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Meissner effect and critical fields in an inhomogeneous $Ba_2HoCu_3O_{7-x}$ high-T_c superconductor

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The Meissner and diamagnetic shielding effects and the upper, lower, and thermodynamical critical fields have been studied in a $Ba_2HoCu_3O_{7-x}$ sample using magnetization measurements in fields up to 55 kOe. The diamagnetic shielding curve shows the existence of a transition at $T_c = 91.5$ K followed by a broad transition extending from 85 to 25 K which may be related to inhomogeneities in the oxygen content of the sample. A rather low flux expulsion (13.5%) is observed which we attribute to flux pinning or trapping. We show that the coexistence of superconducting and nonsuperconducting regions within the sample at temperatures just below T_c leads to strong reductions in the critical magnetic fields.

One of the more striking physical characteristics of the new family of high-T_c superconductors[1,2] is the prediction of very high upper-critical fields H_{c2} (Refs. 3 and 4) which make these materials very attractive for technological applications. For instance, from measurements of the upper-critical field slope at T_c, and by using the standard Werthamer-Helfand-Hohenberg dirty-limit theory, upper-critical fields at $T = 0$ K above 1 MG have been predicted.[5] Nevertheless, a rather wide spread of upper-critical field values has been reported up to now for the Ba_2RCu_3- O_{7-x} (R = Y, rare earths) series[3-8] without any evident relationship with normal-state electrical resistivity or rare-earth magnetic moments. Moreover, very stringent differences in H_{c2} values have been reported by Kupfer *et al.*[8] from electrical resistivity or ac susceptibility measurements in the same sample. All these experimental results suggest, first, that there is no exchange effect in H_{c2} associated with the rare-earth paramagnetic moments, and second, that the differences in upper-critical fields reported up to now in the $Ba_2RCu_3O_{7-x}$ series arise from uncontrolled effects in the microstructure or stoichiometry. Furthermore, some care must be taken when comparing experimental results obtained from different experimental techniques on polycrystalline samples. This is mostly because of the strong H_{c2} anisotropy[8-11] of the $Ba_2RCu_3O_{7-x}$ systems, a feature which, as is well known, may lead to misleading conclusions unless the characteristics of the different experimental techniques are properly considered.[12]

In this work, we report isothermal magnetization measurements of a high-T_c $Ba_2HoCu_3O_{7-x}$ superconducting sample performed with a SQUID magnetometer in applied fields to 55 KOe. The thermodynamical critical field and the lower and upper-critical fields have been measured at temperatures near T_c and the dimensionless Ginzburg-Landau parameter has been determined.

Our results show that the critical fields and the Ginzburg-Landau parameter are much smaller than those reported in other $Ba_2RCu_3O_{7-x}$ samples from resistive or magnetization measurements. We argue that the reduction of the critical fields is associated with the heterogeneous character of our superconducting sample. The existence of sample inhomogeneity, probably associated with oxygen nonstoichiometry, is evidenced from low-field Meissner and diamagnetic shielding measurements.

The $Ba_2HoCu_3O_{7-x}$ samples were prepared by reacting a stoichiometric mixture of $BaCO_3$, Ho_2O_3, and $Cu(NO_3)_2$. After grinding and heating in air several times at 950 °C, the samples were pelletized and annealed in oxygen at 700 °C for 2 h and slowly cooled to room temperature under the oxygen flow. The apparent density of our sample was about 0.6 of the ideal density, as estimated from lattice parameters. Chemical analysis and thermogravimetric studies of samples prepared under this procedure lead systematically to an oxygen content of about 6.9 per formula unit. X-ray-diffraction patterns indicted an unique phase with an orthorhombic unit cell close to that reported by several authors (Refs. 1 and 2): $a = 3.819(1)$ Å, $b = 3.900(1)$ Å, $c = 11.669(2)$ Å. dc-resistivity measurements showed a superconducting transition temperature at $T = 91.5$ K and a width (10%-90% of normal resistance) of about 1.5 K. dc isothermal magnetization has been carried out by means of a SQUID magnetometer (quantum design) after zero-field cooling processes. In the magnetization measurements, the sample consisted of a parallepiped having the largest direction (axial ratio 1:4) oriented along the external field in order to minimize the demagnetizing factor.

