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Giant T_c shift in $HgBa_2CaCu_2O_{6+\delta}$ and $TlBa_2CaCu_2O_{7-\delta}$ superconductors due to Hg-Tl exchange

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The irreversibility lines of epitaxial thin films of $HgBa_2CaCu_2O_{6+\delta}$ and $TlBa_2CaCu_2O_{7-\delta}$, whether deduced from field-induced magnetoresistive broadening or onset of nonhysteretic magnetization, were found to coincide when plotted against reduced temperature, showing the same exponential-decay temperature behavior for $T/T_c<0.8$ and power-law behavior for $T/T_c>0.8$ (where T_c is zero-field, zero-resistivity critical temperature). These results indicate that replacing Tl with Hg has no noticeable effect on the anisotropy and suggests that T_c is not determined by anisotropy. [S0163-1829(99)04601-9]

The mechanism of high-temperature superconductivity has largely been a mystery since its discovery by Bednorz and Müller[1] more than a decade ago. A particularly pressing question is how high critical temperatures (T_c) could be realized in these materials. One well-known fact is that T_c can change significantly when one or more cation in a high-T_c superconductor (HTS) is replaced by another. A striking example is in comparing $HgBa_2Ca_{n-1}Cu_nO$ and $TlBa_2Ca_{n-1}Cu_nO$ systems, such as Hg-1212 and Tl-1212 phases, where replacing the Tl with Hg has the effect of increasing the T_c by about 30 K. As described in Table I, it is clear that Hg-1212 and Tl-1212 have nearly identical crystalline structures except that in the Hg-O plane, the oxygen site is generally empty while in the Tl-O plane, the oxygen site is generally occupied. This agrees with the fact that the different valences of Tl (+3) (Ref. 13) and Hg (+2) causes a difference in the distribution of oxygen in these two systems.

However, the mechanism by which the distribution of oxygen causes this large T_c difference is not yet completely understood. The oxygen distribution in the Hg-O/Tl-O plane can modify both intraplane and interplane properties of the system. In the former case, this modification would result in a different electronic band structure, yielding a different T_c. In the latter case, changing the interlayer coupling of the Cu-O blocks or the anisotropy could also vary the T_c. It is well known that increasing the number of Cu-O layers in the same homologous system increases the T_c, since the distance (d_i) between Cu-O blocks (so-called active blocks[2]) decreases with the number of Cu-O layers, improving the coupling between active blocks, as expected from the Lawrence-Doniach model of Josephson-coupled Cu-O layers.[3]

To be able to distinguish between these two effects on T_c would provide new insights into the mechanism behind the T_c enhancement effect of replacing Tl with Hg. It is well known[4–12] that the irreversibility line (IL) is determined by the anisotropy of HTS's. In the reduced-temperature scale (T/T_c or $1-T/T_c$), the irreversible field (H_{irr}) for a less anisotropic HTS such as $YBa_2Cu_3O_{7-\delta}$ (YBCO) is much higher than that for a highly anisotropic HTS including $[Bi/Tl]_2[Sr/Ba]_2CaCu_2O$ (Bi/Tl-2212) systems, with the IL's for the intermediate species HgTl-1212 and -1223 falling somewhere inbetween. Measuring and comparing the IL's of Hg-1212 and Tl-1212, which is the core of this study, is therefore a potentially effective probe into the effect of Tl-Hg exchange and the induced T_c variation.

High-quality, *c*-oriented thin film samples, described in Table I, were examined. Details of the fabrication process and physical properties of these thin films are reported elsewhere.[13,14] Each set of films is from the same batch whose quality is proven to be highly reproducible, with zero-resistivity T_c of 120–123 K for Hg-1212 and 90–93 K for Tl-1212. Critical current density J_c (5 K, 0 T) is $2-4\times10^7\,\mathrm{A/cm^2}$ for Hg-1212 and about $10^7\,\mathrm{A/cm^2}$ for Tl-1212, and J_c (77 K, 0 T) is $2-5\times10^6\,\mathrm{A/cm^2}$ for Hg-1212 and about $2\times10^4\,\mathrm{A/cm^2}$ for Tl-1212. The Hg-1212 films show smooth surface morphology by scanning electron microscopy (SEM), and XRD pole figure measurements confirm the film growth to be epitaxial.[13] The Tl-1212 film surface is black and mirrorlike and practically featureless in the SEM, and growth has also been confirmed to be epitaxial. From XRD the *c*-axis lattice parameter of the two different species are, to within small uncertainty, identical. Based on measurements by Huang *et al.*[4] and Kim *et al.*,[10] it can be safely assumed that the d_i are practically identical for these two systems.

