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Thermoelectric power of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$: Contributions from CuO_2 planes and CuO chains

C. Bernhard
Universität Konstanz, Fakultät für Physik, D-78434 Konstanz, Germany

J. L. Tallon
Rutherford Institute for Physical Sciences, P.O. Box 31310, Lower Hutt, New Zealand

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The thermoelectric power (TEP) has been studied for polycrystalline $(Y,Yb)_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with variable Ca and O content. The partial substitution of Y^{3+} by Ca^{2+} introduces additional hole carriers into the CuO_2 planes and allows the 123 system access far into the overdoped regime. Consequently, the CuO chains can be strongly deoxygenated until they are nonmetallic (and no more contribute to the TEP), while the CuO_2 planes still are optimally doped ($T_c = T_{c,\max}$) or even slightly overdoped. Over a fairly wide range of doping this enables us to study the TEP of the 123 system as it arises solely from the CuO_2 planes (''plane contribution''). This ''plane contribution'' is in good agreement with the general trend reported for various Bi and Tl compounds [S. D. Obertelli, J. R. Cooper, and J. L. Tallon, Phys. Rev. B **46**, 14 928 (1992)]. For samples with almost fully oxygenated CuO chains, assuming independent TEP contributions from CuO_2 planes and CuO chains, we deduce a ''chain contribution'' which is very similar to the results obtained on untwinned single crystals [J. L. Cohn *et al.*, Phys. Rev. B **45**, 13 140 (1992)]. [S0163-1829(96)04738-8]

INTRODUCTION

Recent experiments revealed a close relationship between the unusual electronic properties of the cuprate high-T_c superconductors and the charge (hole) carrier concentration of the CuO_2 planes, p_{pl}.[1] Scaling relations upon p_{pl} have been reported for several electronic properties in the superconducting and in the normal state, including the critical temperature T_c,[2] the magnetic penetration depth λ,[3] the resistivity,[4] the Hall number,[5] the spin susceptibility,[6] and the thermoelectric power (TEP).[7]

The TEP is a very impressive example where the characteristic features of the unusual temperature dependence and even the absolute values have been shown to vary with p_{pl} in a systematic way.[7] Almost identical results have been obtained for various compounds spanning the entire doping range from the very underdoped to the strongly overdoped regime.[7,8] p_{pl} was determined here either using a bond valence sum (BVS) analysis,[9] assuming a unique dependence of $T_c/T_{c,\max}$ upon p_{pl},[2] or from the chemical substitution level x in $La_{2-x}Sr_xCuO_4$ and $Y_{1-x}Ca_xBa_2Cu_3O_6$.[8]

As shown in Fig. 1, the characteristic features of $S(T)$ and their variation with p_{pl} can be summarized as follows. For the entire underdoped to the optimally doped regime $S(T_c<T<290\ \mathrm{K})$ typically has positive values. $S(T>T_c)$ first rises towards a maximum at a temperature T^* before $S(T>T^*)$ decreases almost linearly with temperature (at least up to room temperature). The negative slope of $S(T>T^*)$ does not change very much with the doping state of the CuO_2 planes and is very similar for the various compounds. The absolute values of $S(T)$ and T^*, however, exhibit a strong and systematic decrease with p_{pl}. The room temperature value, $S(290\ \mathrm{K})$, as a convenient parameter, falls nearly exponentially with p_{pl} from $S(290\ \mathrm{K})\sim 500\ \mu\mathrm{V/K}$ for the undoped samples ($p_{\mathrm{pl}}=0$) towards $S(290\ \mathrm{K})=1\text{–}2\ \mu\mathrm{V/K}$ in case of optimal doping ($p_{\mathrm{pl}}\sim 0.16$). T^* appears to be higher than room temperature for the strongly underdoped samples but falls systematically with p_{pl} as well and is already very close to T_c in the case of the optimally doped samples. Recent experiments have indicated that T^* is closely related with the temperature at which a ''pseudogap'' starts to develop in the excitation spectrum of the normal state[10] as evidenced for example in the specific heat,[11] the NMR relaxation rate and Knight shift[12] and the resistivity.[13] In the overdoped regime T^* seems to fall below T_c (Refs. 10 and 11) and the upturn of $S(T>T_c)$ starts to diminish while

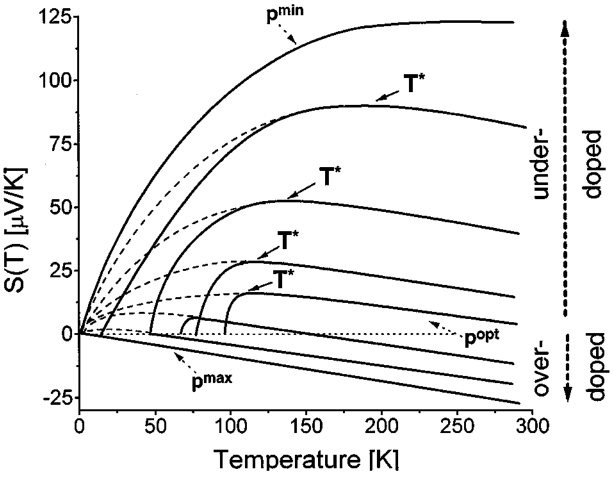

FIG. 1. The evolution of $S(T)$ as a function of the doping state of the CuO_2 planes (in the superconducting regime) is sketched by the solid lines. The dashed lines indicate the expected $S(T)$ in the absence of superconductivity. Labeled by $p^{\min}$ ($p^{\max}$) are the points where superconductivity disappears on the underdoped (overdoped) side. $S(T)$ for optimally doped CuO_2 planes (corresponding to $T_c = T_{c,\max}$) is labeled by p^{opt}. The solid arrows indicate the position of the maxima in $S(T)$ at T^*.

$S(T>T_c)$ still decreases almost linearly with temperature.[7] $S(290\text{ K})$ therefore changes sign shortly past optimum doping and is negative, growing in magnitude more or less linearly related to p_{pl}.

Deviations from this general trend so far have been observed only for two classes of systems. For the YBCO compounds $YBa_2Cu_3O_{7-\delta}$ (Y-123),[14] $YBa_2Cu_4O_8$ (Y-124),[10] and $Y_2Ba_4Cu_7O_{15-\delta}$ (Y-247),[15] they occur when the CuO chains are almost fully oxygenated and become metallic. In $La_{2-x}Sr_xCuO_4$ (La-214) and structurally related compounds[7,16] they appear when the carrier concentration exceeds $p_{\text{pl}}\sim 0.12$.

