Evidence of unusual hybridization: Electrical resistivity and specific heat of $Y_{1-x}Tb_xBa_2Cu_3O_7$ single crystals

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The electrical resistivity $\rho(T,x)$ ($4 \le T \le 300$ K) and specific heat $C(T,x)$ ($0.3 \le T \le 15$ K) have been measured on single crystals of $Y_{1-x}Tb_xBa_2Cu_3O_7$. T_c is 91 K and irrespective of Tb doping. However, the T-linear slope of $\rho(T,x)$ for $T > T_c$ increases rapidly with increasing x, and a fit of $\rho(T,x)$ to $A+BT$ indicates that the Tb doping primarily alters the slope and much more weakly impacts on the $T \to 0$ intercept. The results of the low-temperature $C(T,x)$, on the other hand, show an anomalously enhanced electron contribution to $C(T)$, γ. The enhancement of γ, along with a large temperature-independent magnetic susceptibility χ_0 reported earlier, strongly suggests the appearance of strong f conduction-electron hybridization. It becomes apparent that the Tb-doped system possesses properties that largely deviate from the well-known behavior of the other high-T_c and doped high-T_c systems, thus standing out as being anomalous.

In previous papers[1-3] we have presented preliminary results of our earlier studies on magnetic and transport properties for Tb-doped $YBa_2Cu_3O_7$ (YBCO) single crystals and epitaxial thin films. These studies have revealed a wide range of unusual properties, which largely deviate from the well-known behavior of the other doped high-T_c cuprates. In particular, the superconducting transition temperature T_c is insensitive to Tb doping which is unexpected in that Tb, like Ce and Pr, is known to show mixed-valent behavior in many oxide systems and other compounds and, like Ce, does not form in the $TbBa_2Cu_3O_7$ structure. The insensitivity of T_c to Tb doping is, thus, in sharp contrast to the cases of Pr and Ce doping which have been shown to be very deleterious to the superconductivity. In addition, the magnetic susceptibility $\chi(T,H)$ for $Y_{1-x}Tb_xBa_2Cu_3O_7$ is extremely anisotropic, and this anisotropy cannot be explained by simple models including only single-ion crystal electric-field effects (CEF). $\chi(T,H)$ for $Y_{1-x}Tb_xBa_2Cu_3O_7$ also displays a large temperature-independent contribution which scales with Tb concentration similar to that reported for $Y_{1-x}Pr_xBa_2Cu_3O_7$. Finally, a rapid increase in the linear-T slope of $\rho(T,x)$ with Tb doping is observed for the epitaxial thin films and single crystals. This feature coupled with the independence of T_c on Tb doping is puzzling since many of the models proposed to explain the linear-T dependence of $\rho(T)$ are based on excitations which also mediate the pairing.

In view of these striking features, it is clear that this system indeed differs markedly from the other doped cuprates, and further understanding of how the $4f$ electron hybridize with other states and the impact of this hybridization on current models of the physical properties of these unconventional superconductors may provide some valuable insight into various theories related to these systems and superconductivity.

In this paper, we report data on the concentration dependence of $\rho(T,x)$ and $C(T,x)$ obtained on a series of single crystals of $Y_{1-x}Tb_xBa_2Cu_3O_7$ ($0 \le x \le 0.4$) and compared these results to the behavior previously reported for the Pr- and Zn-doped YBCO and for the Tb-doped YBCO epitaxial thin films.

The single crystals used in this study were grown using standard flux methods[4] and characterized by x-ray diffraction, scanning-electron microscopy, and energy-dispersive x-ray analysis. These studies have confirmed that the crystals are of high quality with Tb ions uniformly distributed throughout the crystals. All the crystals were oxygen annealed at 450 °C in a high-pressure oxygen furnace and after annealing had sharp superconducting transitions at 91 K. The typical size of the crystals is of the order $1.5 \times 1.5 \times 0.2$ mm^3. The electrical resistivity was measured using standard four-probe techniques and the Montgomery method, the magnetization was measured using a commercial superconducting quantum interference device magnetometer, and the specific heat was performed using a time constant method.

