

$(\text{Cu}_{0.5}\text{C}_{0.5})\text{Ba}_2\text{Ca}_{m-1}\text{Cu}_m\text{O}_x$ for $m=3$ and 4 under hydrostatic pressure

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(Received 8 September 1999)

The hydrostatic pressure effects on the superconducting transition temperatures (T_c 's) of the oxycarbonate cuprates $(\text{Cu}_{0.5}\text{C}_{0.5})\text{Ba}_2\text{Ca}_{m-1}\text{Cu}_m\text{O}_x$ [(Cu,C)-12($m-1$) m], have been determined for $m=3$ and 4 with different dopings of x 's. We found that, similar to $\text{YBa}_2\text{Cu}_3\text{O}_x$, dT_c/dP depends strongly on x for (Cu,C)-1223 and increases from -0.7 to $+1.2$ K/GPa as x decreases and the compound changes from overdoped to nearly optimally doped, consistent with the prediction of the phenomenological model on the pressure effect on T_c . In contrast to the prediction, dT_c/dP depends only slightly on x for (Cu,C)-1234 and decreases from 0.75 to 0.6 K/GPa as x decreases from nearly optimally doped to underdoped. The dT_c/dP difference is attributed to the possible different electronic contribution of the CuO chains in the two compounds, as implied by the distinct temperature dependences of their thermoelectric power.

I. INTRODUCTION

While a commonly accepted microscopic mechanism responsible for the occurrence of high-temperature superconductivity (HTS) is still elusive, several general relationships among various physical parameters of the cuprate high-temperature superconductors (HTS's) have been reported. For instance, the superconducting temperature (T_c) was found¹ to depend on the carrier number per CuO_2 (n) parabolically, i.e., $T_c(n) = T_c^{\text{max}}[1 - a(n - n_0)^2]$, where $T_c = T_c^{\text{max}}$ when the compound is optimally doped with $n = n_0 \sim 0.16$ hole/ CuO_2 , and $a = 82.6$ which determines the superconducting doping range. HTS's with $n < n_0$ are known as underdoped, and those with $n > n_0$ overdoped. A correlation of n with the thermoelectric power (TEP) measured near room temperature was also observed,² providing a simple secondary method to determine the doping state of a HTS.

High pressure can provide an effective test for the generality of the above correlation¹ without introducing chemical complexities to the compound system under investigation. Several versions of the phenomenological model³ have been advanced to account for the n dependence of the pressure effect on T_c (dT_c/dP) in terms of an n shift due to a pressure-induced charge-transfer based on the parabolic $T_c(n)$ relation described above. According to one version, $dT_c/dP = c - 2aT_c^{\text{max}}(n - n_0)dn/dP$, with c being a positive constant, and hence decreases from positive to negative as n increases from the underdoped to the heavily overdoped region. Indeed, this was observed in the $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) system.⁴ However, this is no longer true for the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) and the $\text{HgBa}_2\text{Ca}_{m-1}\text{Cu}_m\text{O}_{2m+2+\delta}$ [Hg-12($m-1$) m] compound systems, strongly suggesting that the pressure affects T_c through parameters other than n .⁵⁻⁷ It is interesting to note that the two systems also exhibit only a negligible pressure effect on n , as evident from the Hall and TEP measurements under pressures.^{7,8} Recently, it has been proposed⁹ that the pressure-induced charge-transfer in cuprate HTS's is determined by the existence and the filling of oxygen sites of the CuO-chains in the compounds,

such as YBCO, where the CuO_2 -chain band crosses the Fermi surface and contributes to the density of states.

