Role of Nd/Ba Disorder on the Penetration Depth of $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ Thin Films

M. Salluzzo, F. Palomba, G. Pica, and A. Andreone
INFM and Dipartimento di Scienze Fisiche, Università di Napoli Federico II, I-80125 Napoli, Italy

I. Maggio-Aprile and Ø. Fischer
Département de Physique de la Mattière Condensée, Université de Genève, CH-1211 Genève 4, Switzerland

C. Cantoni and D. P. Norton
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, P.O. Box 2008, Oak Ridge, Tennessee 37831-6061
(Received 7 December 1999)

We report on a study on the effect of Nd/Ba disorder on the *ab*-plane penetration depth of epitaxial $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ thin films. While in stoichiometric samples $\lambda(T)$ at low temperature is linear, Nd-rich films exhibit a quadratic law. For low Nd excess ($x < 0.04$), a satisfying fit is obtained using the "dirty" d-wave model assuming that Nd ions at Ba sites act as strong scattering centers. At high x ($x > 0.15$) the data are explained if Nd/Ba disorder becomes less effective as a source of scattering. The effect of localization has been discussed to account for the experimental results.

PACS numbers: 74.76.Bz, 74.72.Jt

The temperature dependence of the penetration depth of high temperature superconductors (HTS) gives unique information on the symmetry of the order parameter and is an important probe for the peculiar properties of the pair condensate. Measurements on clean hole doped HTS $Y_1Ba_2Cu_3O_7$ [1] and $Bi_2Sr_2Ca_1Cu_2O_8$ [2] single crystals show that the in-plane penetration depth λ_{ab} exhibits a linear growth. On the contrary high quality $Y_1Ba_2Cu_3O_7$ (YBCO) single crystals, in which Zn impurities are added deliberately to introduce disorder, exhibit a T^2 law at the lowest temperatures and possibly a crossover to a linear behavior increasing T [3]. This picture is consistent with a d-wave order parameter in which Zn ions present on the Cu sites of the CuO_2 planes act as strong scattering centers [4,5]. The situation seems more complex in the case of thin films where only rarely a linearly temperature dependent $\lambda_{ab}(T)$ has been reported [6], usually characterized by a lower slope compared to crystals [7], while a T^2 law seems more common also in the case of nominally optimally doped and stoichiometric samples [8]. To explain these apparently contradictory results it is assumed that even high quality epitaxial YBCO films present some degree of pointlike disorder. However, a satisfying explanation of the data on thin films is still lacking. From these considerations, the relevance of studying the role of disorder on the superconducting properties of the HTS seems evident, especially in thin films.

Disorder can be introduced in HTS not only by doping the crystal with ions of different species but also by changing the ratio of the cations in respect to the stoichiometric value. In the $R_{1+x}Ba_{2-x}Cu_3O_7$ family (R = rare earth), the $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ (NBCO) shows the highest solubility of the rare earth ion in the crystal structure [9]. In this compound, acting on the Nd/Ba substitution, it is possible, at the same time, to increase the cationic disorder and reduce the carrier density in the CuO_2 planes [10]. One should note that the parameters for the growth of HTS thin films from the vapor phase are far from thermodynamic equilibrium conditions and cationic disorder could be a common pointlike defect independently of the specific limits of the $R_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ solid solution, as indicated by the equilibrium phase diagram. Therefore, the understanding of the role of R/Ba disorder in NBCO samples, where a control of the Nd/Ba substitution can be achieved, is strongly desirable. In spite of its relevance, no similar study has been reported so far. Recently the authors have shown that it is possible to grow epitaxial c-axis NBCO films by Ar + O_2 dc magnetron sputtering in low oxygen partial pressure [11] and by pulsed laser deposition [12]. Samples characterized by various degrees of Nd/Ba substitution and oxygen content are obtained using $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ starting targets ($x = 0, 0.09, 0.12$) and different deposition conditions. Typical rocking curves on the (005) peak show FWHM lower than 0.1° (0.06° in the best case). Moreover, the size effect on the (001) reflection is always observed, indicating optimal layering and providing very precise thickness measurements. Nd-rich films do not present spirals originated by screw dislocations resulting in a smooth surface even in the case of samples deposited on $LaAlO_3$ substrates [13]. *In situ* XPS (x-ray photoemission spectroscopy) and *ex situ* EDX (energy dispersive x-ray) microanalysis show that the excess of Nd is included in the NBCO matrix. X-ray diffraction, together with XPS and EDX, was used to determine the exact composition of our films.