The $\rho_{ab}(T,x)$ for $Y_{1-x}Tb_xBa_2Cu_3O_7$ single crystals is shown in Fig. 1(a) for $x=0.1$, and 0.32. The substitution of Tb for Y apparently has little impact on T_c (91 K), and T_c for all x is sharp with $\Delta T < 1.2$ K. While $\rho_{ab}(T,x)$ for all x displays a characteristic linear-T behavior, i.e., $\rho(T) \approx A+BT$ for $T > T_c$ [above ~ 200 K for $x=0.30$, a slight departure of the data from a straight line is noted, however, to the first-order approximation, the linearity of $\rho(T)$ above T_c is still well preserved], it is uncharacteristic for the slope of the normal-state resistivity to increase rapidly with Tb concentration x. This phenomena is also observed on epitaxial thin films of this system, $\rho(T)$ for the Tb-doped YBCO films is shown in Fig. 1(b) for $x=0.1$, 0.25, and 0.5. A fit of $\rho_{ab}(T,x)$ to $A(x)+B(x)T$ shows that the Tb doping primarily alters the slope and

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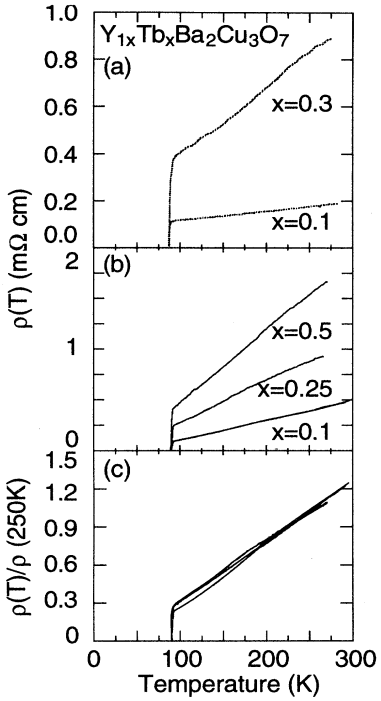

FIG. 1. The resistivity $\rho(T)$ vs temperature for $Y_{1-x}Tb_xBa_2Cu_3O_7$ single crystals with $x=0.10$, and 0.32 (a) and epitaxial thin films with $x=0.1$, 0.25, and 0.50 (b) the reduced resistivity $\rho(T)/\rho(250\ \mathrm{K})$ vs temperature for the epitaxial thin films (c).

much more weakly impacts on the $T\rightarrow 0$ intercept, i.e., $B(x)=d\rho/dT$ changes by 300%, whereas $A(x)$ changes by 100% in comparing $A(x)+B(x)T$ for $x=0.1$ and $x=0.50$. This is evident in a plot of a reduced resistivity $\rho_{ab}(T)/\rho_{ab}(250\ \mathrm{K})$ vs temperature for various x [see Fig. 1(c)] where an approximately universal curve is seen, reflecting a common reduced slope. Such behavior is also illustrated in Fig. 2, where $A(x)$ and $B(x)$ vs x are plotted for both the Tb-doped single crystals and epitaxial thin films. As shown, $B(x)$ for both the crystals and the films increases with x in a similar fashion [Fig. 2(a)]

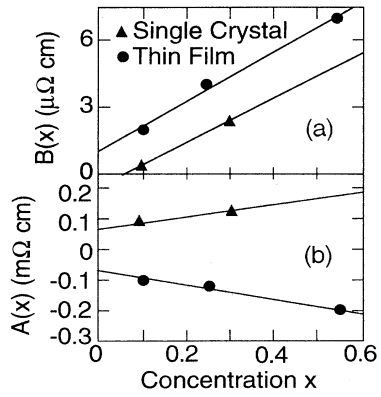

FIG. 2. (a) $B(x)$ vs x and (b) $A(x)$ vs x for $Y_{1-x}Tb_xBa_2Cu_3O_7$ where $\rho(T)=A(x)+B(x)T$.

