Observation of Paramagnetic Meissner Effect in Niobium Disks

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For several superconducting niobium disks, the dc field-cooled magnetization (FCM) shows a paramagnetic response below their superconducting transition temperature $T_c \approx 9.2$ K when the applied magnetic filed is normal to the disk. At 8.6 K, the FCM reaches a maximum in fields of 5 to 10 Oe and becomes diamagnetic for fields larger than 20 Oe. This FCM behavior is qualitatively similar to the paramagnetic Meissner effect (PME) recently observed in high-T_c cuprate superconductors. Various surface treatments to the Nb disks result in changes in both the zero-field-cooled magnetization and the FCM, including the disappearance of the PME.

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One of the characteristic features of a bulk superconductor is the Meissner effect, i.e., the occurrence of perfect diamagnetism below the superconducting transition temperature T_c. The diamagnetism is caused by screening currents associated with the gradient of the magnetic field H near the surface for $H \leq H_{c1}$ and $T \leq T_c$. For an ideal superconductor without flux pinning, the volume susceptibility is $\chi_V = -1/4\pi$ in cgs units. For a superconductor with defects present, flux pinning may occur at these defect sites, causing the field-cooled magnetization (FCM) to be less diamagnetic than the zero-field-cooled magnetization (ZFCM) corresponding to full flux exclusion. Recently, for the high-temperature superconducting granular BiSrCaCuO (2212) materials, several groups [1–7] have even observed a field-cooled magnetic response that is paramagnetic in sign rather than negative as usually associated with superconductivity. This FCM response is typically 20%–60% of $1/4\pi$ for the lowest magnetic fields and becomes negative for fields larger than 0.5 Oe. This abnormal behavior in the FC response is now referred to as the paramagnetic Meissner effect (PME) or Wohlleben effect. Various explanations for the origin of the PME in these granular high-T_c superconductors have been proposed, including spontaneous currents due to π contacts [8–10], vortex-pair fluctuations combined with pinning [1], and spontaneous orbital currents [11]. In fact, the paramagnetic response in these BiSrCaCuO compounds has even been argued [12] as being consistent with d-wave superconductivity in these materials. More recently, the PME was observed in the FCM of a few $YBa_2Cu_3O_{7-x}$ single crystals only when low fields are applied parallel to the crystalline c axis [13]. Although this FCM is only about 3% of the full flux exclusion (ZFCM) at the lowest temperature, the FCM remains positive for fields up to 7 Oe. Because this effect is seen only in fields parallel to the c axis, the PME was attributed to spontaneous currents in the CuO_2 planes of the $YBa_2Cu_3O_{7-x}$ single crystals.

In addition to the uncertainty in the microscopic origin of the PME, it is still unclear why this effect is observed only in some but not all high-T_c superconducting samples. It has been found that the PME is typically observed in ceramic BiSrCaCuO samples that have undergone a melt-casting process during which small crystallites are formed [2,6]. This suggests that structural and/or chemical causes are responsible for the PME observation. During our investigations of flux-trapping phenomena, we have observed a behavior similar to the PME in over a dozen disk-shaped niobium samples when cooled below their superconducting transition temperature of about 9.2 K. The results of the present investigation suggest that the PME phenomenon is more common that in just the high-T_c superconductors, and may be the result of flux trapping arising from microstructural defects on the disk surface as well as from the geometric shape of the sample.

