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# Apparent diamagnetic response of an inhomogeneous ferromagnet

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We present magnetization measurements on a weakly ferromagnetic Pd 0.5 at. % Fe alloy ($T_c = 15$ K). Due to the preparation technique for the sample, it has a thin surface layer with slightly enhanced $T_c$. In fields above 200 mG, the magnetization is typical of a ferromagnet. However, when cooling in very small fields ($H < 25$ mG), the magnetization reverses its direction at low temperatures, apparently becoming diamagnetic. The effect is very similar, but of opposite sign, to that observed in some high-$T_c$ superconducting samples where the magnetization becomes paramagnetic on field cooling (paramagnetic Meissner effect, PME). Whereas the origin of the PME in superconductors is controversial, the effect in our ferromagnetic sample is explained in terms of dipolar polarization of the interior of the sample by the surface layer with enhanced $T_c$. Removing the surface layer eliminates this anomalous effect and the sample behaves like an ordinary ferromagnet, down to the lowest fields. [S0163-1829(97)00626-7]

One of the most intriguing effects observed in high-temperature superconductors (HTSC's) is the so-called paramagnetic Meissner effect (PME). Instead of the normal flux expulsion on cooling into the superconducting state as manifested by the appearance of a diamagnetic signal (Meissner effect), those samples display a positive magnetization at sufficient low magnetic fields. The PME has been observed in polycrystalline Bi- and Tl-based samples, polycrystalline $YBa_2Cu_3O_x$ and $YBa_2Cu_4O_x$, as well as single crystals of $YBa_2Cu_3O_x$ and $La_2CuO_{4+\delta}$.[1–6] The effect was systematically investigated by Wohlleben and co-workers on ceramic Bi-based high-$T_c$ superconductors.[1,2] The paramagnetic signal was explained in terms of spontaneous super currents produced at $\pi$ junctions (formed at grain boundaries), where the superconducting order parameter makes a phase jump of 180°. It was suggested by some investigators that the PME could be seen as evidence for $d$-wave symmetry of the superconducting order parameter.[7,8]

Indeed, a substantial body of evidence has been accumulating to support a $d$-wave pairing mechanism, although evidence to support a more conventional $s$-wave mechanism has also appeared.[9] Since the PME was seen exclusively in HTSC's cuprates, the effect was often cited as providing strong evidence in support of a $d$-wave mechanism for the cuprates. Motivated by these experiments, Minhaj *et al.*[10] and Kostic *et al.*[11] looked for and reported a PME in Nb metal, which is a conventional $s$-wave superconductor. The occurrence of the PME in Nb demonstrated that a $d$-wave mechanism was not required to produce the effect. Further, the similarity in behavior for the PME in both Nb and HTSC's samples suggested that the effect might have a common origin.[11]

In the case of single-crystal $YBa_2Cu_3O_x$, it was shown that the paramagnetic signal was caused by a thin surface layer with enhanced $T_c$. After removal of this layer the effect disappeared and the samples displayed the usual diamagnetic Meissner effect.[4] A very similar behavior was also observed in the conventional superconducting material Nb.[10,11] Here too, the effect is associated with a surface layer with slightly different $T_c$ from the bulk. In this latter case an explanation was given in terms of flux compression which occurs with sample cooling.[12] Similarly, in single crystals of $La_2CuO_{4+\delta}$, which showed the effect,[5] it was also found that $T_c$ is apparently inhomogeneous, probably showing layering variability.[13]

In this paper we report the observation of the corresponding effect in a ferromagnetic material, i.e., the appearance of a diamagnetic signal at low temperatures. We demonstrate that a Pd 0.5 at. % Fe alloy with a small surface layer of increased Curie temperature, $T_c$, shows a sign reversal of its magnetization when cooled in small enough magnetic fields (''diamagnetic ferromagnet''). The temperature and field dependence of the field-cooled magnetization looks very much like that of the anomalous samples displaying the PME, except that the sign change on cooling through $T_c$ is in the opposite direction. As in the case of $YBa_2Cu_3O_x$ crystals and Nb metal, the sign reversal disappears after the surface layer is removed.

In the Pd-Fe case, the apparent diamagnetism observed on cooling in a field can be understood in terms of a polarization of the ferromagnetic interior induced by prior polarization of the surface layer. For the PME superconductors, the mechanism(s) producing the effect is less clear. However, as results for Nb metal demonstrate, the effect can result from a peculiar change in the magnetic-field distribution in an inhomogeneous sample that results in an apparent flux compression (following a brief burst of flux expulsion) as the sample is cooled below $T_c$. It would appear that all superconductors which show the PME are inhomogeneous, in some cases with $T_c$ on the outer surface different from the bulk (Nb and crystal Y-Ba-Cu-O); in some cases $T_c$ shows a layered character ($La_2CuO_{4+\delta}$), and sometimes $T_c$'s are very broad indicating $T_c$ inhomogeneity but with unknown distribution in the sample (ceramics).

