Magnetic properties of $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystals with variable oxygen content

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The reversible magnetization of $Bi_2Sr_2CaCu_2O_{8+\delta}$ crystals was measured for the $H\|c$ direction. Crystals with different stoichiometry were obtained by quenching from different annealing temperatures between 450 °C and 725 °C, resulting in critical temperatures varying from 84 to 93 K. No large variations in the magnetization with T_c were found. The apparent increase of T_c with increasing magnetic field observed in previous work by other authors is not observed, leading to the conclusion that this effect may be caused by inhomogeneities in the oxygen content of the crystals. The magnetization of all specimens approximately followed a logarithmic decrease with increasing magnetic field for a given temperature, allowing the extraction of the magnetic penetration depth λ. The temperature dependence of λ does not follow the empirical $[1-(T/T_c)^m]^{-0.5}$, $m=4$ form, but requires values for m of slightly less than 2. The value for the zero-temperature penetration depth is 0.17 μm, independent of specimen T_c. An attempt to fit the magnetization with a Ginzburg-Landau expression using a temperature dependence for H_c of the type $H_c(T)/H_c(0)=1-(T/T_c)^n$ with $n=2$ was not very successful, indicating that a more sophisticated analysis is needed.

I. INTRODUCTION

In a superconductor complete knowledge of the reversible magnetization as a function of field and temperature enables the determination of all superconducting parameters.[1] Even though a large number of measurements of other superconducting properties have been carried out, the reversible magnetization in $Bi_2Sr_2CaCu_2O_{8+\delta}$ has only very recently been measured.[2,3] However, these measurements are not very consistent. For example, the absolute value of the magnetization (for a given temperature and magnetic field) given by Kritscha *et al.*[3] is almost one order of magnitude smaller than the values measured by Kes *et al.*[2] If only parts of the magnetization in the H-T space are known then theoretical expressions[4-6] allow a fit of the magnetization using a set of parameters like the critical field $H_c(T)$ and the Ginzburg-Landau parameter κ. All of these expressions are based on a solution of the Ginzburg-Landau equations.

In $YBa_2Cu_3O_{7-\delta}$ (1:2:3) it was recognized at an early stage that the oxygen content plays a major role in determining the critical temperature and field.[7-10] Spatial variation of these parameters determine flux pinning and critical currents.[11] The influence of oxygen on crystal properties in $Bi_2Sr_2CaCu_2O_{8+\delta}$ has been neglected in most previous work, with few exceptions.[12,13] Therefore we only know that the critical temperature T_c changes between about 80 K and as high as 97 K (Refs. 13-15) as the oxygen content is changed. However, very little is known how this change in T_c affects the other superconducting properties like, for example, the critical fields. In the current work we attempted to obtain a coherent picture of the superconducting properties in $Bi_2Sr_2CaCu_2O_{8+\delta}$, including the dependence on oxygenation. It should also be noted that the slope of the thermodynamic critical field at T_c determines the size of the specific-heat jump at T_c as well as the magnitude of thermally activated flux creep effects. In previous measurements of the magnetization close to the critical temperature[2,3] no homogenization with respect to the oxygen content was mentioned, and we therefore also carried out some work on the homogenization procedure. The presence of inhomogeneities will of course smear out the specific-heat jump in the actual measurement. As far as we are aware no work has been carried out on how $Bi_2Sr_2CaCu_2O_{8+\delta}$ actually accommodates oxygen defects.

II. EXPERIMENTAL DETAILS

Single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (also referred to as 2:2:1:2, or $n=2$ phase) were grown by quenching polycrystalline material of the composition $Bi_{4.4}Sr_3Ca_3Cu_{3.64}O_x$, maintained in air in a platinum crucible at 870 °C for 45 h. The crystals were obtained as thin platelets of 3-4 mm on the side, with the c axis perpendicular to the plates. After separation the platelets were cleaved to a final thickness of 10 to 20 μm. Electron microprobe analysis of several crystals (as quenched) indicated a composition of $Bi_{2.15\pm0.05}Sr_{1.8\pm0.05}CaCu_2O_{8.15}$. No traces of the $n=3$ phase were observed in x-ray powder diffraction or ac susceptibility versus temperature traces.

