# Inducing the paramagnetic Meissner effect in Nb disks by surface ion implantation

David J. Thompson
*Department of Physics and Astronomy and Institute for Manufacturing Research, Wayne State University, Detroit, Michigan 48202*

L. E. Wenger and J. T. Chen
*Department of Physics and Astronomy, Wayne State University, Detroit, Michigan 48202*

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After implanting Kr ions to a depth of 120 nm below both surfaces of disk-shaped Nb samples, the magnetization in a field-cooling measurement becomes positive at temperatures slightly below the superconducting transition temperature $T_c \approx 9.2$ K. In contrast, the field-cooled magnetization on similar disks prior to the ion implanting was diamagnetic. This behavior confirms earlier evidence that the paramagnetic Meissner effect (PME) is extremely sensitive to the surface microstructure. Furthermore the occurrence of the PME in these ion-implanted Nb disks results from the existence of lower $T_c$ surface defects having a sufficient depth relative to the disk thickness such that the resulting strong flux pinning from these defects gives rise to an inhomogeneous local field distribution. [S0163-1829(96)02346-6]

One of the more intriguing results arising from recent high-temperature superconductivity research is the observation of the so-called paramagnetic Meissner effect (PME) or Wohlleben effect[1–5] in which the field-cooled magnetization (FCM) is positive below the superconducting transition temperature $T_c$ instead of the usual diamagnetic magnetization associated with flux expulsion. In addition, the magnetic-field dependence suggests that in the limit of zero field there is a spontaneous positive magnetization present. This unusual magnetic phenomenon has led to several speculations as to its origin, including orbital currents arising from $\pi$ junctions formed at superconducting grain or crystallite boundaries.[6,7] More recently, the PME has been discovered in certain Nb disks,[8,9] a conventional low-temperature superconductor, and has been found to be sensitive to the surface conditions of the disks. More specifically, mechanical abrasion and polishing of the surfaces of the polycrystalline Nb disks was sufficient to eliminate the PME. Although these results indicate that the PME is not an intrinsic bulk property of these superconductors, the question remains as to why only certain cuprate and conventional superconducting samples demonstrate this phenomenon as well as to the origin of the surface features giving rise to the observation of the PME in these samples.

The earlier work on ceramic $Bi_2Ba_2CaCu_2O_y$ samples[1,2] which were the first to exhibit the PME provides several useful hints to the material characteristics as well as synthesis conditions for observing the effect. These particular ceramic cuprate samples had undergone a melt-casting process for enhancing the critical current density. Subsequent microscopy studies showed that single-crystal platelets were formed during the melt-casting process with the stacking arrangement being predominately one platelet on top of another. Also, the superconducting transition width in the zero-field-cooled magnetization (ZFCM) was fairly broad suggesting possible variations in the $T_c$ and an inhomogeneous superconducting sample. Of course, variations in $T_c$ can arise from different oxygen content in these cuprates as a result of the oxygen diffusion or effusion process during synthesis and subsequent annealing. Another characteristic feature of the PME is the field orientational dependence as measured on $YBa_2Cu_3O_7$ single-crystal samples.[10,11] The PME was observable for magnetic fields applied parallel to the crystallographic $c$ axis (normal to the flat crystalline platelet) whereas an archetypal diamagnetic behavior for a type-II superconductor was observed for fields parallel to the $ab$ plane (parallel to the platelet). Previous work on the Nb disks[8,9] also indicated similar findings of a $T_c$ variation and an orientational dependence of the disk with respect to the magnetic field (i.e., the PME occurs for fields normal to the disk). In addition, our own optical and electron microscopy investigations on Nb disks[8] punched from cold-rolled 0.127-mm thick Nb sheets also indicate the presence of surface defects and voids. Since these Nb superconducting samples exhibiting the PME have a surface microstructure containing defects, which are known to increase the critical current density, it is reasonable to expect that introducing defects through ion implantation, e.g., might enhance or even create the PME in other Nb disks. In the present study, we report that Kr ion bombardment of the surface of Nb disks is a method to artificially create material conditions for inducing a PME in samples previously not exhibiting this effect.