Like the inverse effect in Pd-Fe, the PME arises from a peculiar field distribution that develops about the sample as the sample is cooled in a small applied field. Because of the possible importance of the PME to understanding the pairing mechanism in HTSC's cuprates, it is important to understand how the effect comes about in superconducting systems. As measurements on the Pd-Fe system show, additional insight into this unusual behavior might also be afforded by studies of magnetic systems.

The Pd 0.5 at. % Fe sample used in the present investigation is from a previous research project where we systematically investigated the magnetic properties of dilute Pd-Fe alloys.[14–18] The critical concentration for ferromagnetic order in these alloys is as low as 0.01 at. % Fe.[18] At lower Fe concentration, spin-glass ordering is observed.[18] In order to obtain very homogeneous samples with minimal gradient in the Fe concentration, the samples were subjected to a severe plastic deformation. Upon annealing, to remove the defects introduced by the deformation, partial segregation was observed resulting in a surface layer with slightly enhanced Fe concentration and consequently with slightly higher Curie temperature.[14–17] The sample used in the present investigation was rectangular in shape with dimensions 4×1.5×0.3 $mm^3$ with rounded corners. The field was applied parallel to the long axis.

The magnetization was measured in a noncommercial, low-field superconducting quantum interference device magnetometer, which was previously used extensively in the characterization of high-$T_c$ samples.[11] The magnetic field can be varied between 0 and 100 G, the temperature between 2 and 300 K. With the help of a double $\mu$-metal shield, the residual field was reduced to about 2 mG.[11] As previously described,[11] the sample is stationary during the measurement.

For an ideal soft ferromagnet, the low-field magnetization below $T_c$ is independent of the temperature and is given by $M=VN^{-1}H_a$ (for $H_a<H_{\mathrm{sat}}$), where $V$ is the volume, $N$ is the demagnetization factor, $H_a$ is the applied magnetic field, and $H_{\mathrm{sat}}$ is the saturation magnetic field.[19] If the domain walls are not completely free to move, i.e, if the domain walls are pinned, the thermodynamic equilibrium value of the magnetization is not reached when a magnetic field is applied. When cooling in a field, the magnetization $M$ will be larger than this equilibrium value. After cooling in zero field and warming in an applied field $H_a$, $M$ will be smaller than this value.[14,15,19] Thus, a temperature hysteresis of the magnetization will be observed.

Figure 1 displays the magnetization of a Pd 0.5 at. % Fe sample measured in 200 mG. Displayed are the field-cooled (fc) branch, measured on warming after initially cooling to 4 K in the measuring field, and the zero-field-cooled (zfc) branch, measured after initially cooling to 4 K in zero field. We have previously shown that the fc branch is reversible, i.e., the same curve is measured on cooling and warming.[15–19] Because of the construction of the magnetometer it is easier to measure on warming. The observed hysteresis between the fc and zfc branch is typical of a ferromagnet with some pinning of the domain walls. The two branches meet at the Curie temperature with $M$ for both branches reaching the demagnetization limit of $VN^{-1}H_a$. As can be seen in the inset of Fig. 1, the two branches actually meet slightly above $T_c$. This is indicative of an inhomogeneous sample, with a small part of the sample having a higher $T_c$ than the bulk (see Ref. 14).

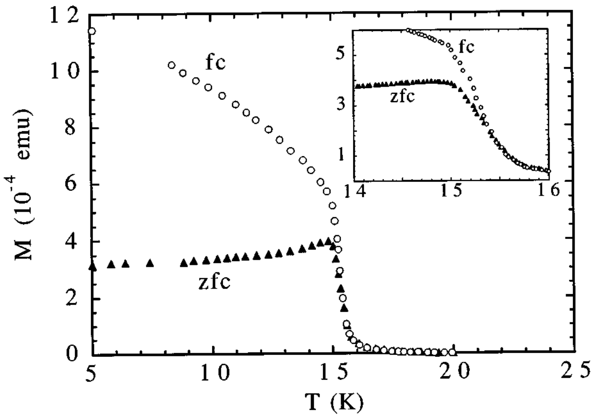

FIG. 1. Field-cooled (fc) and zero-field-cooled (zfc) magnetization of a Pd 0.5 at. % Fe sample in a magnetic field of 200 mG. Inset: enlargement of the transition region.