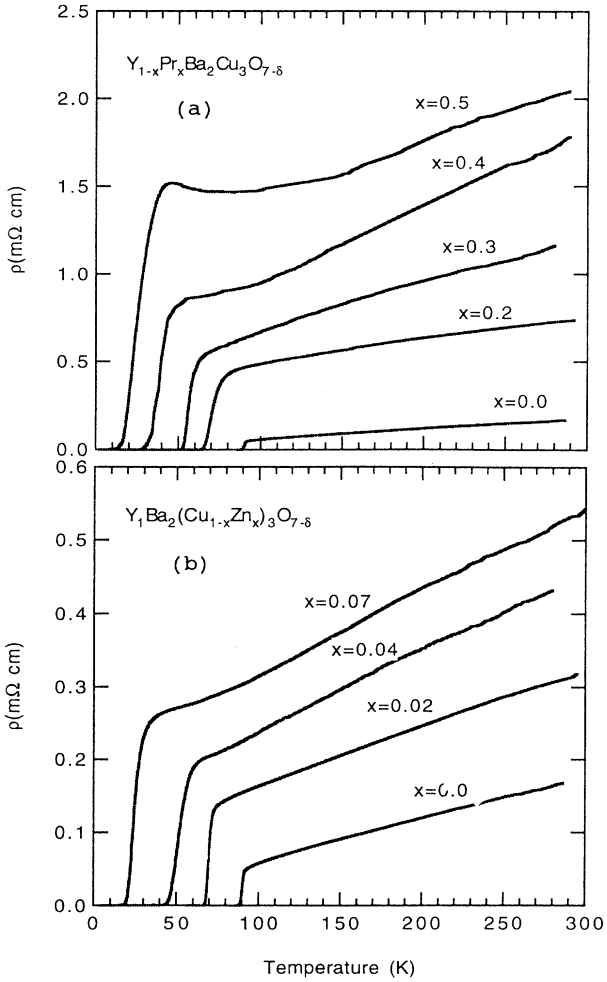

FIG. 3. The resistivity $\rho(T)$ vs temperature for the epitaxial thin films of $Y_{1-x}Pr_xBa_2Cu_3O_7$ (a) and $YBa_2(Cu_{1-x}Zn_x)_3O_7$ (b).

whereas the normalized change in $A(x)$ with Tb doping is much weaker, [Fig. 2(b)], i.e., $A(x)$ increasing (decreasing) slightly with doping for the single crystals (thin films). Although the value of $B(x)$ and $A(x)$ for the crystals and films are not exactly the same, the differences between the single crystals and epitaxial thin films shown in Fig. 2 may be a reflection of the differences in morphology between the thin films, which are c-axis-oriented crystals, and the untwinned single crystals. Nevertheless, the data suggests that the scattering mechanism for carrier transport in the CuO_2 planes leading to the linear-T dependence is dependent on Tb doping, reflecting a systematic change of the scattering rate and/or effective mass of carriers. This coupled with the independence of T_c on Tb doping is puzzling. Many of the models proposed to explain the linear-T dependence of $\rho(T)$ are based on phonons, spins or other excitations that also mediate the pairing. The behavior described above should be contrasted with $\rho(T,x)$ for Pr- and Zn-doped YBCO. Shown in Figs. 3(a) and 3(b) is $\rho(T,x)$ for Pr- and Zn-doped YBCO thin films, respectively. Both Pr and Zn doping in YBCO tends to increase the

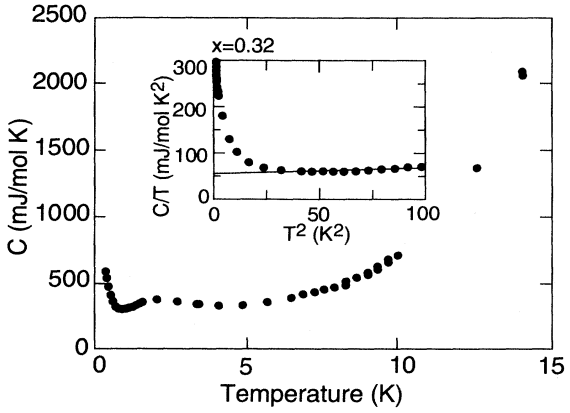

FIG. 4. The specific heat $C(T)$ vs T for a $Y_{0.68}Tb_{0.32}Ba_2Cu_3O_7$ single crystal. Inset: $C(T)/T$ vs T^2.

