Probing the Order Parameter and the c-Axis Coupling of High-T_c Cuprates by Penetration Depth Measurements

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We have measured the low-temperature (T) dependence of the anisotropic penetration depth $\lambda(T)$ of magnetically aligned powders of $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n = 1$ and 3) down to 1.2 K. For both members the T dependence of the in-plane penetration depth $\lambda_{ab}(T)$ is strongly linear, whereas the out-of-plane component $\lambda_c(T)$, for $n = 1$ and 3, varies as T^5 and T^2, respectively. For comparison, we also report $\lambda_c(T)$ data for grain-aligned $YBa_2Cu_3O_{7-\delta}$ ($\delta = 0.0$ and 0.43) which vary as T and T^2, respectively. The results are discussed in terms of $d_{x^2-y^2}$-wave symmetry of the order parameter in cuprates. [S0031-9007(97)04087-8]

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The high-T_c superconductors (HTSC) containing CuO_2 planes are layered materials with anisotropic physical properties. Evidence is now growing that the energy gap in HTSC has "d-wave" symmetry with nodes in the order parameter in certain directions in **k** space [1,2]. Detailed knowledge of the behavior of the superfluid density and the symmetry of the energy gap are important for understanding various properties of the superconducting state including the pairing mechanism in these materials. One of the best probes of the superfluid density and the energy gap morphology at the Fermi surface is the penetration depth (λ). Many early studies of the temperature (T) dependence of λ on single crystals, films, and aligned powders of yttrium barium copper oxide (YBCO) gave evidence for non-s-wave pairing, usually in the form of a T^2 behavior for $\lambda(T)$ at low temperatures rather than exponential dependence expected for s wave. However, this was not widely accepted until the work of Hardy *et al.* [3] on high quality YBCO crystals which showed a linear temperature dependence in the in-plane penetration depth from 1.3 to 20 K. We have found that in some cases, structural and chemical defects near the surface of YBCO crystallites have significant effects on λ at low temperatures and that heat treating the crystallites after grinding in air, or grinding under argon, helped obtain higher quality surfaces and thus intrinsic information from aligned powder composites [4]. Most studies of λ have concentrated on YBCO [1,3,5] and Zn doped YBCO [5,6]. Relatively few studies have examined other materials such as $La_{2-x}Sr_xCuO_4$ [7], $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ [8], $Bi_2Sr_2CaCu_2O_8$ [9–12], and $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) [13].

The Hg-based cuprates are very interesting because of their high T_c's and the fact that there can be one or more CuO_2 planes per unit cell. In this Letter we report the values and temperature dependences, down to 1.2 K, of the in-plane (λ_{ab}) and out-of-plane (λ_c) penetration depths for c-axis grain aligned tetragonal [14] $HgBa_2CuO_{4+\delta}$ (Hg-1201). We find characteristic T dependences, T^1 for λ_{ab} and T^5 for λ_c, which are completely consistent with $d_{x^2-y^2}$ symmetry of the order parameter. For comparison, we report new low-T anisotropic penetration depth data for tetragonal [15] Hg-1223 and $\lambda_c(T)$ of orthorhombic [16] $YBa_2Cu_3O_7$ ($YBCO_7$) and $YBa_2Cu_3O_{6.57}$($YBCO_{6.57}$).

The Hg-1201 and Hg-1223 samples were prepared by a simple single-step technique, described in detail elsewhere [17,18]. Initial characterization by x-ray diffraction showed the phase purity of Hg-1201 to be at least 95% and that of Hg-1223 to be at least 90% with no other superconducting phases present. The Hg-1201 and Hg-1223 samples had $T_c = 93$ and 134.5 K, respectively (T_c represents the temperature where the onset of superconductivity occurs in the ac susceptibility data for a measuring field $H_{ac} = 1$ G rms and frequency $f = 333$ Hz). Bulk pieces were ground in argon atmosphere using a glove box to minimize surface degradation [4]. The collected powders were sieved, kept in an argon atmosphere for 30 min, and then magnetically aligned as described earlier [13]. Part of the collected powders was used to determine the grain size distribution by analyzing scanning electron microscopy (SEM) photographs. The average grain diameters corresponding to the 50% cumulative volume point were 4 and 10 μm for the Hg-1201 and Hg-1223 samples, respectively. Quantitative and qualitative checks of the sample alignment were made by x-ray diffraction using a new high resolution technique [19]. The fraction of the unoriented powder in both Hg-1201 and Hg-1223 was estimated to be $\sim$5%. In both cases rocking curve analysis of the aligned samples gave a full width at half maximum of $\sim$1.6°.