The Meissner effect and diamagnetic shielding effect were measured in an applied field of 18.8 Oe by performing field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements, respectively (Fig. 1). The results of Fig. 1 clearly show that after an abrupt diamagnetic signal beginning at $T = 92.5$ K, a broad bump appears in the ZFC curve below $T \simeq 85$ K extending down to $T \simeq 25$ K where the magnetization saturates at a constant value. The observation of these bumps below T_c, in magnetic susceptibility studies of the $Ba_2RCu_3O_{7-x}$ superconductors, has been already reported before[7,13] and it indicates the existence of oxygen inhomogeneities leading to regions with lower transition temperatures.[14,15] As is observed in Fig. 1 the flux expulsion measured in the FC magnetization curve saturates at the value measured when the broad bump in the ZFC curve starts and even shows a small, but experimentally significant, minimum value (inset, Fig. 1). This observation clearly indicates that a strong flux pinning or trapping occurs when the regions of the sample with a low oxygen content become superconducting. For instance, if this low-temperature transition involves the formation of superconducting loops, a strong flux trapping within the closed regions should occur. It is then very tempting to think that the sample inhomogeneities occur mostly at the surface of the grains. This would be consistent with the observations of Van *et al.*[16] pointing to the fact that the $Ba_2YCu_3O_{7-x}$ samples are very sensitive to air humidity. In fact, our $Ba_2HoCu_3O_{7-x}$ sample was measured after a delay of about three weeks since the preparation procedure and this could be enough to produce some surface degradation. In this context, it is not clear which is the origin of the minimum in the FC curve but a possible explanation is that it reflects the reduction of the penetration depth within the regions with a low temperature transition. This should make more effective the trapping of the flux enclosed within a loop.

In any case, it is clear that the amount of flux expulsion measured in the FC curve must only be considered as a lower limit of the superconducting volume in the sample. The saturated susceptibility of the FC curve corresponds to 13.5% of $-1/4\pi$, after compaction correction, which is much smaller than that observed in more homogeneous samples.[2,17] The susceptibility measured in the ZFC diamagnetic shielding curve corresponds to 63% of $-1/4\pi$ if no compaction correction is applied and 95% when the compaction correction is taken into account. This is a further indication of the granular nature of the superconducting pellets where the grain boundaries behave as weak links allowing flux penetration into the intergranular voids even in fields as low as 18.8 Oe (Refs. 17–19).

The paramagnetic susceptibility of our $Ba_2HoCu_3O_{7-x}$ sample was measured with an external magnetic field of $H=10$ kOe. The temperature dependence of the susceptibility was fitted to a law $\chi=\chi_0+C/(T+\Theta)$ with $C=15.09$ emu/mol and $\Theta=-16.1$ K. The χ_0 term contains mostly the diamagnetic core contribution and the Pauli paramagnetism of the conducting electrons[4] while the Curie-Weiss term is mostly associated with Ho ions with a small contribution of localized electrons in Cu^{2+} ions. In fact, if we assume that the Curie constant C is only associated with Ho ions we get $\mu_{\text{eff}}=10.9\mu_B$/ion, slightly higher than the free-ion value ($\mu_{\text{eff}}=10.6\mu_B$/ion), thus indicating that some contribution of copper ions as well. Finally, the rather strong Θ value indicates important antiferromagnetic interactions among the Ho ions leading to a low-temperature antiferromagnetic transition.[20,21]

The isothermal magnetization curves measured at temperatures close to T_c show a remarkably ideally reversible behavior in the mixed phase (inset of Fig. 2) indicative of very low intragrain critical currents.[22] This allows one to determine the thermodynamical critical field from the relationship[23]

$$\int_0^{H_c^2}(M_s-M_n)dH=-\frac{H_c^2}{8\pi}, \tag{1}$$

where M_s is the magnetization in the superconducting phase and M_n is the extrapolate paramagnetic magnetization which at these temperatures behaves linearly ($g_J\mu_BJH/k_B\ll 1$).

