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Surface-sensitive paramagnetic Meissner effect in $YBa_2Cu_3O_x$ single crystals

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It is demonstrated that the paramagnetic Meissner effect observed in some of our $YBa_2Cu_3O_x$ single crystals is associated with an anomalous surface layer. This surface layer, which has a superconducting transition temperature slightly higher than the bulk, develops when the crystals are annealed below 400 °C. When the layer is mechanically removed, the paramagnetic Meissner effect disappears and the crystals behave as normal. Our results demonstrate that the Meissner effect can be masked by unusual properties of a thin surface layer. Thus the measured field-cooled magnetization may not represent the bulk Meissner effect.

In a recent publication[1] we have reported that several $YBa_2Cu_3O_x$ single crystals show evidence for a paramagnetic contribution to the field-cooled magnetization (Wohlleben effect), in addition to the normal Meissner effect. This paramagnetic contribution was attributed to current loops in the **ab** planes, spontaneously produced by so-called π junctions.[2,3] Previously, such effects were seen only in ceramic samples of high-T_c materials.[2,3] We had pointed out that special defects (not just regular twin boundaries) must be at the origin of the effect.[1] In our ongoing search for the origin of the paramagnetic Meissner effect, we found that annealing normal crystals at 375 °C in flowing oxygen often produced anomalous crystals with a paramagnetic contribution to the field-cooled magnetization. We are thus able to systematically investigate the properties of these anomalous crystals.

In this paper we report that the observed paramagnetic magnetization is not a bulk effect but originates in a surface layer. After removing this layer, all crystals behave as normal.

The single crystals were grown in Y_2O_3-stabilized ZrO_2 crucibles as described earlier.[4] They all displayed the usual twinning. Magnetization measurement in applied magnetic fields of $0 \leq H \leq 2$ mT as function of temperature were performed in a superconducting quantum interference device magnetometer as described previously.[1]

Figure 1 (upper part) displays the magnetization of crystal **A**, measured in 0.1 mT on warming, after initially cooling in zero field to temperatures well below T_c [zero-field-cooled (zfc) magnetization]. In the original state as received after crystal growth (state 1), the crystal had been annealed under flowing oxygen at 440 °C and subsequently furnace cooled to room temperature. The transition in this state, defined as the midpoint of the diamagnetic transition in 0.1 mT, is 90.5 K. According to the T_c vs oxygen concentration relation, recently calibrated with

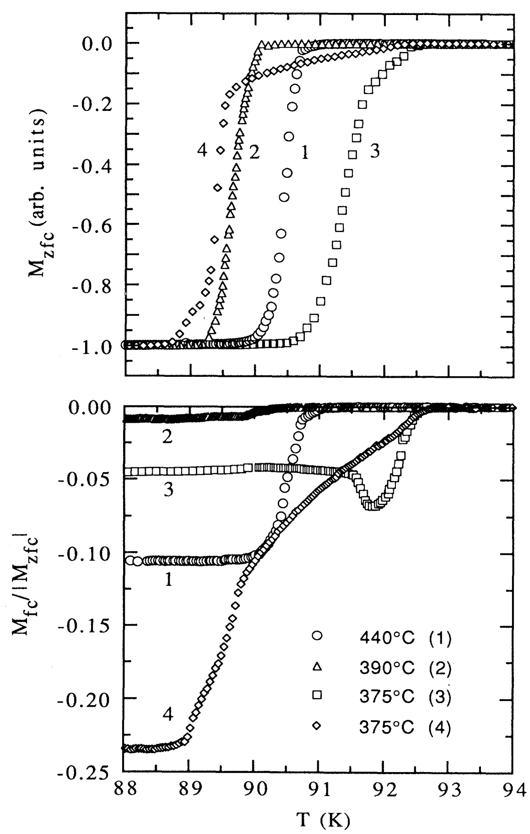

FIG. 1. Zero-field-cooled magnetization M_{zfc} (upper part) and field-cooled magnetization M_{fc} (lower part) in 0.1 mT of crystal **A** in four different states: annealed at (1) 440 °C, (2) 390 °C, (3) 375 °C, and (4) after cutting off a surface layer from the 375 °C state.

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neutron-scattering results,[5] this corresponds to an oxygen concentration of $x = 6.96$. The oxygen concentration was then increased by annealing the crystal in flowing oxygen at 390 °C (state 2). T_c in this state is 89.6 K. This corresponds to an increase in the oxygen concentration to 6.97 (overdoped region).[5] We then tried to increase the oxygen concentration even more by annealing the crystal at 375 °C (state 3). An increase in oxygen concentration would correspond to a further decrease of T_c.[5] Instead, an increase of about 2 K is observed in this state (see Fig. 1). This behavior cannot be easily explained.

