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Surface-barrier effects in grain-aligned $HgBa_2CuO_{4+\delta}$, $HgBa_2CaCu_2O_{6+\delta}$, and $HgBa_2Ca_2Cu_3O_{8+\delta}$ compounds

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We have studied the magnetic hysteresis and relaxation processes of grain-aligned $HgBa_2CuO_{4+\delta}$, $HgBa_2CaCu_2O_{6+\delta}$, and $HgBa_2Ca_2Cu_3O_{8+\delta}$ compounds. The penetration field, H_p, the width of the magnetization loops, ΔM, and the irreversibility field, H_{irr}, of each compound were found to exhibit an exponential temperature dependence [i.e., H_p, H_{irr}, $\Delta M \propto \exp(-cT/T_0)$]. This suggests that their magnetic relaxation is controlled by the penetration of two-dimensional pancake vortices over the Bean-Livingston surface barrier.

The discovery of superconductivity in the single layer CuO_2 compound, $HgBa_2CuO_{4+\delta}$ (Hg-1201), with $T_c=94$ K by Putlin *et al.*[1] has generated a great deal of interest in systems with the general composition $HgBa_2Ca_{n-1}Cu_nO_{2(n+1)+\delta}$. The double layer ($n=2$, Hg-1212) (Refs. 2 and 3) and triple layer ($n=3$, Hg-1223) (Refs. 3–5) compounds have also been synthesized with respective T_c's of 128 and 135 K. Each of these compounds contain blocks of CuO_2 layers separated by insulating BaO-Hg-BaO layers with separation distances of approximately 9.5 Å between their superconducting blocks.[1–3,5,6] Welp *et al.*[7,8] have measured the irreversibility lines of randomly oriented, polycrystalline Hg-1201, Hg-1212, and Hg-1223 and found their temperature dependence to lie between that of the Bi- and Tl-based compounds and the more isotropic $YBa_2Cu_3O_{7-\delta}$. Given their respective T_c's, the highest known values for one, two, and three layer compounds as well as their irreversibility line dependencies, the Hg-based HTSC's are of both technological and fundamental interest.

Recent work by Sun *et al.*[9,10] highlighted the importance of surface pinning effects in random, polycrystalline Hg-based samples, but neglected to fully explore their influence on the magnetization processes of these compounds. Bean-Livingston (Ref. 11) surface barriers are known to play an important role in the vortex dynamics of high-T_c superconductors.[12–16] The BL barrier provided by the ideal surface of type-II superconductors impedes the entry or exit of vortices due to two competitive effects: (i) the repulsion of a vortex from the surface due to the interaction of the flux line with the induced shielding current, and (ii) the attraction of an entering flux line toward the surface due to its mirrored image (or "antivortex") line. In the case of weak bulk pinning, surface barriers can control the penetration field[12,14] and could also determine the position of the irreversibility line.[16] Here, we report their effect on the penetration and irreversibility fields as well as on the magnetic relaxation processes of grain-aligned Hg-based compounds. Our work suggests that the vortex dynamics of these compounds are controlled by the penetration of two-dimensional (2D) pancake vortices over the BL surface barrier at moderate temperatures and applied magnetic fields, and provides additional insight into their anisotropic nature.

Due to the current unavailability of Hg-based single crystals, grain-aligned samples were prepared for this study. Nearly 100% phase-pure Hg-1201, Hg-1212, and Hg-1223 compounds were synthesized as described in Refs. 3 and 6. The samples were milled in acetone and characterized by light scattering (Horiba CAPA-700 Particle Size Analyzer, centrifugal sedimentation mode) to determine their average particle size (D_{av}) and size distributions which are reported in Table I. Each powder (15 wt. %) was mixed with epoxy and cured in a 7 T applied field as described in Ref. 17. X-ray diffraction (XRD) (Scintag Model PAD X diffractometer) was used to characterize the degree of c-axis texture in the aligned samples, which was further quantified by θ rocking curve measurements (Rigaku D-Max diffractometer) of their strongest ($00l$) peaks. A summary of these results is also given in Table I, where $P_{00l}=1-\beta, \beta=(I_{h0l}/I_{00l})^{\text{aligned}}/(I_{h0l}/I_{00l})^{\text{unaligned}}$, I_{h0l}, and I_{00l} are their strongest relative intensities, and the full width at half maximum (FWHM) values are determined from θ rocking curve measurements.

TABLE I. Properties of grain-aligned Hg-based samples.

