High field paramagnetic effect in YBCO single crystals with different oxygen contents

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Abstract. Magnetization vs. temperature measurements were carried out on superconducting YBa2Cu3Ox (YBCO) single crystals. Samples with oxygen concentrations corresponding to x = 6.90, 6.85, 6.78 and 6.72 were studied. Zero field cooling (ZFC), field cooled cooling (FCC) and field cooled warming (FCW) prescriptions were employed. Measurements were performed in the temperature interval between 20 K and 120 K in constant magnetic fields ranged from 0.05 T to 5 T. A negative slope was observed in the FCC and FCW curves below a field-dependent minimum located in temperatures less than the irreversibility point (Tirr). This negative slope is identified as the high-field paramagnetic effect (HFPE). With a fixed magnetic field, the magnitude of the observed HFPE increases as the temperature decreases. The field dependence of the HFPE at fixed temperatures is not trivial. The overall magnitude of the measured HFPE depends on the oxygen content and becomes smaller when x decreases. The results are discussed on the basis of the effects of flux compression and spin moment polarization inside the vortex cores.

1. Introduction

Below some specific values of magnetic field and temperature superconductors go into Meissner state, i.e. they expel the magnetic flux from the inside. Above those field and temperature values, type II superconductors remain in the superconducting phase but rather develop a mixed state with partial penetration of the magnetic flux. In the mixed state, type II superconductors should still re-create a diamagnetic response when submitted to external magnetic fields. Surprisingly, in the late eighties, it was experimentally shown that some samples of high temperature cuprate superconductors (HTSC) exhibit in fact, a paramagnetic response when cooled in the presence of very low magnetic fields (B < 1 mT) [1, 2]. The effect is eventually suppressed when the field intensity surpasses a given value. This phenomenon was called the Wohlleben effect or Paramagnetic Meissner Effect (PME). Later on, it was found in textured YBCO monoliths that above a “neutral zone” of fields, where the expected diamagnetic response was observed, the paramagnetic effect reappeared at relatively higher fields and became stronger as the field was increased. This high field effect was then named as the High Field Paramagnetic Effect (HFPE) [3, 4].

When first discovered, it was thought that the PME was exclusive of unconventional granular superconductors. It was argued that the development of a paramagnetic response could be
produced by the d-wave symmetry of the order parameter [5] and formation of spontaneous currents. Those currents would be caused by the occurrence of Josephson $\pi$ junctions between grains [6]. However, since it was found that the effect can be observed in single crystals [7, 8] and conventional s-wave superconductors such as Nb [9, 10], the mechanism of Josephson $\pi$ junctions may not be the only cause of the PME.

Since then, some attempts to explain both, the PME and the HFPE, have been proposed. These explanations include the formation of a giant vortex state [11] and compression of magnetic flux [12, 13]. The HFPE is the least studied and continues to be an open question. Here, we present some magnetization measurements as an effort to elucidate some possible causes of the appearance of the HFPE in deoxygenated YBCO single crystals.

2. Experimental details

Single crystals of YBCO were growth by the auto-flux method. The complete preparation process is published elsewhere [14]. The crystals were oxygenated by performing a thermal treatment in oxygen atmosphere. In order to obtain deoxygenated samples, some crystals were selected for new thermal processes in air atmosphere. These crystals were separately submitted to a 48 h annealing process at 500 °C, 520 °C and 540 °C. Then, the crystals were fastly cooled to room temperature. Samples with four different oxygen contents were obtained (see Table 1).

We carried out Magnetic measurements by using a SQUID magnetometer model XL5-MPMS by Quantum Design, Inc. Magnetic fields up to 5 T were applied parallel to the c axis. Demagnetization corrections were carried out according to calculations in Ref. [15] by approaching the geometry of our samples to ellipsoids. Three sets of measurements were performed for each sample and each value of magnetic field. ZFC curves were obtained by cooling the sample through the critical temperature in zero field and registering the magnetic response while the temperature was increased. FCC curves were obtained by measuring the sample while cooling it in the presence of the field. For the FCW curves, magnetization measurements were carried out while heating the sample to high temperatures in the presence of the previously applied magnetic field.

3. Results

The critical temperatures of our samples were estimated from the intersection point of the extrapolated straight lines which fit the ZFC measurements in the superconducting and normal states performed in a magnetic field of 1 mT. The correspondence between $T_c$ and $x$ in the formula YBa$_2$Cu$_3$O$_x$ was estimated by using the graphs in Ref. [16]. Those data are presented in Table 1. We use both $T_c$ and $x$ for naming the samples.

| $T_c$ | $x$  |
|------|------|
| 91.5 | 6.90 |
| 88.9 | 6.85 |
| 81.9 | 6.78 |
| 71.5 | 6.72 |

In Fig. 1, we present the FCC results for all samples in several applied fields. The FCW data (not shown) have a closely similar behavior to results shown in Fig. 1.
Figure 1. FCC magnetization vs. temperature results for YBCO crystals with different oxygen contents. The applied magnetic fields range between 0.05 T and 5 T.