The deviations in the TEP of the YBCO compounds can be explained by the CuO chains that become metallic when nearly fully oxygenated ($\delta<0.30$) and provide a contribution to the TEP (''chain contribution'') additional to the CuO_2 planes (''plane contribution'').[7] The metallicity of the fully oxygenated CuO chains has been demonstrated by a number of experimental techniques including NMR,[17] IR reflectivity,[18] and dc conductivity.[13,19,20] Recent muon-spin-relaxation (μSR) experiments[21] and optical reflectivity measurements[22] have indicated that the CuO chains also become superconducting. Direct evidence for the ''chain contribution'' to the TEP comes from experiments on untwinned single crystals where a pronounced anisotropy has been observed between the components parallel (S_b) and perpendicular (S_a) to the CuO chains.[23,24]

For polycrystalline samples the measured TEP consists of the powder average as weighted by the electrical conductivity σ. Due to its very low conductivity $\sigma_c \ll (\sigma_a,\sigma_b)$ the component along the c axis can be neglected. Assuming that CuO_2 planes and CuO chains contribute independently to the TEP along the b direction parallel to the CuO chains according to $S_b=(2\sigma^{\text{pl}}S^{\text{pl}}+\sigma^{\text{ch}}S^{\text{ch}})/(2\sigma^{\text{pl}}+\sigma^{\text{ch}})$, while only the CuO_2 planes are conducting along the a direction perpendicular to the CuO chains with $S_a=S^{\text{pl}}$, one derives that

$$S^{\text{poly}}=\frac{4\sigma^{\text{pl}}S^{\text{pl}}+\sigma^{\text{ch}}S^{\text{ch}}}{4\sigma^{\text{pl}}+\sigma^{\text{ch}}}. \tag{1}$$

For almost fully oxygenated $YBa_2Cu_3O_{7-\delta}$ with $\delta<0.3$,[7] Y-124,[10] and Y-247,[15] it was shown that the appearance of the ''chain contribution'' is accompanied by clear changes in the temperature dependence of $S^{\text{poly}}(T)$. While the ''plane contribution'' typically gives rise to a negative slope, the ''chain contribution'' has a large positive slope.[7,10,15] It is interesting to note that in case of Y-123 the absolute values of $S(290\text{ K})$ are only moderately affected by the ''chain contribution'' indicating that $S^{\text{ch}}(290\text{ K})$ and $S^{\text{pl}}(290\text{ K})$ around optimum doping are rather similar.[7]

The ''chain contribution'' disappears once the CuO chains are sufficiently deoxygenated for $\delta>0.30$.[7,14] Such a deoxygenation of the CuO chains, however, is accompanied by a reduction of p_{pl} and $YBa_2Cu_3O_{7-\delta}$ is already strongly underdoped when $\delta>0.30$. For polycrystalline samples of $YBa_2Cu_3O_{7-\delta}$ it is therefore not possible to study solely the ''plane contribution,'' S^{pl}, over a wider range of doping without the admixture of the ''chain contribution.''

Less well understood are the deviations that occur in the TEP of the system $La_{2-x}(Sr,Ba)_xCuO_4$ (La-214). While $S(T)$ follows the trend of the other compounds in the low doping regime for $p_{\text{pl}}<0.12$,[7] clear deviations have been shown to occur towards higher carrier concentration when $p_{\text{pl}}>0.12$.[7,16] The magnitude of $S(T)$ decreases here much more slowly with p_{pl} and $S(290\text{ K})$ stays positive even for heavily overdoped samples.[16] A similar effect has been observed for T^* which appears to be almost independent from doping for $p_{\text{pl}}>0.12$.[16] The reasons for these deviations in the TEP of the $La_{2-x}(Sr,Ba)_xCuO_4$ system are not yet clear. We can only speculate that they may arise from scattering effects associated with the increasing concentration of oxygen vacancies within the CuO_2 planes which occur especially for $x>0.12$.[25] Structural instabilities that are related to the orthorhombic-tetragonal transition may also have some effect.[26]

Others have suggested that $La_{2-x}Sr_xCuO_4$ provides an ideal model system for studying the ''plane contribution,'' S_{pl} as it arises solely from the charge carriers within the CuO_2 planes.[16] For all the Bi and Tl systems, they have argued that an additional contribution to the TEP arises from the BiO and TlO layers (like the ''chain contribution'' in the YBCO compounds) and accounts especially for the negative values of $S(T)$ in the overdoped samples.[16] It is quite hard to imagine, however, that the different layers of $(Bi,Pb)_2O_2$, $(Tl,Pb)_2O_2$, and (Tl,Pb)O, with the incorporation of various amounts of lead and excess oxygen, should provide the same contribution to the TEP as controlled solely by the doping state of the CuO_2 planes, p_{pl}. The same applies for the Hg cuprates for which the TEP correlates in the same way.[27]

One way to clarify this controversial situation is to measure the ''plane contribution'' to the TEP as it arises for an optimally doped 123-type sample when the CuO chains are strongly deoxygenated and any ''chain contribution'' is known to be absent. The trend of the $La_{2-x}(Sr,Ba)_xCuO_4$ system then would be confirmed if one finds that $S(T)$ is largely positive with $S(290\text{ K})\sim 20\ \mu$V/K. In case one finds $S(290\text{ K})\sim 1$–$2\ \mu$V/K, however, it becomes clear that the TEP of the various Bi and Tl compounds[7] represent the general trend for the ''plane contribution'' as a function of p_{pl}. The TEP obtained for the La-214 system then should be regarded as an exception to the otherwise general trend.

SAMPLE PREPARATION AND CHARACTERIZATION

We addressed this issue by studying the TEP of polycrystalline samples of the system $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with different Ca concentrations of $x=0$, 0.05, 0.10, 0.15, and 0.20 and variable oxygen content of $0.04\leqslant\delta\leqslant 0.98$. The idea is that the substitution of Y^{3+} by Ca^{2+} introduces additional hole carriers into the CuO_2 planes, independently from the (de)oxygenation of the CuO chains, δ. The counterproductive doping effect due to the Ca substitution and the depletion of the CuO chains then allows the preparation of samples of the 123-system with optimally-doped CuO_2 planes (corresponding to $T_c=T_{c,\max}$) but strongly deoxygenated CuO chains ($\delta>0.30$) that are nonmetallic and do not contribute to the TEP.