The disks of diameter 6.4 mm were punched from two different 0.127-mm-thick sheets of niobium (99.98% purity) [14]. Some of these disks also underwent surface treatments including O_2 annealing, etching, and mechanical sanding. Each disk was then positioned at the center of the second-order gradiometric detector coil in a commercial SQUID magnetometer [15] with the dc magnetization measurements being performed on the disk in both parallel and perpendicular orientations with respect to the magnetic field. Throughout the measurements the disk samples were kept stationary, thereby eliminating any spurious paramagneticlike responses that might arise from field inhomogeneity with sample position [16]. The analog voltage output from the SQUID amplifier, i.e., the magnetic flux change through the SQUID pick-up coils, was then recorded on an X-Y plotter while the temperature was slowly increased or decreased ($\sim$1 mK/s) through the transition temperature. The voltage changes were later expressed in terms of a magnetization which was determined from the magnetometer's fitting routine to the dipole response of the ZFC sample moving over a 4-cm span. For field strengths ranging from 50 mOe to 5 Oe, the fields were produced by a copper-wire solenoid [17] and later by the copper-wire solenoid incorporated in the ultra-low-field MPMS-S5 option [15]. For larger fields, measurements were performed using the magnetometer's superconducting solenoid after the completion of the low-field measurements for all disk samples. Dur-

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ing the actual cooling in zero field, the residual longitudinal field at the sample location was attenuated to less than 1 mOe by using an offset current through the copper-wire solenoid in combination with a Mumetal cylinder that surrounds the magnetometer dewar.

Figure 1 shows the field dependence of both the ZFCM and FCM for fields applied perpendicular to the surface of a typical (untreated) Nb disk. At the lowest temperatures, the ZFCM/H shows complete shielding with the diamagnetic response being approximately 22 times larger than $-V/4\pi$. This large diamagnetic response is due to the local field enhancement arising from the geometric demagnetization factor for a disk-shaped sample when the applied field is normal to the disk. The demagnetization correction to the magnetization is given by

$$M_{\mathrm{ZFC}} = -\frac{VH}{4\pi(1-n)} = -\chi_{\mathrm{ZFC}} H ,$$

where n is the demagnetization factor. For a flat disk of radius r and thickness t, the correction factor is $(1-n)^{-1} \approx r/t$. For our disks, $r/t = 25$, which agrees fairly well with the experimental result of 22. In all cases the susceptibility χ $(= M/H)$ will be normalized to the complete shielding value of $|\chi_{\mathrm{ZFC}}|$.

With increasing temperatures the ZFC data indicate the presence of two different superconducting transitions at 9.06 and 9.26 K. The strong field-dependent behavior as well as the large change in the magnitude of the χ_{ZFC} $(=$ ZFCM$/H)$ suggest that the local field $H/(1-n)$ is larger than the lower critical field $H_{c1}(T)$ in the vicinity of 9.20 K. Identical temperature and field characteristics are also observed in the inductive component of the ac susceptibility (not shown) for ac fields perpendicular to the disks measured at 250 Hz [18].

The appearance of the two transition temperatures is also seen in the field-cooled measurements with decreasing temperature; however, the FCM/H does not exhibit the archetypal Meissner behavior. Initially the FCM

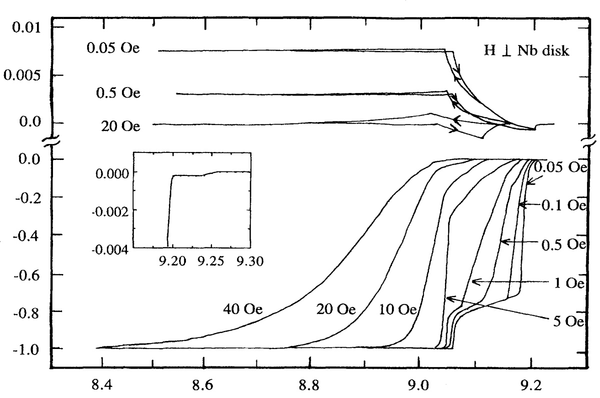

FIG. 1. The ZFCM/H (lower) and FCM/H (upper) data for a Nb disk with magnetic fields applied normal to the disk surface. The data are scaled to the complete shielding value of $|\chi_{\mathrm{ZFC}}|$. The inset shows an enlargement of the ZFCM/H around 9.26 K.

