

Chain contribution to the Seebeck coefficient in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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Measurements of the Seebeck coefficient $\alpha(T)$ and the resistivity $R(T)$ of polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ quenched from different temperatures T_q and of polycrystalline $(\text{Y}_{1-x}\text{Ca}_x)(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_{6.96\pm0.01}$ were made to distinguish the contributions to $\alpha(T)$ from the $\text{Cu}(1)\text{O}$ chains and the CuO_2 sheets. The CuO_2 sheets give a positive contribution to $\alpha(T)$ that is composed of a weakly temperature-dependent part α_0 that decreases sensitively with increasing oxidation and an enhancement part $\delta\alpha$ that gives a broad maximum to $\alpha(T)$ at a $T_{\text{max}} \approx 140^\circ\text{C}$. These two features together have been shown to distinguish the superconductive compositions from the parent and overdoped compositions in other copper-oxide superconductors. In fully oxidized $\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$, the contribution to $\alpha(T)$ from the CuO_2 sheets is obscured by a dominant, competitive negative contribution to $\alpha(T)$ from the chains that has a similar, but negative, $\delta\alpha$ enhancement.

In a previous study¹ we have shown that a distinguishing feature of the superconductive CuO_2 sheets in the p -type high- T_c copper oxides is a Seebeck coefficient

$$\alpha = \alpha_0 + \delta\alpha > 0, \quad (1)$$

where a dopant-dependent α_0 is only weakly temperature dependent and $\delta\alpha$ is an enhancement term giving rise to a broad maximum in α at a temperature $T_{\text{max}} \approx 140$ K. Overdoped CuO_2 sheets were found to retain the $\delta\alpha$ enhancement, but to have a small and dopant-independent α_0 ; the underdoped CuO_2 sheets showed no $\delta\alpha$ term. Moreover, optimally doped CuO_2 sheets that were semiconductive rather than superconductive also gave no $\delta\alpha$ term. In that paper, we restricted our investigation to copper oxides having single CuO_2 sheets separated by an insulating nonsuperconductive layer in order to ensure that only the CuO_2 sheets were contributing to α .

We argued that the appearance of a $\delta\alpha$ term requires an electron-energy dispersion curve and a well-defined Fermi surface, but that a $T_{\text{max}} \approx 140$ K is too high to be accounted for by a conventional $\delta\alpha$ enhancement arising from electron interactions with acoustic phonons. We postulated that a $\delta\alpha$ with a $T_{\text{max}} \approx 140$ K is a signature for a *vibronic* state with strong coupling of electrons to optical-mode lattice vibrations and valence fluctuations. In the overdoped CuO_2 sheets, the *vibrons* would be distributed uniformly over all the Cu atoms of a CuO_2 sheet; in the superconductive samples they would be confined to the volume within *correlation polarons* that are condensed into a *polaron liquid* having a relatively flat vibron-energy dispersion curve with a gap at the midband position. The

strong dependence of α_0 on doping in the superconductive samples was attributed to a dopant-dependent transfer of spectral weight from the upper and lower Hubbard bands of the parent phase to the vibronic states having energies in the gap between them.

A skepticism toward this interpretation may be encouraged by reports in the literature of quite different temperature dependences of the Seebeck coefficient for more complex superconductive oxides.² In this paper, we point out that the data for more complex systems may contain a dominant contribution to α from metallic non-superconductive layers. We show, by way of example, that suppression of the contribution to α from the $\text{Cu}(1)\text{O}_x$ chains in the 123 superconductive copper oxides reveals an $\alpha > 0$ from the CuO_2 sheets that exhibits both the $\delta\alpha$ term and the dopant-dependent α_0 that are distinguishing features of the normal state of p -type copper-oxide superconductors.

