PHYSICAL REVIEW B VOLUME 51, NUMBER 13 1 APRIL 1995-I

Transport characterization of calcium-doped $YBa_2Cu_3O_{7-\delta}$ thin films

J. T. Kucera and J. C. Bravman
Department of Materials Science and Engineering, Stanford University, Stanford, California 94305-2205

(Received 7 September 1994)

We report systematic studies of the normal-state conductivity and thermopower of epitaxial $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films with $0 \leq x \leq 0.3$ as a function of oxygen content. The superconducting transition temperature T_c is found to be parabolic in conductivity σ for each sample, with a universal scaling behavior for all films with $x \leq 0.2$. The room-temperature thermopower, $S_{295\ \mathrm{K}}$, follows the universal correlation between T_c and $S_{295\ \mathrm{K}}$ reported by S. D. Obertelli *et al.* [Phys. Rev. B **46**, 14 928 (1992)] for all films studied, despite the reduction in maximum T_c with increasing calcium content. The thermopower is found to be superior to the conductivity as a measure of the hole concentration because of its reduced sensitivity to extrinsic contributions such as grain boundaries. By assuming that all the charge from oxygen deficiencies and Ca substitution is transferred to the Cu-O planes, and by using Obertelli's empirically-derived expression for hole concentration, we show that $S_{295\ \mathrm{K}}$ can be used to determine the oxygen content of the films. The equilibrium oxygen content is found to be reduced to compensate for the additional carriers introduced by Ca substitution in these films, just as has been previously observed in bulk $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$.

I. INTRODUCTION

Understanding the manner in which the electronic properties of cuprate superconductors change with carrier doping is crucial for understanding the underlying mechanism of high-temperature superconductivity. All copper oxide superconductors can be transformed from antiferromagnetic insulators, to superconductors, to metals as the doping is increased. In many systems, such as $YBa_2Cu_3O_{7-\delta}$ (YBCO), the change in doping can be performed reversibly by varying the oxygen stoichiometry δ through a series of relatively low-temperature anneals. The carrier concentration on the copper oxide planes is usually determined by doping on layers which are well separated from the planes, thus allowing one to adjust the carrier concentration without introducing additional scattering centers in the actively conducting regions.

Cation substitution can also be used to dope cuprate superconductors. In YBCO, Ca^{2+} can be partially substituted for Y^{3+} in quantities up to nearly 0.3 calcium ions per formula unit,[1–6] introducing one additional carrier (hole) per substituted ion. In this case, the dopant ion sits directly in the active superconducting region (planes) and results in a 10 K reduction in the maximum obtainable T_c.[7,8] Calcium substitutes primarily on the yttrium site because its ionic radius is close to that of yttrium,[3] but there have been reports of partial calcium substitution on the barium site that increases as the calcium content is increased.[8,9]

The role of calcium doping on the transport properties of bulk YBCO has been widely discussed.[2,8,10–13] However, bulk samples consist of a network of randomly oriented grains separated by unoriented, high-resistance grain boundaries which complicate the interpretation of the results. It is, therefore, important to understand the effects of calcium doping on more intrinsic samples such as single crystals or epitaxial thin films.

In addition to obtaining a more fundamental understanding of the role of cation substitution on the intrinsic transport properties of YBCO, calcium-doped YBCO films can be used as a model system to quantify the amount of overdoping expected from small amounts of cation disorder in pure YBCO thin films. It has been proposed that Ba-Y disorder or Ba substitution for Y could account for the higher critical current densities, lower transition temperatures, and expanded *c*-axis lattice parameters observed in "fully oxygenated" YBCO films, as compared to bulk samples of the same material.[14–18] This disorder is thought to result from the nonequilibrium growth of thin films in low oxygen pressures (≤ 200 mTorr),[14–19] but is not expected to occur during higher-oxygen-pressure bulk synthesis.[19] The substitution of divalent barium for trivalent yttrium should result in films which are overdoped as compared to unsubstituted samples with the same oxygen content.

Recently Feenstra *et al.*[17,18] have used transport measurements of the resistivity and T_c to investigate possible cation disorder in films grown in low oxygen partial pressures. In these experiments YBCO films were initially annealed in 1.0 atm O_2 at 550 °C to establish a fully oxygenated state. Then the T_c's and conductivities at 100 K were monitored as the films underwent a series of anneals at reduced oxygen partial pressures. Changes in the conductivity relative to that in the fully oxygenated state, $-\Delta\sigma/\sigma_0$, were used to parameterize the oxygen content of the films. The authors found that some films achieved their maximum T_c's after annealing in reduced oxygen partial pressures, and concluded that this results from additional fixed carriers introduced by Ba-Y disorder. However, the amount of overdoping was not readily quantifiable in these experiments since there was no absolute measure of the oxygen content in the films. In addition, the interpretation of their results requires knowledge of the oxygen content of fully oxygenated films. In

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Ref. 17 it was implicitly assumed that the oxygen content of fully oxygenated films was unaffected by possible cation disorder, while in Ref. 18 assumptions about the oxygen content were tailored to each class of films in order to explain trends in the experimental results.

In our work we have attempted to improve the measurement of overdoping by establishing an independent measure of the carrier concentration, and by calibrating the amount of overdoping using well-characterized $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ films with known amounts of cation substitution. We found that the room-temperature thermopower could be used to determine the carrier concentration in our films using the empirical correlation between thermopower and carrier concentration found by Obertelli *et al.*[20] However, the substitution of calcium for yttrium was accompanied by a reduction in the equilibrium oxygen concentration of fully oxygenated films, which completely compensated for the additional carriers introduced by the calcium. This shows that the technique used by Feenstra *et al.*[17,18] does not provide unambiguous evidence of cation substitution in the range of calcium concentration we have investigated. It further suggests that recent reports about the overdoping of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films do not reflect the equilibrium oxygen stoichiometry.[12,21–23]

A brief outline of this paper is as follows. We will first describe the sample fabrication and experimental technique. Then we will discuss the experimental results including correlations between T_c and the normal-state conductivity, and between T_c and the thermopower. We will show that the room-temperature thermopower gives a much better measure of the carrier concentration than the conductivity, because the thermopower is less sensitive to extrinsic influences, such as grain boundaries, which inevitably contribute to the resistivity of these films. Finally, using a simple model of charge transfer that we believe to be applicable near the region of optimal doping, we will show that most of the additional charge introduced by the substitution of calcium is compensated by oxygen defects, just as has been observed in bulk polycrystalline samples.[1,3,6] The consistent explanation of our results with that observed in bulk helps support the use of thermopower as a measure of the planar hole concentration.