Here we present experimental results on two films deposited by dc magnetron sputtering, from $Nd_{1.09}Ba_{1.91}Cu_3O_7$ and $Nd_{1.12}Ba_{1.88}Cu_3O_7$ targets, and on a stoichiometric film, deposited by pulsed laser deposition using the $Nd_1Ba_2Cu_3O_7$ target, on 10×10 mm^2 (100) $LaAlO_3$ substrates. The structural and transport properties of these films are summarized in Table I. The samples are

 0031-9007/00/85(5)/1116(4)$15.00

TABLE I. Structural and superconducting properties of NBCO films. The $\lambda_L(0)$ and $\lambda_{\rm fit}(0)$ are obtained from the number of carriers and from a fit using a phenomenological two fluid approximation for the penetration depth.

Name	c axis (Å)	$T_{c(R=0)}$ (K)	$n \times 10^{21}$ (cm^{-3})	x	$\lambda_L(0)$ (nm)	$\lambda_{\rm fit}(0)$ (nm)
A	11.755 ± 0.005	85	2.5 ± 0.1	0.00 ± 0.025	225 ± 5	240 ± 25
B	11.740 ± 0.005	86	2.6 ± 0.1	0.04 ± 0.025	220 ± 5	230 ± 25
C	11.705 ± 0.005	56	1.0 ± 0.1	0.20 ± 0.025	360 ± 18	380 ± 40

slightly underdoped with a carrier concentration obtained from Hall effect measurements in the range of 1.0–2.6 $\times$ 10^{21} holes/cm^{-3} (in our optimally doped stoichiometric films $n = 4.8 \times 10^{21}$ holes/cm^{-3}). In Nd-rich films the hole content is lower than the optimal doping as a consequence of the Nd for Ba substitution ($x > 0$), which correlates with a c-axis parameter smaller than bulk stoichiometric samples [10]. In the stoichiometric samples a larger c-axis parameter is related to a slightly oxygen deficient composition. The reported results are representative of a series of data taken on various films characterized by similar structural and superconducting properties.

We used an inverted microstrip resonator technique to measure the microwave penetration depth of our films [14]. The fundamental mode of the resonator is $f_0 = 1.3$ GHz. Measuring the frequency resonance shift we can determine the change of the penetration depth with an accuracy better than 5 Å at low temperature. In order to estimate the absolute value of $\lambda(T)$ we have chosen to fit the data in the full temperature range using a modified two fluid approximation:

$$\lambda(T) = \frac{\lambda(0)}{\sqrt{(1 - T/Tc)^{\alpha}}}. \tag{1}$$

This relation reproduces quite well the penetration depth of $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$, $Tl_2Bi_2Ca_1Cu_2O_{8+\delta}$, and $Y_1Ba_2Cu_3O_{7-\delta}$ single crystals in the full temperature range [15]. In our case the parameter α is very similar for each set of data ($\alpha = 0.65$–0.71) and corresponds to the value reported in literature for HTS single crystals [15]. An independent check of our estimated $\lambda(0)$ [$\lambda_{\rm Fit}(0)$ in Table I] has been obtained comparing these values to the zero temperature London penetration depth $\lambda_L(0) = \sqrt{m^* c^2/4\pi n e^2}$, calculated using the number of carriers from the Hall effect coefficient at 100 K (an effective mass $m^* = 4.5 m_e$ has been used [16]). As shown in Table I, the agreement between the fitted $\lambda_{\rm Fit}(0)$ and the calculated $\lambda_L(0)$ is remarkable. In Fig. 1 the change of the penetration depth normalized to the zero value vs T/T_c is shown. While the overall behavior in $\lambda_{\rm ab}(T)$ is very similar for each sample in the full temperature range (inset in Fig. 1), major differences are clearly seen in the low temperature region. In spite of the slight oxygen deficiency, a linear behavior is observed in the case of the stoichiometric sample (A), which is consistent with a d-wave order parameter. In this case it is possible to fit the results using the well-known formula [17]

$$\frac{\Delta\lambda}{\lambda_0} = \ln(2)\,\frac{K_B T_c}{\Delta(0)}\,\frac{T}{T_c}. \tag{2}$$