The upper-citical field H_{c2} was defined as the field where the magnetization M_s reaches the paramagnetic value at the corresponding temperature. A typical magnetization curve is represented in Fig. 2 where it is made evident that the polarization of Ho ions within the vortices dominates the diamagnetic contribution of the superconducting electrons. The fitting procedure followed to get a proper determination of H_{c2} was as follows. High-field points in the magnetization curves were fitted to a straight

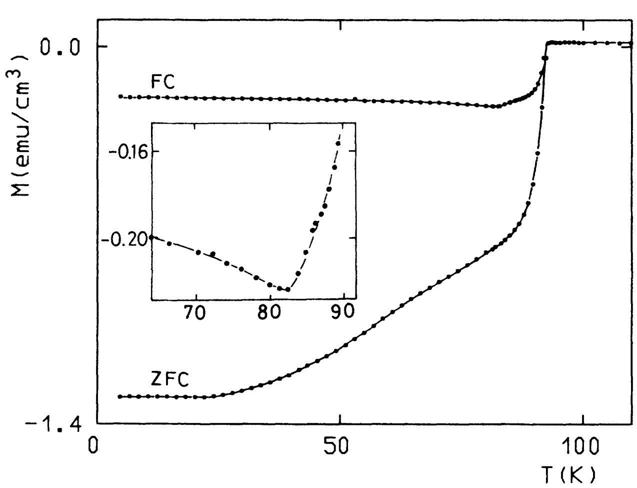

FIG. 1. Meissner effect (FC) and diamagnetic shielding curve (ZFC) as measured at $H=18.8$ Oe. Inset: detail of the FC-magnetization curve at temperatures around the setting of the low-temperature broad bump in the ZFC curve.

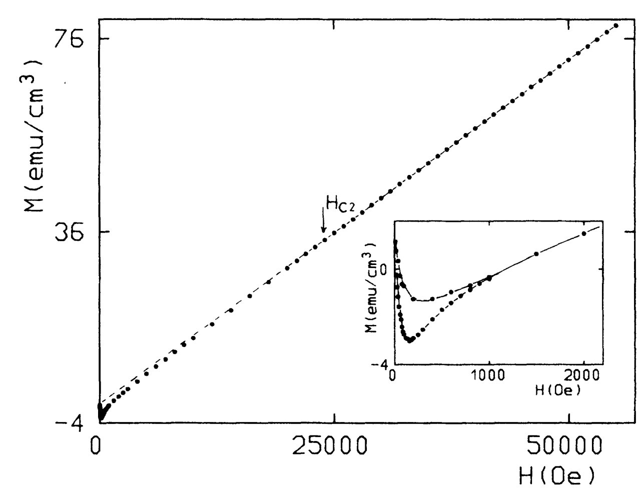

FIG. 2. Magnetization curve measured at $T=83$ K together with the paramagnetic straight-line magnetization fitted from high-field points. Inset: low-field irreversibility observed among increasing and decreasing field curves.

line constrained to go through the origin thus deducing the paramagnetic susceptibility values $\chi_n(T)$ at temperatures below T_c. The upper-critical field was taken as that where the measured magnetization deviates from the high-field straight lines, within the experimental uncertainty in the magnetization values. The self-consistency of this procedure may be ascertained by plotting the temperature dependence of the paramagnetic susceptibilities $\chi_n(T)$ below T_c together with the paramagnetic susceptibility $\chi(T)$ measured at constant field above T_c (Fig. 3).

Finally, the lower-critical field H_{c1} was defined as the field where a deviation of the linear behavior in the isothermal magnetization curve, after zero-field cooling, is observed. This is, in fact, the point above which the diamagnetic shielding effect is broken and which marks the onset of relaxation effects in the magnetization curves.[24] In Fig. 4, we show a typical low-field magnetization curve which makes clear that our determination of H_{c1} is uncertain because of the difficulty in determining the point where linearity no longer holds.

The temperature dependences of H_{c1}, H_{c2}, and H_c, as deduced from the analysis described above, are represented in Figs. 4 and 5 where it may be observed that they extrapolate to $T_c = 91.5$ K which we define as the transition temperature, in agreement with resistivity and Meissner effects measurements. Our results for H_{c2} and H_c clearly show a nonlinear behavior near T_c, at variance with earlier results reported for $Ba_2RCu_3O_{7-x}$ compounds[3-8] while the temperature dependence of H_{c1} remain linear in the investigated temperature range.