Two methods of measuring the IL are used. The more customary method of measuring the onset of reversible magnetization from hysteresis loops was employed. Since this could yield a large noise to signal ratio for small thin film samples, a transport method was also performed by measuring the field-induced broadening of magnetoresistivity. Magnetization was measured with a Quantum Design superconducting quantum interference device (SQUID) magnetometer from 5 K to within 90% of T_c. Isotherms of critical current density $J_c(H)$ were calculated with the Bean model $30\Delta M/d$ where the average radius d of the whole film was used. The field, H_{irr}, corresponding to the onset of reversible

TABLE I. Properties of Hg/Tl-1212 thin film samples used in the study. Note that data for d_i and a are from the references cited, included here for comparison of the two species.

	d_i(Å)	a(Å) [a]	c(Å)	Sample	T_{c0} ($H=0$)	Transport bridge dimensions	Magnetic sample dimensions
Tl-1212	9.51 [b]	3.84	12.66±0.01 Å	No. 1	93 K	1.20 mm×16±1 μm	3×3.5 mm^2
thickness: 0.18 μm				No. 2	92	0.72 mm×31±7 μm	–
Hg-1212	9.57 [c]	3.86	12.67±0.01 Å	No. 1	122	0.40 mm×59±6 μm	–
thickness: 0.26 μm				No. 2	120	–	2×3 mm^2
				No. 3	123	–	2×3 mm^2

[a] Reference 31.
[b] Reference 10.
[c] Reference 4.

magnetization, is defined from these isotherms, using the criterion of $J_c(H_{\mathrm{irr}})=10^3\,\mathrm{A/cm^2}$, to which the H_{irr} values are interpolated. From these values, $H_{\mathrm{irr}}(T)$ is obtained.

For the transport measurement, a standard four-probe configuration was used. Ag pads were rf-magnetron sputtered onto the corners of the film and then annealed for 20 min at 300 °C in flowing oxygen. Pt wire leads were placed on these pads using conductive Ag paint (Ted Pella PELCO 415). The film was then patterned using standard photolithography techniques into microthin lines (Table I). The measurement uncertainties become less significant when resistivity is normalized. Resistivity (ρ) was measured in magnetic fields of 0 to 5 T, in the same SQUID magnetometer, using a current of 1 μA which was oscillated at about 1/3 Hz to eliminate offset signals. For Hg-1212 No. 1, Tl-1212 No. 1, and Tl-1212 No. 2, this gives a current density of about 7, 35, and 18 A/cm^2, respectively, which are well within the range of current density where the resistivity readings do not vary.[15] The temperature for the transport experiment was measured with an Au/Fe(7%)-Chromel thermocouple which has a temperature uncertainty of less than 1%. The normalized resistivity curves $[\rho/\rho_n(T)]$ of two samples are shown in Fig. 1. The zero-ρ critical temperature T_c is defined using a criterion of $\rho/\rho_n=0.001$ and then ascertained by interpolation. These are then defined as the temperatures associated with the field H^* marking the onset of dissipative flux motion.

Both $H_{\mathrm{irr}}(T)$ and $H^*(T)$ are plotted in linear scale in Fig. 2. As expected, there seems to be no clear correlation between IL's of different species and IL's from two different measurements, aside from the consistency in T_c values at around 120 and 90 K as indicated in Table I. However, the IL's for the same species and the same type of measurement coincide; the small spread seen is well within the range of film quality reproducibility. The error bars for $H_{\mathrm{irr}}(T)$ are associated with the uncertainty in interpolation; for $H^*(T)$, they represent the small uncertainty in the temperature measurement. For each species, the $H^*(T)$ curves are larger than $H_{\mathrm{irr}}(T)$ in the phase diagram by about one order of magnitude, as expected from the higher sensitivity (i.e., criterion for definition of IL) of the magnetic measurement. Indeed, if equivalent criteria for the definition of magnetic J_c and transport T_c were used in the two different types of measurement,

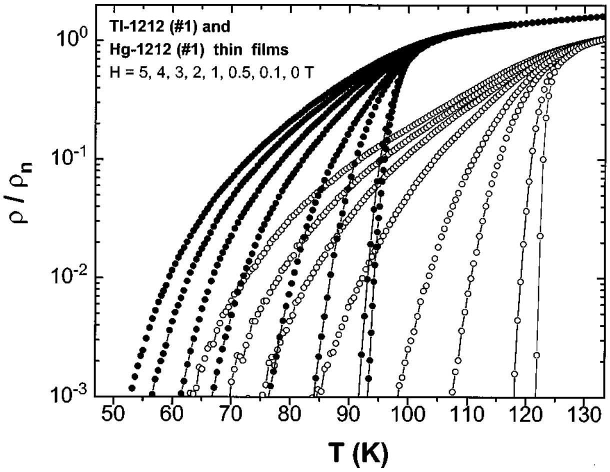

FIG. 1. Semilog plots of resistivity versus temperature for two transport samples at fields from 0 to 5 T.