The preparation of such samples with a large amount of Ca on the Y site requires a careful protocol which has been described previously.[8] From neutron scattering experiments it was shown that we managed to incorporate the Ca almost exclusively on the Y site up to Ca concentrations of

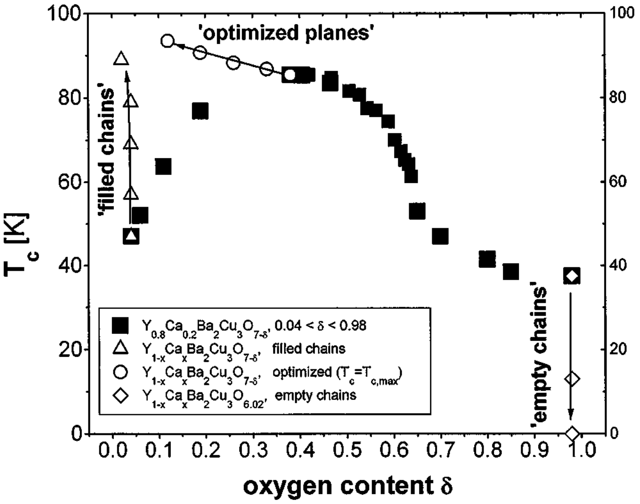

FIG. 2. The critical temperature T_c plotted as a function of the oxygen deficiency, δ, in the CuO chains for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$. The solid squares represent $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ with $0.04 \leqslant \delta \leqslant 0.98$. The open symbols are a series of samples with different Ca content $x=0$, 0.05, 0.1, 0.15, and 0.2, where the CuO chains are fully oxygenated with $\delta \leqslant 0.04$ (open triangles), the oxygen content of the CuO chains is reduced specifically for each Ca content in such a way that the CuO_2 planes are optimally doped (open circles), and the CuO chains are completely deoxygenated ($\delta \sim 0.98$) (open diamonds). The solid arrows always point in the direction of decreasing Ca content.

$x=0.15$.[8] Only for Ca concentration in excess of $x>0.15$ a small fraction of the Ca starts to occupy the Ba site ($x_{eff}<x$) and minor amounts of $BaCuO_2$ start to appear. Furthermore, we investigated the changes in the (hole) carrier concentration of the CuO_2 planes (Δp_{pl}) that are induced by the substitution of Y^{3+} by Ca^{2+}. For a series of samples with equally oxygenated CuO chains (with a fixed amount of charges transferred from the CuO chains), either fully oxygenated ($\delta=0.04$) or completely deoxygenated ($\delta=0.98$) (as confirmed by the neutron experiments), we studied the evolution of the critical temperature, T_c, as a function of the Ca concentration on the Y site, x_{eff}. Assuming that T_c exhibits a unique dependence upon p_{pl} as reported in Ref. 2 we deduced that all the holes incorporated by the substitution of Y^{3+} by Ca^{2+} are transferred into the CuO_2 planes, corresponding to $\Delta p_{pl}=x_{eff}/2$.[8] Such a variation of p_{pl} upon x_{eff} was confirmed independently by a bond valence sum (BVS) analysis based on the results of the neutron scattering experiments.[8]

RESULTS AND INTERPRETATION

A. Critical temperature

Shown in Fig. 2 is the evolution of the critical temperature, T_c, as a function of the oxygen content, δ. Represented by the full squares are our data for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ with $x_{eff}=0.18$ and a variable oxygen content of $0.04 \leqslant \delta \leqslant 0.98$. The fully oxygenated sample with $\delta=0.04$ is strongly overdoped with $T_c=46$ K. Upon a reduction of the oxygen content, and thus of p_{pl}, T_c increases up to the maximal critical temperature of $T_{c,max}=85.5$ K for $\delta=0.38$ at optimal doping. Upon a further deoxygenation of the CuO chains beyond $\delta>0.38$ the CuO_2 planes become underdoped and T_c is suppressed down to $T_c=38$ K for $\delta>0.8$. No further changes occur in T_c in the range $0.8 \leqslant \delta \leqslant 0.98$, indicating that no charge carriers are transferred to the CuO_2 planes as long as the CuO chains are only lightly oxygenated. This circumstance was recognized earlier for the Ca-free $YBa_2Cu_3O_{7-\delta}$ where the Néel temperature is almost unaffected for $0.8<\delta<1$, even though T_N is known to be rapidly suppressed already by a very small amount of charge carriers within the CuO_2 planes.[28] This effect was quantified using bond valence sums determined from neutron diffraction data[8] and the results reported below concur numerically with this.

Shown by the open triangles are the samples which have fully oxygenated CuO chains with $\delta \leqslant 0.04$. While $YBa_2Cu_3O_{6.98}$ is only slightly overdoped with $T_c=89$ K, the CuO_2 planes are progressively overdoped and T_c is successively diminished towards higher Ca content to $T_c=79$ K for $x=0.05$, $T_c=69$ K for $x=0.10$, $T_c=57$ K for $x=0.15$, and $T_c=46$ K for $x=0.20$ ($x_{eff}=0.18$). The open circles represent a series, where for each Ca content of $x=0$, 0.05, 0.10, 0.15, and 0.20, the CuO_2 planes have been optimally doped corresponding to $T_c=T_{c,max}$. Optimum doping was ensured for each Ca content specifically by the depletion of the CuO chains until any further reduction (increase) of the oxygen content caused T_c to decrease towards the underdoped (overdoped) side. The corresponding δ values have been determined from the mass changes relative to the fully-oxygenated samples. They are $\delta=0.38$ for the samples with $x=0.20$ ($x_{eff}=0.18$) and $T_{c,max}=85.5$ K, $\delta=0.32$ for $x=x_{eff}=0.15$ and $T_{c,max}=86.3$ K, $\delta=0.26$ for $x=x_{eff}=0.10$ and $T_{c,max}=87.9$ K, $\delta=0.19$ for $x=x_{eff}=0.05$ and $T_{c,max}=91$ K and $\delta=0.12$ for $x=0$ and $T_{c,max}=93.5$ K. The changes in the oxygen deficiency, δ, of the CuO chains and the Ca content, x, appear to be almost linearly related. Assuming that the optimal doping of the CuO_2 planes always occurs at the same carrier concentration (independent of the oxygenation of the CuO chains) and furthermore, that the hole carriers created by the substitution of Y^{3+} by Ca^{2+} are transferred directly into the CuO_2 planes [as indicated by the changes of T_c for the fully (de)oxygenated samples[8]] we derive that about 1/3 of the charge carriers introduced into the CuO chains are subsequently transferred to the CuO_2 planes, corresponding to $\Delta x_{eff}/2-\Delta\delta/3 \sim \Delta p_{pl} \sim$const. This value is in good agreement with previous estimates for $YBa_2Cu_3O_{7-\delta}$.[8] Moreover, the open diamonds represent the underdoped samples which have completely deoxygenated CuO chains ($\delta=0.98$). Here, only the sample for $x=0.15$ and $x=0.20$ ($x_{eff}=0.18$) are superconducting with $T_c=13$ and 38 K.

