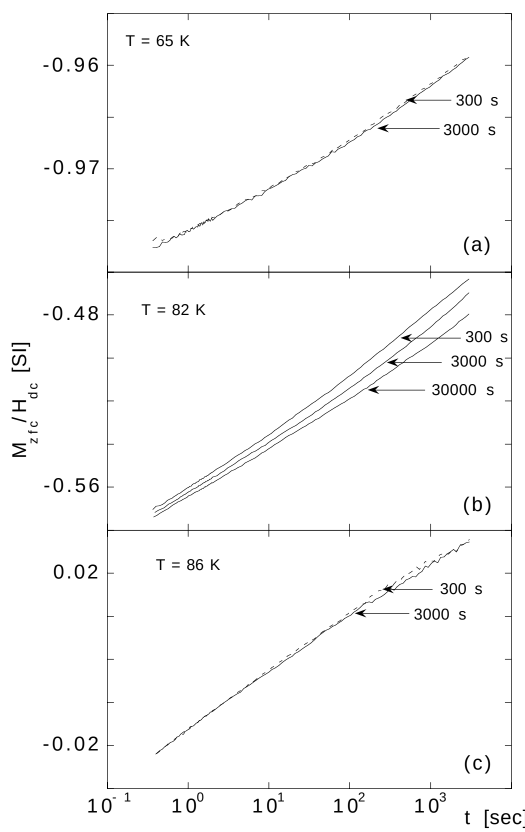


FIG. 2. $M_{\mathrm{zfc}}/H_{\mathrm{dc}}$ is plotted vs observation time for $H_{\mathrm{dc}} = 0.02$ G at the temperatures (a) 65 K, (b) 82 K, and (c) 86 K. The wait times used were 300 and 3000 s; in (b) the result for $t_w = 30\,000$ s is also included.

[18], but it has never been observed in a superconducting system before. The dependence of aging on the temperature is also seen in Fig. 2. At temperatures close to the superconducting transition and at temperatures much lower than the transition temperature, no aging can be resolved within our experimental resolution. On the contrary, in the temperature range 80–85 K, this phenomenon is clearly displayed.

In Fig. 3 $M_{\mathrm{zfc}}/H_{\mathrm{dc}}$ is plotted against the observation time for different fields, at 82 K, and for $t_w = 300$ and 3000 s. At low fields, the aging effect is clearly revealed, but with increasing field, the effect gradually becomes more difficult to observe. Finally, for sufficiently large magnetic fields, fields larger than approximately 1 G, the aging effect is no longer observable.

The aging effect reveals a collective behavior of the spontaneous orbital currents and that intrinsically the system is both disordered and frustrated. We discuss two possibilities in order to explain the observed zero field aging behavior.

It has been shown recently that the PME effect is an intragranular property since it is present in isolated grains with dimensions of the order of 1 $\mu$m [19]. We first consider the case where each grain consists of only a few single crystalline domains and that single $\pi$ loops are

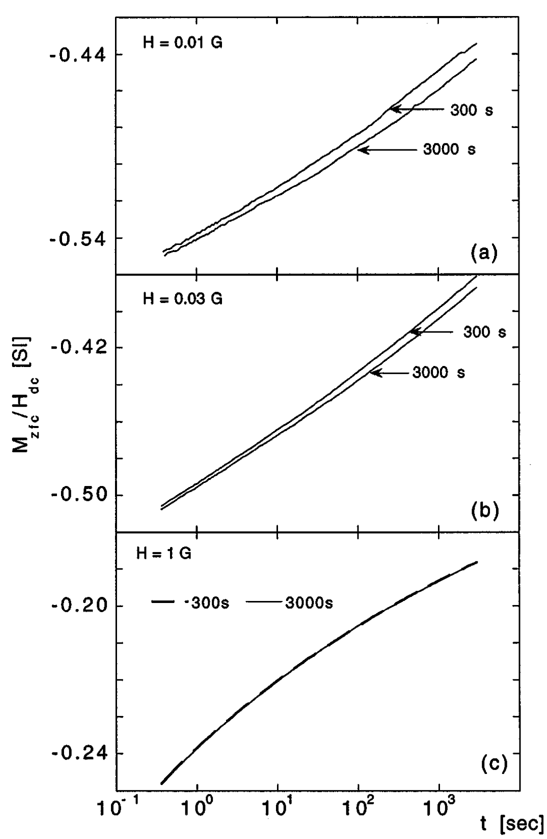


FIG. 3. $M_{\mathrm{zfc}}/H_{\mathrm{dc}}$ plotted vs observation time at 82 K for the fields (a) 0.001 G, (b) 0.03 G, and (c) 1 G. The wait times used were 300 and 3000 s.

formed in some of these grains. The magnetic moment of a $\pi$ loop can point in one of the two possible directions corresponding to the two energy minima of its potential energy and the interaction in this case will correspond to dipole-dipole interaction between the magnetic moments of different $\pi$ loops. This is close to the case of dipole-dipole interacting magnetic nanoparticle systems [18,20]. The disorder and frustration in such systems arise due to the random distribution of spontaneous magnetic moments inside the sample. The $\pi$ loops will behave collectively, in the sense that the direction of the current in a loop will be affected by the magnetic field due to neighboring magnetic moments, when the dipole-dipole pair interaction energy is comparable to the energy barrier separating the two states of an isolated $\pi$ loop. Thus, a necessary requirement here is that the volume fraction of the $\pi$ loops is high, so that the grains are close enough to one another to allow a sizable interaction.