Compound	D_{av} (μm)	$D<10\mu$m (%)	$P_{(00l)}$	($00l$) peak	FWHM
Hg-1201	3.7	100	0.997	(004)	2.3°
Hg-1212	3.1	90	0.991	(005)	3.5°
Hg-1223	7.8	90	0.992	(006)	4.0°

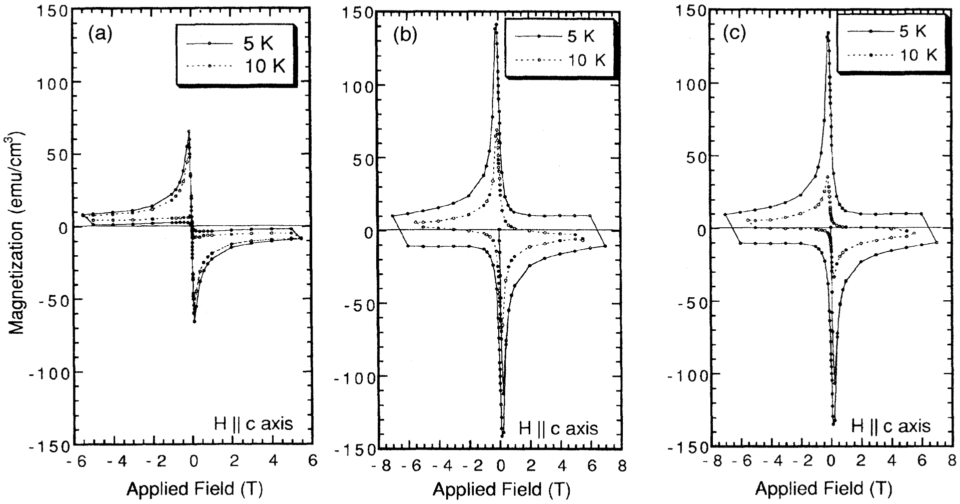

FIG. 1. Magnetic moment hysteresis loops measured at $T=5$ and 10 K for grain-aligned (a) Hg-1201, (b) Hg-1212, and (c) Hg-1223 powders oriented $H\|c$.

Magnetic hysteresis measurements were carried out in a SQUID (Quantum Design Model MPMS magnetometer) in magnetic fields up to ± 7 T between 5 and 100 K. In general, the hysteresis (M-H) loops exhibit an asymmetry with respect to the field ascending and descending branches indicative of surface pinning, where flat curves with values near zero are observed for the field descending branches over a wide range of applied fields. Representative M-H loops for these compounds oriented $H\|c$ are shown in Figs. 1(a)–1(c), respectively. The M-H loops for Hg-1201 display this asymmetry at all temperatures investigated ($T=5-77$ K). In contrast, the M-H loops for Hg-1212 and Hg-1223 are symmetric at 5 K indicative of a higher bulk pinning contribution which dies out with only a modest increase in temperature (refer to data at $T=10$ K where the characteristic asymmetry identified with surface pinning is now observed). The linear Meissner part of each M-H loop is followed by a sharp drop in the magnetization at $H=H_p$ (the penetration field), which also suggests that bulk pinning does not play an important role in these compounds. The temperature dependencies of the penetration field, H_p, the width of the magnetization loops (ΔM), and the irreversibility field ($H_{\rm irr}$) are shown in Figs. 2(a)–2(c) for grain-aligned Hg-1201, Hg-1212, and Hg-1223 compounds, respectively, where $\Delta M=(M^+-M^-)$ at $H=1$ T, and $H_{\rm irr}$ corresponds to the field where $\Delta M=0.25$ emu/cm^3. These semilog plots show that each of these parameters exhibit an exponential temperature dependence. Furthermore, the width of the magnetization loops, ΔM, also exhibits this dependence at higher fields ($H=1-5$ T) with slopes nearly identical to those found at $H=1$ T for each compound [as illustrated in the lower inset of Fig. 2(b) for Hg-1201].

Magnetization decay measurements on the grain-aligned Hg-based samples oriented $H\|c$ were carried out by zero field cooling (ZFC) or field cooling (FC, $H=5$ T) to a given temperature between 5 and 50 K and then applying a magnetic field of 1 T. The time-dependent decay of the magnetization, M, was measured using the SQUID magnetometer. The initial magnetization of each sample was measured 180 s after the application of the 1 T magnetic field. Between each temperature change, the sample temperature was raised well above their respective T_c's to expel any trapped flux remaining in the specimen. Differences in the rate of flux entry $[R_{\rm en}=dM_{\rm en}/d\ \ln(t)]$ and flux exit $[R_{\rm ex}=dM_{\rm ex}/d\ \ln(t)]$ were observed for each compound, which is an additional signature of the surface-barrier effect.[14] These ratios ($R_{\rm en}/R_{\rm ex}$) varied from 3.7 to 1.7 between 5 and 40 K. These values are in good agreement with those reported previously for Hg-1201.[9]

