Anisotropic magnetic penetration depth of grain-aligned $HgBa_2Ca_2Cu_3O_{8+\delta}$

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The temperature (T) dependence of the anisotropic magnetic penetration depth $\lambda(T)$ of magnetically aligned powders of crystalline $HgBa_2Ca_2Cu_3O_{8+\delta}$ is reported. Measurements were performed in the Meissner state using the ac-susceptibility technique. The temperature dependences of the in-plane, $\lambda_{ab}(T)$, and out-of-plane, $\lambda_c(T)$, penetration depths are markedly different. This is believed to arise from the large anisotropy ratio $\gamma=[\lambda_c(0)/\lambda_{ab}(0)]\simeq30$. The behavior of $\lambda_{ab}(T)$ is indicative of d-wave superconductivity while $\lambda_c(T)$ is similar to the behavior expected for a superconductor with intrinsic Josephson coupling between the CuO_2 planes. Similar measurements were performed on $Ba_{0.6}K_{0.4}BiO_3$ powders for comparison.

There is mounting evidence for d-wave superconductivity[1] and intrinsic Josephson coupling[2,3] in high-T_c superconductors. The measurement of the magnetic penetration depth λ is a useful initial probe[4–9] of the energy-gap morphology at the Fermi surface and of the superfluid electrodynamics. Most studies have concentrated on $YBa_2Cu_3O_{7-\delta}$ (YBCO),[4,7,8] and only a few[5,6,9] have examined highly anisotropic materials such as $Bi_2Sr_2CaCu_2O_8$. Various experimental methods have been used to determine the value of $\lambda(0)$ and its temperature dependence $\lambda(T)$ for high-T_c copper oxides. A direct method is to measure the diamagnetism of powder composites of known grain-size distribution using the conventional ac-susceptibility technique.[8]

The $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) compound has the highest known critical temperature.[10–13] On the basis of its crystal structure[14] the transport properties are expected to be highly anisotropic. In this paper, we report the values and temperature dependences of the in-plane, λ_{ab}, and out-of-plane, λ_c, magnetic penetration depths for c-axis aligned Hg-1223 powders obtained using the ac-susceptibility technique. For comparison, the penetration depth of the cubic oxide superconductor $Ba_{0.6}K_{0.4}BiO_3$ was also investigated using the same technique.

Sample preparation was carried out in a simple single-step method, and is reported in detail elsewhere.[15] In brief, appropriate stoichiometric mixtures of binary oxides (HgO, BaO, CaO, and CuO) were ground and pelletized. These mixtures were sealed in quartz tubes under ambient conditions. Following the reports of Lee *et al.*[16] space filling was utilized in the quartz tubes to give optimum phase purity. Sealed tubes were encased in steel bombs as a safety precaution, and fired in a muffle furnace at 750 °C, for 10 h. As prepared samples had a $T_c\sim117$ K (hereafter T_c represents the temperature where the onset of superconductivity occurs in the ac-susceptibility data for a measuring field $H_{ac}=3$ G rms and frequency $f=333$ Hz). The material was then heated at 300 °C in flowing oxygen to raise the T_c to 134.5 K. The $Ba_{0.6}K_{0.4}BiO_3$ (BKBO) powders were produced by grinding large single crystals, whose synthesis has been described elsewhere.[17]

To magnetically align the Hg-1223 samples, the oxygenated powder was first lightly ground by hand to remove lumps and passed through a 20 μm sieve. This was carried out in an argon atmosphere using a glove box, in order to minimize surface degradation which can influence the low-temperature behavior of the magnetization.[18] The powder was kept under argon atmosphere for 30 min before being mixed with a 5 min fast curing epoxy (Double Bubble; Perma Bond Europe) with a weight ratio Hg-1223:epoxy =1:5, and placed in a static field of 7 T at room temperature for 5 min. Part of the collected powder was used to determine the grain-size distribution by analyzing scanning electron microscopy (SEM) photographs. The grain-size distribution of the powder is shown in the inset of Fig. 1(a). ac susceptibility, χ, measurements were performed using a commercial Lake Shore ac susceptometer (model 7000) with the ac field applied either in the ab-plane or along the c-axis. Measurements were performed for $H_{ac}=1$, 2, and 3 G rms at $f=333$ Hz but for all data presented here $H_{ac}=3$ G rms and $f=333$ Hz. The temperature was swept slowly at 1 K/min with the sample positioned in the bottom coil throughout. The separation of the grains and the absence of weak links were confirmed by checking the linearity of the pick-up voltage at 4.2 K for H_{ac} from 1 to 10 G rms and f from 16 to 667 Hz. The background signal was measured in a separate run and subtracted from the data at each temperature. The apparatus was calibrated using a Pb sphere (99.99% pure) at a low enough frequency to eliminate eddy current effects above T_c.

