Paramagnetic Meissner Effect in Bi High-Temperature Superconductors

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For certain ceramic samples of the Bi-based high-temperature superconductors, the dc field-cooling signal becomes paramagnetic in fields below a few 100 mOe. This effect correlates with an anomaly in the low-field microwave absorption. The data are consistent with orbital paramagnetic moments due to the appearance of spontaneous supercurrents in fields smaller than the lower critical field H_{c1a} parallel to the CuO planes.

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The field-cooling (FC) Meissner effect of ceramic samples of the high-temperature superconductors (HTSC's) is known to remain incomplete down to fields which can be much smaller than the lower critical field H_{c1c} parallel to the c axis [1-6]; H_{c1c} is a few tens to a few hundreds Oe. This incomplete flux expulsion was initially attributed to low superconducting volume fractions and later to pinning [2,4]. However, it persists in high-quality samples (see, e.g., Fig. 1) and can then also be attributed consistently to an *equilibrium effect* [3,5,6], namely, to the *magnetic transparency* of grains with cross dimensions $\lambda_{min} < d < \lambda_{max}$ for field components parallel to the CuO planes. Here λ_{min} and λ_{max} are the London penetration depths in fields perpendicular and parallel to the CuO planes. $\lambda_{min} < d < \lambda_{max}$ applies in most HTSC ceramics, in particular in those of the Bi HTSC's, where $(\lambda_{min} \approx 0.4\ \mu m) < d < (\lambda_{max} \approx 30\text{-}50\ \mu m)$. In fields lower than H_{c1c}, the induction then penetrates each grain fully, mainly parallel to the CuO planes, whose spatial orientation varies randomly from grain to grain. The resulting bulk equilibrium magnetization is then only about $\frac{1}{3}$ of the value $M = -H/4$ for full flux expulsion. This is seen clearly in the dc (FC) susceptibility (see [3-6] and Fig. 1), and often even in the ac susceptibility [7,8].

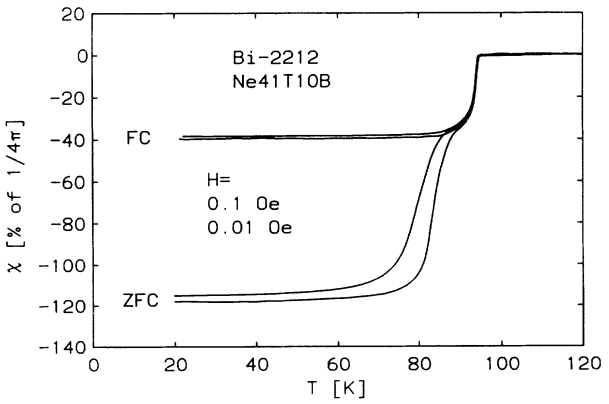

FIG. 1. Zero-field cooling (ZFC) and field cooling (FC) data of a high-quality ceramic Bi-2:2:1:2 sample in 0.1 and 0.01 Oe. The FC flux expulsion reaches only $\frac{1}{3}$ of the fully screening ZFC signal. This is a characteristic of the equilibrium state of "magnetic transparency" and of very weak links between the grains [6].

Eventually, many of these ceramic samples are observed to go over to full flux expulsion at some field H_m, which can be many orders of magnetic smaller than H_{c1c} [1-6]. This field is not an intrinsic property of the HTSC crystals, but rather one of the mesoscopic defect structure: H_m is determined by the strength of the weak links between the "blocks" of crystalline material [6], similar to the (low) critical currents of these ceramics. The weak links are formed across the grain boundaries and across defect surfaces within the grains. Since the full expulsion is approached spontaneously, it is again an equilibrium state, which prevails when the external field puts less than one quantum of flux onto the average mesh of the Josephson network [6].