The experimentally extrapolated slopes at T_c for the different critical fields are $dH_{c2}/dT = -3.9$ kOe/K, $dH_c/dT = -93.5$ Oe/K, and $dH_{c1}/dT = -3.6$ Oe/K. We note first that all these values are considerably smaller than those reported by other authors for any member of the $Ba_2RCu_3O_{7-x}$ series of high-T_c superconductors. From the experimental slopes of H_{c2}, H_c, and H_{c1} the dimensionless Ginzburg-Landau coefficient as generalized

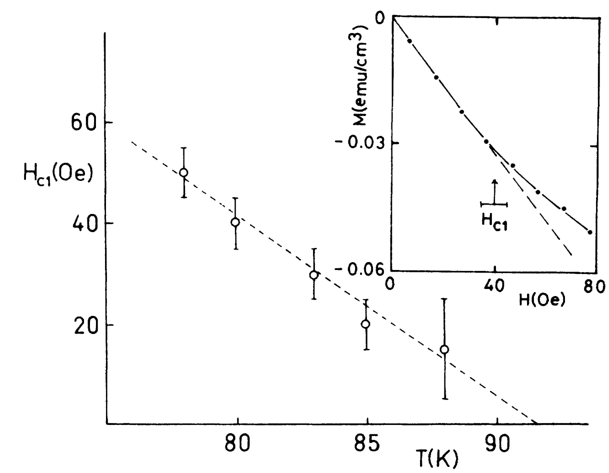

FIG. 4. Temperature dependence of lower critical field H_{c1} near T_c. Inset: low-field magnetization curve measured at $T = 80$ K allowing to determine H_{c1}.

by Maki may be evaluated through the relationship[25]

$$\left.\frac{dH_{c2}}{dT}\right|_{T_c} = \sqrt{2}\kappa \left.\frac{dH_c}{dT}\right|_{T_c}, \tag{2}$$

$$\left.\frac{dH_{c1}}{dT}\right|_{T_c} = \frac{\ln\kappa}{\sqrt{2}\kappa} \left.\frac{dH_c}{dT}\right|_{T_c}. \tag{3}$$

From Eq. (2) we get $\kappa \simeq 30$ while from Eq. (3) we obtain $\kappa \simeq 80$, thus indicating strong type-II superconductivity, even if these values are slightly smaller than those reported by other authors.[4,7]

A clue to the low values of the thermodynamical critical fields may be obtained if we reexamine their definition through Eq. (1). In this definition, it is assumed that the sample is fully superconducting and then H_c is a measure of the condensation energy of the superconducting phase. However, if part of the sample is nonsuperconducting in

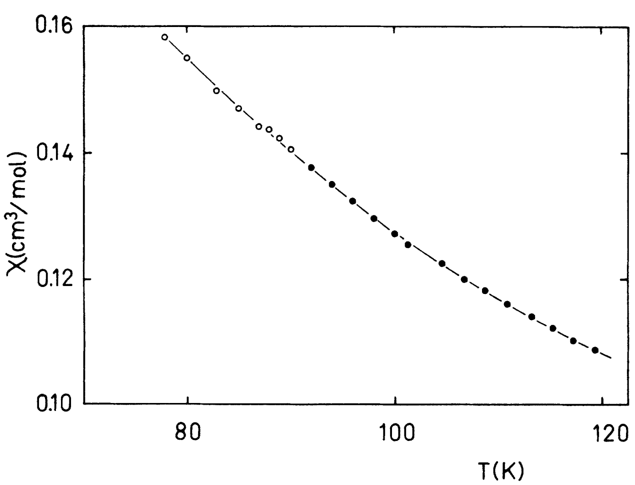

FIG. 3. Paramagnetic susceptibility measured near T_c. Solid points indicate susceptibility values measured at constant field ($H = 10$ kOe) above T_c, open points indicate susceptibility values deduced from isothermal magnetization curves measured below T_c.