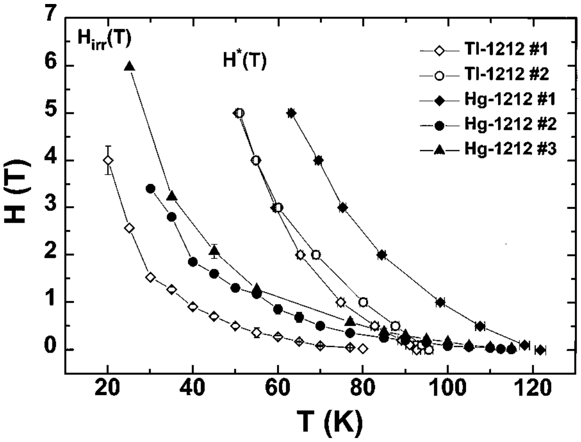

FIG. 2. Linear plot of $H^*(T)$ and $H_{\mathrm{irr}}(T)$ for Tl-1212 samples (open symbols) and Hg-1212 samples (solid symbols).

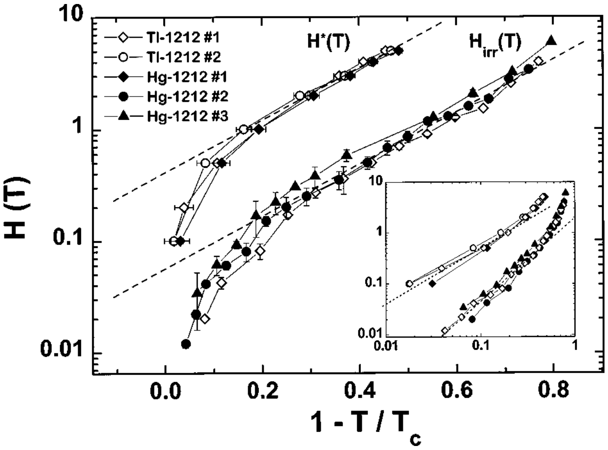

FIG. 3. Semilog plot of $H^*(1\text{-}T/T_c)$ and $H_{\mathrm{irr}}(1\text{-}T/T_c)$. Deviation from apparent linearity occurs between $T/T_c = 0.7$ and 0.8. Average of slopes for $T/T_c < 0.7$ is 5.6 ± 0.3. Inset: log-log plot showing $(1\text{-}T/T_c)^{\alpha}$ behavior for $T/T_c > 0.8$. $\alpha \sim 1.1$ for H^* and ~ 1.6 for H_{irr}.

this could conceivably cause the transport and magnetic IL's of one species, e.g., the curves for Hg-1212 No. 1 and Hg-1212 No. 2, to move together. Also noticeable is the roughness of the magnetically determined $H_{\mathrm{irr}}(T)$, due to the large noise to signal ratio owing to the small mass of the samples measured, compared to the much smoother $H^*(T)$ whose measurement is more well-suited to thin film samples on which it is much easier to make an electric contact.

When these curves are replotted against $(1-T/T_c)$, where T_c is the value for zero field, the IL's of both species *collapse into one* $H_{\mathrm{irr}}(1-T/T_c)$ curve and *one* $H^*(1-T/T_c)$ curve over about three decades, as shown in Fig. 3. This overlap is more clear for the smoother, transport-determined H^* than for the magnetically measured H_{irr}. This result confirms that *the two species have nearly identical anisotropy*; in other words, replacing Tl with Hg increases the T_c by 30 K *without significantly changing the anisotropy*. At this point it should be emphasized that anisotropy has been defined in different ways in the literature. Kim *et al.*[10] used d_i to characterize the anisotropy of HTS's and found this definition to be fairly consistent from system to system. On the other hand, other groups have adopted the ratio of either the resistivities ρ_c/ρ_{ab} or effective masses m_c/m_{ab} perpendicular or parallel to the Cu-O planes.[16] Qualitatively, the geometrically and electronically defined anisotropy have been found to agree with each other. However, a *quantitative* characterization of the anisotropy and its relation to the IL have not yet been fully established. Nevertheless, the coincidence of the IL's for Tl- and Hg-1212 indicates that the anisotropy of the two systems, whether defined geometrically or electronically, are the same.