II. EXPERIMENTAL PROCEDURE

A. Film preparation

Epitaxial thin films of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ were grown *in situ* by off-axis sputtering from composite targets having calcium concentrations of $x = 0, 0.1, 0.2$, and 0.3. The films were deposited onto 13×6 mm^2 $LaAlO_3$ substrates at a deposition temperature of 790 °C in a mixture of 120 mTorr Ar and 80 mTorr O_2 using an rf power of 100 W. Following deposition, the chamber was backfilled with oxygen, and the heater was shut off to allow the films to cool over a period of about 1 h. The resulting films were epitaxial with the *c* axis perpendicular to the substrate and were from 75–175 nm thick. Further details of the deposition system and procedure can be found in Ref. 24.

In contrast to pure YBCO films which were cooled in 300–500 Torr of oxygen, calcium-substituted films were cooled in reduced oxygen pressures of 5–20 Torr in order to achieve as-deposited T_c's near the bulk values of 80–85 K.[7,8] Calcium-doped films that were cooled in higher oxygen pressures had reduced T_c's of from 45 to 65 K, suggestive of overdoping. However, the T_c's of these films could not be increased by more than about 7 K by subsequent anneals, suggesting that they had additional defects or disorder. Because of this, only films cooled in reduced-oxygen partial pressures were used in this study.

B. Annealing

The films were annealed at atmospheric pressure in mixtures of 1%–100% oxygen in flowing argon at 480–500 °C for 2–4 h. The partial pressure of oxygen in the O_2/Ar mixture was determined to within ±5% of the measured value and was continuously monitored by a commercial zirconia-cell oxygen sensor.[25] The annealing conditions were chosen to ensure that the films reached their equilibrium oxygen content while maximizing the amount of oxygen which could be incorporated at the highest oxygen pressure. A series of successively longer anneals on similar films were used to establish that the annealing time was sufficient to ensure an equilibrium oxygen content. The required annealing time is very sensitive to the microstructure of the film because oxygen diffusion along the *a*-*b* plane is many orders of magnitude faster than along the *c* direction.[26–28] The relatively long annealing times required suggests a high degree of *c*-axis texturing and a low density of grain boundaries in these films.

The oxygen content of the films could be changed in a completely reversible manner in all but the $x = 0.3$ sample. The films with $x < 0.3$ were cycled from superconducting to insulating and back to superconducting by varying the oxygen content, and recovered to within better than 10% of their original resistivities and to within 0.8 K of their original T_c's. The film with $x = 0.3$ did not become insulating after the lowest P_{O_2} anneal, and T_c returned to a value 4.9 K *higher* than its original value of 73.9 K. The resistivity of this sample increased by 37% after cycling, suggesting that it was initially overdoped by some mechanism which was irreversible with annealing. The amount of overdoping was estimated to be 0.015 holes per plane based on thermopower measurements. The irreversible behavior of the $x = 0.3$ film is not likely to have resulted from a lower chain oxygen mobility, because this film had a more heterogeneous microstructure than the others, and because the addition of calcium to bulk YBCO has been shown to increase the oxygen diffusion rate by more than a factor of 10 at 500 °C.[29]

C. Transport measurements

The thermopower was measured in vacuum with respect to copper, and was confirmed to have an absolute accuracy of about 7% using a 99.999%-pure Pb standard. We used the room-temperature value of 2.07 μV/K for the thermopower of copper for all measurements, which is the value determined by Cusack and Kendall[30] corrected for the new absolute scale of Roberts.[31] The thermopower was measured using a differential technique by clamping one end of the sample to a large copper block which served as a heat reservoir, and the other to a smaller copper block to which was attached a resistive heater. The temperature gradient was measured by a 0.13 mm diam differential Chromel-Alumel (type K) thermocouple whose ends were embedded in either block. Evaporated silver contacts across the entire width of the sample at either end of the film ensured uniform, low thermal and electrical resistance contacts to the copper blocks. All residual silver paste was removed from the back side of the samples in order to ensure a uniform temperature gradient across the entire thickness of the substrate. The thermocouple and sample voltages were measured to within ±20 nV by Keithley 182 nanovoltmeters, and ΔV was verified to be proportional to the ΔT for 4–5 ΔT's up to $\Delta T \approx 2$ K for each measurement.

The resistivity was measured using a conventional four-point technique with a calibrated Si diode as the thermometer. All films were patterned into four-point resistance bridges 460 μm wide by 7.1 mm long. The sample thickness was determined by a commercial profilometer to within ±10 nm for samples with $x = 0$ and 0.1, and to within ±20 nm for samples with $x = 0.2$ and 0.3. The temperature measurement was accurate to within ±0.1 K. All reported values of the superconducting transition temperature in this paper refer to the "$R = 0$" T_c which was defined as the point where the resistivity dropped to below 1% of its value at 100 K.

III. RESULTS

A. Film properties

The as-deposited films had excellent transport properties with T_c's of up to 89 K (for $x = 0$) and $\rho(T)$'s which extrapolated through $\rho = 0$ at $T = 0$. These films were then annealed for 2 h at 480 °C in 1.0 atm O_2 to establish the fully oxygenated state. After the initial anneal the room-temperature resistivities increased slightly and the extrapolated $T = 0$ intercepts became approximately 10% of the room-temperature resistivity for all films. The T_c of the undoped film was not changed by the initial anneal, but the T_c's of the calcium doped films increased by 2–4 K.