B. The TEP for samples with fully oxygenated CuO chains

We have further investigated these samples by measuring the thermoelectric power (TEP) $S(T)$ as a function of temperature ($T<300$ K) using conventional methods.[7] Shown in Fig. 3 is $S(T)$ for the samples with fully-oxygenated CuO chains and different Ca concentrations of $x=0$, 0.05, 0.10, 0.15, and 0.20. For all these samples $S(T)$ exhibits features that are characteristic of the presence of a significant ''chain contribution'' to the overall TEP.[7,14,15] A fall in $S(T>T_c)$ to large negative values just above T_c is followed by nearly

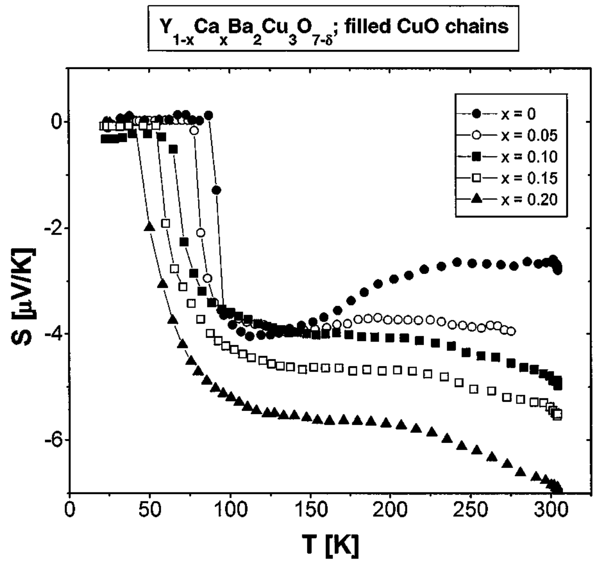

FIG. 3. The TEP plotted as a function of temperature for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with fully oxygenated CuO chains ($\delta \leqslant 0.04$) but different Ca content of $x=0$ (solid circles), $x=0.05$ (open circles), $x=0.01$ (solid squares), $x=0.15$ (open squares), and $x=0.2$ (solid triangles).

constant or moderately increasing values of $S(T>120\text{ K})$ towards room temperature. It can be seen from Fig. 3 that the negative values of $S(T)$ increase in magnitude towards higher Ca content where the CuO_2 planes are more strongly overdoped (as evident from the reduced T_c values). Irrespective of the peculiar temperature dependence of $S(T)$, this demonstrates that the overdoped CuO_2 planes give rise to a negative TEP, similar to what is observed in the case of overdoped Bi and Tl compounds,[7] but in clear contradiction to the case of overdoped $La_{2-x}Sr_xCuO_4$ where $S(T)$ stays positive.[16] We would like to point out that the negative shift of the TEP with increasing Ca content cannot be explained in terms of an increase of the negative "chain contribution." First of all, it is confirmed from neutron refinement that all these samples have almost the same oxygen content of $\delta \leqslant 0.04$.[8] Furthermore, the neutron scattering experiments indicate that the incorporation of Ca enhances the occupancy of the "off-chain" O(5) position and so introduces additional disorder into the CuO chains which should reduce the "chain contribution" to the TEP.[8] Indeed, using the slope of $S(T>120\text{ K})$ as a rough estimate for the relative weight of the "chain contribution" (the "plane contribution" always has a negative slope,[7] while the slope of the "chain contribution" is positive[7,14,15]) such a trend may be seen in Fig. 3. Finally, with increasing overdoping the TEP is weighted more strongly to S^{pl} as σ^{pl} continues to increase.

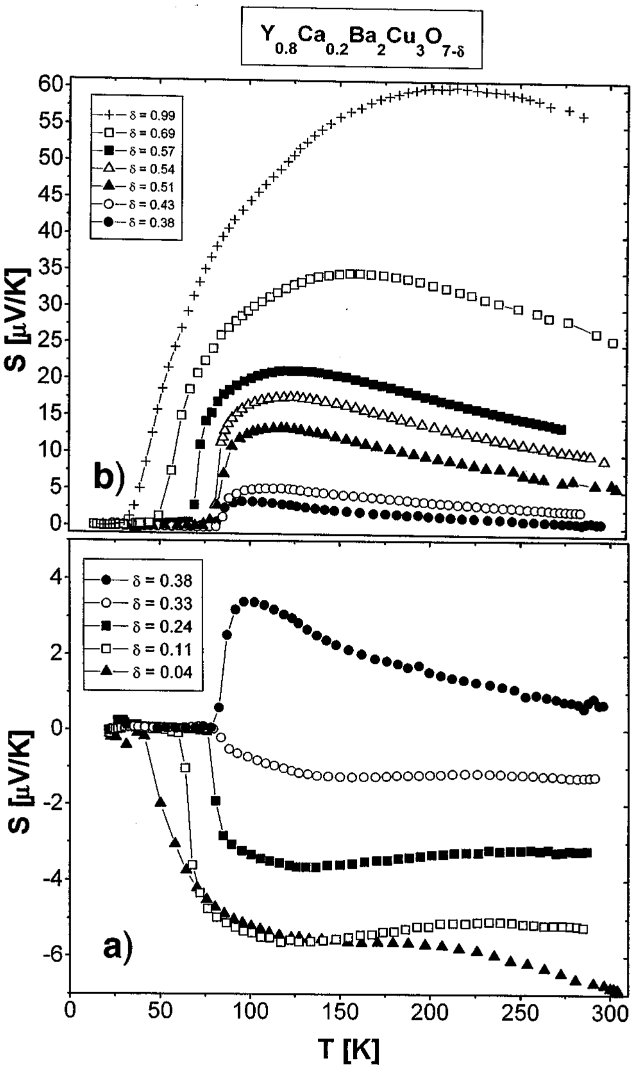

FIG. 4. The TEP plotted as a function of temperature for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$: (a) for overdoped to optimally doped samples with $\delta=0.04$ (solid triangles), $\delta=0.11$ (open squares), $\delta=0.24$ (solid squares), $\delta=0.33$ (open circles), and $\delta=0.38$ (solid circles); (b) for optimally to underdoped samples with $\delta=0.38$ (solid circles), $\delta=0.43$ (open circles), $\delta=0.51$ (solid triangles), $\delta=0.54$ (open triangles), $\delta=0.57$ (solid squares), $\delta=0.69$ (open squares), and $\delta=0.99$ (crosses).