The 123 structure of fully oxidized $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\delta < 0.05$, contains—on traversing the c axis—superconductive CuO_2 -Y- CuO_2 layers with double CuO_2 sheets of Cu(2) atoms in square-coplanar oxygen coordination oriented along the orthorhombic b axis. Resistivity measurements on twin-free single crystals³ have not only established the metallic character of the chains, but also a chain conductivity comparable to or larger than the conductivity of the CuO_2 sheets; and two-dimensional positron annihilation has revealed a Fermi surface associated with the chains.⁴ Moreover, measurements of surface resistance in the microwave region below T_c have indicated the presence of two energy gaps at the Fermi energy, one of which was assigned to the $\text{Cu}(1)\text{O}$ chains.⁵

Seebeck data for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been reported by many groups as cited, for example, in Refs. 6–8; however, meaningful comparison of the data with those for copper oxides having insulating nonsuperconductive layers requires subtraction from the measured net $\alpha(T)$ the contribution from the $\text{Cu}(1)\text{O}$ chains, a contribution that has either been ignored or left undetermined in previous reports. Since the conductivity of the chains is comparable to that of the CuO_2 sheets, the chain contribution to $\alpha(T)$ cannot be ignored; it may even prove to be dominant.^{9,10}

In $\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$, the mean formal oxidation state of a Cu atom is +2.31. From valence-bond sums, the CuO_2 sheets of this optimally doped composition have been estimated¹¹ to contain $\text{Cu}(2)$ atoms with an oxidation state +2.18, which would give the $\text{Cu}(1)$ atoms an oxidation state of +2.56. The CuO_2 sheets of the superconductive copper oxides having insulating nonsuperconductive layers and a copper oxidation +2.18 all have an $\alpha = \alpha_0 + \delta\alpha > 0$. On the other hand, a $\text{Cu}(1)$ oxidation +2.56 should give a negative contribution to $\alpha(T)$ from the y^2-z^2 chain band. If the sign of the chain contribution to $\alpha(T)$ is negative whereas that from the CuO_2 sheets is positive in superconductive $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, then the sign of the net $\alpha(T)$ would reflect the dominant contribution, which would be that of the more conductive structural element. Since the chain conductivity is reduced by oxygen vacancies or twins that break the linear chains into chain segments, the net $\alpha(T)$ should be sensitive to the oxygen concentration and to the oxygen ordering in the $\text{Cu}(1)\text{O}_{1-\delta}$ planes. Reduction of a negative contribution to $\alpha(T)$ from the chains could result in a change from negative to positive in the sign of the net $\alpha(T)$, and the contribution to $\alpha(T)$ of the superconductive sheets would be fully manifest where the negative contribution from the chains is totally suppressed. Our experiments were designed to show how the net $\alpha(T)$ changes with suppression of the chain contribution to the total conductivity and hence to $\alpha(T)$.

Several ceramic samples of the $(\text{Y}_{1-x}\text{Ca}_x)(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_{7-\delta}$ system were made from La, Y, Cu oxides and Ca, Ba carbonates in proper ratios. Nominal La_2O_3 was preheated to 980°C and cooled to room temperature before weighing. Well-ground mixtures were fired to 900°C and sintered at 920°C in air with several intermediate grindings.

Two sets of samples were studied, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ of variable oxygen content and $(\text{Y}_{1-x}\text{Ca}_x)(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_{7-\delta}$ with optimum oxygen content. To vary the oxygen content and distribution in the $\text{Cu}(1)\text{O}_{1-\delta}$ planes of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, sintered pellets were annealed in air at 900°C and then cooled slowly to a temperature T_q before being dropped into liquid nitrogen. To maximize the oxygen content and ordering for all x in $(\text{Y}_{1-x}\text{Ca}_x)(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_{7-\delta}$, the samples were annealed in pure O_2 at 400°C and then cooled slowly in O_2 . Iodometric titration was used to obtain the oxygen parameter δ . For samples quenched from T_q , $400 < T_q < 650^\circ\text{C}$, the oxygen content varied over the range $6.54 < (7-\delta) < 6.91$. Samples annealed and slow

cooled in O_2 all had an oxygen content 6.96 ± 0.01 independent of x . All samples were single phase to x-ray powder diffraction.