Figure 1 shows the resistive transitions of the films following the initial anneal. The resistivity of the undoped film is about twice that typical of the highest-quality single crystals,[32–34] but is still significantly lower than those for bulk, polycrystalline samples.[35–37] The high resistivity of the $x = 0$ film results partly from twin boundary scattering and partly from underdoping due to the slight oxygen deficiency expected for an annealing temperature of 480 °C.[38] The room-temperature resistivities (listed in Table I) decrease with increasing calcium content except for the film with $x = 0.3$. This is consistent with the increased carrier concentration in calcium-doped films. However, as will be quantified later, the decrease in resistivity is not nearly as much as would be expected for the amount of calcium doping if one assumes that the holes from the calcium ions are all transferred to the copper oxide planes.

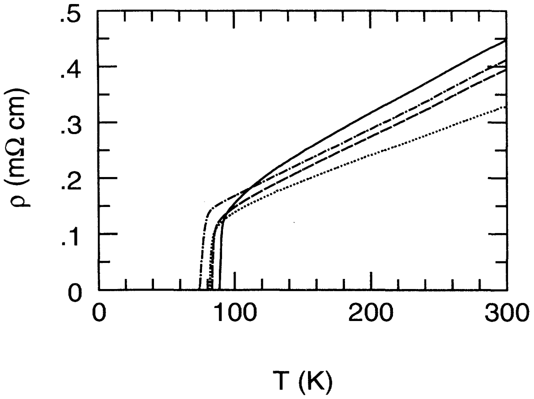

FIG. 1. Resistive transitions of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ films after an initial anneal in 1.0 atm O_2 for 2 h at 480 °C for $x = 0.0$ (solid line), 0.1 (dashed line), 0.2 (dotted line), and 0.3 (dot-dashed line).

The higher resistivity for the $x = 0.3$ sample could be explained by increased grain boundary resistance in this film. Scanning electron microscope (SEM) photos of this film reveal the existence of a needle-shaped impurity phase. This impurity phase is not observed in SEM photos of the other films, suggesting that it results from exceeding the solubility limit of Ca in $YBa_2Cu_3O_{7-\delta}$. The solubility limit in bulk $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ is between $x = 0.2$ and 0.3, which is consistent with this observation.[1–6] Scanning electron microscopy has been used to look for possible impurity phases because it is more sensitive than x-ray diffraction to the presence of unoriented material. No second phase peaks were observed in any of the x-ray diffraction θ-2θ scans of these films. The c-axis lattice parameter for all initially annealed films was 11.71 ± 0.02 Å regardless of the calcium content. The expanded c-axis lattice parameters are typical of fully oxygenated YBCO films grown under similar conditions.[15,16,24,39]

Table I summarizes the properties of all samples studied. The quantities (ρ_0) and (T_c^0) refer to the resistivities and transition temperatures, respectively, of the "initially annealed" films. Table I also lists the initial oxygen content of the films (y_0) determined by the procedure described in Sec. III D. The transition temperature and room-temperature conductivity of the films at "optimal doping" is listed as T_c^* and σ^*, respectively. These values were determined from the correlation between conductivity and T_c as described in the following section.

TABLE I. Properties of all $Y_{1-x}Ca_xBa_2Cu_3O_y$ thin films studied including resistivity (ρ_0), transition temperature (T_c^0), and oxygen content (y_0) of films after initial anneal in 1.0 atm oxygen, and conductivity (σ^*), and transition temperature (T_c^*) of samples at "optimal" doping.

Ca	d (nm)	$\rho_0(300\,\mathrm{K})$ ($\mu\Omega\,\mathrm{cm}$)	T_c^0 (K)	y_0	σ^* ($\Omega^{-1}\,\mathrm{cm}^{-1}$)	T_c^* (K)
0	165	450	88.7	6.98	2350	88.7
0.1	175	390	83.3	6.96	2250	84.0
0.2	76	330	81.5	6.90	3060	81.6
0.3	170	410	73.9	6.87	1730	83.4

The transition temperatures of initially annealed films decrease with increasing calcium content. This decrease could be caused by either a deviation of the carrier concentration from the optimal value, or by additional scattering introduced by the calcium impurities. In bulk polycrystalline samples, the maximum T_c obtainable is reduced to slightly over 80 K for $x \geq 0.05$.[7,8] Thus, there are at least two factors which influence T_c: doping and disorder. The conventional way to separate these factors is to determine the maximum T_c as a function of oxygen content using a series of anneals in various partial pressures of oxygen as has been done in this study. We will later demonstrate that measurement of the room-temperature thermopower provides a much simpler procedure for separating these effects.

B. Conductivity

We now discuss the correlation between the superconducting transition temperature and the normal-state conductivity.

In all cuprate superconductors the transition temperature has been found to go through a maximum with increasing carrier concentration.[40–44] Although the exact functional form of $T_c(p)$ is still disputed,[43,44] many authors have approximated $T_c(p)$ as being parabolic about $p^* \approx 0.16$ holes per CuO plane.[42,43,45–47] This can always be done for any symmetric peak since a parabola is the first term in the Taylor expansion about the maximum. Let us write

$$\frac{T_c(p)}{T_c^*} = 1 - \left(\frac{p^* - p}{p^* - p_1}\right)^2 + \mathcal{O}(p^* - p)^4 , \tag{1}$$

where p_1 is the carrier concentration which causes T_c to go to zero. The normal-state conductivity (σ) has been found to be nearly linear with carrier concentration[48] in $La_{2-x}Sr_xCuO_4$ for hole concentrations greater than some mobility threshold, p_c, giving

$$\sigma = \mu e(p - p_c). \tag{2}$$

If we can extend these results to the case of YBCO and neglect corrections of order $(p^* - p)^4$, then we expect that T_c should be parabolic in σ.

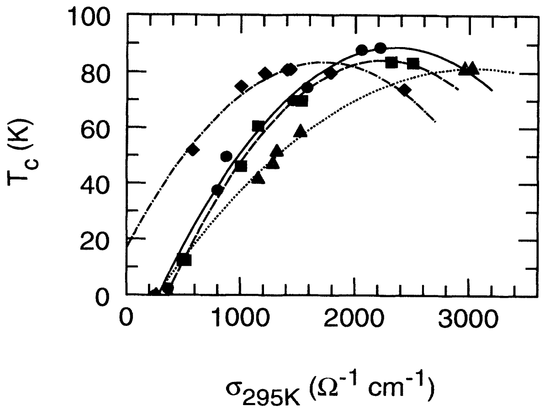

FIG. 2. Superconducting transition temperature versus room-temperature conductivity for samples with Ca = 0.0 (circle), 0.1 (square), 0.2 (triangle), and 0.3 (diamond). Curves are parabolic fits to the data.