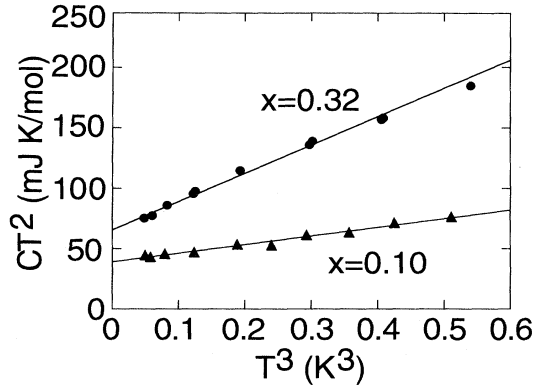

FIG. 5. $C(T)T^2$ vs T^3 for $x=0.10$ and 0.32 for $Y_{1-x}Tb_xBa_2Cu_3O_7$.

temperature-independent contribution to $\rho(T,x)$, i.e., $A(x)$ in $\rho(T,x)=A(x)+B(x)T$ with $B(x)$ remaining essentially unchanged.

These differences between Tb- and Pr-doped YBCO become more interesting after comparing the low-temperature specific heat $C(T)$ for these systems. There are several types of excitations which may contribute to the measured $C(T)$. In particular, $C(T) = C_e(T)+C_{ph}(T)+C_{sch}(T)+C_m(T)+C_{sf}(T)$, where $C_e(T)(=\gamma T)$ is the electronic contribution, $C_{ph}(T)(=\beta T^3)$ is the phonon term, $C_{sch}(T)(\sim T^{-2})$ represents a contribution due to a Schottky anomaly resulting from a multileveled system, $C_m(T)$ and $C_{sf}(T)$ are due to magnetic ordering and spin or magnetic fluctuations, respectively.

Shown in Fig. 4 is $C(T)$ vs T ($0.3 \le T \le 17$ K) for a single crystal with $x=0.32$ and mass of 3.3 mg. There are atypical features displayed by this data. The rapid upturn for $T<1$ K, which becomes more evident in a plot of C/T vs T^2 (see the inset of Fig. 4), may correspond to a Schottky contribution, which is reportedly seen but relatively weaker in the YBCO and the Pr-doped YBCO (Ref. 6) or due to $4f$-electron correlations with a very low characteristic energy scale. The origin of the broad maximum near $T=2$ K is unknown and appears not to be magnetic ordering based on the results of magnetic susceptibility.[3] Interestingly, this maximum resembles ones found in the heavy-fermion superconductors $CeCu_2Si_2$ and UBe_{13}, incidently also occurring in the vicinity of 2 K, and so far there is no accounting for these anomalies. Measurements of the specific heat in magnetic field which are being pursued may help address this issue.

The major feature of the data is a large enhancement of the electron specific-heat coefficient γ. Fitting the $C(T)$ for $4 \le T \le 10$ K to an electron and phonon contribution, i.e., $\gamma T+\beta T^3$, leads to the value of $\gamma \approx 180$ mJ/mol Tb K^2 (see the inset of Fig. 4). This value of γ is extraordinarily large when compared to typical values of metals ($\le \sim 7$ mJ/mol K^2 for YBCO, for instance) and comparable with γ values obtained for Pr-doped YBCO, i.e., $\gamma \approx 200$ mJ/mol Pr K^2 which has been known to show heavy-fermion-like behavior.[6,7] The magnitude of the temperature-independent contribution to magnetic susceptibility $\chi(T)$, $\chi_0(H\|c)$, is also found to be unusually large ($\sim 3.5\times 10^{-3}$ emu/mol Tb) (Refs. 1–3) when compared to that typically reported for the rest of the cuprate oxides, e.g., $\chi_{pauli} \approx 10^{-5}-10^{-4}$ emu/mole for YBCO. In fact, the Wilson ratio (χ_0/γ in units of $3\mu_B^2/\pi^2 k_B^2$) is, approximately, 4. This parallel increases in both γ and χ_0 for Tb-doped YBCO is characteristic of strong $4f$-electron hybridization and is similar to that reported for Pr-doped YBCO.