The in-plane $\mathbf{k}$ dependence of the d-wave gap is assumed to be of the $d_{x^2-y^2}$ type. From the fit (see Fig. 2) one yields $\Delta(0)/K_B T_c = 3.3 \pm 0.1$. This result is in agreement with gap values inferred from tunneling on NBCO polycrystalline samples [18] and with those obtained in the case of YBCO single crystals from penetration depth [1] and scanning tunneling spectroscopy [$\Delta(0) = 20$–25 meV] [19]. On the contrary, the Nd-rich samples (B) and (C) exhibit a T^2 law which is consistent with the d-wave picture if we suppose that Nd at the Ba site acts as a nonmagnetic impurity scattering center. In this case a finite density of states n_0 induced by disorder gives rise to a gapless superconductivity below a crossover temperature T^*, which is related to the scattering rate $\Gamma(0)$ due to the impurities alone by the two-coupled equations [4,5]:

$$T^* \cong \gamma = \frac{\Gamma(0)}{c^2 + n_0^2}\, n_0 = \begin{cases} \Gamma(0)/n_0 & (c = 0), \\ \Gamma(0)/c^2 n_0 = \Gamma_N n_0 & (c \gg 1), \end{cases} \tag{3a}$$

$$n_0 = \frac{2}{\pi} K\!\left(i\,\frac{\Delta(0)}{\gamma}\right). \tag{3b}$$

Here c is the cotangent of the phase shift of the scattered electron wave function, whose value is related to the strength of the scattering center, Γ_N is the normal state scattering rate due to the impurities, n_0 is the disorder induced density of states at the Fermi level, and $K(x)$ is the

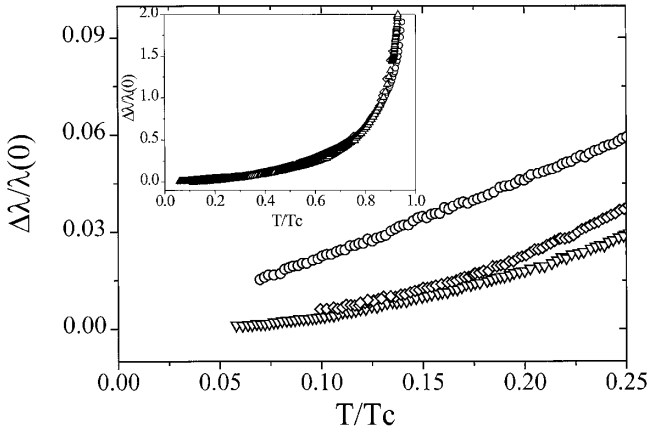

FIG. 1. Normalized change of the penetration depth vs T/T_c. The experimental data for stoichiometric sample (A) (○), for low disordered Nd-rich sample (B) (△), and for disordered sample (C) (◇) are shown at low temperature. In the inset the same graph is shown in the full temperature range.

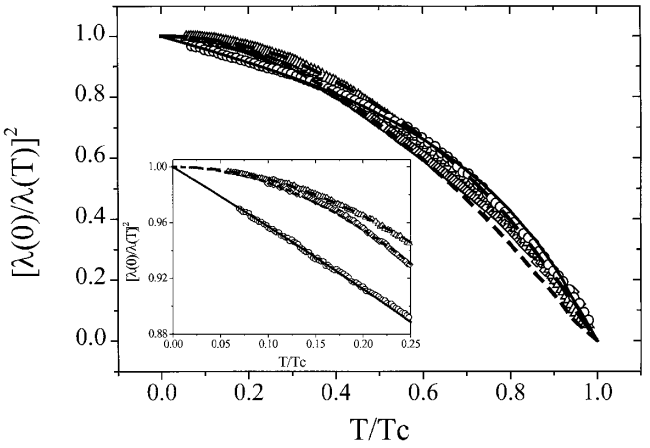

FIG. 2. Fit of the experiment results to the d-wave and d-wave "dirty" models. Here the data are expressed as $[\lambda(0)/\lambda(T)]^2$. The symbols for the data are the same used in Fig. 1, while the lines correspond to the theoretical fit: straight line is for the stoichiometric sample (A), the dashed line is for low disordered Nd-rich sample (B), and the dash-dotted line is for the disordered sample (C). In the inset the same curves are shown at low temperature.