Figure 2 shows T_c versus the room-temperature conductivity $\sigma_{295\,\mathrm{K}}$ for all films with varying oxygen contents. For each film T_c vs $\sigma_{295\,\mathrm{K}}$ can be well fit by a parabola with a maximum at $\sigma = \sigma^*$ and $T_c = T_c^*$. The values for σ^* and T_c^* are given in Table I for all films studied. Note that T_c^* and σ^* are different from T_c^0 and $1/\rho_0$, showing that none of the films were "optimally doped" after the initial anneal in pure oxygen. Also note that none of the samples get very far into the "overdoped" regime where T_c begins to decrease with increasing conductivity. This is an effect which is further confirmed by thermopower measurements in Sec. III C. Although our data are consistent with a parabolic $T_c(\sigma)$, we cannot rule out the possible existence of higher-order terms.

If we assume the conductivity as a function of doping is given by the modified Drude form in Eq. (2), then we can determine p from

$$\frac{\sigma^* - \sigma}{\sigma^*} = \frac{p^* - p}{p^* - p_c} , \tag{3}$$

where p^* is the hole doping at optimal T_c. Note that this expression requires knowledge of the additional parameter p_c to determine $\delta p/p^*$ as in Refs. 17 and 18.

The films have different $T_c(\sigma)$ relations presumably because of different characteristic scattering times (τ) in the Drude form for σ. The scattering time would be expected to be smaller in films with more calcium or other disorder-induced scattering centers. This is consistent with the general trend of decreasing σ^* with increasing x as seen in Table I. However, σ^* can also be affected by extrinsic factors such as grain boundary resistances and errors in the thickness determination. This might explain the increase in σ^* of the $x = 0.2$ film since the relative error in the thickness of this very thin film is nearly ±25%.

It is possible to scale all T_c vs σ data onto a single parabola for all films except for the sample with $x = 0.3$. If we combine Eqs. (1) and (3) and neglect the higher-order terms, we find

$$\frac{T_c(\sigma)}{T_c^*} \approx 1 - \eta^2 \left(\frac{\sigma}{\sigma^*} - 1 \right)^2 , \qquad (4)$$

where $\eta \equiv (p^* - p_c)/(p^* - p_1)$. The scaled $T_c(\sigma)$ curves give $\eta = 1.14 \pm 0.01$ for the samples with $x \leq 0.2$. The fact that the curves can be scaled shows that there are sample-independent values of p^*, p_c, and p_1 which are capable of representing the $T_c(p)$ and $\sigma(p)$ relations. The fact that η is slightly larger than 1 shows that T_c drops to zero just before localization sets in. This behavior is also observed in $La_{2-x}Sr_xCuO_4$.[49,50] One might expect T_c to be suppressed by localization right at the metal-insulator transition. This scenario would still be consistent with our observation of residual conductivity at $T_c = 0$ because we have used the room-temperature value of σ which is nonzero even when the sample is an insulator at $T = 0$. The lack of ability to scale the $x = 0.3$ sample is consistent with the existence of a significant extrinsic contribution to the resistivity in this film.

While it does appear possible to use the conductivity to determine the carrier concentration in thin films, there are a number of difficulties which complicate its use. First, one needs to assume values for p^* and p_c. Second, the inability to scale the T_c vs σ data on the $x = 0.3$ sample provides evidence that not all films behave the same due to possible extrinsic contributions to the conductivity. Finally, the most serious drawback is that one has to determine σ^* through an exhaustive series of anneals before being able to employ this technique.

C. Thermopower

Because of drawbacks in the interpretation of the conductivity, we set out to evaluate the thermopower as a technique to determine the carrier concentration in our films.

Figure 3 shows the correlation between the measured room-temperature thermopower $S_{295\text{ K}}$ and the superconducting transition temperature normalized to its sample-dependent maximum, T_c^*. The solid symbols are our data on calcium-doped YBCO thin films, while the crosses are the data from Obertelli *et al.*[20] The thermopower is plotted against both logarithmic and linear scales on the left and right axes, respectively. This is done because for underdoped samples the thermopower is large and positive and increases rapidly as T_c/T_c^* decreases, while for overdoped samples the thermopower has much smaller magnitude and changes sign in the vicinity of the optimal T_c. The superconducting transition temperature is plotted on the x axis as $\sqrt{1 - T_c/T_c^*}$ which should be linear in p if

$$T_c/T_c^* = 1 - \alpha(p - p^*)^2. \qquad (5)$$

For our films T_c^* was determined from the peaks of the parabolic fits to the conductivity measurements listed in Table I. The data of Obertelli *et al.*[20] was converted from $S(p)$ to $S(T_c/T_c^*)$ using Eq. (5) with $\alpha = 82.6$ and $p^* = 0.16$ [Eq. (1) of Ref. 20]. This was done to put all the data on the same scale for comparison, and results in the unphysical values of $\sqrt{1 - T_c/T_c^*}$ for the extremely underdoped films in Fig. 3.

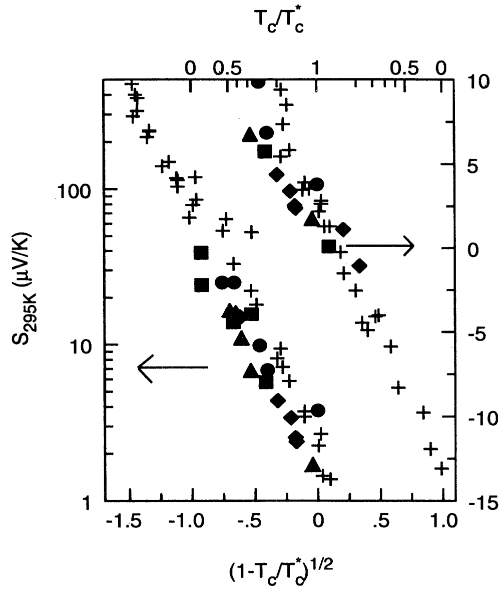

FIG. 3. Room-temperature absolute thermopower on logarithmic (left axis) and linear (right axis) scales as a function of normalized transition temperature for samples with Ca = 0.0 (circle), 0.1 (square), 0.2 (triangle), and 0.3 (diamond). The functional form of the x axis has been chosen to be linear in hole concentration (p) if T_c is parabolic in p. Crosses are data from Ref. 20.