As the magnetic field is lowered we expect the shape of the two branches to remain about the same with some increased hysteresis. However, a qualitatively different effect is observed as demonstrated in Fig. 2. At 30 mG, with decreasing temperature, the fc branch initially increases reaching a maximum value but then decreases again at lower temperatures to a value well below that of the zfc branch. Below about 25 mG the net magnetization of the fc branch even becomes negative, as demonstrated for 10 mG in Fig. 2.

The observed small negative excursion of the zfc branch for 10 mG near $T_c$ is due to the residual field in the magnetometer of about 2 mG, which is opposite in direction to the applied field, i.e., the zfc branch is actually cooled in $-2$ mG. Because of domain-wall pinning, applying $+10$ mG does not reverse all domains and some of them remain trapped in this reversed direction even close to $T_c$. This negative polarization even remains after the bulk loses its ferromagnetic order thus causing the slight negative excursion of the zfc branch. This persistence of the negative polarization in the surface layer points to a relatively strong domain-wall pinning in this layer (see below).

It is surprising how similar, except for the sign inversion, the fc branch looks to that observed in superconducting samples displaying the PME. As mentioned above, for the case of single crystal $YBa_2Cu_3O_x$ and also for some Nb samples, the PME or sign reversal of the fc magnetization was caused by a surface layer with a $T_c$ that is slightly different from that of the sample interior. We also know from our previous work that some of our Pd-Fe samples are inhomogeneous with an Fe-enriched surface layer with $T_c$

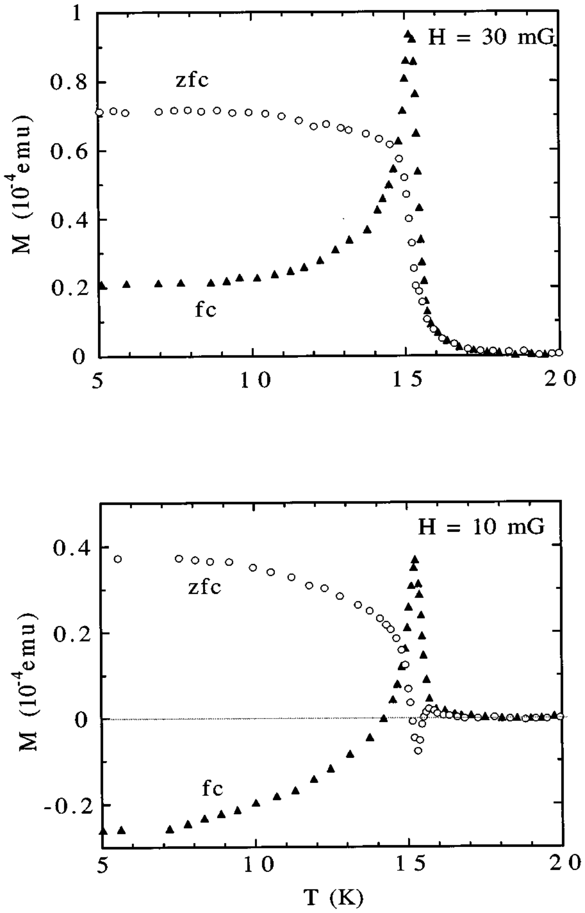

FIG. 2. Field-cooled (fc) and zero-field-cooled (zfc) magnetization for the sample, with surface layer in place, measured in two fields; upper panel: $H$=30 mG, lower panel: $H$=10 mG.

