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# Paramagnetic relaxation and Wohlleben effect in field-cooled Nb thin films

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The ''Wohlleben effect'' (paramagnetic Meissner effect) is found in uniform applied magnetic fields only above a threshold value $H_0 \approx 10^2$ Oe for field-cooled Nb films of thickness less than 1000 Å. The initial diamagnetic magnetization observed upon field cooling to fixed temperatures just below $T_c$ gives way to a logarithmic time relaxation toward paramagnetic values comparable to the critical state magnetization over a period of several hours (normalized rate $S \approx 0.1$), implying that the development of the paramagnetic state is moderated by fast flux creep processes. Small field gradients ≈10–20 mOe/cm are found to influence the occurrence of the effect for applied fields $H < H_0$. [S0163-1829(99)50826-6]

One of the intrinsic properties of superconductivity is the Meissner effect. When a superconductor is cooled below the transition temperature in the presence of an external magnetic field, it expels flux and behaves as a diamagnet. However, occasionally samples have been found to exhibit a *paramagnetic* magnetization below the transition temperature. Initially the effect was observed in high-$T_c$ superconductors,[1–3] and was proposed as evidence for the existence of spontaneous supercurrents in an unconventional pairing state caused by ''$\pi$ boundaries.''[4,5] However, a similar effect was also observed in niobium discs,[6–8] which showed that the ''paramagnetic Meissner effect'' or ''Wohlleben effect'' (WE) is a phenomenon that is not necessarily dependent upon an unconventional mechanism unique to high-$T_c$ superconductors. Subsequent models for the WE, based upon flux compression by Lorentz forces in thin samples, were proposed by Koshelev and Larkin (KL) (Ref. 9) and Moschalkov *et al.* (Ref. 10).

An application of the KL model to data for Nb discs[7] suggested that the paramagnetic magnetization must be small for samples much thicker than the penetration depth $\lambda \sim 500$ Å; however, for very thin samples one can expect a much larger WE due to the macroscopic penetration of Meissner currents into the sample interior (essentially a demagnetization effect). In the present paper we report a study of the WE for Nb films of thicknesses $d \approx \lambda$.

Sample films were prepared via Nb deposition on a $SiO_2$ substrate using dc sputtering in a four-S-gun, high-vacuum system.[11] Although several samples from different depositions were examined, we report our results for two representative films of different thicknesses = 950 Å (designated ''film A'') and 650 Å (''film B''), as measured by a Tencor profilometer. Films A and B had square shape with dimensions $1 \times 1$ mm$^2$ and $3 \times 3$ mm$^2$, and superconducting transition temperatures $T_c = 8.8$ and 8.3 K, respectively.

Magnetic-moment measurements were done using a Quantum Design MPMS5 Superconducting quantum interference device (Squid) magnetometer, both in standard dc (4-cm scan length) and ''reciprocating sample'' (RSO) modes. Both modes yielded similar results, and since the RSO mode is essentially a vibrating sample method (sample motion at 4 Hz and amplitude $\leqslant 1.0$ cm), it is more suitable for time-resolved studies, and we present those results herein. The magnetic field was aligned perpendicular to the plane of the film. A first cycle of experiments was performed in the ''no-overshoot'' magnet charging mode (which generates monotonic field changes); and a second cycle was done later to compare data taken in the ''oscillation'' charging mode (which minimizes field drift) to that taken with the no-overshoot method.

Results of the first cycle of measurements of the temperature dependence of the magnetic moment of film A in field-cooled (FC) and subsequent field-warming (FCW) regimes in external magnetic fields of 150, 250, and 700 Oe are presented in Fig. 1. The temperature was initially swept down from 9.5 to 6 K in increments of 0.1 K, and then reversed. The FC and FCW curves coincide at lower fields, indicating that the temperature dependence of the moment is reversible below about 200 Oe, where the usual diamagnetic Meissner effect is observed. However, at higher fields the FCW curves are always more paramagnetic than the FC curves; in other words, unusual hysteresis behavior develops above a threshold field of around 200 Oe. At a field of 700 Oe, the magnetic moment is positive except for a weak diamagnetic response in a FC regime very close to $T_c$. The data for film B do not exhibit any field threshold for development of paramagnetic relaxation down to 100 Oe, which was the lowest applied field investigated for film B.