C. The TEP for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ with variable oxygen content

Shown in Fig. 4(a) is $S(T)$ for a series of optimally-doped to strongly-overdoped samples of $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ with $0.38 \geqslant \delta \geqslant 0.04$. The Ca content is fixed here and it is the variation of the oxygen content of the CuO chains, δ, that determines the changes in p_{pl}. The fully-oxygenated sample with $\delta=0.04$ is strongly overdoped with $T_c=46$ K. For the samples with oxygen depleted CuO chains the CuO_2 planes are less strongly overdoped and T_c is increased up to its maximum of $T_c=T_{c,\max}=85$ K for $\delta=0.38$. Again, the most negative values of $S(T)$ are found for the most strongly overdoped and fully oxygenated sample as was shown already in Fig. 3. The negative values of $S(T)$ are stepwise decreased for the samples which have less strongly overdoped CuO_2 planes. Simultaneously, however, the negative "chain contribution" is reduced now by the deoxygenation of the CuO chains and accounts at least in part for this effect. The relative weight of the "chain contribution" again may be roughly estimated from the slope of $S(T)$. The "chain contribution" is almost absent for the strongly deoxygenated and optimally-doped sample with $\delta=0.38$. For the only slightly deoxygenated samples with $\delta=0.11$ and 0.19, however, it appears to be even a little increased as compared to the fully oxygenated sample with $\delta=0.04$. At present we are not sure if this effect is real and possibly related to the fact that the oxygen in the O(5) position is removed first upon the deoxygenation of the CuO chains, thereby increasing the ordering and the metallicity of the CuO chains. Neutron scattering experiments are under way that might clarify this point.[29]

Most notable is the TEP for the optimally-doped sample with $T_c = T_{c,\max} = 85.5$ K and $\delta = 0.38$. The monotonic and nearly linear decrease of $S(T > 100\ \text{K})$ indicates that its TEP arises mainly from the charge carriers within the CuO_2 planes while the ''chain contribution'' is almost absent. In fact, there appears a striking similarity to the TEP as it is typically observed for the optimally-doped samples of all the different Bi and Tl compounds.[7] The similarity holds not only for the overall shape of $S(T)$ with T^* being close to T_c and $S(T > T^*)$ decreasing almost linearly with temperature, but also for the absolute values with $S(290\ \text{K}) \sim 1\text{–}2\ \mu\text{V/K}$. Our data therefore support the conclusions that the TEP of the Bi and Tl compounds arises solely from the charge carriers within the CuO_2 planes[7] and thereby leaves the case of the optimally-doped $La_{1.85}Sr_{0.15}CuO_4$ with $T^* \sim 140$ K and $S(290\ \text{K}) \sim 20\ \mu\text{V/K}$ (Ref. 16) as the exception from the otherwise general trend.

Shown in Fig. 4(b) is $S(T)$ for the more strongly deoxygenated and consequently underdoped samples of $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ for $0.98 \geqslant \delta \geqslant 0.38$. For all these samples $S(T)$ exhibits the typical features of the ''plane contribution,'' S^{pl}, i.e., an increase of $S(T > T_c)$ to a maximum at a temperature T^* and an almost linear decrease of $S(T > T^*)$ towards room temperature.

Shown in Fig. 5 are the results for $S(290\ \text{K})$ as a function of p_{pl} represented by the full squares for the fully oxygenated series $Y_{1-x}Ca_xBa_2Cu_3O_{6.96}$ for $0 \leqslant x \leqslant 0.2$ (see as well Fig. 3) and by the full circles for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ for $0.04 \leqslant \delta \leqslant 0.98$ [see as well Figs. 4(a) and 4(b)]. p_{pl} has been calculated from the suppression of the relative critical temperature $T_c/T_{c,\max}$ using the empirical formula

$$T_c/T_{c,\max} = 1 \pm 82.6(p_{\text{pl}} - 0.16)^2 \qquad (2)$$

as given in Ref. 2. Included for comparison are representative results for Bi-, Tl-, and Y-123 systems as they were shown in Refs. 7 and 8. From this plot it becomes obvious that $S(290\ \text{K})$ of the 123 system follows the trend reported by Obertelli, Cooper, and Tallon.[7] Even though the temperature dependence of $S(T)$ is clearly affected by the appearance of the ''chain contribution'' in the case of $\delta < 0.3$ [see Figs. 3 and 4(a)], it appears that the room temperature values (somewhat accidentally) are only weakly modified by the ''chain contribution'' (at least on the relevant scale of the large changes that occur when p_{pl} is varied).

In this context we would like to comment on the seemingly contradictory results that have been reported in a similar work where the ''plane contribution'' to the TEP was investigated for $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_7$ with $x \leqslant 0.4$.[30] It was concluded there that a large positive TEP arises from the optimally-doped CuO_2 planes of the 123-type system with $S(290\ \text{K}) \sim 10\ \mu\text{V/K}$, very similar to the case of $La_{1.85}Sr_{0.15}CuO_4$. The ''chain contribution'' was supposedly suppressed here by the substitution of large amounts of Ba by La, while a constant doping level of the CuO_2 planes (optimally doped) was believed to be ensured by the fully-oxygenated CuO chains combined with the codoping effect that was thought to arise from the substitution of equal amounts of Y^{3+} by Ca^{2+} and Ba^{2+} by La^{3+}. It is the latter point that we doubt, for it is a very complicated task in itself to incorporate large amounts of Ca exclusively on the Y site. Following the conditions of sample preparation as described in Ref. 30 we find that this is not possible, and even under optimized conditions this is possible only up to a limited amount for $x < 0.2$.[8] No indication has been given in Ref. 30 that the doping state of the CuO_2 planes is kept at a constant level. Therefore, it seems more likely to us that the large positive value of $S(290\ \text{K})$ for $x = 0.4$ simply indicates the fact that the CuO_2 planes are slightly underdoped. This point could be easily checked using, e.g., measurement of the NMR Knight shift.[31]