The structural change from orthorhombic to tetragonal symmetry with T_q in the first set of samples and with x in the second was monitored by precise scanning of the x-ray powder patterns in the range 31° – 34° in 2θ ; curve fitting to Lorentzian functions decomposed the overlapping (110), (103), and (013) peaks in this range. The transport data were obtained with homebuilt apparatus; the Montgomery method¹² was used to obtain the pellet resistivity from four-probe measurements.

Figure 1 shows the evolution of the lattice parameters with x in the doubly doped system $(\text{Y}_{1-x}\text{Ca}_x)(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_{7-\delta}$ with $\delta = 0.04 \pm 0.01$. A complete solid solution can be obtained to $x = 0.4$; higher Ca contents are not accessible.^{13,14} An orthorhombic to tetragonal transition is found between $x = 0.3$ and $x = 0.4$, which is consistent with the literature data.¹⁴

Figure 2 presents the Seebeck $\alpha(T)$ and resistivity $R(T)$ data for different values of x in the doubly doped system with maximum oxygen content. The orthorhombic $x = 0$ sample has a $T_c \approx 90$ K and shows a negative α_0 and $\delta\alpha$ whereas the tetragonal $x = 0.4$ sample has a $T_c = 78$ K and shows a positive α_0 and $\delta\alpha$. In the range $0.1 \leq x \leq 0.3$, a temperature-independent α for $T > T_c$ is small, indicative of a near cancellation of negative and positive contributions; the $R(T)$ curves show a shoulder at 90 K before dropping to zero at a T_c that decreases with increasing x .

Figure 3 shows the $\alpha(T)$ and $R(T)$ data for different values of T_q for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples. Samples quenched from $T_q = 650^\circ\text{C}$ exhibit a large, positive net α_0 and $\delta\alpha$ with a $T_c \approx 50$ K whereas those quenched from

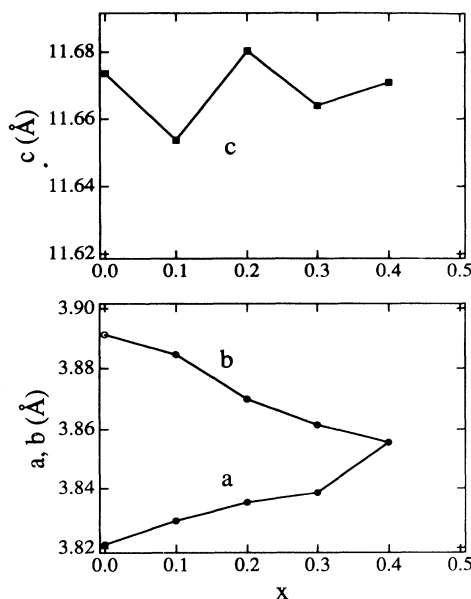


FIG. 1. Variation of room-temperature lattice parameters with compositional parameter x for $(\text{Y}_{1-x}\text{Ca}_x)(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_{6.96 \pm 0.001}$.

$T_q = 400^\circ\text{C}$ have a $T_c \approx 90$ K and a small, positive net $\delta\alpha$. The $R(T)$ curves show T_c decreasing from about 85 K for $T_q = 450^\circ\text{C}$ to $T_c \approx 52$ K for $T_q = 600^\circ\text{C}$; at intermediate temperatures $T_q = 500$ and 550°C , a shoulder near 80 K in the $R(T)$ curves indicates that the organization of pockets of well-ordered Cu(1)O chains begins below 600°C .

Substitution of La for Ba in $\text{YBa}_{2-x}\text{La}_x\text{CuO}_{7\pm\delta}$ introduces extra oxygen into the $\text{CuO}_{1\pm\delta}$ planes so as to maintain a nearly constant oxidation of the CuO_2 sheets; the excess oxygen induces an orthorhombic to tetragonal transition to powder x-ray diffraction.^{15,16} In the system $(\text{Y}_{1-x}\text{Ca}_x)(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_{6.96}$, double doping keeps constant the oxygen content needed to maintain the overall mean oxidation state of the Cu atoms, but the oxygen ordering in the $\text{CuO}_{1-\delta}$ planes is altered by the substitution of La^{3+} for Ba^{2+} in the neighboring planes. This alteration breaks the Cu(1)O chains by displacing oxygen atoms to *a*-axis positions; and at high enough La concentrations, long-range ordering of the chain segments is lost. Therefore, the contribution of the chains to the net conductivity, and hence also to the net $\alpha(T)$, must decrease with increasing x in $(\text{Y}_{1-x}\text{Ca}_x)(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_{6.96}$ even though the overall mean formal oxidation state of the copper remains constant.