shows a weak diamagnetic response below 9.26 K, followed by an abrupt increase in the FCM starting at 9.20 K which eventually attains a positive value (less than 1% of $|\chi_{\mathrm{ZFC}}|$) and then remains essentially constant below 9.06 K. The temperature associated with the abrupt increase is identical to the onset temperature of the large diamagnetic response in the ZFCM for similar field strengths. This FCM behavior for the Nb disks is qualitatively very similar to the temperature and field dependences of the PME characteristics exhibited by the $YBa_2Cu_3O_{7-x}$ single crystals [13]. The importance of keeping the samples stationary during the FC measurements is exemplified by viewing the SQUID voltage response of the sample over a 4-cm scan length for $T \leq 9.06$ K. In addition to the positive, nearly dipole response that is dependent upon the applied field, a contribution arising from a linear field variation of only 0.3 mOe over the 4-cm scan length is clearly evident. Thus the utilization of the term FCM for the flux change in the FC data and the numerical conversion of the flux change to a magnetization is valid and is consistent with experimental techniques used in previous PME work [1–7]. The magnitude of the FCM response at the lowest temperatures is essentially independent of time as well as cooling rate (0.7–20 mK/s) through the transition region. Furthermore, Nb disks measured after a period of three years still showed the same qualitative behavior.

Another similarity to the $YBa_2Cu_3O_{7-x}$ single crystal [13] results is the hysteretic behavior in the FCM between cooling and warming measuring cycles. As also shown in Fig. 1, the field-cooling data FCCM are typically more positive than the FCWM data measured during the warming cycle. This behavior is consistent with the viscous nature of flux expulsion below T_c. On cooling, the magnetic flux must overcome activation-type processes in order to be expelled, and correspondingly the FCCM will be more positive than the equilibrium magnetization. Similarly, during the warming cycle, the flux cannot easily penetrate the sample and thus the magnetization is more diamagnetic. This type of hysteretic behavior is very common in type-II superconductors and is consistent with a recent theoretical interpretation based on critical-state model calculations [19]. Furthermore, one observes only a small difference in the temperatures of the "sharp" FCM features between the cooling and warming cycles. This suggests that the movement of magnetic vortices is not solely responsible for the PME. This is further supported by the characteristic shape of the M vs H curves (see Fig. 2). The nearly field-independent behavior of the magnetization above 0.5 Oe, the polarity change upon field reversal at 4.5 Oe, and the overall "square-like" hysteretic behavior in the temperature range between 9.10 and 9.20 K are indicative of flux pinning in this temperature regime. In contrast, the M vs H curves at lower temperatures ($T \lesssim 9.05$ K) are more reminiscent of a type-II superconductor with the magnetization becoming less diamagnetic as the

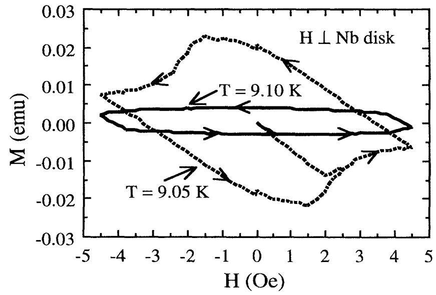

FIG. 2. Magnetization versus magnetic field H curves at various temperatures for H normal to the Nb disk surface.

flux penetrates into the sample for $H \geq H_{c1}$. Another similarity to the earlier work on the YBaCuO crystals is that the magnitude of the FCM at 8.6 K initially becomes more positive with increasing magnetic field before reaching a maximum in the 5–10 Oe range, as shown in Fig. 3. The FCM remains positive until the field exceeds 20 Oe and then exhibits a nearly linear decrease with increasing field. If one assumes this linear dependence (∂FCM$/\partial H \sim$ const) reflects the Meissner contribution to the overall FCM response, the PME contribution would be just the difference between the FCM and a line going through the origin with a slope of ∂FCM$/\partial H$. Thus the PME contribution for these Nb disks appears to saturate at approximately 20 Oe, about 4 times larger than the saturation field found for the $YBa_2Cu_3O_{7-x}$ single crystals.