The threshold field value $H_0 = 200$ Oe for film A, and our tentative limit $H_0 < 100$ Oe for film B, may be related to the influence of sample shape on the first penetration field $H_p \propto (d/w)^{1/2}$, consistent with estimates by Zeldov *et al.*,[12] where $d$ is the thickness (650 Å and 950 Å, respectively), and $w$ the width (3 mm and 1 mm, respectively) of the film. Our observation of the persistence of the WE to fields of order $10^2$ Oe and beyond, and the existence of the threshold field for film A, differ from published results for thick (25–127 $\mu$m) Nb discs[6,7] studied at much lower magnetic fields ($10^{-2}$–25 Oe).

A remarkable linear temperature dependence (in auto-

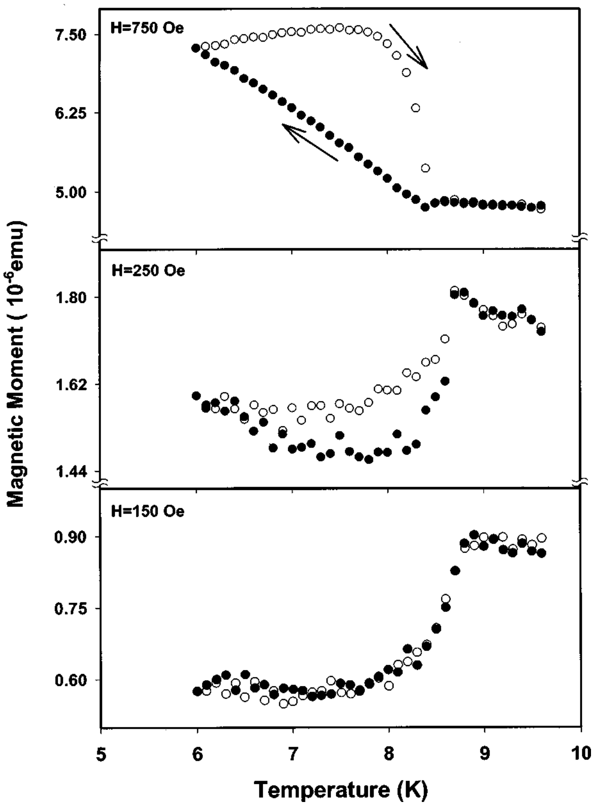

FIG. 1. Magnetic moment versus temperature for Nb film A for different magnetic fields shown. The closed circles denote data taken on the initial FC run, the open circles the FCW run (arrows indicate the temperature sweep direction).

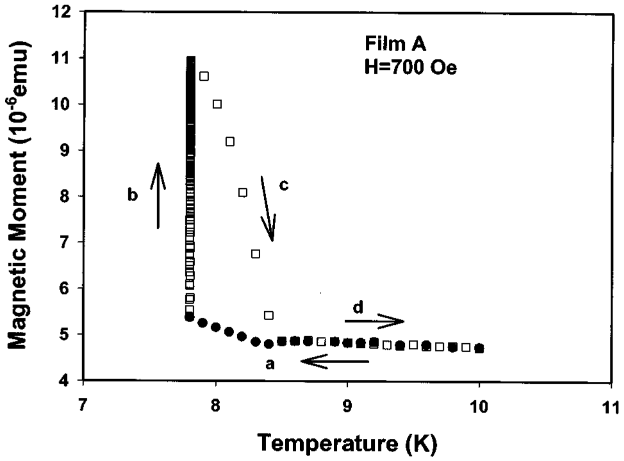

FIG. 2. Magnetic moment versus temperature for Nb film A in an applied magnetic field of 700 Oe. Curve a (solid circles) is composed of data taken by FC to 7.8 K; curve b (open squares) shows the time dependence of the moment at fixed $T = 7.8$ K over a 10-h period [see also Fig. 4(a)]; curve c (open squares) is composed of FCW data taken above $T = 7.8$ K after the 10-h waiting time.

mated data acquisition) of the FC magnetic moment was observed (upper panel of Fig. 1) in the temperature range 6–8.4 K, but we surmised that this was due to a time-dependent relaxation of magnetization. To check this, we halted the FC temperature sweep at $T = 7.8$ K and repeatedly measured the magnetic moment for about 10 h, followed by the usual FCW temperature sweep, as shown in Fig. 2, which confirms the existence of a remarkable time relaxation of magnetization toward a very large paramagnetic response. The subsequent FCW sweep restored the magnetic moment of the sample to precisely the same value observed in the FC sweep at temperatures just above $T_c$, which precludes complications caused by instrumental drift during the 10-h relaxation experiment. Similar behavior was observed for film B.