Disks of 6.4-mm diameter were punched from an untreated, cold-rolled, 0.25-mm thick sheet of niobium (99.8% purity)[12] as well as from a 1 in.$^2$ section of the same sheet that had both sides ion implanted with 200 keV $Kr^+$ ions at a dose of $6\times10^{16}/cm^2$. Each disk was then positioned at the center of the second-order gradiometric detector coil system in the Quantum Design superconducting quantum interference device (SQUID) magnetometer[13] with the dc magnetization measurements being performed on the disk in both parallel and perpendicular orientations with respect to the applied magnetic field. Throughout the measurements the disk samples were kept stationary, thereby eliminating any spurious paramagneticlike responses that might arise from the magnet's field inhomogeneity with sample position.[14,15] The analog voltage output from the SQUID amplifier, i.e., the magnetic flux change through the SQUID pickup coils,

 

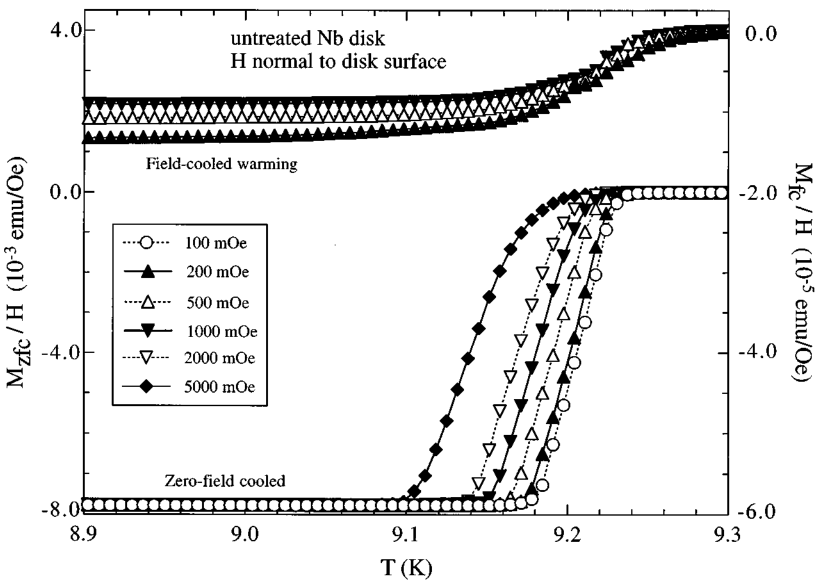


FIG. 1. The zero-field-cooled (lower) and field-cooled-warming (upper) susceptibility data for an untreated Nb disk with magnetic fields applied normal to the disk surface.

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 calibration routine for 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 the copper-wire solenoid incorporated in the ultra-low-field MPMS-*S*5 option.[13] During the actual cooling in zero field, the residual longitudinal field at the sample location was zeroed to less than 1 mOe by using an offset current through the copper-wire solenoid.

Figure 1 displays the field dependence of both the ZFCM and FCM for fields perpendicular to the surface of a typical disk from the original untreated 0.25-mm thick Nb sheet. The overall characteristics of the ZFCM/$H$ and FCM/$H$ data are consistent with an essentially homogeneous superconductor in a perpendicular field orientation. At the lowest temperatures, the susceptibility ZFCM/$H$ is independent of field and indicates complete flux exclusion (or shielding) with a magnitude about 12 times larger than $-V/4\pi$ where $V$ is the volume of the superconducting disk. This enhancement is due to the geometrical demagnetization factor for the disk-shaped sample with the correction factor to the susceptibility being on the order of $R/t$ for a flat disk of radius $R$ and thickness $t$. For our 0.25-mm disks, $R/t=13$ which agrees fairly well with experimental result of 12. With increasing temperatures, the ZFCM/$H$ shows a field-dependent transition of approximately 50-mK width with the disappearance of any appreciable diamagnetic signal occurring at 9.24 K. The departure from the susceptibility field independence is associated with the local field at the circumferential edges exceeding the lower critical field $H_{c1}(T)$ and with magnetic flux entering the sample. On the other hand, the FCM/$H$ exhibits a more complex but diamagnetic behavior, including a hysteresis depending upon whether the sample is being cooled or subsequently warmed through the transition as shown in Fig. 2. The field-cooled magnetization data taken during cooling (designated as FCCM) are typically more positive than the field-cooled data measured during the subsequent warming cycle (FCWM) because of the viscous nature of flux motion into and out of the superconducting sample below $T_c$. Furthermore, the observation that the hysteretic behavior extends down to the lowest measuring temperatures suggests a rather low viscosity with respect to flux motion and the presence of rather weak flux pinning. The absence of the PME in the untreated 0.25-mm thick Nb disks points out that the presence of surface defects themselves are not the sole factor for the PME occurrence since these Nb disks have essentially identical surface structural features as disks from thinner Nb sheets of 0.127-mm thickness [8] which exhibited the PME. Thus disks with similar surface features but different thicknesses exhibit different FCM behaviors.