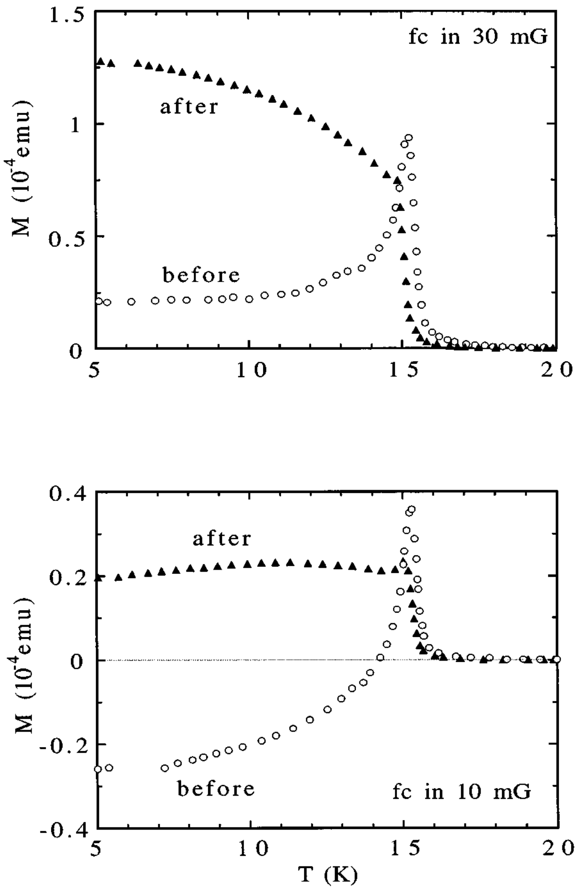

FIG. 3. Field-cooled magnetization of a Pd 0.5 at. % Fe sample. Upper panel: $H$=30 mG, lower panel: $H$=10 mG. ''Before'' and ''after'' refers to the two states of the sample; with the surface layer in place (before) and after its removal (after).

slightly higher than the bulk. Thus we removed the surface of our sample by grinding and chemical etching. In doing so, we reduced the thickness of the sample by about 0.02 mm or about 7%. Figure 3 displays the fc branches in 30 and 10 mG, before and after the surface removal. After the surface removal, the fc magnetization behaves normally. Also note, in Fig. 3, that the higher $T_c$ of the surface layer can now be recognized. With the surface layer in place, the first increase in the magnetization on cooling in a field occurs several tenths of a degree higher than after its removal. Because of the similar dependence on sample inhomogeneity for the superconducting and ferromagnetic samples, it is natural to assume that the sign reversal of the fc magnetization has a similar origin in both classes of materials.

Figure 4 displays the fc magnetization at 5 K as a function of the magnetic field in place during cooling. Data in the upper panel were taken with the surface layer in place and, in the lower panel, after the surface layer was removed. Again, the similarity, except for the inverted sign, with the behavior of $M(H)$ for the PME samples is striking.[3,4,11]

The anomalous behavior in the case of our ferromagnetic sample arises from an interplay of demagnetization fields and domain-wall pinning. On cooling in a small field, the surface layer with the higher $T_c$ first becomes ferromagnetic with its magnetization creating a dipolar field in the sample interior that is opposite in direction to the applied field. When the applied field is less than the average field produced by the surface dipoles (about 25 mG in our case), the interior of the sample sees a negatively biased field and responds with a negative magnetization when it becomes ferromagnetic. However, the thermodynamic equilibrium value of the total magnetization (surface plus interior) is always positive (see below). Thus the appearance of a net diamagnetic signal requires that domain-wall pinning must occur in the inside of the sample as it cools, i.e., it is necessary to frustrate the thermodynamic equilibrium state.

It is instructive to use thermodynamic arguments. The solid line in Fig. 5 shows the magnetization curve for an ideal soft ferromagnet. At small enough fields, magnetic domains are spontaneously formed yielding a net magnetization of $M = VN^{-1}H_a$, independent of temperature (shearing curve). This $M(H)$ dependence minimizes the Landau free energy, $F = -MH_a + NM^2/2$. In order to keep $M$ on the shearing curve (minimum of free energy) as $H_a$ is increased, magnetic domains that are favorably oriented relative to the applied field will grow at the expense of the other domains. This process continues until all domain walls are driven out