YBCO was prepared in the standard way by solid state reaction from CuO_2, Y_2O_3, and $BaCO_3$. The bulk

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product was ground in air, sedimented in acetone (to obtain a narrow grain size distribution), and finally heat treated at 845 °C in flowing oxygen for 12 h to repair the damaged surface of the grains [4]. The fully oxygenated, $\delta = 0.0$ ($YBCO_7, T_c = 92$ K) samples were prepared by annealing in pure oxygen atmosphere at 380 °C for 24 h and then slowly cooled to room temperature. The oxygen deficient, $\delta = 0.43$ ($YBCO_{6.57}, T_c = 55$ K) samples were prepared by annealing in 0.2% O_2/N_2 atmosphere at 550 °C for 12 h and then quenching into liquid nitrogen. The annealed powders were then magnetically aligned, as described in earlier publications [4,6,19].

Low field susceptibility, χ, measurements were performed using both commercial equipment and a home built susceptometer down to 1.2 K. For the latter, the Earth's field was screened out using a mu-metal shield. Measurements were performed for $H_{ac} = 0.3-3$ G rms at $f = 333$ Hz. For all data presented here $H_{ac} = 1$ G rms at $f = 333$ Hz. As in previous work [6] the separation of the grains and the absence of weak links were confirmed by checking the linearity of the signal at 4.2 K for H_{ac} from 0.3 to 3 G rms and f from 33 to 333 Hz. Taking the grains of the composites to be approximately spherical, as indicated by SEM, the data were analyzed using London's model [20], and the variation of λ with temperature was obtained for both orientations [5,6,13].

The values of $\lambda_{ab}(0)$ and $\lambda_c(0)$ obtained for Hg-1201 are 1710 ± 250 and $13\,600 \pm 1600$ Å, respectively. Figures 1(a) and 1(b) show characteristic plots of the T dependence of the ac susceptibility (plotted as fractional diamagnetism) for the ab plane and the c axis Hg-1201 data, respectively. The temperature dependences of λ_{ab} and λ_c are shown in the respective insets. The linear term in $\lambda_{ab}(T)$ seen in Fig. 1(a), characteristic for d-wave superconductivity [1], has a slope of 6.5 Å/K. In contrast, the data for $\lambda_c(T)$, Fig. 1(b), are much flatter at low T. The $\lambda_c(T)$ data fit the expression suggested by Xiang and Wheatley for tetragonal HTSC with relatively low anisotropy [Eq. 3 in Ref. [21]]: $\lambda_c(T) \sim \lambda_c(0)[1 + \alpha(T/T_c)^5]$, with $\alpha \sim 3$. The parameter α depends strongly on the ratio of the superconducting transition temperature and the zero temperature energy gap, namely $\alpha = 255(T_c/\Delta_0)^5$. The experimental value of α yields $(\Delta_0/T_c) \sim 2.37$. This is very close to the weak coupling BCS value $(\Delta_0/T_c) = 2.14$ for a d-wave superconductor. We also tried to fit the data using an exponential or other power-law functions of T/T_c but found that these were less satisfactory than the above expression for $\lambda_c(T)$. Furthermore, it is physically unlikely for λ_{ab} to vary linearly with T, as observed experimentally, while the c-axis penetration depth shows an exponential T dependence.

We believe that the weaker T dependence of λ_c compared to λ_{ab} is a consequence of the unusual c-axis electronic structure of high-T_c oxides. In clean tetragonal samples, the c-axis hopping of holes mainly occurs through large radius Cu 4s orbitals [22]. It has been