The data for our films follow the same universal curve as that of Obertelli *et al.*[20] despite the additional disorder introduced by the calcium substitution. This shows that the mechanism responsible for the striking correlation between $S_{295\text{ K}}$ and T_c/T_c^* is not influenced by the additional disorder, even though T_c^* is. It also means that a single measurement of T_c and $S_{295\text{ K}}$ can be used to determine T_c^* without requiring a series of oxygenating anneals. This observation may be extremely useful in determining whether a film with a reduced T_c is merely underdoped or is defective in some other way.

For higher thermopowers (lower doping) the data for our films begins to systematically deviate to values about 30% lower than those seen by Obertelli *et al.*[20] This deviation occurs for all films regardless of the calcium content, suggesting a systematic discrepancy that is not related to the calcium. This discrepancy is not significantly larger than the scatter in the data of Obertelli *et al.*,[20] and actually improves the extrapolation of the highest-thermopower data into the lower-thermopower regime. Alternatively, the discrepancy could result from an error of about 0.02 holes per CuO plane in converting the data of Obertelli *et al.*[20] from $S(p)$ to $S(T_c)$. In Ref. 20, p was determined by bond valence sums[40,51] for most samples in the low-doping regime, and so the discrepancy could also result from a small error in the determination of p.

The fact that the thermopower versus T_c correlation holds for our films also suggests that $S_{295\text{ K}}$ is measuring something intrinsic to the material. One might expect the thermopower to be less sensitive than the conductivity to extrinsic defects, such as grain boundaries, because the temperature gradient is supported by phonons and is locked to the gradient across the substrate, whereas the electric field gradient can be appreciable across the narrow, but relatively poorly conducting grain boundaries. Thus, the thermopower is a much more intrinsic measurement than the conductivity, making it more directly applicable to evaluating the carrier concentration in the films.

If we use the calibration of Obertelli *et al.*[20] of $p(S_{295\ \mathrm{K}})$, we can plot T_c/T_c^* as a function of p for the calcium-doped films. This plot is shown in Fig. 4. The data for all films lie on a single parabola with maximum T_c/T_c^* at $p = p^* = 0.167$. Although this is not surprising given the method in which p was determined, Fig. 4 provides another way of expressing the fact that the empirical correlation between $S_{295\ \mathrm{K}}$ and T_c/T_c^* holds for all films regardless of the suppression of T_c^* from the additional disorder introduced by calcium doping.

D. Oxygen content

The results of Fig. 4 suggest a quantitative discrepancy between the amount of calcium doping and the increase in carrier concentration. Because the calcium is substituted directly between the copper oxide planes, the excess holes should be directly transferred to the planes yielding $p(x) = p(x = 0) + x/2$. However, we find that the maximum hole concentration in calcium-doped films does not greatly exceed that of the undoped samples. With $x = 0.3$ the doping level in films with oxygen $y \approx 7.0$ should be nearly $p = 0.17 + 0.15 = 0.32$. This is far less than observed. Even the conductivity (Fig. 2) shows far less overdoping; based on Eq. (3), the conductivity, would be expected to nearly double for this level of carrier concentration. The thermopower, normal-state conductivity, and transition temperatures all indicate quantitatively less overdoping than would be expected for any of the calcium-substituted films.

We can quantitatively explain the lack of overdoping in our $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ films by a compensation effect in which the additional carriers introduced by calcium doping are almost completely compensated by the creation of oxygen vacancies. Consider the fully oxygenated films which were initially annealed in 1.0 atm O_2. We model the system near equilibrium as one in which all of the holes from added calcium go onto the copper oxide planes, and all of the holes removed by loss of chain oxygens are removed directly from the planes. This results in an expression relating the oxygen deficiency δ, the calcium doping x, and the planar hole concentration p by

$$p = p^* + x/2 - (\delta - \delta_0) \ , \tag{6}$$

where $p^* = 0.167$ is the planar hole concentration at optimal doping determined in Fig. 4. The quantity $(\delta - \delta_0)$ in expression (6) is the oxygen deficiency relative to that of a pure YBCO film at optimal doping. Equation (6) simply says that for a calcium-free film ($x = 0$) the hole concentration per plane is p^* at optimal doping ($\delta = \delta_0$). The hole concentration decreases by 1 hole per plane for every oxygen atom removed and increases by 1/2 hole per plane for every Ca^{2+} substituted for a Y^{3+}.

Figure 5 shows the equilibrium oxygen content ($y = 7.00 - \delta$) as a function of calcium doping for all fully oxygenated films. Also included in Fig. 5 is the data of Gledel *et al.*[6] on the oxygen content of bulk $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ powders that were annealed in 1.0 atm oxygen. Here we have chosen $\delta_0 = 0$ as the equilibrium oxygen content of calcium-free YBCO at optimal carrier doping. This choice is merely convenient for comparing our results to the bulk data, and does not affect the validity of our argument.

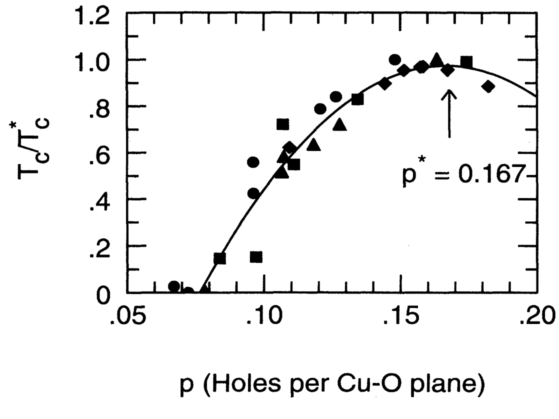

FIG. 4. Normalized transition temperature as a function of hole concentration per plane (p) for samples with Ca = 0.0 (circle), 0.1 (square), 0.2 (triangle), and 0.3 (diamond) using the scale of Obertelli *et al.* (Ref. 20) for p. All curves fall onto a single parabola with optimal hole concentration of $p^* = 0.167$.