elliptic integral of the first kind. The scattering rate depends on the impurity concentration n_i, on the density of electrons n, and on the density of electronic states at the Fermi level g_F through the relation [5]

$$\Gamma(0) = \frac{n_i n}{\pi g_F}. \tag{4}$$

To calculate the penetration depth we use the well-known expression valid in the clean local limit:

$$\left[\frac{\lambda(0)}{\lambda(T)}\right]^2 = 1 - \int_{-\infty}^{+\infty} d\omega\, N(\omega)\left[-\frac{\partial f}{\partial \omega}\right]. \tag{5}$$

In Eq. (5) $N(\omega)$ is the density of states determined in the case of a d-wave order parameter, taking into account the effect of nonmagnetic impurities [5]. The assumption here is that the clean limit applies even in the case of the more disordered sample (C). This hypothesis is based on the fact that the mean free path of quasiparticles at low temperature in clean HTS thin films is typically of the order of hundreds of angstroms and therefore much higher than the in-plane and out-of-plane coherence lengths. This is confirmed by the scattering rates $\Gamma_{\rm calc}(0)$ and mean free path $\ell_{\rm calc}$ listed in Table II and derived from Eq. (4) in the framework of a quasi-2D-electron gas model. It is clear that, even for sample (C), $\ell_{\rm calc}$ is at least 1 order of magnitude higher than ξ_0, which agrees also with results of normal state resistivity which is only a factor of 5 higher than that of a clean sample. The best fit for each sample using Eq. (5) is plotted as $\lambda(0)^2/\lambda(T)^2$ in Fig. 2 (in the inset the fitting curves are shown in the low temperature region). In the case of sample (A) the fitting curve has been determined using the value of $\Delta(0)/K_BT_c$ deduced from the linear dependence of $\lambda(T)$ for $T < 0.3T_c$. In this case no other fitting parameter is needed. For the Nd-rich samples (B and C) two parameters are required to fit the data, namely, γ/K_BT_c, which depends on the impurity scattering, and $\Delta(0)/K_BT_c$. In Table II the results of the fitting procedure are summarized. In the same table also shown are the scattering rates $\Gamma_{\rm fit}(0)$ which reproduce the fitted γ/K_BT_c according to Eqs. (3) and (4) in the unitary limit ($c = 0$) and, as stated before, the calculated $\Gamma_{\rm calc}(0)$ and $\ell_{\rm calc}$. For sample (B) the assumption that Nd at the Ba site acts as a strong impurity scattering center seems reasonable. A very good fit is obtained in the complete temperature range and the scattering rate obtained is very similar to what is expected in the case of such a density of impurities. On the contrary, in order to get $\gamma = 0.26K_BT_c$ in the Born limit ($c \gg 1$), $\Gamma(0)/c^2 = \Gamma_N$ must be larger than 6.6×10^{12} s^{-1}, in strong disagreement with the estimated $x = n_i$. A picture in which an impurity outside the CuO_2 plane would act as a strong scattering center is at first surprising, since it is generally believed that the pairs condensate is mainly confined to the 2D planes. However, it is well known that the superconducting properties of the NBCO compound are extremely sensitive to the Nd/Ba disorder, as revealed by a complete suppression of T_c for $x > 0.3$ [11]. In the case of the strongly disordered sample (C) the fit parameters seem to be not consistent with the case of unitary limit for which we expect $\gamma = 0.65 \pm 0.07K_BT_c$. Indeed, as shown in Table II, the best fit was obtained with a lower normalized gap $\Delta(0)/K_BT_c = 2.6$ and $\gamma = 0.25K_BT_c$. On the contrary, this value of γ can be reproduced by an intermediate strength of the scattering, i.e., $c \approx 0.9$ in Eq. (3a). Moreover, it is not possible to obtain a satisfying fit in the whole temperature range since the theoretical curve does not match the experimental data in the region $T > 0.6T_c$.