The corresponding field-cooled (fc) magnetization curves are shown in Fig. 1 (lower part). They were obtained on warming in 0.1 mT, after initially cooling in the same field to well below T_c. In the original state 1, the sample shows the usual incomplete Meissner effect with about 10% flux expulsion. Annealing at 390 °C considerably decreases this flux expulsion to less than 1%. In the anomalous state 3, obtained after annealing at 375 °C, the fc magnetization is rather anomalous. With decreasing temperature, the magnetization first decreases at T_c but then increases again a few tenths of a degree below T_c. This behavior is typical of a paramagnetic contribution superimposed on the normal Meissner effect.[1] If the normal Meissner effect would have remained as low as that in the state 2, the net magnetization in state 3 would now become positive a few degrees below T_c. The crucial test for the presence of a paramagnetic contribution is to measure the field dependence of the field-cooled magnetization at a temperature where it is independent of the temperature, say at 88 K. This is shown in Fig. 2. For crystal **A**, the fc magnetization at low fields has a negative curvature which, as we demonstrated in Ref. 1, is the signature of a paramagnetic contribution to the fc magnetization. Also shown in Fig. 2 is the fc magnetization for

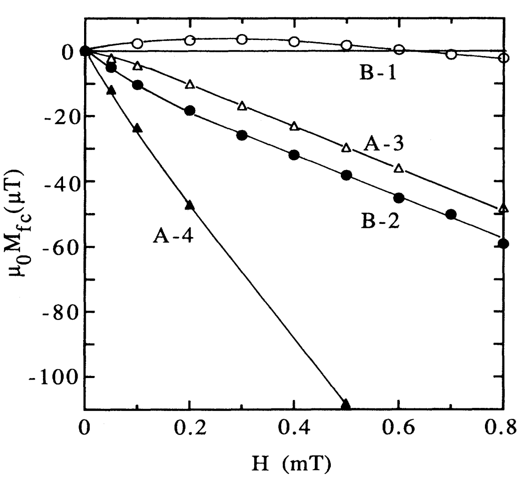

FIG. 2. Field dependence of the field-cooled magnetization M_{fc} at 88 K as a function of the magnetic field for the two crystals **A** and **B**; open symbols: crystal **A** in state 3 and crystal **B** in state 1, before the surface layer is removed; closed symbols: crystal **A** in state 4 and crystal **B** in state 2, after the removal of the surface layer.

the anomalous crystal **B** for which the fc magnetization actually becomes positive at low fields. This crystal had been investigated previously by us (labeled as sample 1 in Ref. 1). The data reported here in Fig. 2 are essentially identically to those reported earlier for this crystal, although a time interval of about two years had elapsed between the two measurements. The behavior of the two crystals is similar, except that for crystal **B**, at low fields, the paramagnetic contribution overcompensates the normal Meissner effect and the net fc magnetization becomes positive.

To check if the anomalous state, observed after annealing crystal **A** at 375 °C, is a bulk effect we removed a surface layer from both **ab** faces of the crystal **A**. This was accomplished by cutting off 10 μm with an ultramicrotome using a diamond knife. This state is referred to as state 4. The cutting procedure did not significantly alter the size of the crystal. Its original dimensions were about 1×2 mm^2 in the **ab** plane and 0.3 mm in **c** direction. The removal of the very thin surface layer, however, has dramatic consequences on the behavior of the crystal, as can be seen in Figs. 1 and 2.

The zfc magnetization in Fig. 1 (upper part) for the state 4 demonstrates that the bulk of the crystal has a T_c of 89.4, slightly below that of state 2. The 2° higher value observed in state 3 thus appears to be due to a small surface layer, apparently formed during the 375 °C anneal. This layer completely shielded the bulk of the crystal. Only after most of this surface layer is removed can the bulk be seen. The remaining tail in the zfc magnetization in state 4 extending from 89.5 up to 92.6 K is probably due to the incomplete removal of the surface layer.

The effect of the removal of the surface layer on the fc magnetization is shown in Fig. 1 (lower part). In the state 4, similar to the zfc magnetization, the transition is very broad due to remaining parts of the surface layer. The surprising result is that the anomalous behavior in state 3 has disappeared, the sample now showing 24% flux expulsion. Thus the observed paramagnetic contribution in state 3 must have originated in the surface layer produced during the 375 °C anneal. This is further elaborated in Fig. 2 which shows the field dependence of the fc magnetization at 88 K. In state 4, with the surface layer removed, the behavior is quite normal with a positive curvature at low fields.

Our experiments clearly have demonstrated that the paramagnetic contribution to the fc magnetization originates from a small surface layer with rather anomalous properties. This layer has a transition temperature which is more than 2 K higher than that of the bulk and has a paramagnetic contribution to the fc magnetization which, in part, compensates the normal Meissner effect of the bulk. The question immediately arises as to whether this behavior is restricted to our crystal **A** or it is generally true for other anomalous crystals as well. We thus decided to cut off a 10 μm surface layer from crystal **B**, the only crystal which showed a net positive magnetization in its original state (see Fig. 2).