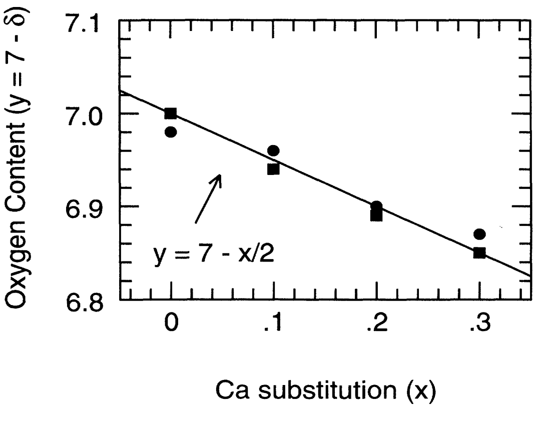

FIG. 5. Equilibrium oxygen content (y) as a function of calcium content for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ films annealed in 1.0 atm O_2 at 480 °C. For these films (squares) the extra holes introduced by calcium substitution is almost completely compensated by oxygen defects just as is seen in bulk (circles) (Ref. 6).

The fixed charge introduced by calcium doping is completely compensated by oxygen defects in both the bulk and the films. This phenomenon is absolutely typical of oxides where the thermodynamics is driven by equilibrium ionic valences rather than by total oxygen content. The phenomenon is most familiar in highly ionic solids such as yttrium-stabilized zirconia where the well-defined valences of Y and Zr do not confuse the issue. Substitution of Y^{3+} for Zr^{4+} results in the creation of oxygen vacancies to compensate for the change in ionic charge. In $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$, the variable valence of copper has to be reconciled with the variable oxygen content of the material. The correct way to think of it is that the minimization of thermodynamic free energy (enthalpy) requires a particular copper valence which is dependent, in part, on the crystal structure of the material. The oxygen content is therefore adjusted to create the appropriate copper valence at the given temperature and oxygen pressure. Our results show that when calcium is partially substituted for yttrium, the equilibrium average copper valence for a given temperature and oxygen pressure is unchanged to first order. The transition temperature is slightly reduced by the disorder from the calcium located in between the actively conducting copper oxide planes, but there is no significant change in equilibrium copper valence.

Exactly the same results of compensation of cation charge by oxygen vacancies have also been observed in bulk $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ by many other researchers.[1,3,6,52] In those reports the oxygen content was determined by iodometric titration,[1,52] thermogravimetry,[3,6,52] and neutron diffraction,[3] all of which confirm the loss of oxygen upon substitution of calcium. The fact that we see the same results in thin films validates our technique of using the thermopower to determine the carrier concentration and hence the oxygen content.

There have been several claims of overdoping in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films.[12,21–23,53] While the reduced transition temperatures and upwardly curved resistive transitions reported by these authors suggest overdoping, only Matijasevic *et al.*[22] and Sun *et al.*[12] have attempted to confirm the overdoping by observing an increase in T_c upon reducing the oxygen content. If we use the parabolic relationship between T_c and p from Presland *et al.*[43] to determine the carrier concentration of the three films from Ref. 22, the maximum amount of overdoping observed was $\Delta p = 0.027$, 0.045, and 0.064 for films with $x = 0.1$, 0.2, and 0.4, respectively.[53] This is less than half that expected from simple cation substitution, confirming the presence of compensating oxygen defects in these films.

The slight overdoping reported by other researchers might result from a nonequilibrium oxygen content. The annealing conditions of $T = 400\,^\circ\mathrm{C}$ for 1 h reported in Ref. 21 were insufficient to establish an equilibrium oxygen content in our epitaxial thin films of similar thickness. Alternatively, these films might have additional disordered defect structures which allow for some amount of overdoping. The film in Ref. 22 which showed the most overdoping had a maximum T_c of only 72 K, similar to the defective films we produced by cooling in higher oxygen pressures. While it is possible to produce calcium substituted films with reduced T_c's, overdoping may not be the only factor which contributes to the T_c reduction.

IV. DISCUSSION

Our model for oxygen compensation [Eq. (6)] represents the simplest model that can be proposed for the YBCO system. It assumes that the addition of calcium only changes the carrier concentration, and that there is complete charge transfer from the chains to the planes. The latter assumption may seem crude given the belief that, in unsubstituted YBCO, as little as 1/3 of the charge from the chains gets transferred to the planes, depending on the ordering of oxygen vacancies for $\delta < 0.5$.[54–60] However, in the present case we are considering the charge transfer involved in compensating for extra holes on the copper oxide planes, rather than the charge transfer for oxygen intercalation on the chains. If there is less than full chain-to-plane hole transfer, then there must be even more oxygen loss to compensate for the addition of calcium on the planes. This would result in a decrease in the equilibrium chain copper valence since the total charge difference must be twice the number of oxygen atoms. We think this would be unlikely given that equilibrium is determined by the copper valences rather than the actual oxygen content. In any case δ is a lower bound on the number of compensating oxygen defects, and is a measure of the amount of charge transferred to the copper oxide planes.

The lack of any significant amount of overdoping in these films is not caused by a lack of calcium. Extensive composition analysis has been performed by Rutherford backscattering spectroscopy on a dozen films deposited onto MgO substrates from the target with $x = 0.3$. The calcium content of nine amorphous films deposited at ambient temperature and three crystalline films deposited under conditions nearly identical to those used for films in this study was $x = 0.30 \pm 0.03$ when normalized to Cu $= 3$. This confirms previous studies which have shown that the composition of films sputtered in our chamber closely matches that of the target.[24] We have no reason to believe the film composition would vary from that of the target in the cases of $x = 0.1$ or $x = 0.2$. At the very least we would expect a monotonic increase in the amount of calcium in films sputtered from targets with increasing x. We know that calcium is actually incorporated into the YBCO unit cell because the maximum T_c is reduced for samples with $x > 0$. The fact that we observe a calcium solubility limit in our films which exactly agrees with that in the bulk[1–6] provides the strongest evidence that the calcium is incorporated into the unit cell in the amounts expected.