In this Letter we show that the magnetically transparent state does not always go over to a state of full expulsion at some field $H_m \ll H_{c1c}$, but sometimes rather to the opposite: In certain Bi HTSC ceramics, a *paramagnetic* magnetization is found in the field-cooling mode below a field of order 1 Oe. Since this magnetization appears spontaneously, suggesting another equilibrium state, we shall henceforth speak of it as the paramagnetic Meissner effect (PME). This state seems again to be associated with the mesoscopic defect structure, rather than being an intrinsic property of the ideal HTSC crystallites. It is nevertheless of fundamental interest, since it is to our knowledge the first experimental manifestation of a superconductor with a "negative critical Josephson current" [9], or of spontaneous orbital currents in the ground state of a metal [10].

A paramagnetic field-cooling signal was reported once before for a ceramic Bi-2:2:1:2 ($Bi_2Sr_2CaCu_2O_8$) sample, but was interpreted as a pinning effect in a Kosterlitz-Thouless transition [11]. We (and others) have observed such signals occasionally in ceramic samples for more than three years, in vibrating sample and SQUID magnetometers. Recently, we begin a systematic study of this effect [12]. Since conventional SQUID magnetometers have been reported to produce spurious paramagnetic moments on superconductors [13], we shall describe our apparatus in some detail. We use a commercial rock

magnetometer [14], which works with an rf SQUID, but without a superconducting magnet. The magnetometer is inside a double-walled Mumetal tube to shield the Earth's field. There is also a superconducting shield surrounding the sensitive region. The residual field at the sample position was measured by axial and transverse Foerster probes. Both the parallel and the transverse residual field were found to be less than 1 mOe. The SQUID pickup coils are wound Helmholtz-like to achieve a 3-cm-wide area where the signal is not sensitive to the sample position [14]. The output signal was calibrated with a Cu coil to give absolute signals. In its conventional mode, rocks at room temperature are moved mechanically through the sample access hole into the SQUID sensitive region. For our measurements, we have added a cryogenic insert and Helmholtz coils inside the Mumetal shield to apply a low external dc field. The cryogenic insert is made of nonmagnetic and nonmetallic materials (mainly glass); the only metal in the sensitive region is that in the Si-diode thermometer, which is fixed below the sample, and in its leads (metallic materials are not recommended, because differential thermocurrents can produce severe noise in the SQUID). The dc field is applied while the superconducting shield is in its normal state. It is then trapped in the shield, after which the current in the coils is turned off. The cryogenic insert holds the sample mechanically fixed at the center of the pickup coil system. The sample is cooled by He gas streaming past it. The SQUID signal is recorded while changing the temperature. *The sample is never moved during the measurement*, which guarantees that its does not experience any change in the applied field during the run. This is an essential point, since sample movement in an inhomogeneous field (e.g., in the rest field of a superconducting magnet, which of course is not present here) was able to produce apparent paramagnetic moments, while the sample was actually weakly diamagnetic, as explained in [13].

The common run proceeds as follows. (a) Zero-field cooling (ZFC): The sample is cooled down in zero field ($|H| < 1$ mOe) from far above T_c to about 20 K $\ll T_c$. The field is applied. Then the ZFC signal is recorded, while slowly warming the sample to at least 120 K, well above the T_c of the Bi-2:2:2:3 phase. (b) Field-cooling: Without changing the field, the FC signal is then recorded while cooling the sample again down to 20 K. Note that in Figs. 1 and 2, the ZFC signal is somewhat larger than $M/H = -1/4\pi \equiv 100\%$, because in ZFC the calibrated signal measures the volume enclosed by the screening currents (induced on the sample's surface when turning on the field at $T \ll T_c$). In a ceramic sample, this volume is somewhat larger than the "100%" volume, which we calculate from the weight of the sample with the x-ray density.