The $(\text{Cu}_{0.5}\text{C}_{0.5})\text{Ba}_2\text{Ca}_{m-1}\text{Cu}_m\text{O}_x$ [(Cu,C)-12($m-1$) m] compound system¹⁰ has been shown to exhibit the basic crystal structure of the Hg-12($m-1$) m but retains certain features of the CuO chains that exist in $\text{YBa}_2\text{Cu}_3\text{O}_x$. We have therefore decided to determine the n dependences of dT_c/dP of (Cu,C)-12($m-1$) m for $m=3$ and 4 , and to compare them with predictions of the phenomenological model. We found that the dT_c/dP of (Cu,C)-1223 depends strongly on n in a fashion similar to that of YBCO, increasing from -0.7 K/GPa to $+1.2$ K/GPa when the oxygen content x decreases from overdoped to nearly optimally doped, as qualitatively predicted by the phenomenological model. However, the dT_c/dP of (Cu,C)-1234 decreases slightly as x decreases from nearly optimally doped to underdoped. The difference observed in dT_c/dP between the two compounds is attributed to the possible difference in their CuO-chain electronic contributions. This is consistent with the different temperature dependences of TEP displayed by the two compounds.

II. EXPERIMENTAL

Powders of cation oxides BaO, CaO, and CuO were thoroughly mixed with cation ratios of Ba:Ca:Cu = 2:1.5:3.5 and 2:2.5:4.5, for (Cu,C)-1223 and -1234, respectively. The mixed powders were calcined in an alumina crucible at $650-900^\circ\text{C}$ for 40-48 h in flowing O_2 with several intermittent grindings. CaCO_3 was later added to the calcined oxide powders as the carbon source to make the precursors of the stoichiometric $(\text{Cu}_{0.5}\text{C}_{0.5})\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ [(Cu,C)-1223] and $(\text{Cu}_{0.5}\text{C}_{0.5})\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_x$ [(Cu,C)-1224]. These precursors were then mixed with appropriate amounts of oxidizing agent Ag_2O_2 , pressed into pellets, wrapped in Au foil and heated in a high-pressure cell inside a multianvil Walker module from Rockland Research under 5-6 GPa at $1000-1100^\circ\text{C}$ for 1-4 h before they were furnace quenched to room temperature. The furnace used was made of Ca-doped LaCrO_3 and the pressure medium employed was MgO. The pressure was determined using the load vs pressure curve provided by Rockland Research, and the tempera-

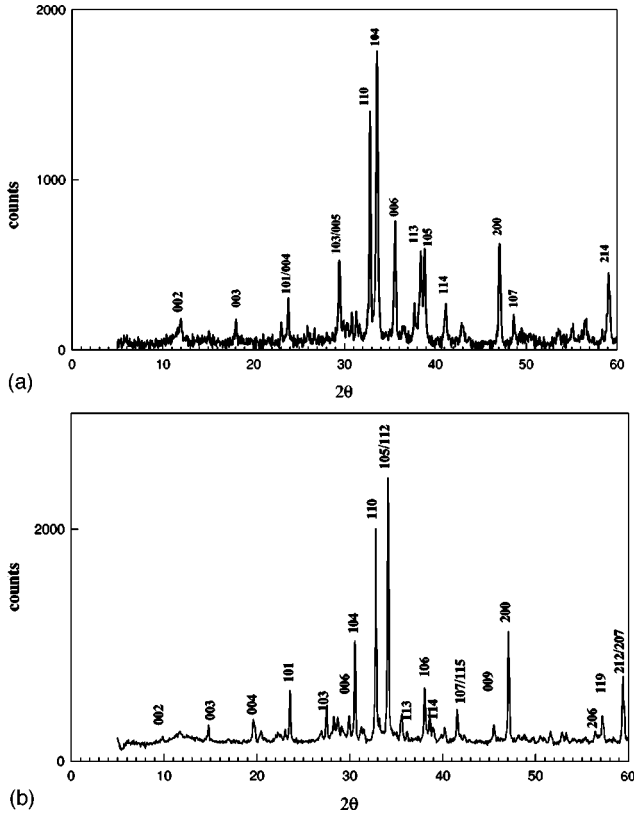


FIG. 1. XRD patterns of (Cu,C)-1223 (a) and -1234 (b), respectively.

ture by a *D*-type thermocouple (W + 3% Re/W + 25% Re) located next to the sample inside the high-pressure cell.