After the ion implanting of 200 keV $Kr^+$ ions, the Nb disks exhibit several strikingly different characteristics in the ZFCM and FCM, including the appearance of the paramagnetic Meissner effect (see Figs. 2 and 3). The ZFCM/$H$ data now indicate the presence of at least one additional superconducting transition at 9.07 K, even though the magnitude of the ZFCM/$H$ at the lowest temperatures remains the same as that for the untreated disk. Above 9.07 K, the field-dependent behavior suggests that the local field exceeds the lower critical field $H_{c1}$, but at temperatures lower than those observed for the untreated disk at similar field strengths. Also the strong field-dependent diamagnetic transition has been lowered to 9.17 K from the previous 9.24 K with a barely perceptible diamagnetic signal still persisting up to 9.26 K. In comparison, the FCM/$H$ with decreasing temperature shows a diamagnetic signal also beginning at 9.26 K and increasing in magnitude until about 9.17 K whereupon the data show a marked upturn and an eventual positive magnetic response. Finally at 9.07 K, the FCM/$H$ abruptly flattens, extending down to the lowest measuring temperatures. The field dependences in the FCM/$H$ are consistent with the previous studies on both conventional and cuprate superconductors exhibiting the PME since the positive FCM/$H$ becomes less positive and eventually diamagnetic with increasing field strengths (data not shown). In fact, both the ZFCM/$H$ and FCM/$H$ behaviors for the Nb disks after the ion implanting are qualitatively very similar to the tempera-

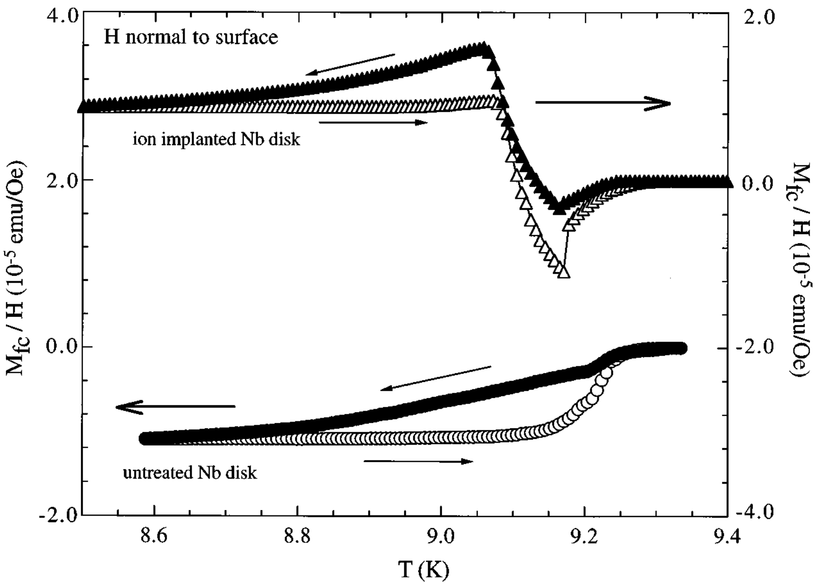


FIG. 2. The hysteretic behavior between the field-cooled-cooling (solid symbols) and field-cooled-warming (open symbols) susceptibility data for an untreated Nb disk (circles) and an ion-implanted Nb disk (triangles) for a 500 mOe field applied normal to the disks surface.

ture and field dependences of the data for the 0.127-mm thick Nb disks that exhibited the PME characteristics without ion implanting.[8] It should be further pointed out that subsequent mechanical polishing of both surfaces of the ion-implanted Nb disk to a thickness of 0.205 mm resulted in the elimination of the PME and the subsequent appearance of magnetic behaviors more consistent with the untreated 0.25-mm-thick disks.

In order to further our understanding of the effect that the ion implanting has upon the magnetization characteristics, one should note that the $Kr^+$ ions penetrate uniformly to a depth of 40 nm below the surface and then the concentration drops off to a negligible value beyond 120 nm.[16] Thus the observed magnetic behavior is strongly affected by just the first 120 nm below the two surfaces of the disks. Clearly the ion bombardment has created an inhomogeneous superconducting sample with a $T_c$ variation as evidenced by the appearance of a second diamagnetic transition at 9.07 K. It is known, e.g., that the $T_c$ of Nb is easily reduced by oxidation and strains.[17] Furthermore Halbritter[18] has shown enhanced oxidation is promoted around defects and serrations on the Nb surfaces so that the defect regions can extend down to several microns below the surface. Consequently it is plausible that the Kr ions have the greatest impact on these regions by reducing the $T_c$ and extending their depth below the surface. Secondly, the ion implanting has produced sites with extremely strong flux pinning as indicated by the narrowing of the ZFCM/$H$ transition width of the largest diamagnetic change. For the 50 mOe data, the transition width is about 15 mK, a factor of 3 times smaller than the 50-mK width observed for the untreated disks. This appearance of stronger flux pinning is also consistent with the characteristic behavior displayed by the $M$ vs $H$ traces (e.g., see Fig. 2 of Ref. 8) in the temperature range between 9.07 and 9.17 K. The nearly field-independent behavior for the magnetization above the lower critical field suggests that the magnetic vor-