Extending the above analysis, without considering Schottky contributions to $C(T)$, might be controversial. Analyses of the low-temperature $C(T)$ data for $x=0.1$, and 0.32 of the interval $0.3 \le T \le 0.9$ K and including just the γT term and a T^{-2} Schottky term were performed. It is worth mentioning that an extrapolation of the higher-temperature ($4 \le T \le 10$ K) phonon contribution ($\beta=0.2$ mJ/mol K^4) indicates that C_{phonon} at $T=1$ K is less than 1% of the measured $C(T=1\text{ K})$, C_{phonon} is, thus, totally negligible. As shown in Fig. 5, the γ value is represented by the x-proportional slope which corresponds to $\gamma \approx 720$ and 760 mJ/mol Tb K^2 for $x=0.1$ and 0.32, respectively. Yet above ~ 0.80 K for $x=0.32$ the data slightly deviate from a straight line, however, this should not invalidate the assumption (which is evident in Fig. 5 especially in lower temperatures), i.e., in the lower-temperature region the γT term and the T^{-2} Schottky term are dominant, and, thus, results from such analyses are believed to be justifiable. The linear dependence displayed in Fig. 5 indicates that γ has saturated and is T independent within T-range analyzed here. These γ values obtained are substantially larger than that defined above and may reflect a T-dependent γ value indicative of a low characteristic energy scale. In fact, such a strong temperature dependence of γ at low temperatures is a common feature of many heavy-fermion systems, and is a striking contrast to the temperature-independent γ usually observed in an ordinary metal. At the present time, with so many possible contributions to $C(T)$ at low temperatures, it may not be easy to unambiguously separate these various contributions to $C(T)$

without additional data including $C(T)$ measurements in magnetic fields where the Schottky or hyperfine and magnetic ordering contributions could be more clearly defined. However, it is unlikely that any specific-heat contribution other than an electron contribution to $C(T)$ could be responsible for the large γ values obtained above for either the $4 \leq T \leq 10$ K or $0.3 \leq T \leq 0.9$ K intervals. Actually, contributions from the magnetic ordering due to Tb ions, if any, could be very small. For $BaTbO_3$, for example, which antiferromagnetically orders at 34 K, the magnetic ordering contributions to $C(T)$ obtained from the temperature range of $1.5 \leq T \leq 5$ K are less than 10 mJ/mol e K^2.[4,8] In addition, there is preliminary evidence that the Tb-doped YBCO with $x=0.32$ magnetically orders in the vicinity of $T \approx 16$ K, i.e., at much higher temperatures compared to the T interval used in the analysis presented here.[2,3]

Indeed, regardless of the ultimate resolution of the γ value, it is clear that the electron specific-heat coefficient γ is highly enhanced and extraordinarily large compared with those typical of ordinary metallic systems. Such behavior is reflective of strong hybridization of $4f$ electrons with charge carriers near the Fermi surface in the Tb-doped system. Similar values of γ and χ_0 in the Pr-doped YBCO have been reported.[3,6,7] However, it is by no means plausible to assume that the same hybridization mechanism(s) is operative in these two systems, otherwise it would be difficult to simultaneously explain the similarities in the impurity concentration dependence of χ_0 and γ and at the same time address the difference in the concentration dependence of $T_c(x)$ and $\rho(T)$ behavior reported for these systems.