The magnetization decay of each grain-aligned Hg-based compound at $T=5$ K (ZFC) is shown in Figs. 3(a)–3(c), respectively. Significant differences in the time dependence of the magnetization are observed between these respective curves. The Hg-1201 curve exhibits a constant slope over the entire experimental time window. In contrast, the Hg-1212 and Hg-1223 curves exhibit a crossover in their flux creep behavior at intermediate times yielding two different slopes (refer to Fig. 3). Such behavior has been discussed previously by Chikumoto *et al.*[18] and Burlachkov[14] who have identified the short- and long-time regimes with bulk and surface pinning, respectively. The differences in the M-H loops for these compounds at $T=5$ K (refer to Fig. 1) suggest that the curve for Hg-1201 lies solely in the long-time (or surface-barrier) regime, and that the curves for Hg-1212 and Hg-1223 exhibit both bulk pinning (short-time) and surface-barrier (long-time) regimes.

The observed exponential dependencies of $H_p(T)$, $\Delta M(T)$, and $H_{\rm irr}(T)$ (refer to Fig. 2) suggest that the vortex dynamics of these compounds are controlled by the penetration of 2D pancake vortices over the BL surface barrier. Burlachkov *et al.*,[16] building on earlier work by Kopylov *et al.*[12] and Clem,[19] derived the following expressions [Eqs. (1)–(3)] for the penetration of individual pancake vortices over such barriers. The temperature dependence of the penetration field, H_p, is given by

$$H_p \cong H_c \exp(-T/T_0), \tag{1}$$

where the characteristic temperature $T_0=\varepsilon_0 d/\ln(t/t_0)$, $\varepsilon_0(\Phi_0/4\pi\lambda)^2$, λ is the penetration depth ($H\|c$), d is the period of the layered structure, Φ_0 is the magnetic flux quan tum, H_c is the thermodynamic field, and t and t_0 are the experimental and some microscopic time scale, respectively. The temperature dependence of the width of the magnetization loop (ΔM) follows straightforwardly from the intermediate fields, $H \gg H_p$, expression $-M \approx H_p^2/2H$ as

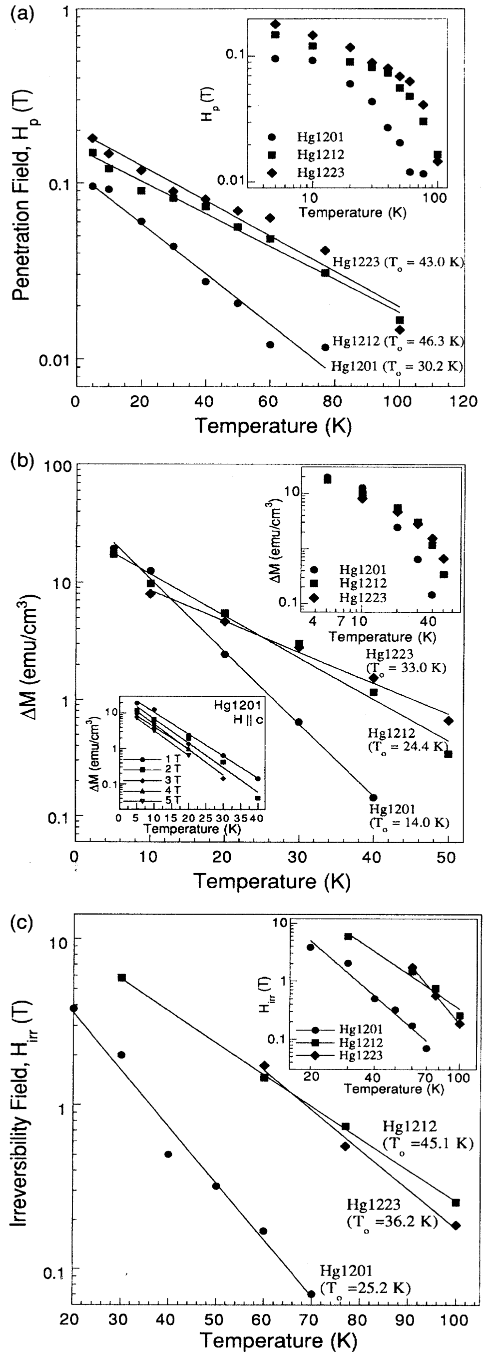

FIG. 2. The temperature dependence of the magnetization loops for each grain-aligned Hg-based compound: (a) the penetration field (H_p), (b) the magnetization width (ΔM), and (c) the irreversibility field ($H_{\rm irr}$). [Note: logarithmic plots of these respective data are given the upper insets of (a)–(c). In addition, a semilog plot of $\Delta M(T)$ at $H_{\rm app}=1-5$ T is given in the lower inset of (b).]