The crystals were equilibrated in flowing oxygen at 1 atm. Annealing times were different for different annealing temperatures: 5 h at 725 °C, 20 h at 600 °C, and 48 h at 450 °C. At 725 °C annealing times were varied from 2 to 20 h, but only small differences in the magnetization were found. Reproducibility for different crystals was good. We have not attempted to use higher annealing temperatures (leading to a T_c increase) because of a possible change in cation stoichiometry that can result from evaporation. A controlled low-oxygen partial pressure environment was not available. Two different quenching

procedures were used. (i) The crystals were rapidly cooled inside the quartz furnace tube in oxygen by removing the tube from the furnace and moving the crucible to the cold part of the tube. This process does not expose the crystal to air. (ii) The crystals were removed quickly from the furnace and quenched to room temperature by exposing them to air of ambient temperature. This cool-down process is faster than the first one, but it allows the crystal to exchange oxygen in the first moments before the cool down.

Magnetic measurements were carried out in a commercial Quantum Design superconducting quantum interference device-magnetometer. A 5-cm scan length was used. The magnetic moment was measured in both increasing and decreasing magnetic fields, allowing a determination of the irreversibility line. The magnetization was calculated using the volume of the crystal deduced from its weight. The error in the crystal weight is the major source of the error when comparing measurements on different crystals. A more extensive description of the measurement process was given previously.[10]

III. RESULTS

The reversible magnetization of a crystal quenched from 725 °C as a function of magnetic field and temperature is shown in Fig. 1. Only small differences in the magnetization were found between crystals produced by the two quenching methods. Differences do exist at T_c (see below). The solid line is a fit of the data to a theoretical Ginzburg-Landau expression (see discussion). The field dependence of the magnetization at a given temperature shows an approximately logarithmic decline with increasing magnetic field. This is shown in the inset of Fig. 1.

The influence of the oxygenation treatment on the reversible magnetization in a 1-T applied field is shown in Fig. 2. Aside from a shift in the critical temperature there are only small changes in the absolute magnitude of the magnetization. This is in contrast to previous measurements in the $YBa_2Cu_3O_{7-\delta}$ system.[10] The crystal annealed at 600 °C actually has the largest magnetization by a small margin, even though its T_c is not the highest in the series. The absolute values of the magnetization are comparable to the values given by Kes *et al.*,[2] and about one order of magnitude larger than the values given by Kritscha *et al.*[3] T_c values determined from low field (5 mT) flux expulsion measurements are also shown as arrows in the figures. Alternating-current transitions are typically about 2 K wide. The onset critical temperature decreases from about 93 K to 89 K to 84 K for anneals at 725 °C, 600 °C, and 450 °C, respectively. We are not abso-

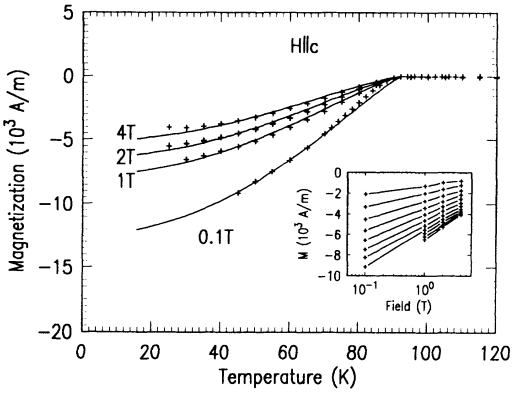

FIG. 1. Reversible magnetization vs temperature for crystal equilibrated at 725 °C. The solid lines are Ginzburg-Landau fits to the data. Inset: field dependence of reversible magnetization from 30 to 80 K. The difference in temperature between the curves is 5 K.

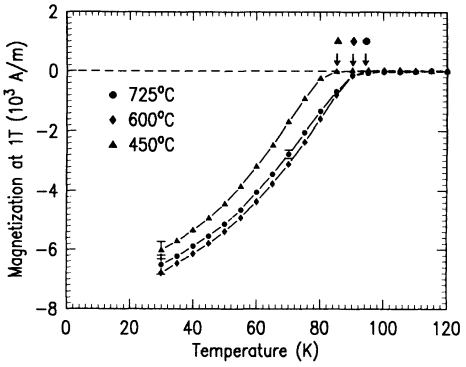

FIG. 2. Reversible magnetization at 1 T for crystals equilibrated at different temperatures. Onset critical temperatures measured in low magnetic field (5 mT) are marked by arrows. The lines are a guide to the eye.