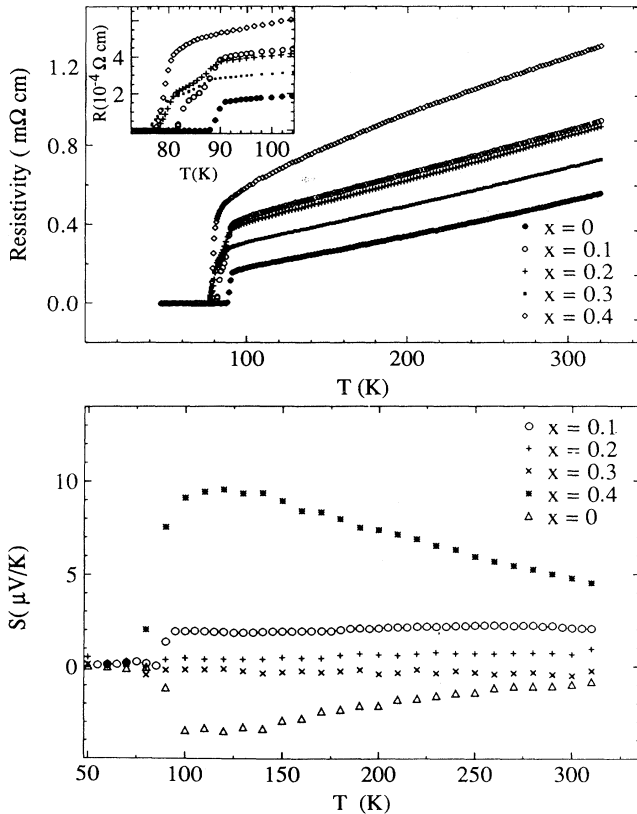


FIG. 2. Temperature variation of the Seebeck coefficient and resistivity for various values of x in polycrystalline $(\text{Y}_{1-x}\text{Ca}_x)(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_{6.96\pm 0.01}$.

Although the charge distribution between chains and CuO_2 sheets may vary with increasing x , the small change in T_c suggests it changes little. A nearly constant value of T_c in the range $0.2 \leq x \leq 0.4$ signals an essentially constant oxidation of the CuO_2 sheets in this compositional range, so we can attribute the remarkable change in $\alpha(T)$ between samples $x = 0.3$ and $x = 0.4$ in Fig. 2 to a change in the contribution from the Cu(1)O chains. The change from orthorhombic to tetragonal symmetry between $x = 0.3$ and $x = 0.4$ testifies to a breakup of the long-range ordering of the chains, or chain segments; and the jump in $R(T)$ indicates that in the orthorhombic phase the chain conductivity is comparable to, if not greater than, the conductivity of the CuO_2 sheets. In the $x = 0$ sample, the Cu(1)O chains give the dominant contribution to the conductivity and to $\alpha(T)$; in the $x = 0.4$ sample, the contribution from the CuO_2 sheets is dominant. It is therefore significant that $\alpha(T)$ for $x = 0.4$ is positive and exhibits a $T_{\text{max}} \approx 125$ K, which is typical of what is found in other *p*-type copper-oxide superconductors.¹ Surprising to us is the character of the negative contribution from the Cu(1)O chains made manifest in the $x = 0$ sample; it also exhibits a $\delta\alpha$ enhancement with a $T_{\text{max}} \approx 125$ K, but of opposite sign to that of the $x = 0.4$ sample. This finding implies a strong coupling between the vibrons of a CuO_2 sheet and those of the neighboring chains. In the intermediate compositions $0.1 \leq x \leq 0.3$, where the contributions to $\alpha(T)$ from the Cu(1)O chains and CuO_2 sheets are comparable, a nearly temperature-