The consequence of the surface removal is demonstrated in Figs. 2 and 3. Figure 3 displays the zfc (upper part) and the fc magnetization (lower part) in 0.1 mT, before and after the surface layer was cut off. The effects are dramatic. Similarly to crystal **A** the bulk has a 0.4 K lower transition temperature than the surface layer. When both surface layers are present the bulk is completely shielded. The zfc magnetization in 0.1 mT in the original state of the crystal has a positive value below T_c as shown in Fig. 3 (lower part). After the removal of the surface layer, the crystal shows a normal Meissner effect with about 10% flux expulsion in 0.1 mT. The field dependence of the fc magnetization at 88 K is displayed in Fig. 2. The positive fc magnetization vanishes in small fields after surface removal, and M vs H shows normal behavior, with a positive curvature at low fields.

At the moment it is not clear what happens to the surface layers of the crystal during the low 375 °C anneal. It should be mentioned that crystal **B** was furnace cooled after the original oxygen loading procedure. It therefore has been exposed to 375 °C; however, we have no record of how long. We have annealed other samples at higher and lower temperatures and have found similar behavior upon thermal cycling as reported for crystal **A**. The observed surface layer with different properties than the bulk may be related to other anomalies reported in the literature. One is the observation that overdoped ceramic $YBa_2Cu_3O_x$ samples sometimes consist of two phases with different transition temperatures as seen in specific heat measurements.[6] Similarly, two phases with different lattice parameters and T_c values were observed in some $YBa_2Cu_3O_x$ single crystals annealed in a certain temperature range.[7] However, the connection between those anomalies and the anomalous surface layer discussed here still needs to be established. Regarding the origin of the paramagnetic Meissner effect, it could well be that the required π junctions do only form in a surface layer (i.e., the layer we removed with the microtome), perhaps near surface-characteristic defects. It is not clear at the moment if our observation is at all related to the paramagnetic Meissner effect in ceramic materials.[2,3] More work will be required to answer all these questions. One thing is certain, however. The Meissner effect in irreversible type-II superconductors should not be regarded as a bulk probe. It may be in large parts determined by a surface layer with properties very much different from the bulk. Regardless of the question of a paramagnetic Meissner effect, the apparent Meissner fraction varies strongly for different low-T annealing stages as demonstrated in Fig. 1.

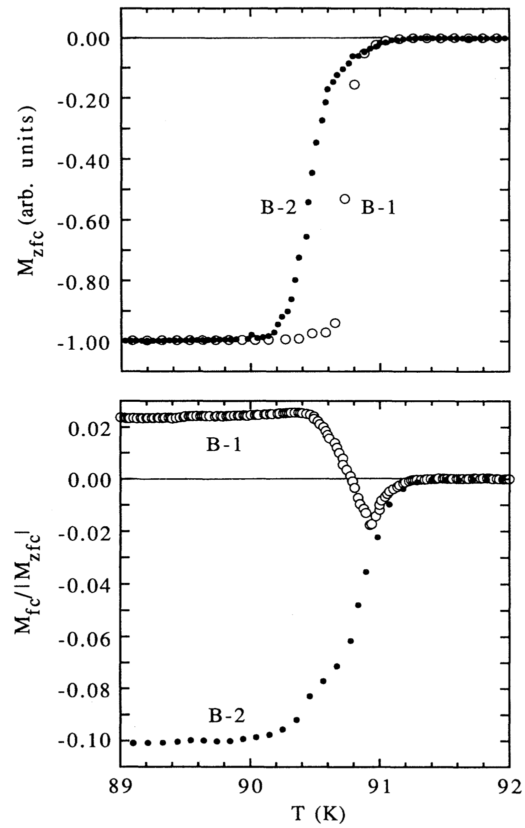

FIG. 3. Zero-field-cooled magnetization M_{zfc} (upper part) and field-cooled magnetization M_{fc} (lower part) in 0.1 mT of crystal **B** in its two states; open symbols: *B*-1, before the surface layer is removed; closed symbols: *B*-2, after the removal of the surface layer.

There have been recent reports that a similar effect as observed for our $YBa_2Cu_3O_x$ single crystals is seen in commercial Nb foil; i.e., a positive fc magnetization which disappears when the surface is sanded down.[8,9] Future work will have to clarify how these reports relate to our observations.

In summary, we have demonstrated that the paramagnetic Meissner effect observed in $YBa_2Cu_3O_x$ single crystals originates in an anomalous surface layer. This layer is produced by annealing the crystals below 400 °C, a temperature at which bulk oxygen diffusion is very small.

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