Both films exhibit logarithmic time relaxation beyond time delays $\approx 10^3$ s, although some differences in behavior can be seen in Fig. 3. Film A exhibits smooth relaxation and obeys a logarithmic time dependence over most of the observation time, but the initial 70-min period reflects a substantially slower response. Film B also exhibits a slow, fairly smooth relaxation during an initial 15-min period, followed by a faster logarithmic dependence interrupted by increasingly unstable behavior, including step jumps, for time delays $\approx 10^4$ s (this is correlated with the many jumps observed in field-sweep data). Nevertheless the rough (interpolating through jumps) time dependence of the relaxation follows the logarithmic behavior defined for waiting times well beyond $10^3$ s.

It is possible that the abrupt jumps in the relaxation and magnetic moment curves of film B are due to thermomagnetic instabilities. It is well known that a combination of large sample size and low temperature can cause the critical state to become unstable when heat is generated during small flux jumps, and to undergo larger instabilities involving macroscopic redistributions of flux[13] when the driven flux generates more heat than the superconductor can absorb over a relevant time interval.[14] Two recent studies have demonstrated development of thermomagnetic instabilities of the critical state in Nb films[14,15] in the form of irregular jumps in magnetic moment and local field in field-sweep and relaxation data. The apparent stability of film A is therefore consistent with film B having a larger size and a lower $T_c$, but we cannot rule out structural inhomogeneities and impurities as possible contributors to the unstable behavior of film B.

A logarithmic relaxation of the magnetization towards zero in type-II superconductors is commonly considered to be the result of the decay of a Bean critical state via thermally activated flux creep in zero-field-cooled ZFC experiments,[16,17] whereas the FC magnetization is expected to remain constant in time. In contrast, in our *FC experiments* we observed a time evolution of the magnetic moment toward *large positive values* typical of the Bean critical state. The overall relaxation process is also unusual in that it initially slowly evolves from a diamagnetic state, but accelerates into a stronger logarithmic process that shows some tendency toward saturation for waiting times greater than $10^4$ s.

We performed measurements of the moment hysteresis curves (taken by zero field cooling the samples) at a reduced temperature $t \equiv T/T_c = 0.88$ in order to compare the paramagnetic moment values developed as a result of slow relaxation, to those attained in Bean's critical state (see Fig. 4). While the ZFC magnetic moment curves for film A are relatively smooth, curves for film B exhibit many irregular jumps (only the envelope of the film B data are shown in Fig. 4). The width of the hysteresis loop for film B is approximately ten times larger than for film A. Taking into account the size difference between the two films, we can use the

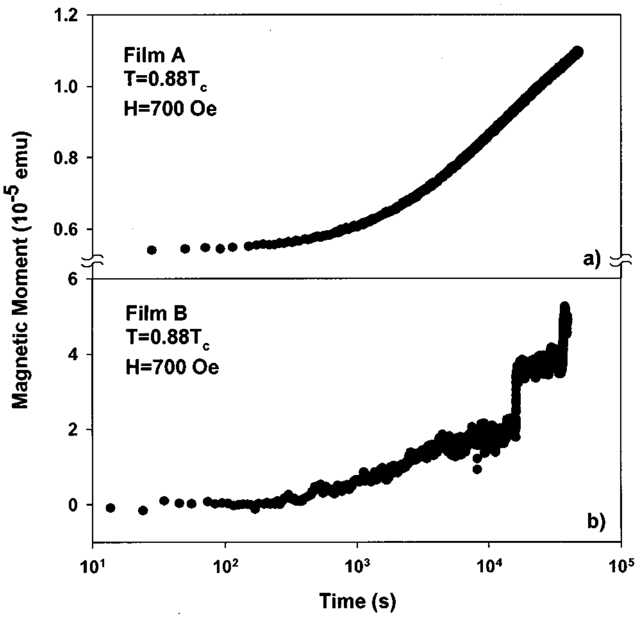

FIG. 3. Time dependence of the magnetic moment of Nb films FC to $T = 0.88T_c$ in an applied field of 700 Oe. (a) Data for film A (“curve b” from Fig. 2). (b) Data for film B. Note the larger magnitude of the moment, stronger pinning (see Fig. 3), and increased scatter and jumps in the film B data.