$$\Delta M \propto \exp(-2T/T_0). \tag{2}$$

The temperature dependence of the irreversibility line of highly anisotropic, layered high-T_c superconducting compounds, is given by

$$H_{\rm irr} \cong [H_{c2}/\ln(\eta H_{c2}/H_{\rm irr})]\exp(-2T/T_0), \tag{3}$$

where η is on the order of unity.

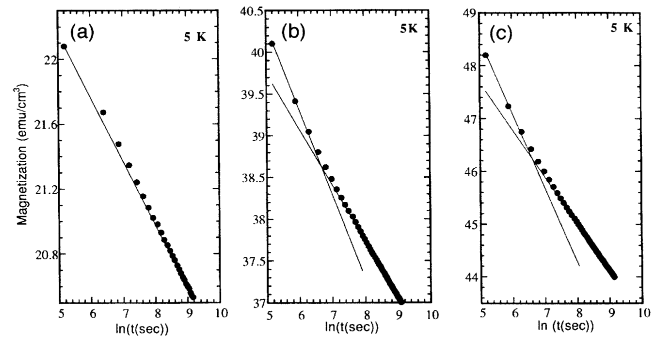

FIG. 3. A plot of the magnetization, M, as a function of $\ln(t)$ for the grain-aligned Hg-based samples at $T=5$ K (ZFC): (a) Hg-1201, (b) Hg-1212, and (c) Hg-1223.

Using this theoretical framework, we have analyzed our experimental results to determine whether the vortex dynamics of these Hg-based compounds are controlled by the penetration of 2D pancake vortices over the BL barrier. The respective characteristic temperatures (T_0) were estimated from the above expression for T_0 to be 26, 35, and 43 K for Hg-1201, Hg-1212, and Hg-1223 using a penetration depth (λ) of 1500 Å, periodic spacings (d) of 9.51, 12.7, and 15.8 Å, respectively, and $\ln(t/t_0)=30$ which is representative of values typically reported in the literature.[16] To compare these values to those obtained experimentally, the $\ln[H_p(T)]$, $\ln[\Delta M(T)]$, and $\ln[H_{\rm irr}(T)]$ curves of the data shown in Figs. 2(a)–2(c) were fitted by a least squares analysis to determine their respective slopes. T_0 values were then calculated using Eqs. (1)–(3), and were found to be 30.2, 46.3, and 43.0 K from the $H_p(T)$ dependence, 14.0, 24.4, and 33.0 K from the $\Delta M(T)$ dependence, and 25.2, 45.1, and 36.2 K from the $H_{\rm irr}(T)$ dependence for Hg-1201, Hg-1212, and Hg-1223, respectively. Only the values determined from the $\Delta M(T)$ dependence scale with the respective periodic spacings (d) as predicted above. The deviations observed in the T_0 values obtained from the $H_p(T)$ and $H_{\rm irr}(T)$ dependencies are believed to arise from errors associated with assessing these values from the M-H data. In contrast, ΔM values are directly obtained from the M-H curves. The consistency of this data is revealed in the inset in Fig. 2(b), where the slopes of the $\Delta M(T)$ curves are nearly identical at applied fields between 1 and 5 T for Hg-1201. As stated previously, similar trends were also observed for Hg-1212 and Hg-1223. Thus although differences exist between each set of experimentally determined T_0 values, the averaged results $[T_{0,\rm avg}=1/3(T_{0,H_p}+T_{0,\Delta M}+T_{0,H_{\rm irr}})]$ agree quite well with those estimated above supporting our interpretation, where $T_{0,\rm avg}$ is 23.1, 38.6, and 37.4 K for Hg-1201, Hg-1212, and Hg-1223, respectively.