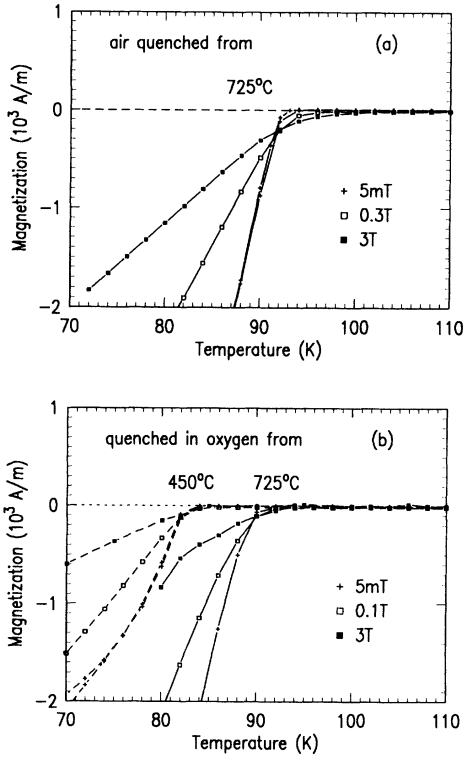

FIG. 3. Expanded view of the magnetization close to the critical temperature for (a) air-quenched crystal equilibrated at 725 °C, (b) crystal quenched in oxygen, equilibrated at 450 °C and 725 °C. The connecting lines are a guide to the eye.

lutely certain what the maximum obtainable T_c is for our crystals, but the maximum value given by Triscone *et al.*[13] is 94.4 K, whereas Deshimaru *et al.*[14] claim an even higher value of about 97 K. Different cation stoichiometry may play a role in producing different maximum T_c values.

Figure 3(a) shows an expanded view of the magnetization close to T_c for an air-quenched crystal. The magnetization shows a crossover effect, where the magnetization above the low-field diamagnetic onset temperature becomes more diamagnetic as the field is increased, in effect leading to an apparent increase of the critical temperature with increasing magnetic field. In Fig. 3(b) similar data are shown for two crystals equilibrated at 725 °C and 450 °C, using quench method 1 (no exposure to air). For the lower-T_c crystal, the crossover effect is absent, and for the higher-T_c crystal the effect is strongly reduced in magnitude, but not completely absent.

IV. DISCUSSION

A. Magnetization close to T_c

Quite large differences between crystals were found in the behavior of the magnetization close to the critical temperature. Most interesting is the crossover effect depicted in Fig. 3(a). This effect was also observed in a series of recent reports[2,3] and has been attributed to thermodynamic fluctuations. Since we have produced specimens that do not show this effect, other causes have to be investigated.

First, we will consider inhomogeneities in the oxygen content. The two different quenching procedures—not being perfectly instantaneous—will have different effects on the inhomogeneities created. The critical temperature for 2:2:1:2 in this regime decreases as the oxygen content is increased. Therefore keeping the crystal in oxygen during quenching will completely suppress the development of regions with a higher T_c value than the bulk of the crystal. This is entirely consistent with the results shown in Fig. 3(b). However, if the crystal is exposed to air, then, depending on how fast the crystal cools, it may lose oxygen (the partial pressure of oxygen in air is only 0.2 atm) since its vapor pressure is 1 atm at the equilibration temperature. Lowering the oxygen content creates regions of higher critical temperature. In order to create a magnetization consistent with Fig. 3(a), a necessary condition is that these regions must be much smaller than a magnetic penetration depth, and not connected. In principle, in this interpretation these regions should be magnetically visible, but only if high sensitivity is used.

We notice that the magnetization at 3 T in Fig. 3(a) is diamagnetic up to a temperature of 99 K. If the effect were caused purely by inhomogeneities in the oxygen content, then that would necessitate the existence of regions in the specimen with a T_c value as high as 99 K. The highest onset critical temperature (measured resistively) in the $n=2$ phase is indeed 99 K,[15] with zero resistance occurring at 96 K. No magnetic data were reported. Deshimaru *et al.*[14] report a maximum T_c value of 97 K. Certainly fluctuations could cause an apparent resistive onset temperature above the mean-field transition, so that there is some uncertainty about the maximum zero-field T_c value of the 2:2:1:2 phase. Fluctuations may account for the finite diamagnetic signal (and resistance drop) above 96 or 97 K.

However, if the crossover phenomenon were caused entirely by fluctuations, then a change in the quenching procedure should not be able to cause its disappearance, unless the superconducting properties show a strong dependence on this procedure, which does not seem to be the case, at least for $H\|c$. Even in the event that the anisotropy were to change drastically for crystals with different T_c, the influence of this possible change on the broadening of the in-field transition would be minor [see Fig. 3(b)]. It must therefore be concluded that the crossover phenomenon is probably caused by inhomogeneities in the oxygen content of the crystal, while thermodynamic fluctuations play a minor role.