Figure 1 shows data for a high-quality Bi-2:2:1:2 ceramic sample with $T_c = 94.5$ K (for the quality criteria, see [7]). Note the sharp onset of the signal at T_c, and

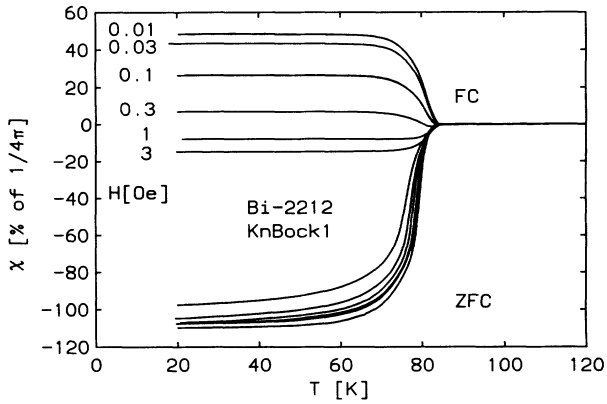

FIG. 2. ZFC and FC signals of a ceramic Bi-2:2:1:2 sample exhibiting the paramagnetic Meissner effect (PME).

that the FC signal is rather accurately $\frac{1}{3}$ of the ZFC signal at $T \ll T_c$. In the FC mode, this sample shows no indication of final full flux expulsion down to 10 mOe; apparently here we have $H_m \ll 10$ mOe. There are, of course, some weak links; otherwise, the ZFC signal would coincide with the FC signal.

Figure 2 shows data for another Bi-2:2:1:2 sample. Its $T_c = 83$ K is lower because it was only annealed in air, not in Ar, as was the sample in Fig. 1 [7]. The transition is rounded, which speaks for some inhomogeneity. The ZFC signal is normal. However, at 3 and 1 Oe, the FC signal, while being diamagnetic, is already relatively small, and in fields lower than 0.5 Oe, it becomes *paramagnetic*. This behavior is perfectly reproducible: The run in 0.1 Oe was repeated six times, and all the data coincided within the noise. One of these runs was done with reversed external field direction (for which the magnetization reversed sign), some after measurements in other fields, some with ZFC, and some without; some of these runs were done after the sample had been removed from the cryostat for 3 weeks. To check the thermal stability, we stopped the temperature in one of these runs for 30 min each in the ZFC and in the FC branches at 77 K, a few K below but near T_c. During this time, the ZFC signal *decreased* (by 3%), as expected for this nonequilibrium state, while the FC signal *did not move* outside of the noise. After these measurements, one part of the sample was powdered to an average grain size of 2–3 μm. The powder showed a reduced ZFC signal, as expected from the looser contact between the grains, but in the lowest fields, the FC signal showed actually a slight *increase* of the paramagnetic signal. Another part of the sample was subjected to various heat treatments in an Ar or O_2, in order to move T_c between 75 and 93 K. All these versions showed the PME, starting at the respective T_c's, with some minor variations of the final paramagnetic susceptibilities at $T \ll T_c$ [15].

The samples exhibiting the PME also show an anomaly in their low-field microwave power absorption [Figs. 3(b) and 3(c)]. The absorption of a "normal" sample (with-

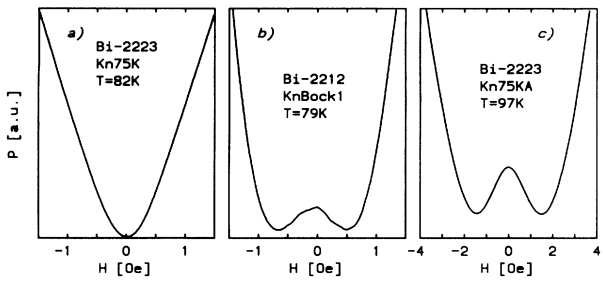

FIG. 3. (a) The magnetic-field induced change of the microwave absorption (MWA) typical for a powdered HTSC sample, which does not show the PME. The changeover from parabolic to linear occurs around 0.6 Oe, near the lower critical field H_{c1a} of the Bi HTSC's in the a-b direction [17]. (b) The MWA signal for the sample of Fig. 2. The minima are located at ± 0.6 Oe, near the field, where the FC signal of this sample changes over from paramagnetic to diamagnetic. (c) The MWA signal of a Bi-2:2:2:3 sample, in which a weak PME was found later, guided by this MWA signal [15].