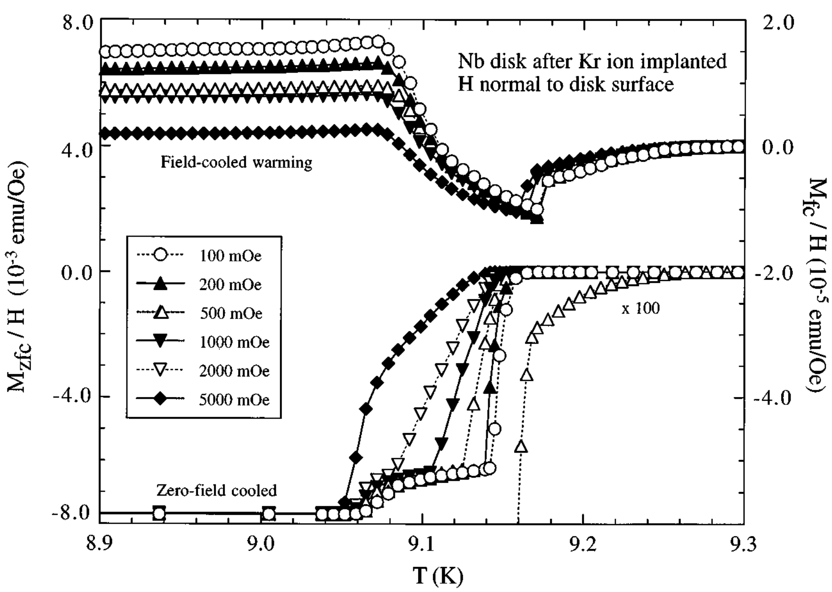


FIG. 3. The zero-field-cooled (lower) and field-cooled-warming (upper) susceptibility data for a Nb disk after $Kr^+$ ion implanting. The magnetic fields are applied normal to the disk surface.

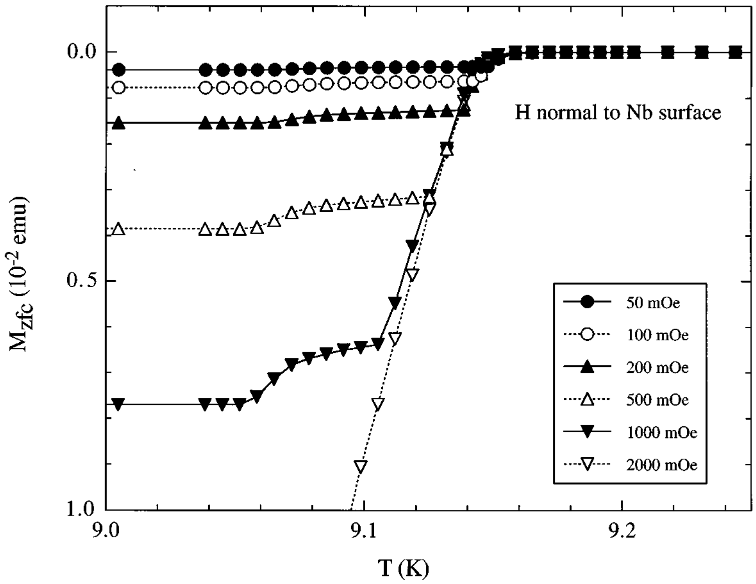


FIG. 4. The zero-field-cooled magnetization as a function of the temperature for a Nb disk after $Kr^+$ ion implanting. The magnetic fields are applied normal to the disk surface.

tices do not easily penetrate the sample at these temperatures. This behavior is shown in an alternate fashion in Fig. 4, where the temperature dependence of just the ZFCM is shown. With increasing temperatures, the ZFCM becomes essentially field independent below a characteristic temperature $T_{c1}(H)$. Thus, the ion implanting appears to have not only created non-negligible regions with a lower $T_c$ at the defect and serration sites on the surface, but also to have extended the depths of these regions so that they are more effective pinning sites. This leads to the conclusion that the geometric ratio of the depths of these lower $T_c$ regions to the thickness of the disk is a factor in the development of the PME.