B. Magnetic penetration depth

The field dependence of the magnetization in the intermediate-field regime can be shown to follow a logarithmic behavior.[16] In this field regime the penetration depth λ can be simply expressed as (in SI units)

$$\lambda=\sqrt{\Phi_0/8\pi\mu_0 S}\ , \tag{1}$$

where $s=dM/d(\ln H)$, Φ_0 is the magnetic flux quantum, and $\mu_0=4\pi 10^{-7}$ V s/A m. The resulting values for the penetration depth as a function of temperature for two crystals are plotted in Fig. 4. The temperature dependence clearly does not follow the empirical form of $\lambda(t)/\lambda(0)=(1-t^n)^{-0.5}$ with $n=4$. In this case $n=1.7$ and $\lambda(0)=0.19$ μm is a good fit. Reducing the value for n causes a larger dependence of λ on temperature at low temperature (for $t<0.6$), which is required to match the experimental data. The BCS weak-coupling temperature dependence for λ found by Weber *et al.*[17] is a better fit than the empirical form, but shows deviations close to T_c. It also results in a slightly higher value of the penetration depth at $T=0$ of 0.2 μm.

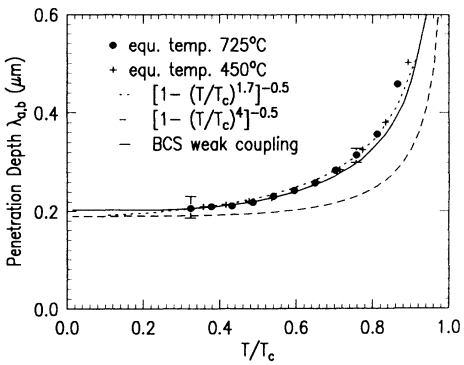

FIG. 4. Magnetic penetration depth vs temperature deduced from the logarithmic field dependence of the magnetization for crystals equilibrated at 450 °C and 750 °C. Also shown are fits to the temperature dependence using $\lambda(0)=0.19$ μm (power-law fits) and 0.203 μm (BCS weak-coupling fit).

According to Hao and Clem[18] the absolute values of λ obtained by this procedure need to be corrected since core contributions to the magnetic energy were neglected in the derivation of Eq. (1). For a superconductor with $\kappa=200$ this correction is about 10%.[18] Taking this correction into account we obtain a value for $\lambda(0)=0.17$ μm (or 0.18 μm, if the BCS weak-coupling fit is used) in the a,b plane. This value is still slightly larger than the value determined from muon spin relaxation measurements of Weber *et al.*[17]

In previous work on a variety of high T_c superconductors the connection between the critical temperature and the carrier concentration has been pointed out.[19] The magnetic penetration depth is also directly related[1] to the carrier concentration n: $\lambda \propto n^{-0.5}$. Therefore, if n (and T_c) is decreasing a larger penetration depth should result. For our crystals there is (within the error bars) virtually no dependence of the penetration depth on the value of T_c. However, if there was a linear dependence of T_c on n, then the change in λ due to the change in n falls within our error bars, making it undetectable.

C. Critical fields

In order to estimate values of the thermodynamic critical field H_c and the upper critical field H_{c2}, it was attempted to fit the magnetization data to a form described by the Ginzburg-Landau equations. The fitting procedure used was identical to the one used successfully before,[10] and is very similar to the procedures used by Hao *et al.*[5] for $YBa_2Cu_3O_{7-\delta}$, and by Almasan *et al.*[20] (using the Hao *et al.* expressions) in the Sm-Ce-Cu-O system. Briefly, the fitting parameters used are the Ginzburg-Landau parameter κ, the bulk critical temperature T_c^{GL}, and the critical field $H_c(T=0)$. The numerical solution of the Ginzburg-Landau (GL) equations derived by Koppe and Willebrand[4] was used to compute the field dependence of M_{rev}. This expression agrees well with other approximations,[6,21] and smoothly spans the range from lower to upper critical field. As in previous work,[10] a temperature dependence for the critical field of the type $H_c(T)/H_c(0)=1-t^2$ was assumed (here $t=T/T_c^{GL}$). If, for simplicity, the small temperature dependence[21] of κ is neglected, then all of the temperature dependence of the magnetization is contained in a term containing $H_c(T)$. A master curve can then be generated [in which the field and magnetization axes are normalized by $\sqrt{2}H_c(T)$] which only depends on κ.