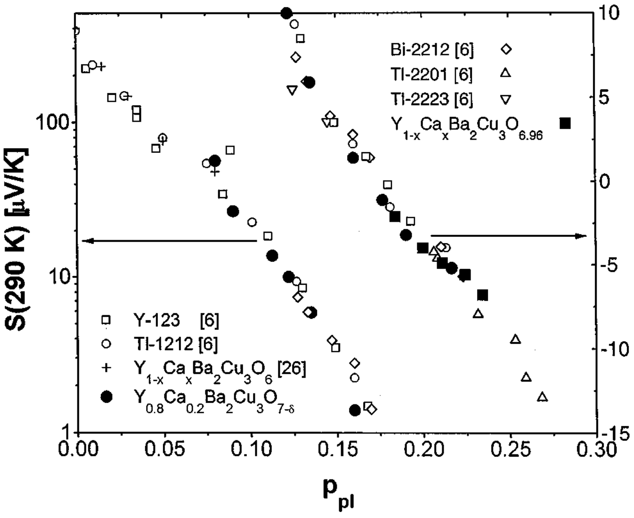

FIG. 5. The TEP at room temperature, $S(290\ \text{K})$, as a function of the hole concentration of the CuO_2 planes, p_{pl}. The values for p_{pl} have been estimated from the ratio of $T_c/T_{c,\max}$ assuming the relationship $T_c/T_{c,\max} = 1 \pm 82.6(p_{\text{pl}} - 0.16)^2$ (Ref. 2). The results for the underdoped to optimally doped samples are shown on a logarithmic scale, while those for the optimally doped to overdoped samples are shown on a linear scale (as indicated by the solid arrows). The solid squares represent our results for the fully oxygenated samples with different Ca content [for $S(T)$ see Fig. 3]. The solid circles are data for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ with variable oxygen content δ [for $S(T)$ see Figs. 4(a) and 4(b)]. Included by the open symbols (as labeled in the figure) are representative results for various Bi-, Tl- and Y-123 systems from Refs. 7 and 8.

D. Additional disruption of the CuO chains by Co substitution

We have further investigated the TEP of $Yb_{0.7}Ca_{0.3}Ba_2Cu_{2.9}Co_{0.1}O_{7-\delta}$, a 123-system where the CuO chains have been additionally disrupted by the substitution of Co on the Cu(1) site. The idea is that the substitution of Cu(1) by Co should ensure that the metallicity of the CuO chains is destroyed even faster upon deoxygenation of the CuO chains. When the ''chain contribution'' to the TEP has disappeared the CuO_2 planes then still might be in a slightly overdoped state. Using Yb instead of Y we attempted to reduce the size mismatch between the Ca^{2+} and the R^{3+} which assists the incorporation of larger amounts of Ca^{2+} on the site of the R^{3+}. For this series no neutron experiments

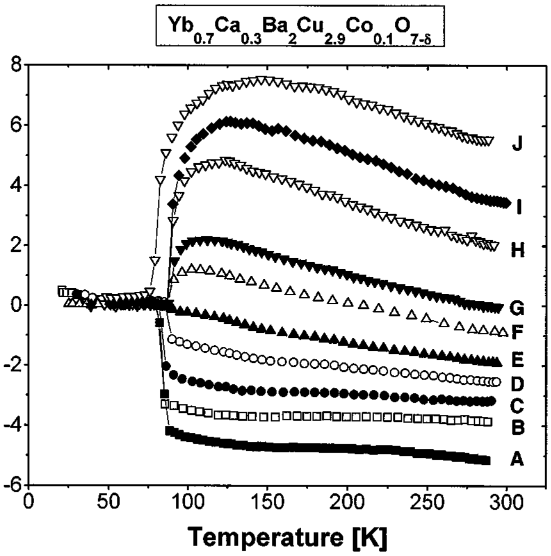

FIG. 6. The temperature dependence of the TEP for the system $Yb_{0.7}Ca_{0.3}Ba_2Cu_{2.9}Co_{0.1}O_{7-\delta}$. Samples A–G are overdoped with T_c=69, 81.8, 84.3, 86.1, 86.5, 87.3, and 87.9 K; T_c is increased upon the deoxygenation of the CuO chains. Sample H is optimally doped with $T_c=T_{c,\max}$=88.5 K and samples I and J are slightly underdoped with T_c=87.7 and 79.7 K. The negative slope of $\alpha=dS(T>T^*)/dT$, that occurs typically for samples where the ''chain contribution'' to the TEP is absent, can be seen to persist for the optimally doped sample H and even for the slightly overdoped samples G–E. A significant ''chain contribution,'' as indicated by a change towards positive slope, occurs only for the fully oxygenated samples where the CuO_2 planes are strongly overdoped.

have been performed to check for the Ca occupancy on the Yb site or for the absolute oxygen content. For a similar sample of $Lu_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$, however, neutron scattering experiments indicate that we managed to incorporate $x_{\mathrm{eff}}=0.235$ Ca on the R site.[29] Our fully oxygenated sample again is strongly overdoped with T_c=68 K. When oxygen is removed from the CuO chains T_c is increased towards the maximum value of $T_c=T_{c,\max}$=88.5 K, before it is decreased again on the underdoped side. The results of our TEP measurements are summarized in Fig. 6. Clear signatures of a ''chain contribution'' appear only for the fully oxygenated and strongly overdoped samples A–D. Even for the weakly deoxygenated samples E–G, for which the CuO_2 planes are still slightly overdoped, it can be seen that $S(T)$ exhibits the features that are typical for the ''plane contribution'' [i.e., the linear decrease of $S(T>T^*)$]. The overdoped state of these samples is apparent from the increase in T_c with the oxygen depletion and from the negative values of S(290 K) where $S(290\ \mathrm{K})=-1.9$ µV/K and T_c=86.5 K for sample E, $S(290\ \mathrm{K})=-0.9$ µV/K and T_c=87.3 K for sample F, and $S(290\ \mathrm{K})=-0.1$ µV/K and T_c=87.9 K for sample G. For the optimally doped sample H with T_c=88.5 K we find $S(290\ \mathrm{K})=2$ µV/K in good agreement with the results obtained on the optimally doped sample $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.62}$ shown above and indeed with most other cuprates. Finally, for the underdoped samples I and J S(290 K) is positive and grows in magnitude, while the negative slope of $S(T>T^*)$ is almost unchanged. Clearly, our data support the essential conclusions of Ref. 7. S^{pl}(290 K) changes sign and becomes negative shortly past optimum doping towards the overdoped side. The slope $\alpha=dS^{\mathrm{pl}}(T>T^*)/dT$ is almost unchanged and stays negative on the overdoped side. Our data demonstrate that the sign change in $\alpha=dS(T)/dT$ is related to the onset of the ''chain contribution'' to the TEP. The sign change in α, as it is observed for Ca-free $YBa_2Cu_3O_{7-\delta}$ around optimum doping, therefore is related to the onset of the ''chain contribution'' that coincides here rather accidentally with the optimal doping of the CuO_2 planes. In particular, this coincidence is specific to the composition $YBa_2Cu_3O_{7-\delta}$ and is not related to the electronic properties of the CuO_2 planes and in particular the presence of a van Hove singularity at the Fermi surface.[32,33]