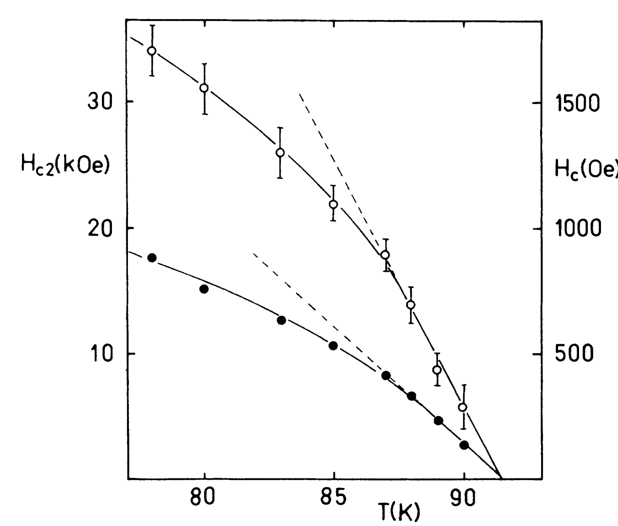

FIG. 5. Temperature dependences of upper critical field H_{c2} (○) and thermodynamical critical field H_c (●) near T_c.

the investigated temperature range, as indicated by the low-field diamagnetic shielding curve, then our evaluation of H_c is underestimated. For instance, measurements by Bezinge, Jorda, Junod, and Mupper[4] for $Ba_2YCu_3O_{7-x}$ samples give $dH_c/dT = -180$ Oe/K at T_c. Therefore, it is very likely that our experimental H_c values have been reduced because of the heterogeneous character of our sample. If we assume that the slope reported by Bezinge *et al.* corresponds to a fully superconducting sample and that the penetration-depth effects[26] are similar in both cases, we conclude that about 13% of our sample remains nonsuperconducting in the 85 K $\leq T \leq$ 91.5 K temperature range. This amount of nonsuperconducting volume seems quite reasonable and could be consistent with a surface degradation phenomena as pointed out above.

Now concerning the upper-critical field H_{c2} several preliminary comments are in order. It is usually observed that, in anisotropic superconductors, electrical resistivity and dc-magnetization measurements in polycrystalline samples lead to strongly diverging results, typically with lower critical fields in the magnetization measurements.[12] This is probably because vanishing small superconducting volumes, having the highest H_{c2} and not detected in the magnetization measurements, may still have a percolation path and thus, zero resistance. One should then expect that dc-magnetization measurements should provide upper critical fields approaching the low values of H_{c2} determined from electrical resistivity drops but definitely higher than those determined from zero resistivity criteria. Moreover, in the study of the new high-T_c superconductors, extreme care must be taken when comparing results from different authors because, due to their very high H_{c2} anisotropy, any nonrandom distribution of the crystallites in the sample may lead to considerable diverging results.

For instance, electrical resistivity results on the $Ba_2RCu_3O_{7-x}$-type high-T_c superconductors give H_{c2} slopes at T_c of about 4–12 T/K for 90% of normal resistivity and of about 0.3–1.2 T/K for 10% of normal resistivity.[3,5,6,8] On the other hand, H_{c2} slopes determined from magnetization measurements are in the range 2–5 T/K.[4,7] It is then obvious from the comparison of all these H_{c2} slopes with that which we have determined in our $Ba_2HoCu_3O_{7-x}$ sample, that we are on the low end of the large range of H_{c2} slopes reported up to now. Furthermore, some authors found a straight-line-type behavior near T_c while others found an upward curvature. Our results show an initial constant slope at T_c and a progressive downward curvature which is very similar to the behavior found by Day *et al.* from critical current measurements.[27]

In light of our own measurements on the $Ba_2HoCu_3O_{7-x}$ superconductor, we must then conclude that the upper critical fields display a strong sensitivity to sample inhomogeneities or microstructure. As it is well known, heterogeneous superconductors usually present anomalous H_{c2} temperature dependences because the percolation correlation length may play the role which should be attributed to the superconducting correlation length.[28–30] In the new high-T_c superconductors it has been recently suggested[31] that the existence of copper-oxygen chains is an essential feature and so we should expect a strong sensitivity of the superconducting state to the introduction of defects or inhomogeneities which could interrupt the coherence along these chains.

In conclusion, our investigation shows that the new high-T_c superconductors have critical fields which are very sensitive to the existence of oxygen inhomogeneities and suggests that a close relationship exists among this defective structure and the observance of low flux expulsion.[32] We suggest then that a very careful characterization of the oxygen stoichiometry must be carried out in order to get reliable fundamental parameters such as critical fields or the dimensionless Ginzburg-Landau parameter.

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