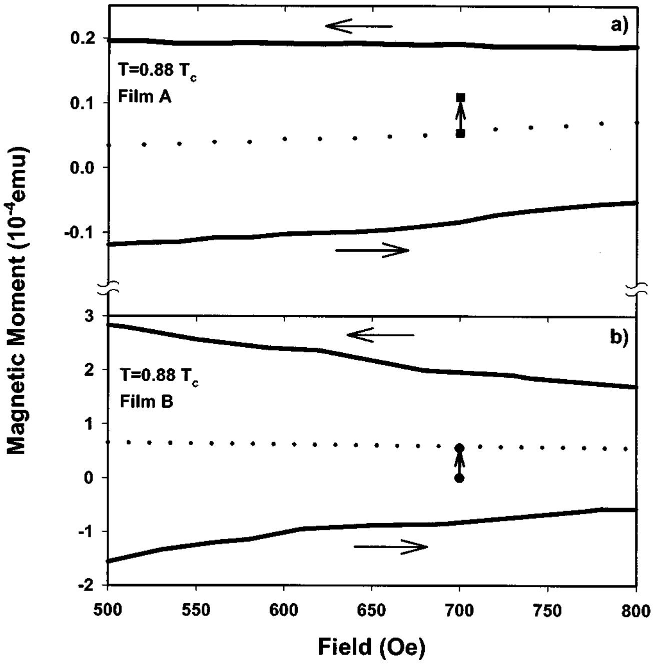

FIG. 4. Critical state hysteresis curves for Nb film A (a) and B (b) ZFC to $T = 0.88T_c$. The dotted curves represent the reversible magnetic moment estimated as $(m_+ + m_-)/2$, where “+” corresponds to the field-decreasing data (large right-hand arrow), and “−” to the field-increasing data (large left-hand arrow). The smaller arrows connect the initial moment values to the final ones (first and last points of the relaxation curves in Fig. 4) obtained after 10 h of relaxation in an applied field of 700 Oe.

critical state model to estimate that the critical current density ($j_c \propto [m_+ - m_-]/2w^3d$, where “+” corresponds to the field-decreasing moment data and “−” to the field-increasing data) of film A is ~1.4 times higher than that of film B. The paramagnetic shift of the magnetic moment of film A attained after 13 h is $\approx 1.1 \times 10^{-5}$ emu, which is about half of the critical state moment derived from the envelope of the hysteresis curve [see Fig. 4(a)]. The corresponding shift after 11 h of relaxation is $\approx 5.5 \times 10^{-5}$ emu for film B, which is also approximately half of the critical state moment [see Fig. 4(b)].

We defined a normalized relaxation rate $S = m_c^{-1} dm(t)/d \ln t$, where $m_c$ is the value of the critical state magnetic moment at the same temperature and applied field, to characterize the relaxation process. Taking into account the comparable values of $j_c$ for the two films studied, it is not surprising that the normalized relaxation rates, $S_A = 1.03 \times 10^{-1}$ and $S_B = 0.71 \times 10^{-1}$, for films A and B (where we interpolated through flux jump events in Fig. 4), respectively, are similar. These values are at the high extremum of relaxation rates commonly observed for high-$T_c$ superconductors at much higher temperatures.[12]