The sample alignment was checked by x-ray diffraction. The fraction of the unoriented powder was estimated to be

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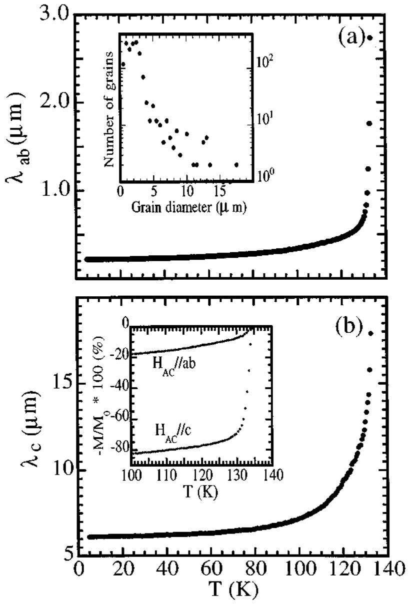

FIG. 1. The temperature dependence of the penetration depth for a grain-aligned sample of $HgBa_2Ca_2Cu_3O_{8+\delta}$ for (a) $H_{ac}//c,\lambda_{ab}$ and (b) $H_{ac}//ab,\lambda_c$. (a) (inset): grain-size distribution of the Hg-1223 powder. (b) (inset): $-M/M_0$, in percent, of the same sample as a function of temperature close to T_c.

5% by comparing the measured intensity of the (110) and (006) lines of an aligned sample with these of an unaligned sample, set in epoxy under the same conditions but in a zero static field. Rocking curve analysis of the (006) and (007) reflections of an aligned sample revealed full width at half maximum of 1.7° each.

Initial x-ray measurements of the oxygenated powder indicated a phase purity greater than 90%. Superconducting quantum interference device measurements of the same powder two months later yielded a Curie term of $75\times10^{-3}/T$ (emu/mol) from fits between 250 and 300 K. This corresponds to 6.7% of the Cu atoms in Hg-1223 having a spin $S=\frac{1}{2}$, and gives an upper limit to the amount of insulating impurity phases. This Curie term is negligible in comparison with the superconducting diamagnetism.

The maximum possible diamagnetism M_0 was calculated from the mass of Hg-1223 in the composite sample, its x-ray density and assuming the individual particles were spherical. The inset of Fig. 1(b) shows the temperature dependence of $-M/M_0$, in percent, near T_c for a c-axis aligned Hg-1223 sample. The onset of superconductivity is observed to be at 134.5 K and the transition width (10–90%) is 2 K. The difference in the diamagnetic susceptibilities for $H_{ac}//c$ at 4.2 K, $\chi_c(4.2)$, and $H_{ac}//ab$ at 4.2 K, $\chi_{ab}(4.2)$, $[\chi_c(4.2)/\chi_{ab}(4.2)]\approx4$, reflects the highly anisotropic nature of Hg-1223. Taking the Hg-1223 grains in the composite to be approximately spherical, as indicated by SEM, the data were analyzed on the basis of the model suggested by Shoenberg,[19] and the variation of λ with temperature for both orientations[8] was obtained [Figs. 1(a) and 1(b)]. To calculate $\lambda(T)$ from $\chi(T)$ one needs to know the form of the grain-size distribution. Uncertainties in the grain-size distribution did not affect significantly our penetration depth values. For example, measuring only half the number of grains gave a

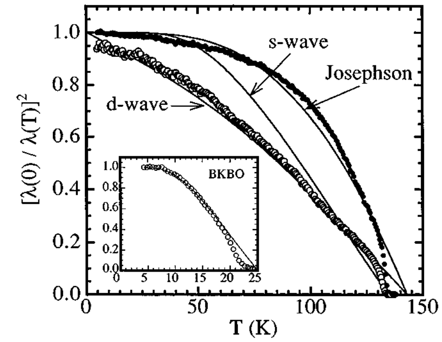

FIG. 2. Plots of $[\lambda_{ab}(0)/\lambda_{ab}(T)]^2$ (open circles) and $[\lambda_c(0)/\lambda_c(T)]^2$ (closed circles) as functions of T for Hg-1223. Also shown, as solid lines, are the theoretical predictions for the normalized superfluid density from the weak-coupling BCS theory for s-wave,[22] the weak-coupling BCS theory for d-wave,[23] and the normalized superfluid density as calculated for a Josephson coupled d-wave superconductor.[24] Inset: similar plot for BKBO: data (open circles) and s-wave weak-coupling BCS fit (solid line).