Recently it has been proposed that the suppression of the order parameter at impurity sites may have a substantial effect on the pair condensate, introducing an additional source of quasiparticles scattering [20]. This is possible in HTS because the coherence length is very short and therefore for small concentration of point defects

TABLE. II. The first two columns are the fitting parameters using the d-wave predictions. The third column is the scattering rate $\Gamma_{\rm fit}(0)$ which reproduce the fitted γ/K_BT_c from Eq. (3) in the unitary limit. Finally, the last two columns are the scattering rates $\Gamma_{\rm calc}(0)$ calculated using Eq. (4) and the correspondent values of the mean free path $\ell_{\rm calc}$ in the framework of a quasi-2D-electron gas model.

Sample	$\frac{\Delta(0)}{K_BT_c}$	$\frac{\gamma}{kTc}$	$\Gamma_{\rm fit}(0)$ ($\times 10^{12}$ s^{-1})	$\Gamma_{\rm calc}(0)$ ($\times 10^{12}$ s^{-1})	$\ell_{\rm calc}$ (nm)
A	3.3 ± 0.1	...	...	...	...
B	3.0 ± 0.1	0.28 ± 0.02	2.3 ± 0.2	2.6 ± 0.2	54
C	2.6 ± 0.1	0.25 ± 0.02	1.8 ± 0.2	3.6 ± 0.2	19

the order parameter could be not uniform, becoming zero at the impurity site. Recently Hudson *et al.* and Pan *et al.* [21,22], using a cryogenic scanning tunneling microscope, demonstrated that a quasiparticle scattering resonance occurs around an isolated Zn impurity. Moreover, they found that within an area of about 15 Å the superconductivity is strongly suppressed. In our opinion this is similar to what happens in the case of Nd/Ba disorder, giving a natural explanation of the fact that isolated Nd ions at Ba sites behave as unitary scattering centers, as in sample (B). Moreover, one should note that a crossover is expected when the average distance d_i between the impurities becomes comparable with the coherence length ξ_{ab} [23]. Indeed if d_i is larger than the coherence length ξ_{ab}, the order parameter is not spatially uniform and is suppressed at the impurity site, but inside the superconducting matrix the gap maximum is identical to that of a clean sample. If increasing disorder d_i becomes comparable to ξ_{ab}, the order parameter is spatially averaged and we have a reduced gap maximum, but at the same time around the impurities we have no more a normal state "hole" but a depressed superconducting region. We expect that in this case the impurity will be less effective as a scattering center. To be more quantitative we can compare d_i to ξ_{ab} in the case of low impurity content (sample B) and in the case of high disorder (sample C). Using $d_i = 2a_0/\sqrt{\pi n_i}$ [23], we have $d_i \approx 30$ Å for sample (B), i.e., a value certainly higher than $\xi_{ab} = 10$–15 Å, while $d_i \approx 10$ Å for sample (C) which is comparable or even smaller than ξ_{ab}. In spite of its crudity the agreement of the experimental results with this picture is remarkable. If our approach is correct the important effect of local suppression of the order parameter at impurity site needs to be carefully taken into account in the study of any superconducting properties of HTS.

The idea outlined above strongly suggests dominant d-wave symmetry of the order parameter. In fact, an s-wave picture can be reconciled with the experimental data only supposing that magnetic impurities are introduced by Nd/Ba substitution, but it is difficult to justify quantitatively the data. The magnetic properties of the NBCO compound have been carefully investigated by neutron scattering [24]. The main results are that no free spins are created in both the CuO_2 and CuO layers in the case of $Nd_1Ba_2Cu_3O_x$ ($x > 6.5$), as it happens in YBCO, while Nd ions at the Ba site may induce free spins in the CuO layer by disordering of the chains. We cannot rule out some role of these free spins in the case of Nd-rich samples. An alternative model, which considers the effect of magnetic scattering in the chains in an s-wave framework, is the two-gap model [25]. Using this approach we have obtained a fit of the data with quality comparable to the d-wave dirty model. However, the magnetic scattering rate Γ_M, which mainly governs the low temperature behavior, is found to be larger in the case of the stoichiometric sample (A) (120 K) compared to the Nd-rich sample B (90 K), contrasting what is observed by neutron scattering experiments.