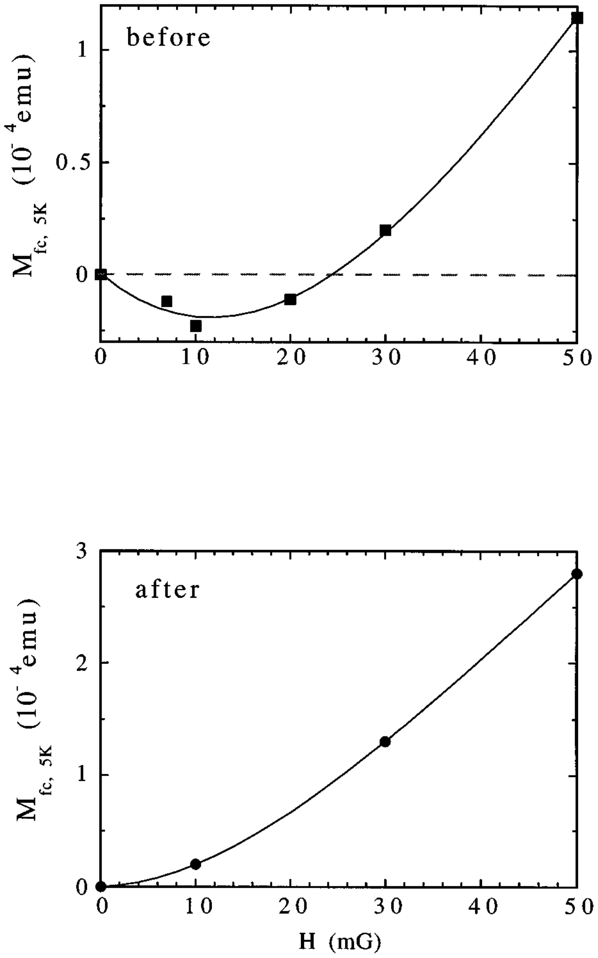

FIG. 4. Field-cooled magnetization at 5 K measured as a function of the magnetic field. Upper panel: with surface layer (before), lower panel: after surface layer has been removed.

of the sample and $M$ reaches the value $M_s = Vm_s$, where $m_s$ is the spontaneous magnetization density of the sample and $V$ its volume.

Let us now assume that the cooling field $H_1$ produces a magnetic moment of $M_0$ in the surface layer (see Fig. 5). In reality $M_0$ will be temperature dependent, similar to the fc branch shown in Fig. 1. We further assume that due to relatively large domain-wall pinning in the surface layer (see above), this surface magnetization freezes-in rapidly as the temperature is lowered below $T_c$ of the surface, i.e., the domain structure of the surface is not changed when the interior becomes ferromagnetic. Thus the surface layers are equivalent to surface domains with a large in-plane anisotropy.

For the following discussion, the solid curve in Fig. 5 is taken to represent the thermodynamic equilibrium magnetization of the total sample, interior plus surface layer (note that $M_s$ and $M_0$ are not to scale; because of the small volume in the surface layer, $M_0$ is only a few percent of $M_S$). As the interior of the sample (fc in field $H_1$) becomes ferromagnetic with cooling, the net magnetization of the total sample will move toward $M_1$, its thermodynamic equilibrium value. The sample can achieve this by creating a negative magnetization in the inner part of the sample equal to $M_i = M_1 - M_0$ ($M_0 > M_1$, see Fig. 5). Just below $T_c$ of the interior, the spontaneous magnetization density of the interior is rather small and to obtain a magnetization equal to $M_i$, the domains are predominantly aligned with the surface generated field (opposing the applied field in the sample interior); i.e., a rather large part of the interior has a negative magnetization.

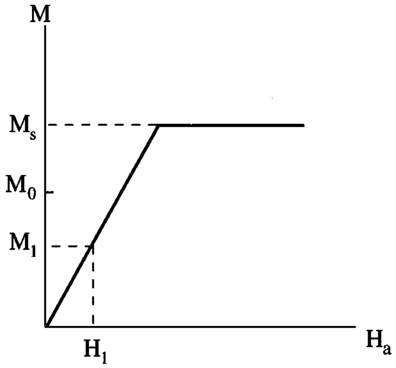

FIG. 5. Magnetization vs field curve for an ideal soft ferromagnet. $M_0$ represents the magnetic moment of the surface layer and $M_s$ the saturation magnetization of the sample. $H_1$ is the cooling field and $M_1$ the thermodynamic equilibrium value of the magnetization in the ferromagnetic state (see text).

As the temperature is further lowered, minimization of the free energy (for a sample with an ideally soft interior part) will demand that the magnetization remains at the value $M_1$. To accomplish this, the domains in the interior part of the sample that are oriented against the applied field must shrink by domain-wall motion since the spontaneous magnetization density increases as the temperature is lowered. However, if the domain walls get pinned, as in our case, the minimization process of the free energy will be stopped and the negative magnetization of the interior will grow along with the spontaneous magnetization density as the temperature is lowered. If the negatively polarized part of the sample is large enough, the net magnetization of interior plus surface can now become negative. At larger cooling fields, $M_1$ will eventually be larger than $M_0$ and the net magnetization $M$ will remain positive at all temperatures.

In summary, we have demonstrated that the magnetic response of an inhomogeneous ferromagnet at very low magnetic fields can be rather complicated and great care must be taken in the interpretation of the results. We have shown that in special circumstances, a negative (‘‘diamagnetic’’) magnetization, opposed to the external field, can be produced. The appearance of this anomaly is surprisingly similar in nature, except for a change in sign, to the PME observed in various superconducting samples. This similarity suggests that the mechanisms causing the effect in the two cases may be closely related.

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