In contrast to the results for fields perpendicular to the disk surface, the ZFCM and FCM data for fields parallel to the Nb disk surface (see Fig. 4) indicate only diamagnetic responses with an onset of superconductivity at 9.2 K and a large diamagnetic increase beginning at 9.06 K with a weak field dependence. The magnitude of the ZFCM at 8.5 K is nearly equal to the bulk value of $-V/4\pi$, and the FCM magnitude is about 25% of the ZFCM. This anisotropic behavior indicates that there is a preferred orientation of the sample with respect to the magnetic field direction in order to observe the PME; i.e., the magnetic field should be perpendicular to the flat surface of the disk. This corroborates a recent report [10] that BiSrCaCuO samples showing the PME consist of platelike crystallites that are predominantly oriented parallel to one another. Moreover, the PME in the 123 single crystals [13] was observed only for fields parallel to the c axis, i.e., perpendicular to the crystalline platelet surface.

Since the appearance of the PME in the Nb disks seems to be related to the presence of strong pinning and multiple superconducting phases as well as sample geometry and orientation, the effect of the surface microstructure was investigated by altering the surface through mechanical sanding, O_2 annealing, and chemical etching. The most dramatic effect occurred when both the top and bottom surfaces were abraded as the PME was reduced and even eliminated, while abrading the circumferential edge had a minimal effect on the PME. After slightly abrading both surfaces of the Nb sheet with no detectable thickness change (<2.5 μm), two disks were punched out and measured. Both the ZFCM and FCM for fields perpendicular to the disk (see Fig. 5) are diamagnetic for all magnetic fields with a single transition at 9.2 K in the ZFCM. The absolute magnitude of the ZFCM is identical to the ZFCM ($T < 9.0$ K) for the untreated disk shown in Fig. 1. Likewise, the ZFCM and FCM for fields parallel to the disk have a single transition at 9.2 K. It should be noted that the PME may not be completely eliminated in this sample as the FCM shows some structure in the temperature range between 9.2 and 9.06 K. Two other untreated disks which showed similar magnetization behaviors, as shown in Figs. 1 and 4, were subsequently subjected to a series of sandings. The PME in the FCM and the structure at 9.06 K in the ZFCM gradually diminished after each set of sandings until both effects completely disappeared. An average thickness reduction of 10 μm was required for the elimination of the PME; however, the sanding process was not uniform since some inadvertent rounding of the originally sharp

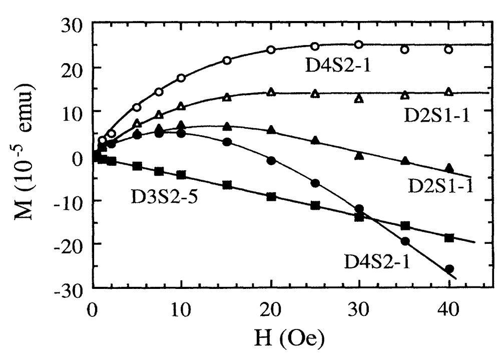

FIG. 3. The FCM at 8.6 K with H normal to the Nb disk for two different (untreated) samples. The open symbols represent the paramagnetic contribution to the FCM (see text). The closed squares are the FCM after abrading the surfaces of another disk (D3S2–5).

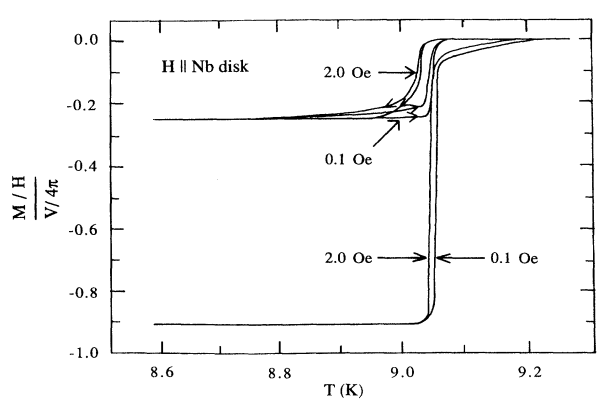

FIG. 4. The ZFCM$/H$ (lower) and FCM$/H$ (upper) data for a Nb disk surface. The data are scaled to the complete shielding value of $V/4\pi$.