5% change in the λ(0) values. Shifting the grain-size distribution by ±1 μm changed λ(0) by less than 3%. In both the aforementioned cases the temperature dependence of λ remained unchanged. We note that when $\lambda_c \gg \lambda_{ab}$ one can safely take $\lambda_{eff}\sim0.7\lambda_c$ for grains of arbitrary sizes in order to estimate λ_c,[8] where λ_{eff} is the effective value of the penetration depth derived from the measured susceptibility for $H_{ac}//ab$.

The values of $\lambda_{ab}(0)$ and $\lambda_c(0)$ are 2100 and 61 000 Å, respectively. Our estimates of $\lambda_{ab}(0)$ are very sensitive to the phase purity and alignment. If these were both 96 wt. % rather than 100 wt. % the estimated value of $\lambda_{ab}(0)$ would be as small as 1500 Å but its temperature dependence would not change. However, the value $\lambda_{ab}(0)=2100$ Å is in good agreement with that reported earlier for grain aligned Hg-1223 from high-field magnetization studies.[20] Further, the estimated anisotropy ratio $\gamma=[\lambda_c(0)/\lambda_{ab}(0)]\simeq30$ is close to that expected from resistivity results from Hg-1223 single crystals at 300 K, $\rho_c/\rho_{ab}\sim1000$.[21]

Figure 2 shows plots of the temperature dependence of the normalized superfluid density $[\lambda(0)/\lambda(T)]^2$ for the ab-plane and the c-axis data, respectively. The data are compared with weak-coupling theory for an s-wave[22] and a d-wave superconductor,[23] with a maximum gap $\Delta(0)=2.14k_BT_c$.[23] It can be seen that the d-wave curve fits the data for $\lambda_{ab}(T)$ reasonably well. There is a small deviation at low temperatures which perhaps could arise because there is more than one type of CuO_2 planes in the unit cell or because of disorder. In other words, the behavior of $\lambda(T)$ for d-wave superconductors on these closely coupled inequivalent CuO_2 planes might conceivably be different from that of a single plane. Since $\delta\cong0.4$ for $T_c\sim135$ K,[14] the excess oxygen atoms do perhaps introduce some disorder. In contrast the data for $\lambda_c(T)$ are much flatter at low T and fit the expression suggested for Josephson coupling[24] $[\lambda(0)/\lambda(T)]^2=[\Delta(T)/\Delta(0)]\tanh[\Delta(T)/2k_BT]$ reasonably well, where $\Delta(T)$ is the weak-coupling d-wave superconducting gap.[23] A similar behavior has been reported for $\lambda_c(T)$ of $La_{1.85}Sr_{0.15}CuO_4$ single crystals by Shibauchi *et al.*[3] but they used an s-wave $\Delta(T)$. There are some deviations from the Josephson fit for λ_c in Fig. 2 at low T corresponding to a T

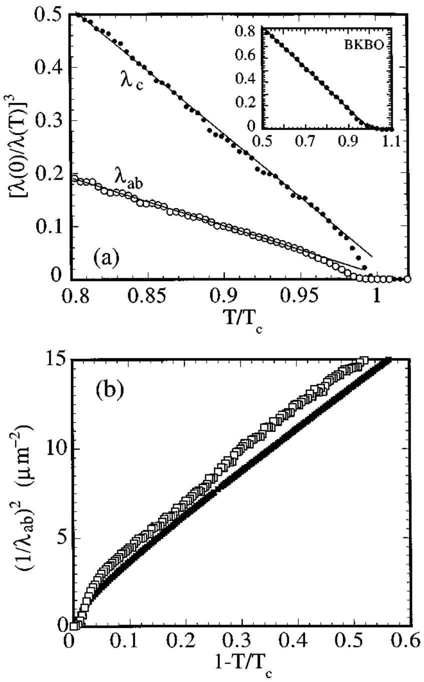

FIG. 3. (a) $\lambda^3(0)/\lambda^3(T)$ versus T/T_c for the ab-plane and c-axis penetration depths of Hg-1223. Solid lines are drawn as a guide to the eye. Inset: $\lambda^3(0)/\lambda^3(T)$ versus T/T_c for the BKBO sample. (b) $1/\lambda^2_{ab}(T)$ versus $1-T/T_c$ (open squares) for Hg-1223 compared to the theory of Baraduc and Buzdin (Ref. 30) (closed squares).

or T^2 power law. This behavior is consistent with the Josephson-coupled layer model of Clem *et al.*,[25] where the Josephson and the quasiparticle contributions to $\lambda_c{}^2$ are simply additive. The significant deviations seen in both λ_{ab} and λ_c near T_c are due to thermodynamic fluctuation effects as discussed below.