The second case is taking under consideration a sample consisting of large grains, where each grain has an extremely polydomain microstructure. Thus, each grain can be described as a Josephson junction network and the collective behavior of the moments arises from the fact that the spontaneous orbital currents in $\pi$ junctions share common paths. Disorder and frustration originate from the random distribution of $\pi$ junctions in the network. Kawamura [21] recently proposed that a novel thermodynamic phase, the chiral-glass phase, might occur in zero external field in such a system. This thermodynamic phase is characterized by a spontaneously broken time-reversal symmetry [22]. The order parameter is a "chirality," a quantity associated with half a vortex, generated by frustrated rings of $\pi$ loops. The model describing the chiral-glass phase was developed in analogy to the *XY* spin glass. In the model, the superconducting system is viewed as an infinite network of Josephson junctions, in which the Josephson coupling is positive for 0 loops and negative for $\pi$ loops. The existence of the chiral-glass phase is revealed by the negative divergence of the nonlinear susceptibility and the aging of the magnetic relaxation [23,24]. One requirement for an experimental system to show a transition is that the connections between domains and grains should form an infinite cluster or at least a network large enough so that the divergence of the nonlinear susceptibility is not significantly rounded by finite-size effects. It should be noted though that even finite systems may show aging in the magnetic relaxation.

In both scenarios, the energy of the collective state is characterized by a multivalley energy landscape with energy barriers separating different metastable states. Even in zero field, after having cooled the sample from a temperature above the superconducting transition temperature to some low temperature, the system is out-off equilibrium and the equilibration process proceeds by thermally activated flipping of the orbital magnetic moments. Since the collective system will go through many metastable states before reaching equilibrium, the equilibration process is expected to be logarithmically slow in time. By allowing the system to "age," we allow it to go through more metastable states and thus to be closer to equilibrium when we start measuring the magnetic relaxation.

TEM studies performed on our melt-cast material [14] have shown that it is characterized by a polydomain microstructure, with the orientation of the *a* and *b* axes of different domains slightly disordered. It is believed that under these conditions the formation of $\pi$ junctions is inevitable. The typical grain size is approximately 100 $\mu$m in the *ab* plane and 1 $\mu$m along the *c* axis. Within the grains, the average size of each domain is approximately 0.3 $\mu\text{m} \times 1$ $\mu$m along the *ab* plane. If their size along the *c* direction is also of the order of 1 $\mu$m, then there can be many thousands of domains inside each grain and therefore the intragrain regions in the melt-cast sample can be modeled as Josephson junction networks. However, the mere existence of $\pi$ loops in the network is not the only requirement for the development of spontaneously generated orbital currents [19]. For a single loop containing only one $\pi$ junction the condition $\eta = 2\pi L I_c/\Phi_0 > 1$ must be fulfilled, where $L$ is the self-inductance of the $\pi$ loop with critical current $I_c$. This means that the critical current of the $\pi$ junction has to be large. One should be cautious though using this condition for loops containing several $\pi$ junctions. It has been shown that the spontaneous flux may remain nonzero in a multiple-junction loop [22] even when $\eta \ll 1$ but that the flux becomes small since it will be proportional to $\eta$. Thus, $\eta$ should not be too small for the paramagnetic contribution not to be masked by the diamagnetic contribution.

Previous relaxation measurements performed on sintered samples of the Bi-2212 system revealed no aging effect [25]. One possible reason for this is that the grain size in such samples is too small to host more than a few single crystalline domains. This implies that the PME effect, which essentially is a local effect, is observed, while the aging effect, which is a cooperative phenomenon, will be inhibited, at least if the dipole-dipole interaction between orbital magnetic moments is also weak enough.

From Fig. 2 we see that the aging effect is not observable at low temperatures. This is not surprising since here the external field is screened from the bulk of the sample and, thus, cannot probe the collective behavior of the Josephson junction network. Monte Carlo simulations performed by Kawamura *et al.* [23] showed that the chiral-glass phase is stable even in the presence of moderate screening; strong screening is however expected to destroy the chiral-glass state. In order to really see if there is some evidence for the chiral phase at the lower temperatures, measurements of the nonlinear susceptibility must be performed. We do not know though if the grains are large enough to reveal a negative divergence of the nonlinear susceptibility, or if the links between different grains, which should be considerably weaker as compared to links between different domains, allow the sample to be considered as an infinite, or large enough, network, in order for the divergence to be observed experimentally.

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