Several of our observations on both pure and calcium-substituted YBCO films suggest that the carrier concentration immediately after deposition exceeds that expected in equilibrium. Even though our calcium-substituted YBCO films were cooled in reduced partial pressures of oxygen (0.007–0.026 atm) their carrier concentrations were not significantly increased by subsequent anneals in pure oxygen at 480 °C for 2 h. Annealing these films again in 0.035 atm O_2 reduced the T_c's of the $x = 0.1$ and $x = 0.2$ films to 12.8 K and 41.7 K, respectively, although the T_c of the $x = 0.3$ sample remained nearly unchanged. Even unsubstituted YBCO films had an excess carrier concentration immediately after deposition. Thermopower and resistivity measurements routinely showed that as-deposited YBCO thin films were very slightly overdoped, but after the films were annealed in pure oxygen they became slightly underdoped.

These observations are impossible to explain by a single oxygen diffusion mechanism because the films spend more time at lower temperatures during *ex situ* annealing and therefore should contain more oxygen after annealing. Nor can the observations be explained by oxygen ordering, because the films were cooled more slowly after *ex situ* anneals and therefore should have greater ordering and hence more chain-to-plane charge transfer.

The simplest explanation is the existence of an additional defect structure that results in nonequilibrium overdoping and is frozen in during deposition or during high-temperature annealing in high partial pressures of oxygen. This defect structure might also explain the irreversible annealing behavior of the $x = 0.3$ sample and the reduced T_c's of calcium-substituted films cooled in high partial pressures of oxygen. The irreversibility comes from the fact that the defect structure can be gradually eliminated by prolonged annealing at temperatures used for reversible oxygenation. We note that the $x = 0.3$ sample exhibited an increased T_c^* after undergoing six low-temperature anneals for a total of 15 h at 480 °C.

The fact that such an effect is only seen in thin films suggests that either it occurs during kinetically limited growth or that it is only a "surface effect" in bulk samples. The fact that the slight overdoping is not compensated indicates that the responsible mechanism must also disrupt the equilibrium charge balance. Since the charge balance is determined by the copper valence, which is determined in part by structural considerations, we believe that the nonequilibrium overdoping mechanism must involve a distortion of the lattice.

Because nonequilibrium overdoping in our calcium-substituted films was so dramatically affected by the oxygen pressure during cooling, we believe there are two primary candidates for its origin: either the intercalation of excess oxygen, perhaps in molecular form, within the unit cell or significant amounts of cation disorder driven by the imbalance of cation charges in the presence of high oxygen pressures.

The scenario of excess oxygen incorporation is most appealing to us. Manthiram *et al.*[1] have proposed the formation of molecular oxygen (peroxides) in the basal plane to explain the oxygenation of lanthanum-doped YBCO where equilibrium oxygen contents of $y > 7.00$ would be expected to compensate for the carriers lost to the La substitution. Peroxides would be expected to have a much slower diffusion rate than atomic oxygen because of their larger size. Therefore, they could only be incorporated into very thin films at relatively high substrate temperatures, perhaps above the orthorhombic-to-tetragonal transition. Films with greater amounts of calcium could incorporate more peroxides because of the tremendous enhancement of oxygen mobility observed for calcium-substituted YBCO.[29] While the incorporation of peroxides could explain these anomalies, the issue needs to be resolved by further study.

V. CONCLUSIONS

We have systematically studied the variations of normal-state thermopower and conductivity with oxygen content in high-quality, epitaxial thin films of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with $0 \leq x \leq 0.3$. The superconducting transition temperature was found to vary parabolically with conductivity for all films studied with a universal scaling behavior for single-phase samples. This behavior of $T_c(\sigma)$ is consistent with a linear dependence of the conductivity on carrier concentration with a scattering rate that increases with increasing amounts of calcium.

The room-temperature thermopower $S_{295\text{ K}}$ was found to obey the same universal correlation with T_c/T_c^* as was found by Obertelli *et al.*[20] for a wide variety of hole-doped bulk samples. This correlation holds for films of varying T_c^*'s and calcium contents, suggesting an intrinsic, universal origin of the thermopower that is independent of the additional electronic scattering due to calcium impurities.

Using the empirical correlation between $S_{295\text{ K}}$ and p determined by Obertelli *et al.*,[20] we were able to determine the electronic carrier concentration in our thin films. The thermopower was shown to be far superior to conductivity in determining the carrier concentration because it is less sensitive to extrinsic influences, and does not require normalization to a value determined through an entire series of oxygen anneals. Using the thermopower to determine the carrier concentration, we found that the normalized T_c's of all our calcium-doped films have a single parabolic dependence on p with a maximum at $p^* = 0.167$.

Based on a simple model relating the oxygen content to the carrier concentration, we showed that the additional carriers introduced by calcium doping were completely compensated by the creation of oxygen vacancies under equilibrium oxygen conditions in 1.0 atm O_2 at 480 °C. This is exactly what has been seen in bulk samples of the same materials, confirming that the properties of our thin films are representative of the bulk material.

We speculate that the very slight amount of overdoping observed for the sample with $x = 0.3$ could be caused by the incorporation of low-mobility peroxides during deposition or during post-deposition cooling in oxygen. This mechanism might also explain why other researchers have observed a greater amount of overdoping in calcium-doped YBCO films prepared by different techniques.

ACKNOWLEDGMENTS

We would like to thank T. H. Geballe, J. MacManus-Driscoll, J. L. Tallon, and L. Antognazza for helpful discussions. We would also like to thank T. P. Orlando for a critical reading of the manuscript, and the Electric Power Research Institute (EPRI) for funding.

[1] A. Manthiram, S. J. Lee, and J. B. Goodenough, J. Solid State Chem. **73**, 278 (1988).

[2] A. Manthiram and J. B. Goodenough, Physica C **159**, 760 (1989).

[3] C. Greaves and P. R. Slater, Supercond. Sci. Technol. **2**, 5 (1989).

[4] E. M. McCarron III, M. K. Crawford, and J. B. Parise, J. Solid State Chem. **78**, 192 (1989).