The structure of the sample was characterized by x-ray diffraction (XRD) using a Rigaku D-MAX/B-III powder diffractometer. The T_c at ambient was measured both resistively, by the four-probe method using a Linear Research LR-400 bridge, and magnetically, using a quantum design superconducting quantum interference device (SQUID) magnetometer. It is defined as the temperature where the resistivity is linearly extrapolated to zero from the main transition or where the magnetic transition is halfway completed. The T_c 's so defined agree well with one another. Under pressure, the T_c was determined resistively. The hydrostatic pressure environment was generated at room temperature inside a Teflon cell housed in a Be-Cu high-pressure clamp,¹¹ using 3M fluorinert as the pressure medium. The pressure at low temperature was measured with a superconducting Pb monometer, which was situated next to the sample inside the pressure cell, and the temperature by a chromel-alumel thermocouple above 10 K and by a Germanium thermometer below 10 K.

III. RESULTS AND DISCUSSION

High quality (Cu,C)-1223 and -1234 samples were successfully synthesized. The XRD patterns of the samples are shown in Figs. 1(a) and 1(b), displaying a single phase in each of the samples with less than 5% impurities. These compounds were found to be tetragonal (space-group $P4/mmm$) with lattice parameters $a=3.858 \text{ \AA}$, $c=14.78 \text{ \AA}$ for (Cu,C)-1223 and $a=3.857 \text{ \AA}$ and $c=17.89 \text{ \AA}$ for (Cu,C)-1234. A superstructure with a^*

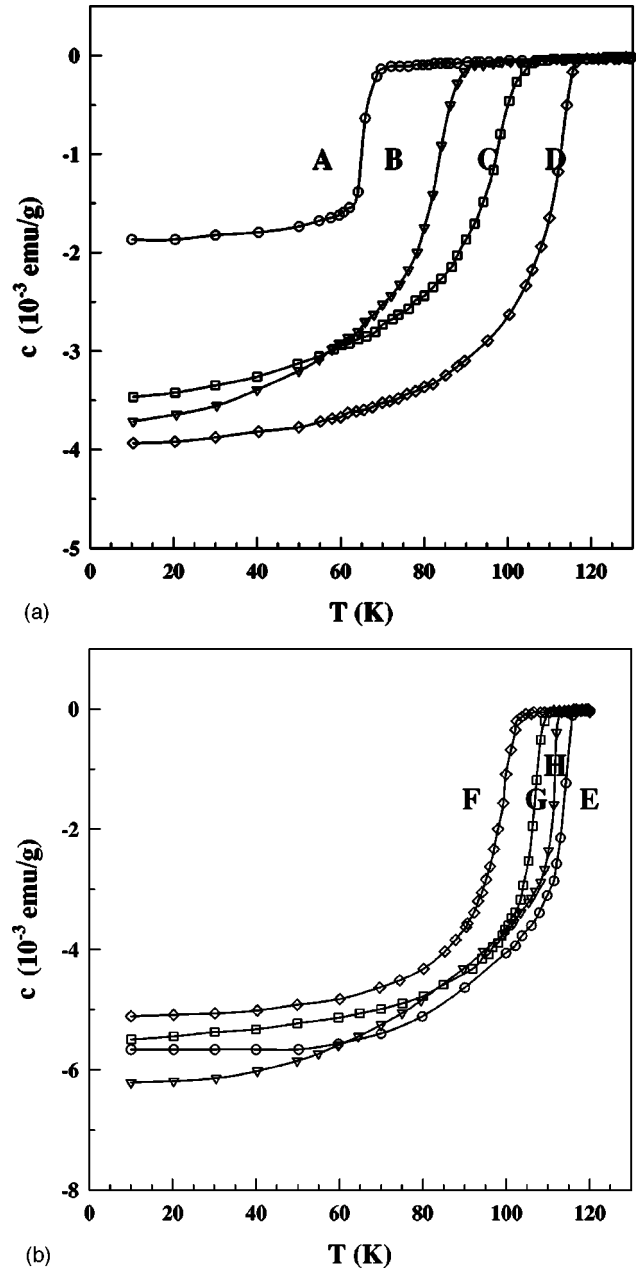


FIG. 2. dc χ vs T for (Cu,C)-1223 (a): \circ as-synthesized, and annealed in Ar at ∇ — 350 °C for 48 h, \square — 450 °C for 48 h, and \diamond — 550 °C for 48 h; and for (Cu,C)-1234 (b): \circ as-synthesized, and annealed in Ar at ∇ — 400 °C for 48 h, \square — 500 °C for 24 h, and \diamond — 600 °C for 24 h.