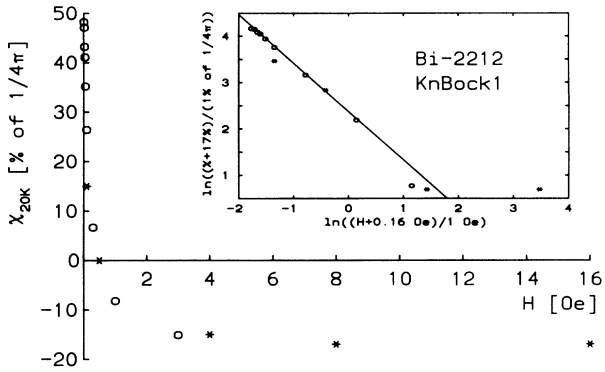

FIG. 4. Collection of the low-temperature data of the sample of Fig. 2, plotted against the applied field. The points indicated by an asterisk were taken in our vibrating sample magnetometer. The log-log plot in the inset can be fitted by Eq. (1), indicating the existence of spontaneous orbital magnetic moments, which are field and temperature independent at $T \ll T_c$ and $H < 0.3$ Oe.

out PME) is shown in Fig. 3(a): There is a minimum of the absorption at $H=0$, followed by a parabolic increase, which turns into a linear increase at $|H| > 0.6$ Oe. The PME sample of Fig. 2 shows instead a maximum of the absorption at $H=0$, followed by minima near ± 0.6 Oe [Fig. 3(b)], close to the field where this sample crosses over from diamagnetism to paramagnetism in the FC measurement. A similar effect was observed in one of our Bi-2:2:2:3 ceramic samples [Fig. 3(c)]. This sample was then checked in the SQUID magnetometer and showed the PME below 50 mOe [15].

The PME *cannot* be caused by paramagnetic or ferromagnetic impurities, i.e., by some *spin* magnetization. In Faraday susceptibility measurements above T_c in fields up to 0.8 T, we found only small traces of paramagnetic impurities (similar to, e.g., Ref. [16]) and no ferromagnetic moments within the accuracy of the measurement. If the PME were due to paramagnetic impurities, they would have to produce the large PME magnetization starting abruptly at T_c, while their magnetization is "invisible" above T_c (no Curie-Weiss-type susceptibility is visible above T_c in Figs. 1 and 2). To achieve this, one has to invoke the sudden appearance of a very strong field at the location of these impurities, by some redistribution of the magnetic flux below T_c, from order 1 to the 10^6-OE range. Residual ferromagnetic impurities with a large initial susceptibility in the 100-K range can also be excluded, since we do not observe any severe hysteresis effects after repetition of the FC experiment, or when measuring in very low fields after measuring in higher field, where the FC signal is diamagnetic, or after switching the field direction.

The only reasonable explanation for the PME seems to be a magnetization M_s due to spontaneous *orbital* (superconducting) currents. These currents are just as spontaneous as those in the ordinary (diamagnetic) Meissner effect and have a very similar temperature dependence, but they go in the *opposite* direction. Moreover, contrary to the ordinary Meissner effect, they seem to turn on below T_c *without the need of an external field.*

Figure 4 shows a plot of the low-temperature signals of Fig. 2 as a function of the applied field (the points at 0.5, 8, and 16 Oe were taken in a vibrating sample magnetometer). M/H tends to diverge for $H \to 0$, with a cutoff at the lowest fields, suggesting that the spontaneous paramagnetic contribution to the magnetization is *field independent*. The inset in Fig. 4 shows a log-log plot of $M/H+\alpha$ vs $H+H_0$; it is linear for $0.03 < H < 3$ Oe with $\alpha = 0.17/4\pi$ and $H_0 = 0.16$ Oe:

$$\frac{M}{H} = -\alpha + \frac{M_s}{H+H_0} = -\frac{0.17}{4\pi} + \frac{0.095\ \text{Oe}}{4\pi(H+0.16\ \text{Oe})}. \quad (1)$$