E. The evolution of the ''chain condensate'' with oxygen depletion

We have further investigated the evolution of the ''chain condensate'' for a series of optimally-doped samples of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with (x=0, δ=0.12), (x=0.05, δ=0.19), (x=0.1, δ=0.26), (x=0.15, δ=0.32), and (x=0.2, δ=0.38). The equally optimally doped CuO_2 planes can be expected to provide an identical ''plane contribution'' to the TEP, so that the evolution of the chain contribution can be studied as a function of the oxygen content of the CuO chains. Our results for $S(T)$ are summarized in Fig. 7. The positive slope of $\alpha=dS(T>120\ \mathrm{K})/dT$ for $YBa_2Cu_3O_{6.88}$ indicates a rather strong ''chain contribution.'' The positive slope α (therefore the ''chain contribution'' to the TEP) can be seen to decrease systematically for the samples with higher Ca content which have more strongly deoxygenated CuO chains. Finally, α becomes negative for $\delta>0.30$ as is expected when the TEP is dominated by the ''plane contribution.'' For $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.62}$, the most strongly deoxygenated sample, $S(T)$ was shown already in Fig. 4(a) and discussed as an example where the TEP arises solely from the charge carriers within the optimally-doped CuO_2 planes. Overall, it appears from Fig. 7 that the ''chain contribution'' has quite a strong influence on shape and especially on the slope of $S(T\gg T^*)$, while the changes in S(290 K) are only minor (±1 µV/K) especially compared with the large changes that occur upon the variation of p_{pl}.

Assuming independent TEP contributions from CuO_2 planes and CuO chains, one can use Eq. (1) to extract the thermoelectric power (TEP) of the CuO chains, S^{ch}, from the measured TEP of the polycrystalline samples, provided one knows the ''plane contribution,'' S^{pl}, and the in-plane anisotropy of the conductivity parallel and perpendicular to the CuO chains, $\gamma=\rho_a/\rho_b=(2\sigma^{\mathrm{pl}}+\sigma^{\mathrm{ch}})/2\sigma^{\mathrm{pl}}$. We derive

$$S^{\mathrm{ch}}=(\gamma-1)^{-1}\{(\gamma+1)S^{\mathrm{poly}}-2S^{\mathrm{pl}}\}. \qquad (3)$$

A reasonably good estimate for S^{pl} can be derived from its unique dependence upon p_{pl} and upon the ratio $T_c/T_{c,\max}$.[7,8] In case of optimally doped samples we can use the experimentally measured TEP of the polycrystalline sample $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.62}$ for which $S^{\mathrm{poly}}\approx S^{\mathrm{pl}}$. The more critical quantity is the in-plane anisotropy of the conductivity, γ, which is experimentally accessible only for untwinned single crystals.[13,19,20,23] Unfortunately, only few such studies have been reported so far and in most cases the oxygen content was not determined very accurately. Even worse, an ad-

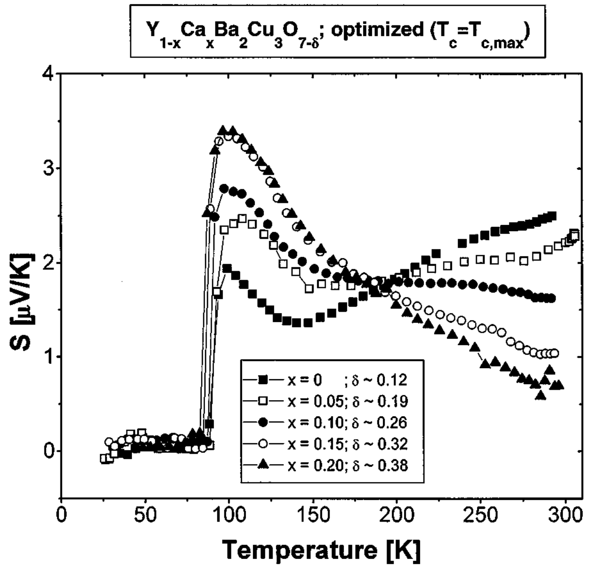

FIG. 7. The TEP plotted as a function of temperature for the series of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ where the depletion of the CuO chains was adjusted specifically for each Ca content in such a way that the CuO_2 planes are optimally doped with $T_c = T_{c,\max}$. Data are shown for $x=0.2$ and $\delta=0.38$ (solid triangles), $x=0.15$ and $\delta=0.32$ (open circles), $x=0.1$ and $\delta=0.26$ (solid circles), $x=0.05$ and $\delta=0.19$ (open squares), and $x=0$ and $\delta=0.12$ (solid squares). The slope $\alpha = dS(T>120\ \mathrm{K})/dT$ decreases successively and changes sign from positive (for $x=0$ and $\delta=0.12$) to negative (for $x=0.2$ and $\delta=0.38$) with the depletion of the CuO chains. The positive α is a characteristic feature of a strong ''chain contribution,'' while the negative α for $S(T>T^{*}\sim 100\ \mathrm{K})$ occurs when the TEP is determined solely by the CuO_2 planes.

ditional source of uncertainty comes from the fact that most single crystals are likely to contain small amounts of impurities like Au or Al which are incorporated mainly in the Cu chains and thereby affect and reduce the anisotropy. Finally, the detwinning of the crystals may not be perfect and may give rise to a reduction of the measured anisotropy. We are aware only of one study on detwinned Y-123 single crystals that have been grown in a specific way to ensure that no impurities like Al or Au are introduced during the melting process.[20] The value of $\gamma=2.15(10)$ is amongst the highest reported so far and the annealing conditions with $T=500$ °C in O_2 and the deduced oxygen content of $\delta\sim 0.1$ are very similar to those of our optimized sample $YBa_2Cu_3O_{6.88}$. The result deduced for S^{ch} is shown in Fig. 8(a) by the open squares together with S^{poly} (full squares) and the TEP for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.62}$ where $S^{\mathrm{poly}} \approx S^{\mathrm{pl}}$ (full triangles) represents the ''plane contribution'' that arises from the optimally doped CuO_2 planes. Shown by the dashed line is S^{ch} as it was derived in Ref. 23 in a more direct way from TEP measurements on a detwinned single crystal that was annealed at 460 °C in oxygen but contained Au as impurity in the CuO chains. Except for the saturation of S^{ch} at higher temperatures which occurs for the detwinned single crystal the results are very similar. S^{ch} for $YBa_2Cu_3O_{6.88}$ is shown again in Fig. 8(b) (open squares) together with S^{ch} as derived for fully oxygenated $YBa_2Cu_3O_{6.98}$ (open circles). For the fully oxygenated sample the CuO chains should be almost perfectly ordered and therefore we have assumed that the anisotropy γ is comparable to that of Y-124 where a value of $\gamma=2.8$ is observed experimentally.[13] The idea is that the electrical conductivity of the one-dimensional CuO chains is limited mostly by the scattering of the charge carriers on oxygen vacancies rather than by the concentration of the charge carriers in the chains. The conductivity of the almost