Using this approach the solid lines in Fig. 1 were generated. The fitting parameters used to generate the fit are $T_c=92.5$, $\mu_0 H_c(T=0)=0.9$ T, and $\kappa=205$. However, the fit is not good with fairly large error sums. This is in contrast to $YBa_2Cu_3O_{7-\delta}$ and the Sm-Ce system, where this procedure leads to good agreement between fit and data.[5,10,20] The quality of the fit can be improved by allowing a stronger temperature dependence for H_c close to T_c. An ansatz of the form $H_c(T)/H_c(0)=1-t^m$, with $m=2.5$, leads to a better fit, with only minor (less than 10%) changes in the superconducting parameters $H_c(0)$ and κ. However, it also leads to a discrepancy between the measured and fitted critical temperature. The penetration depth calculated from the fit (with $m=2$) is about 10% larger than the one obtained from the logarithmic field dependence of the magnetization (20%, if the core correction is taken into account). The upper critical field $H_{c2}(T=0)$ is obtained as about 270 T, which results in a coherence length ξ of about 1.1 nm (at $T=0$). These values yield an upper critical field slope at T_c of about 6 T/K. This result is significant because it indicates that the upper critical field of fully oxygenated $YBa_2Cu_3O_{7-\delta}$ (Refs. 10 and 22) (for $H\|c$) may be larger than for $Bi_2Sr_2CaCu_2O_{8+\delta}$. Therefore the in-plane coherence length may be larger in 2:2:1:2 than it is in the 1:2:3 material.

Using the slope of the critical field at T_c it is predicted that these specimens should show a specific-heat jump $\Delta c/T_c$ of about 25 mJ/K^2 mole, roughly half the size the jump that is observed in fully oxygenated $YBa_2Cu_3O_{7-\delta}$. The fact that no clear jump has been observed in single crystals must be blamed on the same reasons that cause the crossover behavior in the reversible magnetization, namely, inhomogeneities in the oxygen content. Specific-heat measurements by Braun *et al.*[23] on polycrystalline $Bi_2Sr_2CaCu_2O_{8+\delta}$ specimens do show anomalies of magnitude 10 to 20 mJ/K^2 mole at T_c. In fully dense ceramics it may be possible that they are actually more homogeneous with respect to the oxygen content than single crystals simply because they are larger in size. If these specimens are cooled from high temperature, then due to large diffusion distances there may be little or no change of the oxygen content in the interior of a polycrystalline pellet.

It should be noted that the assumptions that we made in order to obtain the fit are rather restrictive. For example, no distinction was made between κ, κ_1, κ_2, and κ_3. κ_2 can increase twofold from T_c to 0 K.[24] This increase in κ_2 will change the temperature dependence of the magnetization without the need for a different temperature dependence for H_c. It is unclear whether these modifications are sufficient to obtain a good fit to the data. A basic deficiency of the formalism used is that it is based upon a classical crystalline vortex lattice. In $Bi_2Sr_2CaCu_2O_{8+\delta}$, the existence of a regular flux lattice above the irreversibility line is uncertain.[25,26] This flux liquid state, which may contain decoupled pancake vortices,[27] in fact may exhibit magnetizations that are quite different from the classical Abrikosov flux line lattice. Since this work is intended to be primarily experimental, this more sophisticated theoretical approach is considered beyond the scope of this article. However, based on the experience with conventional low-T_c materials it should also be noted that refinements of the theoretical description are not expected to drastically change the absolute values of the superconducting parameters given here. We would guess that the magnitude of the error of the values for H_{c2}, H_c, and ξ given here, about 20%, is of the order of, for example, the differences in the value of the penetration depth determined using the logarithmic field dependence of the magnetization or the full fit.

V. CONCLUSIONS

Our conclusions can be summarized as follows:

(i) There is no strong dependence of the reversible magnetization on the oxygen content, even though the critical temperature T_c varies by about 10 K.

(ii) The magnetic penetration depth deduced from the logarithmic decrease of the magnetization does not follow the empirical $(1-t^n)^{-0.5}$ with $n=4$ scaling relationship. A stronger temperature dependence at low temperature is required. This was approximated by choosing $n \approx 2$. At $T=0$, $\lambda=0.17$ μm, independent of the crystal's T_c.

(iii) Values of $H_c(T=0)$ are about 0.9 T, which together with κ values of about 210 leads to values of the upper critical field ($T=0$) of around 270 T. The coherence length computes to 1.1 nm ($T=0$). There is very little dependence on the oxygen content. This coherence length is larger than the one found in recent measurements[10] in fully oxygenated $YBa_2Cu_3O_{7-\delta}$.

(iv) The shape of the magnetization versus temperature curve close to T_c is shown to be strongly dependent on quenching conditions. This raises some doubt about the role of fluctuations in causing diamagnetism above the low-field T_c in some specimens.

(v) The sharp in-field transitions observed in these crystals lead to the conclusion that sharp specific-heat transitions at T_c also should be observable, provided that the crystals have been equilibrated properly. Based on our Ginzburg-Landau analysis of the magnetization, a specific-heat jump of about 25 mJ/K^2 mole is predicted.

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