In a recent study, Zeldov *et al.*[12] have reported a geometrical barrier that is present in a thin superconducting slab placed in a perpendicular magnetic field, and the concentration of vortices in the center of the sample due to the action of a Lorentz force by Meissner currents that penetrate the bulk of the slab (i.e., a demagnetization effect). This leads to the formation of a “flux-free region” near the slab edge. In a similar fashion, KL theory explains the paramagnetic FC magnetization of flat superconductors as due to vortex compression and formation of a “paramagnetic critical state” in the sample center. However, in the KL approach, the compression is induced by an inhomogeneous entry into the superconducting state that occurs when the colder edges of a slab become superconducting (with magnetic flux trapped in the normal sample core). Subsequently, Meissner currents form and push (against pinning forces) vortices nucleated in a phase front that moves toward the middle of the cooling sample. The critical state created near the sample center is supposed to generate a paramagnetic moment that exceeds the diamagnetic moment of the Meissner current. Alternatively, Moschalkov *et al.* have shown that compression of a “giant vortex” nucleated at the edge of a superconductor in the surface state ($H \approx H_{c3}$) can also lead to the positive magnetization of a FC superconductor.[10]

The above theoretical considerations motivated us to carry out a second cycle of experiments on film A to investigate the possible influence of nucleation conditions and very small field inhomogeneities on our data. As expected from the reproducibility of the normal-state magnetic-moment data shown in Figs. 1 and 2, slight variations of temperature history and the use of the oscillation mode to minimize field drift had no discernable effect on the paramagnetic relaxation behavior. However, the occurrence of the WE at low applied fields was found to correlate with the presence of very small residual field gradients created by first ramping the field to the the value $H$ chosen to test for the presence of the WE, then discharging the magnet to a residual field $\approx$5–8 Oe. The nonuniformity of the residual field was then profiled using the Quantum Design flux-gate magnetometer option (which unfortunately cannot be directly used to characterize field uniformity for $H \geqslant 10$ Oe). The WE was found to occur in fields $H < H_0$ only when a residual field gradient ≈10–20 mOe/cm was detected after discharging the magnet to 5–8 Oe, which strongly suggests that similar gradients present at measuring fields below $H_0$ are necessary for the occurrence of the WE. These results may explain other observations[8] of a persistent WE in bulk Nb discs at very low fields.

Additional experiments at fields $1200\,\mathrm{Oe} \geqslant H \geqslant H_0 \approx 200\,\mathrm{Oe}$ revealed paramagnetic relaxation and thermal hysteresis following an initial diamagnetic response for temperatures just below $T_c$ (similar to the behavior in Fig. 1). Careful charging of the magnet resulted in measured residual field gradients ≈10 mOe/cm only for $H \geqslant 500$ Oe, but the possible connection of the WE with inaccessible (via flux-gate magnetometry) field gradients potentially present at the full measuring field is unclear in this regime. The WE without significant hysteresis or relaxation (i.e., a reversible paramagnetic Meissner effect) was found to exist for fields between 1200 Oe and 1600 Oe. Checks of the dependence of the WE on the RSO sample oscillation amplitude (0.05–1.0 cm) did not reveal any clear evidence for an inductive mechanism (moving the film through a small field gradient during the RSO measurements). Additional details of the second cycle experiments will be presented in a future publication.

In conclusion, we found Nb films with thicknesses comparable to the bulk penetration depth exhibit new features of the WE not observed[6,7] for substantially thicker Nb discs in magnetic fields below 30 Oe. First, there is the existence of a sample-dependent threshold field $\approx 10^2$ Oe, above which the WE is observed. Contrary to the behavior of most FC superconductors, whose magnetization remains constant in time, thin Nb films exhibit an unexpected relaxation phenomenon. A *paramagnetic* FC magnetization first develops very slowly, on a time scale of tens of minutes, following an initial *diamagnetic* response. The relaxation then accelerates and follows a logarithmic law, which implies that a flux creep process underlies the relaxation in this regime. The relatively large values of normalized relaxation rate at rather low temperatures (compare to values of $S$ appropriate for high-$T_c$ materials) suggest that the Meissner current provides an additional drive for the relaxation toward a ‘‘paramagnetic critical state.’’

Our observations tentatively support the idea[9] that the paramagnetic state develops as a result of the compression of vortices from the sample edge toward the interior, creating a ‘‘vortex-free’’ region between the edge and the interior. However, the geometrical barrier approach of Zeldov *et al.*, The KL model, and the giant vortex approach by Moschalkov *et al.* consider only a static or metastable distribution of the vortices, and none of these models considers nonuniform applied fields or vortex dynamics, both of which we find play significant roles in the Wohlleben effect.

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