In contrast to the results for fields perpendicular to the disk surface, the ZFCM/$H$ and FCM/$H$ data for fields parallel to the ion-implanted Nb disk surfaces indicate only diamagnetic behaviors, similar to that shown in Fig. 4 of Ref. 8. The ZFCM/$H$ for the ion-implanted Nb disk indicate a lower temperature for the diamagnetic transition of 9.07 K in comparison to 9.18 K for the untreated Nb disk. Also a very weak-field dependence is observed for this sample orientation since the local field should be nearly the same as the applied magnetic field and correspondingly much smaller than $H_{c1}(T)$. 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. This is also consistent with the knowledge that more effective flux pinning is found for fields perpendicular to superconducting films than for fields parallel.

Although the microscopic origins of the PME cannot be completely explained in this study, it is evident that ion-implantation enhances the effectiveness of the flux pinning by creating deeper surface defect regions which have a lower $T_c$. Furthermore the ion-implantation gives rise to a different temperature dependence in the initial flux penetration field in the temperature range above 9.07 K than that given by the intrinsic lower critical field $H_{c1}(T)$. Figure 5 shows a comparison of the applied field vs $T_{c1}(H)$, the temperature where the perpendicular ZFCM/$H$ data of Fig. 3 become field dependent (or the ZFCM data of Fig. 4 become field independent), and the intrinsic lower critical field $H_{c1}(T)$ for Nb with $H_{c1}(0)=1730$ Oe and $T_c=9.26$ K. Because of the enhancement of the local field due to the demagnetization factor in the perpendicular field orientation, $H_{c1}(T)$ has been scaled by the factor $t/R$. The marked change in the temperature behavior of this initial penetration field suggests two scenarios. (i) The magnetic-field profile created by the surface defects in the ion-implanted disks can suppress the $T_c$ in the remaining portion of the disk and thus a smaller $H_{c1}(T)$ will result with increasing temperatures. (ii) Alternatively, the field distribution arising from the microstructural defects has effectively reduced the superconducting volume fraction associated with the $T_c=9.26$ K phase and thus an increasingly larger circumferential local field ($\sim HR/t$) will by generated by a shrinking geometric ratio $t/R$ as the temperature increases. Since the magnetic behavior in this temperature region between 9.07 and 9.17 K is dominated by strong flux pinning, the shielding currents could dominate not only the

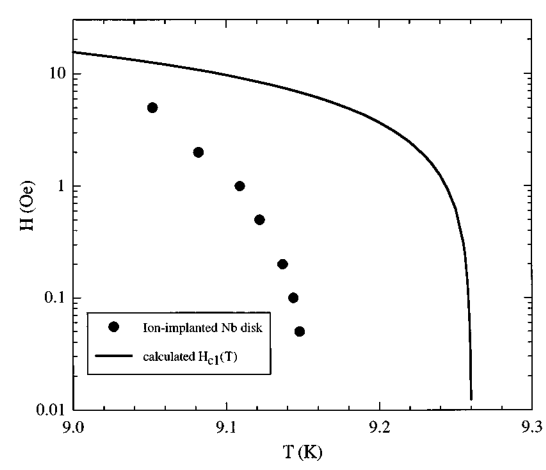


FIG. 5. The temperature dependence of the initial flux penetration field $H$ for the ion-implanted Nb disk. The solid line represents the intrinsic lower critical field $H_{c1}(T)$ for Nb with $H_{c1}(0)=1730$ Oe, $T_c=9.26$ K, and scaled by the demagnetization factor $t/R$.

diamagnetic behavior of the ZFCM, but also the PME since the increasingly positive FCM behavior in cooling measurements occurs in a similar temperature region. For bulk superconducting samples with strong pinning, it is well-known experimentally that small decreases in the field can result in the reversal of the shielding currents and a positive magnetization as characterized by the *M* vs *H* loops for an ideal critical-state superconductor. Rather than having the local field changing due to an external field change, the positive FCM in the Nb disks might arise from a temperature dependence in the local field (a decreasing local field with decreasing temperature).

In summary, the paramagnetic Meissner effect, i.e., a positive magnetization in field-cooled measurements below $T_c$, has been induced in Nb disks by implanting Kr ions to a depth of about 120 nm below the surfaces of the disks. The enhancement of the $T_c$ variation and of the effective pinning strength from surface defects resulting from the ion bombardment are important factors in the development of the PME. By creating a surface defect structure with greater relative depth into the thicker Nb disks, these lower-$T_c$ regions serve as more effective pinning sites which produce inhomogeneous field variations whose temperature dependences could result in the PME characteristic behavior.

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