For comparison, we have performed similar measurements on BKBO powder samples dispersed in epoxy. $\lambda(0)$ was found to be ≅3500 Å which is in good agreement with other results reported in the literature.[26] The temperature dependence of the normalized superfluid density together with the behavior expected from the weak coupling BCS theory[22] are shown in the inset of Fig. 2 for comparison. The temperature dependence of BKBO resembles that predicted from the weak-coupling BCS theory for s-wave superconductors,[22] except near T_c where the deviation seen may also arise from thermodynamic fluctuations.

There is marked curvature in the $[\lambda_{ab}(0)/\lambda_{ab}(T)]^2$, $[\lambda_c(0)/\lambda_c(T)]^2$ versus T plots (Fig. 2) near T_c. Kamal *et al.*[27] have seen curvature in $[\lambda_{ab}(0)/\lambda_{ab}(T)]^2$ of YBCO crystals near T_c. By replotting their data as $[\lambda_{ab}(0)/\lambda_{ab}(T)]^3$, they obtained linear behavior characteristic of three-dimensional (3D) critical fluctuations. As shown in Fig. 3(a), $[\lambda(0)/\lambda(T)]^3$ plots for our data (λ_{ab} and λ_c) are linear from $T/T_c=0.8$ to ~0.97, but there are significant deviations nearer T_c which were independent of the magnitude of H_{ac}. They may be caused by a dimensional crossover[24] when the c-axis coherence length $\xi_c(T)\geqslant d$, where d is the largest distance between CuO_2 planes. For Hg-1223 estimates of $\xi_c(0)$ range from ~1 to 2 Å.[21,28] Taking an average value $\xi_c(0)=1.5$ Å and $d=10$ Å,[14] we obtain $\xi_c(0)/d=0.15$, a value lying in the range empirically found to represent superconductors exhibiting interlayer Josephson coupling.[29] In the usual case where the coupling between CuO_2 planes within a unit cell is stronger than that between cells, d is the c-axis parameter [15.8 Å for Hg-1223 (Ref. 14)].[30] Taking $\xi_c(0)=1.5$ Å and $d=15.8$ Å the 2D-3D crossover should occur at a reduced temperature $r=[2\xi_c{}^2(0)/d^2]=0.018$, i.e., $T/T_c\cong 0.98$ which corresponds rather well to the region where the curvature sets in Fig. 3(a). So one possible description of the results in Fig. 3(a) is that there are critical fluctuations having an exponent $\frac{1}{3}$ both in the 2D and 3D regions but with somewhat different prefactors. The similar behavior of λ_{ab} and λ_c supports this viewpoint but as far as we know there are no theoretical predictions of critical exponents in the 2D region. The inset to Fig. 3(a) shows that BKBO does obey the expected law for 3D critical fluctuations better than the mean-field law (inset in Fig. 2).

A second possibility for Hg-1223 is that the fluctuations are weaker and our data can be described by the theory of Baraduc and Buzdin (BB) for Gaussian fluctuations.[30] As shown in Fig. 3(b) a reasonably good fit can be obtained for the λ_{ab} data using the BB 2D formula, taking $r=0.018$ (as before) and the reduced Ginzburg temperature $T_G=0.089$. (In making these fits we have multiplied $\lambda_{ab}{}^{-2}(0)$ by 1.3, as expected from calculations for a weak-coupling d-wave superconductor near T_c.)[23] BB predict that in the 2D region the effect of fluctuations in $\lambda_c{}^{-2}$ is equivalent to a shift of $[0.5T_c(T_G r)^{1/2}]$ on the temperature axis. For the above values of T_G and r this shift is 3 K and is reasonably consistent with the c-axis data in Fig. 2.

In conclusion, we have investigated the temperature dependence of the anisotropic penetration depth of high-quality grain-aligned Hg-1223. The values of $\lambda_{ab}(0)$ and $\lambda_c(0)$ were found to be 2100 and 61 000 Å, respectively. The ansiotropy ratio $\gamma=[\lambda_c(0)/\lambda_{ab}(0)]\cong 30$ is very high, reflecting the 2D nature of Hg-1223. A kink was observed in $1/\lambda^2(T)$ near T_c indicating a dimensional crossover. The temperature dependence of $\lambda_{ab}(T)$ is indicative of d-wave superconductivity with $\lambda_c(T)$ approximately following the behavior expected for a superconductor with intrinsic Josephson coupling between the CuO_2 planes. The Josephson nature of Hg-1223 is further supported by the ratio $\xi_c(0)/d=0.15$. Briefly, we conclude that Hg-1223 is a highly anisotropic two-dimensional Josephson type d-wave high-T_c superconductor.

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