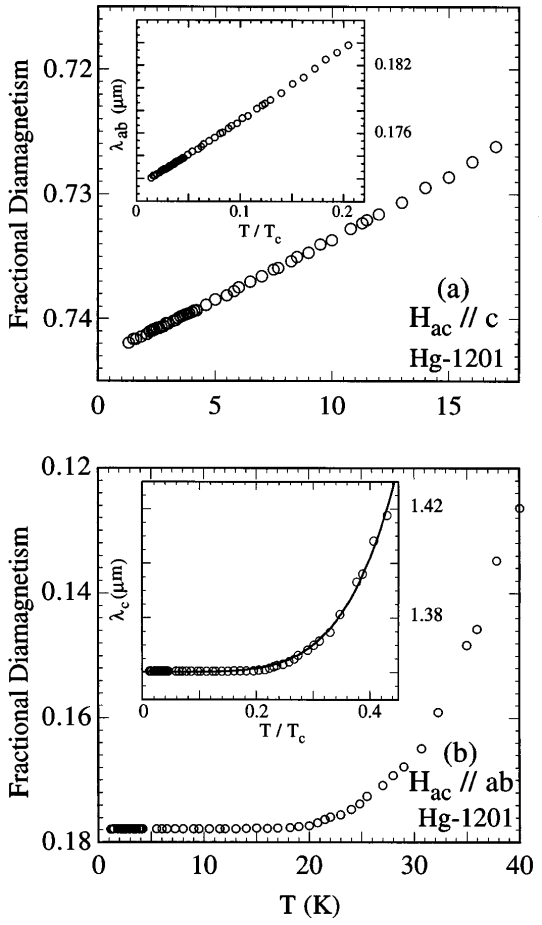

FIG. 1. The low-temperature dependence of the fractional diamagnetism for a grain-aligned sample of $HgBa_2CuO_{4+\delta}$ for (a) $H_{ac} \parallel c$ and (b) $H_{ac} \parallel ab$. The insets in (a) and (b) show the temperature dependences of λ_{ab} and λ_c, respectively, of the same sample. Also shown, by the solid line in the inset (b), is the fit to the expression $\lambda_c(T) \sim \lambda_c(0)[1 + \alpha(T/T_c)^5]$, with $\alpha \sim 3$.

shown [21] that in this case the interlayer hopping constant of holes (t_c) is a function of the in-plane momentum $k_\parallel = (k_x k_y)$, and t_c is proportional to $(\cos k_x - \cos k_y)^2$. This unusual $k_\parallel$ dependence of t_c originates from the wave function overlap between the bonding O 2p orbital and Cu 4s orbital that is proportional to $(\cos k_x - \cos k_y)$. Therefore, t_c vanishes along the lines, $k_x = \pm k_y$, where the $d_{x^2\text{-}y^2}$ wave gap nodes develop and will thus have a strong impact on the low-T behavior of λ_c if the superconducting pairing has $d_{x^2\text{-}y^2}$ symmetry. This leads to the T^5 dependence described above. This $k_\parallel$ dependence of t_c is clearly apparent in band structure calculations for all tetragonal cuprates, including those with more than one CuO_2 layer per unit cell [23]. However, it is strongly violated for YBCO because of the presence of the Cu-O chain bands [22,24].

The agreement between the theoretical analysis and the experimental result for the T^5 behavior of λ_c implies that the gap nodes do in fact lie along the directions where t_c vanishes, i.e., $k_x = \pm k_y$, since otherwise this special $k_\parallel$ dependence of t_c would have little effect and the T

dependences of λ_{ab} and λ_c should be similar. Thus our results indicate not only the existence of the gap nodes but also the positions of the nodes on the Fermi surface. They also show, indirectly, that the single-band picture [25] is valid for high-T_c materials since they imply that only the strongly hybridized Cu $d_{x^2-y^2}$ and O $p_{x,y}$ orbitals contribute to λ_c. [If other bands contributed, λ_c would deviate noticeably from T^5 at low T because simple symmetry arguments show that the effective c-axis hopping constants for these bands would no longer be proportional to $(\cos k_x - \cos k_y)^2$.]

The T^5 term in λ_c is small. It can be observed only in clean tetragonal samples of relatively low anisotropy where the coherent hopping of holes is the main contribution to the c-axis superfluid response. The contribution to λ_c from disorder effects is expected to vary as T^2 at low T [21,26]. If disorder effects are important in the c-axis superfluid response, then the T^5 behavior of λ_c will be completely masked by this T^2 term. We believe this is the reason why the T^5 behavior of λ_c has not been observed in Hg-1223, as discussed below. The effect of impurities was recently seen in penetration depth results of Zn-doped YBCO [6]. It was also found that Zn substitution slightly increases the c-axis coupling which is also consistent with the idea that the c-axis coupling in the cuprates is influenced by the in-plane Cu 4s orbitals.