If ρ_c/ρ_{ab} is unchanged in the Tl-Hg exchange, one might conclude that the change in the charge transport mechanism is either negligible or nearly the same along the a-b plane and along the c axis. The latter is unlikely, since the mechanism is well known to be dramatically different along these two directions for HTS's. This leads one to believe that the major effect of the replacement of Tl with Hg is in the superconducting charge carrier density ρ_s. Indeed, if one defines anisotropy electronically, i.e., as the ratio ρ_c/ρ_{ab}, this ratio would scale with any uniform change in charge carrier density and would therefore not detect such a change, thus keeping the anisotropy constant. Remarkably, a simple consideration of the results of conventional BCS theory reveals another very interesting feature: The fact that the IL's coincide *only when plotted against* $1-T/T_c$ (or T/T_c) clearly shows that the only difference between these species is associated with the superconducting order parameter, which is physically manifested as the superconducting charge carrier density or ρ_s. Both these considerations suggest that the 30-K increase in T_c is largely due to a change in ρ_s.

Exactly how the replacement of Tl with Hg would produce a shift in ρ_s is not yet clear, although it is very likely for the resultant redistribution of oxygen to alter the electronic structure so that the most significant change is in ρ_s. It would seem, then, that optimizing the oxygen distribution in the charge reservoir block (CRB) *while at the same time retaining almost the same crystal geometry* is enough to produce a large shift in the T_c. This is already implied by an intriguing study[17] done on Hg-1223 in which the Hg was partially replaced by Tl and apparently raised the T_c to close to 140 K in ambient pressure. Another hint is in the high-pressure measurements of Hg-based cuprates[18] in which elevated pressures could very well produce an optimum redistribution of oxygen in the CRB. It is possible, then, that the pure Hg-O CRB may not yet have the optimum oxygen distribution for T_c. Further study is needed to explore these possibilities. For instance, a comparative study of the normal-state Hall effect in the 1212 systems would be very interesting. Although Hall data has been reported for Hg-1212,[19] to our knowledge there is still no Hall experiment reported for Tl-1212. It is also fascinating to consider what other cations could be substituted for Hg in the Hg-O CRB of Hg-1212, either partially or entirely, that could enhance the T_c from $\sim$120 K to unprecedented levels. The same could be considered for 1223 systems.

Other possible explanations for the giant T_c shift cannot be excluded, such as those stemming from the subtle differences between the 1212 species which may still be significant despite overall similarities. There might be differences in pinning structures originating from the processing conditions unique to each species, causing different types of disorder potentials with different effects on T_c. However, it is unlikely that the extent of such extrinsic features would not vary from sample to sample, and it is difficult to imagine sample-dependent features inducing a systematic 30-K shift in T_c and yet not causing a significant scatter of IL's in Fig. 3. A recent proton-irradiation study[20] on Hg-1212 and -1223 has shown that random disorder that causes no significant drop in T_c could drastically degrade the critical current density. As for the possible effect of oxygen optimization, an alternative explanation is that TlO and HgO layers may mediate electron-electron interactions in subtly different ways and thus bring about a shift in T_c. Note, however, that this still does not exclude the possibility of a resulting giant shift in ρ_s.

It should be noted that this is not the first time that the IL's of species with similar structural anisotropy have been compared. Maignan *et al.*[21] have done so for Hg- and Tl-1223 but there was no overlap of IL's. This result is most likely due to samples of less than optimum quality. In fact, samples in our study that have degraded[22] yield a lower (reduced temperature) IL than the ones shown.

The rather unusual temperature dependence of these IL's deserves brief mention. At high T/T_c—above 0.70 for $H_{\rm irr}$ and 0.8 for H^*—the dependence is power law (inset, Fig. 3), $(1-T/T_c)^\alpha$. The exponent $\alpha \sim 1.1$ for H^* and ~ 1.6 for $H_{\rm irr}$, which is expected for temperatures close to T_c. At low T/T_c, however—below 0.70 (0.80) for $H_{\rm irr}(H^*)$—the behavior is *exponential decay* for all curves, $\sim \exp(-mT/T_c)$, with $m = 5.6 \pm 0.3$. This temperature dependence is markedly different from that previously reported for Hg-1212 (Ref. 23) *but* has been observed in previous studies of both thin films *and* single crystals of Bi-2212 (Refs. 24–29) and Tl-2212,[24,30] implying that this property may be a symptom of the higher anisotropy of these quasi-two-dimensional systems, although an explanation has not yet been proposed.

In conclusion, the Tl-Hg exchange in the 1212 system is found to cause a large difference in T_c between Hg-1212 and Tl-1212. We speculate that the Tl-Hg exchange induces a shift in the charge carrier density. Further studies such as comparative Hall-effect measurements, should shed more light on this possibility. It would also be interesting to consider other ways in which the oxygen distribution could be *chemically* optimized within the 1212 or 1223 crystal structure and as a result get even higher T_c. The IL's for both 1212 species follows an unusual exponential-decay temperature dependence for low temperatures which is also seen in *only* the highly anisotropic 2212 species, the reason for which is now under investigation.

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