Thus, at $0.03 < H < 3$ Oe and $T \ll T_c$, the spontaneous M_s depends neither on field nor on temperature. If M_s has its origin in spontaneous currents in some loops of mesoscopic size, then $H_0 \approx 0.16$ Oe can be understood as an average field of interaction between these loops, which leads to some glassy antiferromagnetic order at very low fields ($H < H_0$), and then the increase of the PME of the powdered sample at the lowest fields [15] is probably caused by a decrease of H_0 due to an increase of the interloop distances.

The field of the crossover from diamagnetism to paramagnetism, $H \approx 0.6$ Oe, confirms the orbital origin of M_s *independently*: It is near the lower critical field H_{c1a} of the Bi HTSC's for fields applied in the a-b plane. H_{c1a} goes together with the (small) intrinsic critical current density for supercurrents in the c direction and with the (large) penetration depth $\lambda_{max} \approx 30$–50 μm. H_{c1a} is actually detected directly in the MWA, by the crossover from parabolic to linear [see Fig. 3(a) and [17]]. Since the spontaneous M_s appears in fields lower than H_{c1a}, the associated currents run most likely in the c

direction, which means that M_s lies parallel to the CuO planes. This is also the direction of the induction in the magnetically transparent state in fields below H_{c1c} [16].

In short, while isolated perfect grains remain in the magnetically transparent state down to $H \to 0$ [8], the ceramics can leave this state with the aid of the weak link Josephson network, by going either to full flux expulsion at $H < H_m \ll H_{c1c}$ or by going to a state with spontaneous orbital currents at $H < H_{c1a} \ll H_{c1c}$, depending on the mesoscopic geometry of the weak links. (*Both* effects, of course, may also occur in different regions of the *same* macroscopic ceramic sample, which would explain the quite frequent observation of intermediate situations [15,18].)

Then what distinguishes the two types of mesoscopic defect structures? Unfortunately, we have very little information available to answer this question; we know only a trend: Those samples which in FC remain at $\frac{1}{3}$ flux expulsion (Fig. 1), or go to full expulsion at $H < H_m$ [3-6], are more homogeneous than those which exhibit the PME. This shows up as a rounding of the transition in the FC and ZFC data of the samples with PME, which is not observed in those without (compare Figs. 1 and 2). In ceramic Bi HTSC's, there is an anticorrelation between the intrinsic quality of the crystalline material and the strength of the weak links: The ZFC shielding becomes weaker the better the x-ray quality, the sharper T_c, and the more pronounced the superconducting fluctuations in transport and magnetization above T_c and in the specific heat anomaly at T_c [7]. There is an important difference in the preparation procedures: Samples with PME went through a short cycle of heating above the melting temperature T_m, while those without were annealed carefully just *below* T_m. Melt processing is known to increase the critical currents of the ceramics, while simultaneously deteriorating somewhat the crystalline quality. This suggests that the PME occurs when some weak links are above some minimum critical current. The persistence of the PME after powdering indicates moreover that these weak links are *intragranular* (perhaps shorts between the CuO planes).

The possible appearance of spontaneous supercurrents was theoretically anticipated by Bulaevskii, Kuzii, and Sobyanin [9] for certain Josephson loops with a *negative* critical current I_c ("π junctions"), which must also be sufficiently large ($|I_c|L > \phi_0$, where L is the self-inductance of the structure). In their theory, the negative critical current is caused by spin-flip scattering in the tunneling barrier. Spontaneous orbital currents were recently also predicted for a mesoscopic metallic ring made of a nonsuperconducting metal, where the effect is entirely due to the restricted geometry [10]. A restricted geometry alone can probably also cause spontaneous currents in a superconductor; such currents were recently discussed for disordered superconductors [19].

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