We have performed similar measurements on Hg-1223 samples for which the values of $\lambda_{ab}(0)$ and $\lambda_c(0)$ are 1770 ± 300 and $61\,000 \pm 5000$ Å, respectively. Figures 2(a) and 2(b) show the T dependence of the fractional diamagnetism for the ab-plane and the c-axis data, respectively. The T dependences of λ_{ab} and λ_c are again shown in the respective insets. The linear term in $\lambda_{ab}(T)$ has a slope of 4.2 Å/K. In a previous study on Hg-1223 [13], at $T < 20$ K we observed a small deviation from linearity near 4.2 K which is absent in measurements on the same sample to lower temperatures with the new apparatus. The data for $\lambda_c(T)$ are much flatter and a T^2 term develops at low T. As mentioned above, the T^2 behavior of $\lambda_c(T)$ in Hg-1223 at low temperatures [Fig. 2(b) (inset)] could be due to its high anisotropy. In highly anisotropic materials one expects a significant decrease in the coherent tunneling component of the superfluid along the c direction [21]. This takes place without affecting $\lambda_{ab}(T)$ because propagation in the ab plane remains coherent. However, the new $\lambda_c(T)$ data for Hg-1223 agree with those published earlier for $T > 4.2$ K [13] which could be fitted reasonably well to a Josephson tunneling model.

Figure 3 shows typical data for high-quality grain aligned $YBCO_7$ and $YBCO_{6.57}$. For the more isotropic $YBCO_7$ [6] we observe a linear T dependence in λ_c at low temperatures, but the relative change is about a factor of 2 smaller than in $[\lambda_{ab}(T)/\lambda_{ab}(0)]$ (taken from Ref. [6] and shown as an inset in Fig. 3). The weaker T dependence of λ_c may arise from the interband hopping between the planar and chain CuO bands [24,27]. In

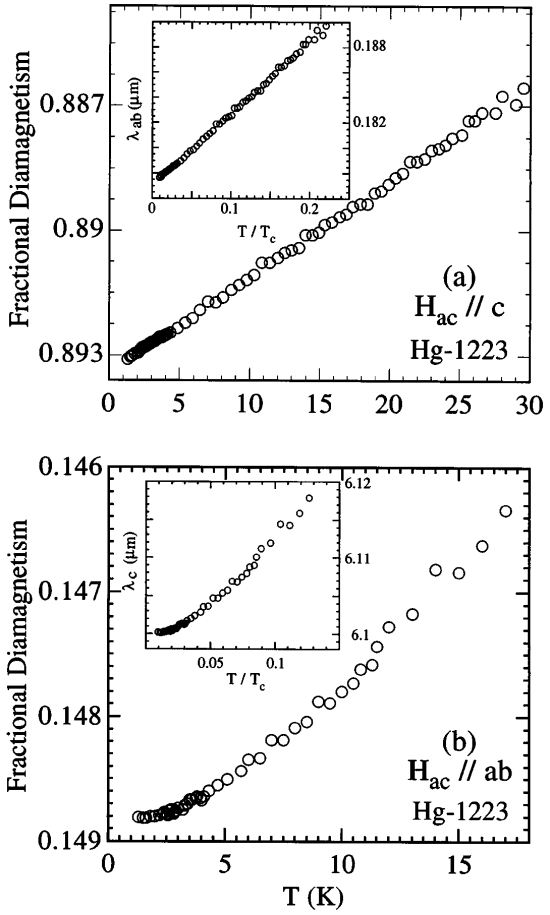

FIG. 2. The low-temperature dependence of the fractional diamagnetism for a grain-aligned sample of $HgBa_2Ca_2Cu_3O_{8+\delta}$ for (a) $H_{ac} \parallel c$ and (b) $H_{ac} \parallel ab$. The insets in (a) and (b) show the temperature dependence of λ_{ab} and λ_c of the same sample.