In general, the slope and magnitude of $\rho(T)$ are sensitive to a weighed average over the excitations spectrum of the electron-excitation interactions and similarly, T_c depends on a different spectral weight. Based on theories of spin fluctuations,[5] for instance, which are favored by a number of experimental results, T_c is directly proportional to the value of the spin-fluctuation frequency $\omega_{SF}(T_c)$, which determines the range of energies over which the spin-fluctuation-induced interaction is effective, and strongly impacting on the slope of $\rho(T)$ as well as on T_c. It has been claimed that a 10% change in $\omega_{SR}(T_c)$ results in a 20% change in the slope of $\rho(T)$.[5] The differences in the experimental data for Zn-, Pr-, and Tb-doped YBCO presented here may suggest an unique $4f$-electron hybridization for Tb-doped YBCO which leads to the anomalous behavior, and is not evident in Pr-doped YBCO. For example, a very qualitative understanding of this difference is evident in the spatial extent of the $4f$-electron ground-state wave function for Pr and Tb in the nearly cubic nearest- and next-nearest-neighbor CEF environment in YBCO. The spatial wave function for Pr favors strong $4f$ hybridization with the O orbitals whereas Tb may slightly favor hybridization with the Cu d orbitals. This subtle difference in the hybridization is consistent with the fact that the thermodynamic quantities, e.g., $\chi(T)$ and $C(T)$, are qualitatively similar for Pr and Tb, whereas the transport and T_c are markedly different. It is not unreasonable to expect such similarities and differences if Pr strongly hybridizes with the oxygen p holes which from Hall-effect measurements are the primary carriers in the Cu-O planes and Tb hybridizes with the Cu d electrons.

This study has led to a wide range of unusual observations concerning the role of Tb in YBCO. The results of electrical resistivity seem to suggest an unconventional scattering mechanism for carrier transport in CuO planes that is dependent on the Tb doping to which T_c, however, is insensitive. The heavy-fermion behavior indicated by the results of the specific heat is, on the other hand, reflective of an enhanced hybridization that is absent in other cuprates, and very likely to be responsible for all observations which largely deviate from well-known common features of the other cuprates. The strong Tb concentration dependence on the $d\rho(T)/dT$, i.e., the slope of the T-linear resistivity for $T > T_c$ along with independence of T_c on Tb doping, appears to be inconsistent with most of the phonon and/or spin-excitation models[9] for the normal and superconducting properties of high-T_c systems.

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[1]G. Cao, R. J. Kennedy, J. W. O'Reilly, J. E. Crow, Pernambuco-Wise, and S. T. Ting, Physica B **186-188**, 1022 (1993).

[2]G. Cao, J. W. O'Reilly, and J. E. Crow, J. Appl. Phys. **75**, 6329 (1994).

[3]G. Cao, F. Freibert, P. F. Henning, S. McCall, M. Shepard, and J. E. Crow, Physica B **206-207**, 749 (1995).

[4]G. Cao, Ph.D. thesis, Department of Physics, Temple University, 1992.

[5]P. Montheux and D. Pines, Phys. Rev. B **49**, 4261 (1994); **47**, 6609 (1993).

[6]N. E. Phillips, R. A. Fisher, R. Caspary, A. Amato, H. B. Radoussky, J. L. Peng, L. Zhang, and R. N. Shelton, Phys. Rev. B **43**, 11 488 (1991).

[7]G. Hilscher, E. Holland-Moritz, T. Holubar, H.-D. Jostarndt, V. Nekvasil, G. Schaudy, U. Walter, and G. Fillion, Phys. Rev. B **49**, 535 (1994), and references within.

[8]J. B. Bulman, M. V. Kuric, R. P. Guertin, S. Foner, E. J. Mcniff, Jr., G. Cao, J. W. O'Reilly, J. E. Crow, P. P. Wise, and T. Yuen, J. Appl. Phys. **69**, 4874 (1991).

[9]K. Miyake, T. Matsuura, and C. M. Varma, Solid State Commun. **71**, 1149 (1989); K. Kadowaki and S. B. Woods, *ibid.* **58**, 507 (1986).