As can be seen in Fig. 1, in all samples a negative slope occurs in the magnetization at low temperatures which we identify as a manifestation of HFPE. All curves present a minimum a few degrees below the critical temperature. This minimum is produced by the escape of the flux trapped in excess during the cooling procedure [4]. As the minimum occurs at temperatures below $T_{irr}$, we conclude that the HFPE is restricted to the irreversible region where the pinning forces acting on the vortices are substantial.

A real paramagnetic behavior is observed in samples with $x = 6.90$ and $x = 6.78$. We believe that a positive signal would be observed also in the sample with $x = 6.85$ in fields above $B = 1$ T and temperatures below 50 K. For the most deoxygenated specimen, a linear extrapolation of the data to temperatures smaller than those measured does not reach a positive value even near the absolute zero. It is clear, however, that the HFPE occurs in this sample, though with a smaller intensity.

In the three more oxygenated samples, we observe a non-monotonic field dependence of the HFPE at fixed temperatures. As can be seen in Fig. 2, an “oscillatory behavior” is observed in the samples with $x = 6.90$ and $x = 6.78$.

In order to compare the HFPE in samples with different oxygen contents, in Fig. 3 we show FCC and FCW curves measured in all samples in several fields. The irreversibility between the FCC and FCW curves is observed in all crystals in low applied fields. However, only in the sample with $x = 6.90$ the FCC-FCW irreversibility remains in the entire range of applied fields. The simultaneous occurrence of HFPE and the FCC-FCW irreversibilities, as revealed by the results in Fig. 3, suggest that flux compression and pinning have an important role to explain the high field paramagnetic effect [3]. As the pinning becomes less efficient in deoxygenated YBCO samples, one expects that the magnitude of the HFPE progressively decreases as oxygen...
is removed, as indeed observed in the series of crystals studied by us.

In the last years, an out-of-plane spin magnetic moment in YBCO and other HTSC structures was discovered [17, 18]. This moment is observed when a moderate magnetic field is applied and is related to the canting of the antiferromagnetically ordered Cu$^{2+}$ spins. The canting is generated by the Dzyaloshinskii-Moriya interaction within the CuO$_2$ planes. This interaction is reported to be non-zero even in samples with doping near the optimum value [18]. Here, we propose that the HFPE could also result from the polarization of those Cu$^{2+}$ magnetic moments inside the vortex cores, where the magnetic induction attains locally significant magnitudes. In that case, the vortex pinning should promote the spin localization, thus contributing to generate a paramagnetic response. By using the unit cell volume ($V_c \approx 1.73 \times 10^{-22}$ cm$^3$), and the value for the magnetic moment in the superconducting planes of an YBCO sample with $T_c = 90$ K, $m_z = 0.019\mu_B/\text{atom}$ [18], we estimate that the contribution of the Cu moments to the magnetization of our most oxygenated sample is approximately $M \approx 2.04 \times 10^3$ A/m for an applied field of 4 T in a temperature of 9 K. This value is one order of magnitude less than the obtained by us, as can be checked by extrapolating the 4 T curve in the upper left panel in Fig. 1. So, even that the Cu atoms magnetization fills most of the HFPE size, it is clear that this is not the only contribution. Finally, as the magnetic moment developed by the Cu ions is larger in La$_2$CuO$_4$ than in YBCO, we anticipate that the HFPE should be higher in that compound if our statement is correct. Observation of the HFPE in La$_2$CuO$_4$ should be helpfull to elucidate if polarization inside the vortices cores is really a relevant mechanism to explain this unexpected though commonly occurring effect.

4. Conclusion
The high field paramagnetic effect was observed in YBCO single crystals with different oxygen contents. This fact reveals that the occurence of the HFPE is more general than previously thought. The effect is observed in low temperatures and relatively high magnetic fields. The temperature dependence of the HFPE reminds that of a superparamagnetic material. This suggests that polarization of the Cu spins inside the vortex cores might be important to explain the effect. However, as the magnetic signal of the localized Cu$^{2+}$ spins is not directly related to the vortex lattice behavior and its contribution do not fulfill the size of the HFPE, we conclude that other mechanisms are also responsible for this effect. These mechanisms are probably pinning and flux compression, as deduced from the observation of FCC-FCW irreversibilities as well as from the progressive decrease of the effect intensity in crystals with lower oxygen contents.
Figure 3. Magnetization of the studied YBCO crystals measured at several applied fields. Filled symbols represent FCC curves and open symbols represent FCW curves.

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