In conclusion, we have performed accurate measurements of $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ penetration depth and studied the effect of Nd/Ba disorder. The experimental results were compared to the d-wave dirty model in the Born and unitary limit. The data support the d-wave picture assuming that Nd at the Ba site acts as a strong nonmagnetic impurity scattering center for low impurity content. Increasing the disorder the same kind of impurity site becomes less effective as a source of scattering and the fit is not satisfactory for $T > 0.6T_c$. The results can be explained taking into account the role of local suppression of the order parameter around the impurity sites.

The authors are grateful to Professor R. Vaglio and Dr. A. Cassinese for stimulating discussions. Professor J. M. Triscone, Dr. M. Decroux, and S. Gariglio are gratefully acknowledged for the Hall effect measurements.

[1] W. N. Hardy *et al.,* Phys. Rev. Lett. **70**, 3999 (1993).
[2] Shih-Fu Lee *et al.,* Phys. Rev. Lett. **77**, 735 (1996).
[3] D. A. Bonn *et al.,* Phys. Rev. B **50**, 4051 (1994).
[4] P. J. Hirschfeld, W. O. Putikka, and D. J. Scalapino, Phys. Rev. Lett. **71**, 3705 (1993).
[5] P. J. Hirschfeld, W. O. Putikka, and D. J. Scalapino, Phys. Rev. B **50**, 10 250 (1994).
[6] L. A. de Vaulchier *et al.,* Europhys. Lett. **33**, 153 (1996).
[7] E. Farber, G. Deutscher, J. P. Contour, and E. Jerby, Eur. Phys. J. B **5**, 159 (1998).
[8] A. Fuchs, W. Prusseit, P. Berberich, and H. Kinder, Phys. Rev. B **53**, R14 745 (1996).
[9] E. A. Goodilin *et al.,* Physica (Amsterdam) **272C**, 65 (1996).
[10] M. J. Kramer *et al.,* Physica (Amsterdam) **219C**, 145 (1994).
[11] M. Salluzzo, I. Maggio-Aprile, and Ø. Fischer, Appl. Phys. Lett. **73**, 683 (1998).
[12] C. Cantoni *et al.,* Appl. Phys. Lett. **74**, 96 (1999).
[13] M. Salluzzo, I. Maggio-Aprile, and Ø. Fischer, IEEE Trans. Appl. Supercond. **9**, 683 (1999).
[14] A. Andreone *et al.,* J. Appl. Phys. **82**, 1736 (1997).
[15] M. R. Trunin, J. Supercond. **11**, 381 (1998).
[16] A. T. Fiory *et al.,* Phys. Rev. Lett. **65**, 3441 (1990).
[17] D. J. Scalapino, Phys. Rep. **250**, 329 (1995).
[18] S. Kasiviswanathan and G. Rangarajan, Physica (Amsterdam) **200C**, 301 (1992).
[19] I. Maggio-Aprile *et al.,* Phys. Rev. Lett. **75**, 2754 (1995).
[20] M. H. Hettler and P. J. Hirschfeld, Phys. Rev. B **59**, 9606 (1999).
[21] E. W. Hudson *et al.,* Science **285**, 88 (1999).
[22] S. H. Pan *et al.,* Nature (London) **403**, 746 (1999).
[23] M. Franz, C. Kallin, A. J. Berlinsky, and M. I. Salkola, Phys. Rev. B **56**, 7882 (1997).
[24] E. Brecht *et al.,* Phys. Rev. B **59**, 3870 (1999).
[25] S. D. Adrian, M. E. Reeves, S. A. Wolf, and V. Z. Kresin, Phys. Rev. B **51**, 6800 (1995).