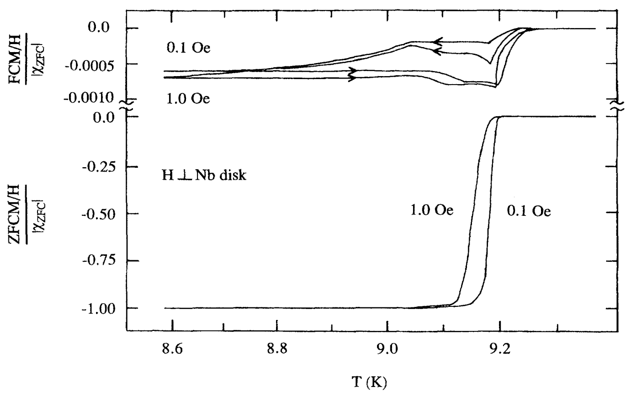

FIG. 5. The ZFCM/H (lower) and FCM/H (upper) data for an abraded Nb disk with magnetic fields applied normal to the disk surface. The data are scaled to the complete shielding value of $|\chi_{ZFC}|$.

circumferential edges occurred. In addition, the SQUID responses over a 4-cm scan length for all the abraded disks indicate the dipole response is now negative after field cooling. Changes in the magnetization data due to an O_2 anneal and chemical etching were more subtle with the PME still remaining. It is well known that an O_2 anneal at 400 °C can reduce surface pinning effects in Nb [20]. After a 5-min anneal on one Nb disk, the ZFCM and FCM behaviors for perpendicular fields were essentially the same as that for the untreated disks, except for a more narrow transition width accompanying the 9.20 K transition. This sharper transition resulted in the positive FCM to increase to about 3% of $|\chi_{ZFC}|$. On the other hand, a 60-s chemical etch with a HF:HNO_3 (1:3) solution produced a decrease in the 9.20 K transition to 9.08 K, which resulted in the magnitude of the positive FCM decreasing by a factor of 3. Thus the surface microstructure plays a key role in the formation and the size of the PME.

Although the microscopic origin of the PME cannot be completely explained based on this study, it is evident that the sample surface and geometry are important aspects. From the abrasion studies, it is evident that the lower temperature feature at 9.06 K in the untreated disks must be associated with a lower T_c superconducting surface layer. These results further suggest that the surface defects reside within the first 5–10 μm of the surface and create nonuniform field distributions as the sample is cooled through 9.2 K in perpendicular fields, leading to positive magnetic responses associated with the pinned vortices. Since flux pinning is known to be easier in superconducting films for perpendicular fields than for parallel fields, this explanation is consistent with the PME results in the cuprates as the PME is observed in perpendicular fields to the platelets of the $YBa_2Cu_3O_{7-\delta}$ single crystals and the smaller BiSrCaCuO crystallites found in ceramic samples. The magnitude of the PME in the various superconductors could be related to the nature of the defects, such as size and density, to the geometrical size of the platelets or samples, and to the anisotropy of the superconducting material. The creation of nonuniform field distributions during the field-cooled process and the appearance of the PME could even result from defect structures arising from a distribution of T_c's as evidenced by broad superconducting transitions in the ceramic BiSrCaCuO samples [2]. Furthermore, since not all BiSrCaCuO and YBaCuO samples exhibit the PME, the PME may not be an intrinsic property even in the cuprates.

In summary, a positive magnetization in the field-cooled response, i.e., the so-called paramagnetic Meissner effect, has been observed in disk-shaped niobium samples for fields perpendicular to the surfaces of the disks. We believe this effect arises from nonuniform field distributions created by strong flux pinning sites on the surface layer of the disk when the sample is cooled through its transition temperature. We also find that the sample orientation and geometry play a role in the observation of the PME.

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