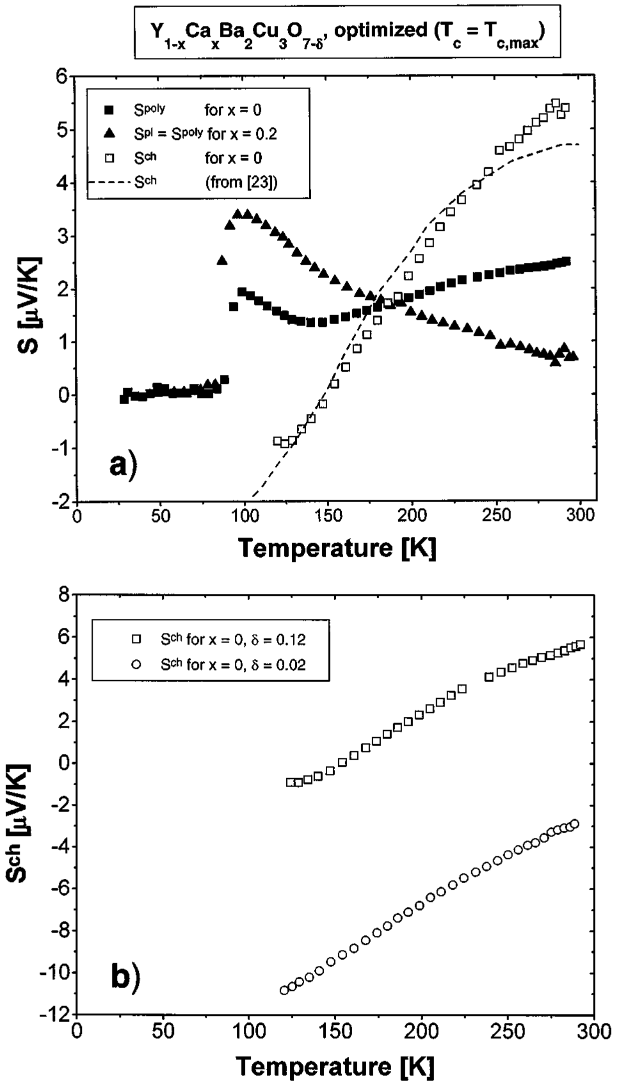

FIG. 8. The temperature dependence of the ''chain contribution'' to the TEP, S^{ch}, for $YBa_2Cu_3O_{7-\delta}$ as extracted assuming independent contributions of CuO_2 planes and CuO chains to the overall TEP of the polycrystalline samples [see Eq. (3)]. (a) The solid squares show S^{poly} for optimally doped $YBa_2Cu_3O_{6.88}$. The solid triangles represent the ''plane contribution,'' S^{pl}, of the optimally doped CuO_2 planes as measured for the optimally doped sample $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.62}$ where $S^{\mathrm{poly}} \approx S^{\mathrm{pl}}$. The open squares show the ''chain contribution'' S^{ch} for $YBa_2Cu_3O_{6.88}$ as deduced using Eq. (3). For comparison the dashed line shows the results for S^{ch} as reported from TEP measurements on a detwinned Y-123 single crystal of similar oxygen content (Ref. 23). Except for small deviations towards higher temperatures the agreement is very good. (b) The open squares show S^{ch} for optimally doped $YBa_2Cu_3O_{6.88}$, while the open circles represent S^{ch} as we deduced it (for details see text) for fully oxygenated and slightly overdoped $YBa_2Cu_3O_{6.98}$. It appears that S^{ch} becomes more negative with the filling of the CuO chains while the positive slope α remains almost unchanged.

perfectly ordered double chains in case of Y-124 and the single-chain for fully oxygenated $YBa_2Cu_3O_{6.98}$ therefore can be expected to be rather similar even though the total concentration of charge carriers is a little different. From the value of $T_c/T_{c,\max}=89/93.5$ we estimate $S^{pl}=S(290\ \mathrm{K})[1-\alpha(290\text{-T})]$ with $S^{pl}(290\ \mathrm{K})=-2\ \mu\mathrm{V/K}$ and $\alpha=0.02\ \mu\mathrm{V/K}^2$. As was concluded in Ref. 23 from the TEP measurements on the detwinned single crystals we find that S^{ch} becomes more negative when the CuO chains are fully oxygenated while the positive slope α is hardly changed.

SUMMARY

In summary we have studied the TEP of polycrystalline samples of the 123 system $(Y,Yb)_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ for $0\leqslant x\leqslant 0.2$ and $0.04\leqslant\delta\leqslant 0.98$. The partial substitution of Y^{3+} by Ca^{2+} introduces additional hole carriers into the CuO_2 planes and makes the 123 system access far into the overdoped regime. The counterdoping effect by Ca substitution and oxygen depletion of the CuO chains enables us to prepare 123 samples which have strongly deoxygenated and nonmetallic CuO chains but still have optimally doped (as determined by $T_c=T_{c,\max}$) and even slightly overdoped CuO_2 planes. Over a fairly wide range of doping we can study the TEP that arises typically from the CuO_2 planes (''plane contribution'') of this 123 system. The observed ''plane contribution'' follows almost perfectly the trend as it was reported by Obertelli, Cooper, and Tallon for various Bi and Tl compounds.[7] In particular, for the optimally doped sample we find that $S^{pl}(T>T^*)$ decreases almost linearly with temperature towards a value of $S(290\ \mathrm{K})\sim 1$–$2\ \mu\mathrm{V/K}$. Shortly past optimum doping towards the overdoped side $S^{pl}(290\ \mathrm{K})$ changes sign and becomes negative. The characteristic negative slope $\alpha=dS^{pl}(T>T^*)/dT$, however, is almost unchanged and remains negative like in the underdoped regime. We find that the sign change in $\alpha=dS^{poly}(T>T^*)dT$ is related to the onset of a significant ''chain contribution'' to the TEP. The coincidence of the sign change of α and $S(290\ \mathrm{K})$ as it is observed in Ca-free $YBa_2Cu_3O_{7-\delta}$ just around optimum doping therefore occurs accidentally only for this specific composition, and is not related to the electronic properties of the CuO_2 planes, i.e., to the presence of a van Hove singularity at the Fermi surface. Assuming independent TEP contributions from CuO_2 planes and CuO chains, we can deduce a ''chain contribution'' which agrees remarkably well with the results that have been obtained more directly from TEP studies on untwinned single crystals.

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