Burlachkov *et al.*[16] also derived expressions for the penetration of individual 3D-vortex lines over BL surface barriers. In this case, the temperature dependencies are $H_p \propto T^{-1}$, $\Delta M \propto T^{-2}$ (at a given field, H), and $H_{\rm irr} \propto T^{-2}$. Logarithmic plots of $H_p(T)$, $\Delta M(T)$, and $H_{\rm irr}(T)$ for each compound are shown in the insets of Figs. 2(a)–2(c). The $H_p(T)$ and $\Delta M(T)$ plots both exhibit a downward curvature over the entire temperature range studied, yielding poor agreement with these 3D expressions. In contrast, the logarithmic plot of the $H_{\rm irr}(T)$ data could be fit to this expression; however, the slopes (m) of the log-log curves of these data, found by least squares analysis, deviated substantially from the predicted value ($m=-2$), where $m=-3.1745$, -2.487, and -4.3639 for Hg-1201, Hg-1212, and Hg-1223, respectively. Given the confidence in the $\Delta M(T)$ data as well as the additional features described above, it appears that the 2D interpretation yields the best fit to our experimental results.

From Eq. (1), the $M(H)$ dependence at $H \gg H_p$, and the expression for T_0, it follows that the magnetization, M, decays according to the power law

$$M(t) \cong (t/t_0)^{-2T/\varepsilon_0 d} \approx t^{-\alpha} \tag{4}$$

for creep of individual 2D pancake vortices over the BL surface barrier.[16] Thus, to further verify our interpretation, we also examined the magnetic relaxation behavior of these compounds within this framework. The exponent, α, was determined from log-log plots of the irreversible magnetization versus time at various temperatures. The normalized form of this exponent (α/T) is plotted as a function of temperature in Fig. 4 for each compound. There is a finite temperature range where α/T is nearly constant for the Hg-1212 and Hg-1223 compounds (i.e., $T \approx 10-40$ and 10–50 K, respectively). In these respective temperature ranges, the characteristic temperatures for Hg-1212 and Hg-1223 compounds were found using Eq. (4) to be 42.9 and 49.6 K, respectively, when $\ln(t/t_0)=30$. The value of T_0 for Hg-1201 could not be determined using this analysis due to the observed decrease of α/T with temperature. The reason for this anomalous behavior is presently unclear. The T_0 values obtained for Hg-1212 and Hg-1223, however, are in reasonable agreement with the experimental values obtained from the M-H analyses and those estimated from the T_0 expression given above. This further supports our interpretation that the vortex dynamics of the Hg-based compounds are controlled by this phenomenon.

Assuming that the 2D interpretation is correct for these Hg-based compounds, one can estimate values of their thermodynamic critical fields, H_c, and anisotropy factors, Γ. H_c values were found using Eq. (1) by extrapolating their respective $H_p(T)$ curves to $T=0$ K where $H_c=0.13$, 0.15, and 0.18 T for Hg-1201, Hg-1212, and Hg-1223, respectively. The penetration of *pancake* vortices is observed in the 2D limit, which means that $B > B_{2D} \approx \Phi_0/\Gamma d^2$ where B_{2D} is crossover field from 3D to 2D behavior, $\Gamma = m_2/m$ (where m_z and m are the effective quasiparticle masses for tunneling between and motion in the planes), and d is the periodic spacing of the layered compound.[20] Using this relationship,

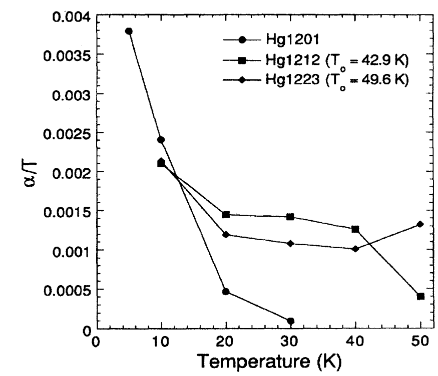

FIG. 4. A normalized plot of α/T as a function of temperature for each grain-aligned Hg-based compound.

we calculated a lower bound for the anisotropy factors of these compounds. As an example, we found Γ to be greater than 2000 for Hg-1201 using a value for B of 1 T. This value ($B=1$ T) was selected based on the magnetic hysteresis and relaxation measurements which indicate that Hg-1201 is dominated by surface-barrier effects at this field over a broad range of temperatures. The calculated anisotropy factor, $\Gamma_{\text{Hg-1201}}$, though intermediate to the values reported for the Bi-Sr-Ca-Cu-O (Ref. 20) and Y-Ba-Cu-O compounds, is much closer to the more anisotropic (Bi- and Tl-based) compounds.

In summary, we present evidence that the vortex dynamics of the layered, Hg-based compounds are controlled by the penetration of 2D pancake vortices over the surface barrier at moderate temperatures and applied magnetic fields in a manner analogous to highly anisotropic HTSC's. The design of technologically relevant devices based on these compounds must account for the presence of strong surface effects and/or rely on additional processing steps (e.g., neutron irradiation[21]) to improve bulk pinning.

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