[5] D. E. Morris *et al.*, in *High Temperature Superconductors: Fundamental Properties and Novel Materials Processing*, edited by D. Christen, J. Narayan, and L. Schneemeyer, MRS Symposia Proceedings No. 169 (Materials Research Society, Pittsburgh, PA, 1990), pp. 237–240.

[6] C. Gledel, J. F. Marucco, and B. Touzelin, Physica C **165**, 437 (1990).

[7] Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzal, Phys. Rev. B **38**, 7156 (1988).

[8] R. G. Buckley *et al.*, Physica C **174**, 383 (1991).

[9] R. G. Buckley, J. L. Tallon, D. M. Pooke, and M. R. Presland, Physica C **165**, 391 (1990).

[10] B. Fisher *et al.*, Phys. Rev. B **47**, 6054 (1993).

[11] G. Xiao and N. S. Rebello, Physica C **211**, 433 (1993).

[12] Y. Sun *et al.*, Physica C **206**, 291 (1993).

[13] C. Legros-Gledel *et al.*, Physica C **175**, 279 (1991).

[14] E. S. Hellman *et al.*, J. Mater. Res. **4**, 476 (1989).

[15] V. Matijasevic *et al.*, J. Mater. Res. **6**, 682 (1991).

[16] K. Shinohara *et al.*, Appl. Phys. Lett. **58**, 756 (1991).

[17] R. Feenstra, D. K. Christen, C. E. Klabunde, and D. J. Budai, Phys. Rev. B **45**, 7555 (1992).

[18] R. Feenstra *et al.*, in *Layered Superconductors: Fabrication, Properties and Applications*, Materials Research Society, edited by D. T. Shaw, C. C. Tsuei, T. R. Schneider, and Y. Shiohara, MRS Symposia Proceedings No. 275 (Materials Research Society, Pittsburgh, PA, 1992), p. 101.

[19] J. L. MacManus-Driscoll *et al.*, Physica C **232**, 288 (1994).

[20] S. D. Obertelli, J. R. Cooper, and J. L. Tallon, Phys. Rev. B **46**, 14928 (1992).

[21] H. M. Appelboom, H. Sato, and M. Naito, Physica C **221**, 125 (1994).

[22] V. C. Matijasevic *et al.*, Physica C **235-240**, 2097 (1994).

[23] L. Antognazza, K. Char, and T. H. Geballe (unpublished).

[24] C. B. Eom *et al.*, Physica C **171**, 354 (1990).

[25] Model TM-1B oxygen analyzer, Ametex, Thermox Instruments Division, 150 Freeport Road, Pittsburgh, PA 15238.

[26] B. M. Lairson, Ph.D. thesis, Stanford University, 1991, p. 36.

[27] S. J. Rothman, J. L. Routbort, and J. E. Baker, Phys. Rev. B **40**, 8852 (1989).

[28] S. J. Rothman, J. L. Routbort, U. Welp, and J. E. Baker, Phys. Rev. B **44**, 2326 (1991).

[29] J. L. Tallon *et al.*, Physica C **171**, 61 (1990).

[30] N. Cusack and P. Kendall, Proc. Phys. Soc. London **72**, 898 (1958).

[31] R. B. Roberts, Philos. Mag. **36**, 91 (1977).

[32] T. A. Friedmann, J. P. Rice, J. Giapintzakis, and D. M. Ginsberg, Phys. Rev. B **42**, 6217 (1990).

[33] T. A. Friedmann, J. P. Rice, J. Giapintzakis, and D. M. Ginsberg, Phys. Rev. B **39**, 4258 (1989).

[34] N. P. Ong *et al.*, Physica C **153-155**, 1072 (1988).

[35] R. J. Cava *et al.*, Phys. Rev. B **36**, 5719 (1987).

[36] J. M. Tarascon *et al.*, Phys. Rev. B **36**, 226 (1987).

[37] R. J. Cava *et al.*, Phys. Rev. B **58**, 1676 (1987).

[38] E. D. Specht *et al.*, Phys. Rev. B **37**, 7426 (1988).

[39] J. Ye and K. Nakamura, Phys. Rev. B **48**, 7554 (1993).

[40] J. L. Tallon, Physica C **176**, 547 (1991).

[41] J. B. Torrance *et al.*, Phys. Rev. Lett. **61**, 1127 (1988).

[42] W. A. Groen, D. M. de Leeuw, and L. F. Feiner, Physica C **165**, 55 (1990).

[43] M. R. Presland *et al.*, Physica C **176**, 95 (1991).

[44] H. Zhang and H. Sato, Phys. Rev. Lett. **70**, 1697 (1993).

[45] H. Takagi *et al.*, Phys. Rev. B **40**, 2254 (1989).

[46] A. Maeda *et al.*, Phys. Rev. B **41**, 6418 (1990).

[47] T. Wada *et al.*, Phys. Rev. B **44**, 2341 (1991).

[48] J. B. Torrance *et al.*, Phys. Rev. B **40**, 8872 (1989).

[49] B. Keimer *et al.*, Phys. Rev. B **46**, 14 034 (1992).

[50] R. J. Birgeneau, Am. J. Phys. **58**, 28 (1990).

[51] J. L. Tallon, Physica C **168**, 85 (1990).

[52] A. Tokiwa *et al.*, Jpn. J. Appl. Phys. **27**, L1009 (1988).

[53] N. Y. Chen, V. C. Matijasevic, J. E. Mooij, and D. van der Marel, Phys. Rev. B **50**, 16 125 (1994).

[54] J. K. Burdett, Physica C **191**, 282 (1992).

[55] B. W. Veal and A. P. Paulikas, Physica C **184**, 321 (1991).

[56] R. J. Cava *et al.*, Physica C **165**, 419 (1990).

[57] J. D. Jorgensen *et al.*, Phys. Rev. B **41**, 1863 (1990).

[58] D. de Fontaine, G. Ceder, and M. Asta, Nature **343**, 544 (1990).

[59] *Oxygen Disorder Effects in High-T_c Superconductors*, edited by J. L. Morán and I. K. Schuller (Plenum, New York, 1990).

[60] R. Beyers and T. M. Shaw, in *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic Press, San Diego, 1989), Vol. 42, pp. 135–212.