$YBCO_7$ or other chain-related materials, t_c is finite around the d-wave gap nodes [i.e., t_c is no longer proportional to $(\cos k_x - \cos k_y)^2$] due to the hybridization between the one-dimensional CuO chains and the CuO_2 planes. Thus the above discussion of the T^5 law is not applicable to $YBCO_7$. By removing oxygen from $YBCO_7$ one can significantly reduce the chain contribution. $YBCO_{6.57}$ has an anisotropy ratio $\gamma = [\lambda_c(0)/\lambda_{ab}(0)] \sim 25$ [28]. As in Hg-1201, Hg-1223, and $YBCO_7$, $\lambda_{ab}(T)$ in $YBCO_{6.57}$ is linear at low temperatures but with a slope 20 Å/K. The systematic variation of λ_{ab} with oxygen content in YBCO will be discussed separately [28]. Here we focus on $\lambda_c(T)$ of $YBCO_{6.57}$, Fig. 3, which at low T obeys a T^2 behavior similar to Hg-1223, which is of similar anisotropy.

Finally, SQUID measurements of the Hg-1201 and Hg-1223 powders used to make the aligned composites yielded normal-state Curie terms $C = 52 \times 10^{-3}/T$ and $75 \times 10^{-3}/T$ (emu/mole), respectively. In principle, such Curie terms could affect our low T ac susceptibility data, especially those for $\lambda_c(T)$. However, because the measurements have been made down to 1.2 K, for both $H_{ac} \parallel c$ and $H_{ac} \parallel ab$, it is clear that a Curie Weiss

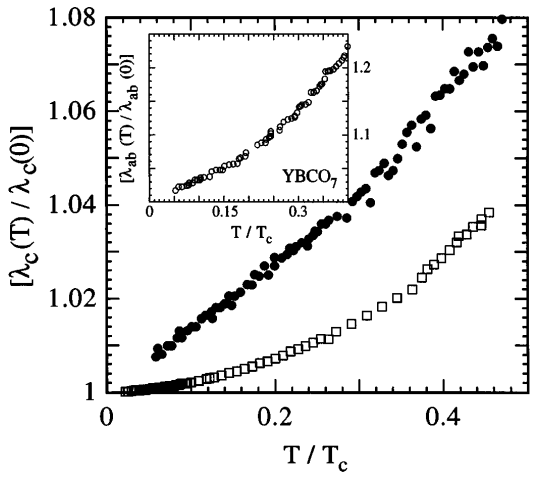

FIG. 3. The low-temperature dependence of $[\lambda_c(T)/\lambda_c(0)]$ for grain-aligned $YBa_2Cu_3O_7$ (closed circles) and $YBa_2Cu_3O_{6.57}$ (open squares). $\lambda_c(0)$ for these samples are 12 600 and 71 700 Å, respectively. For comparison with $[\lambda_c(T)/\lambda_c(0)]$ the inset shows recent $[\lambda_{ab}(T)/\lambda_{ab}(0)]$ data of $YBa_2Cu_3O_7$ [6].

law $\chi = [C/(T + \Theta)]$ with $\Theta = 0$ does not describe the low T data for $H_{ac} \parallel ab$. If $\Theta \geq 10$ then the effects of these Curie terms are completely negligible. The worst case scenario is $\Theta = 2-3$, which gives small correction to $\lambda_c(T)$, of the size of the symbols used in Figs. 1(b) and 2(b), while $\lambda_{ab}(T)$ is unchanged.

In conclusion, we have investigated the low-temperature dependence of the anisotropic magnetic penetration depth of magnetically aligned powders of crystalline $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n = 1$ and 3) down to 1.2 K. The values of $\lambda_{ab}(0)$ and $\lambda_c(0)$ for $n = 1$ and 3 were estimated to be 1710 ± 250 and 13 600 ± 1600 Å and 1770 ± 300 and 61 000 ± 5000 Å, respectively. The T dependence of λ is not affected by this level of uncertainty in $\lambda(0)$. A linear $\lambda_{ab}(T)$ was observed at low temperature for both Hg-1201 and Hg-1223 with slopes 6.5 and 4.2 Å/K, respectively. On the other hand, the out-of-plane component $\lambda_c(T)$ varied as T^5 and T^2 for Hg-1201 and Hg-1223, respectively. Furthermore, $\lambda_c(T)$ for $YBCO_7$ varies as T whereas a T^2 power law was observed for $YBCO_{6.57}$. All the present results are consistent with the picture of $d_{x^2-y^2}$-wave superconductivity in low and high anisotropic cuprates with and without chains, provided one accepts that disorder effects are indeed important for $\lambda_c(T)$ of more highly anisotropic compounds.

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