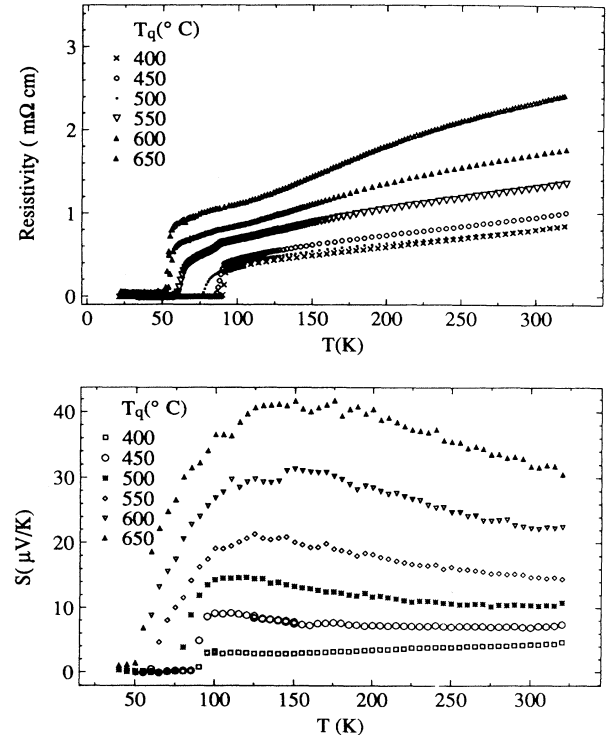


FIG. 3. Temperature variation of the Seebeck coefficient and resistivity for a polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample quenched from different temperatures T_q into liquid nitrogen.

independent α would seem to indicate a cancellation of two $\delta\alpha$ contributions each with a $T_{\max} \approx 125$ K.

At higher temperatures in air, oxygen is both increasingly disordered within and also lost from the $\text{Cu(1)O}_{1-\delta}$ planes of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$; ¹⁷ annealed samples quenched from different temperatures T_q reflect the oxygen concentration and ordering at T_q . Reduction of the CuO_2 sheets with loss of oxygen from the $\text{Cu(1)O}_{1-\delta}$ planes is reflected in the decrease in T_c with increasing T_q in Fig. 3. In this case also, breaking of the chains to suppress their contribution to $\alpha(T)$ reveals an $\alpha = \alpha_0 + \delta\alpha > 0$ for the CuO_2 sheets with a $\delta\alpha$ enhancement having a T_{\max} that increases with T_q over the range $120 < T_{\max} < 150$ K. In addition, α_0 is seen to increase as the oxidation of the CuO_2 sheets decreases, which was the other distinguishing feature of the superconductive CuO_2 sheets found in superconductive copper oxides having insulating nonsuperconductive layers.¹

We turn finally to the shoulder observed in the $R(T)$ curves of Figs. 2 and 3 in the transitional compositions where the contributions to $\alpha(T)$ from the chains and

CuO_2 sheets appear to be comparable. The shoulder probably reflects the presence of domains within which the chain contributions still dominate. Conductive chains (or chain segments) appear to play an important role in raising T_c to its maximum value of about 90 K. However, the $x = 0.4$ and $T_q = 650^\circ\text{C}$ samples exhibit no shoulder; in these samples the contribution to $\alpha(T)$ from the CuO_2 sheets appears to be homogeneously dominant.

In conclusion, we have demonstrated that the dominant contribution to the negative Seebeck coefficient $\alpha(T)$ in fully oxidized $\text{YBa}_2\text{Cu}_3\text{O}_{6.95 \pm 0.01}$ is from the metallic Cu(1)O chains. In fact, suppression of the chain contribution reveals that the CuO_2 sheets have an $\alpha = \alpha_0 + \delta\alpha > 0$ with a $\delta\alpha$ enhancement having a $T_{\max} \approx 140$ K and a dopant-dependent α_0 . These two features, taken together, have been shown to distinguish the superconductive normal state from the underdoped state on the one hand and the overdoped state on the other in p -type copper oxides having an insulating nonsuperconductive layer.

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