$=2a$, $b^*=b$, and $c^*=2c^*$ was also observed using a transmission electron microscope, consistent with previous reports.¹⁰

The T_c 's are $\sim 67 \text{ K}$ and $\sim 115 \text{ K}$, respectively, for the as-synthesized (Cu,C)-1223 and -1234 at ambient. A fairly broad range of doping and thus T_c has been achieved in these samples by removing oxygen from the as-synthesized samples *via* annealing in various atmospheres at different temperatures. Sequential annealing on the same sample to achieve different doping states was adopted to reduce possible effects on T_c or dT_c/dP arising from possible differences in different samples. No effort of ours succeeded in increasing the O content above that of either of the as-synthesized samples by charging O_2 at $\sim 300 \text{ °C}$ and 150

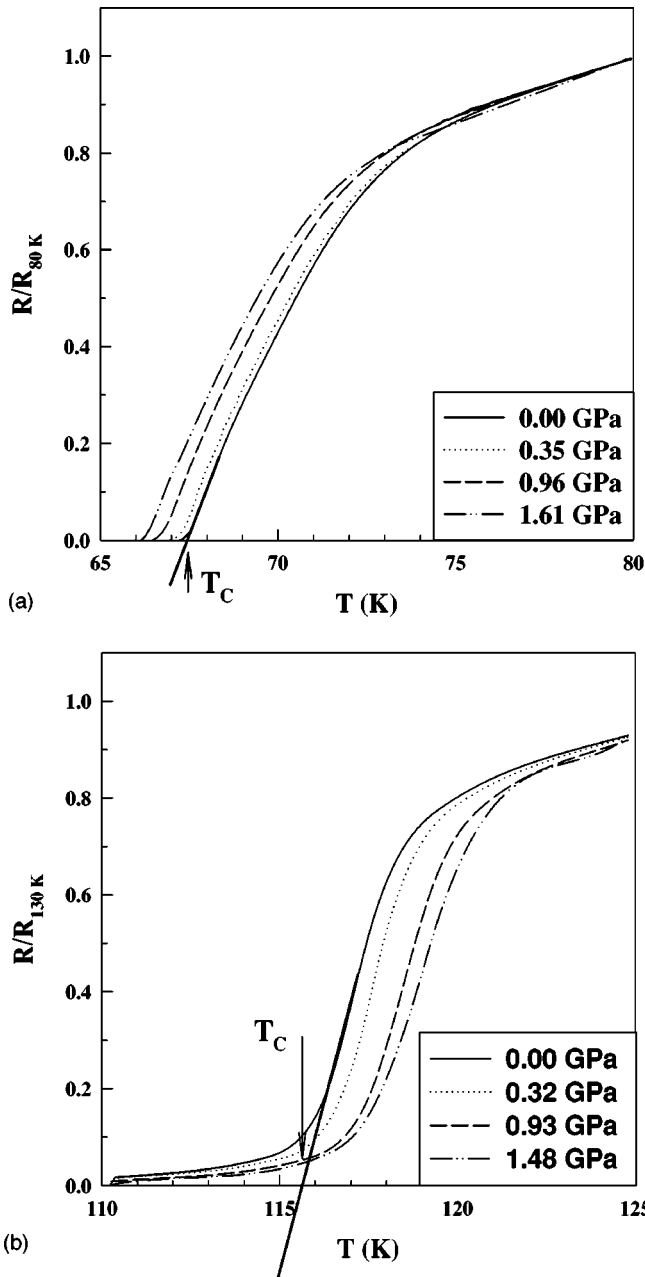


FIG. 3. R vs T for (Cu,C)-1223 as-synthesized (a) and after annealing at 550°C for 24 h (b).

bar, the highest gas pressure used. This can be understood, since all samples were prepared under a partial O pressure of about 5–6 GPa. We estimated n from the TEP measurements according to the empirical correlation, and verified by the ratio of T_c/T_c^{max} .² The doping was found to vary from $n \sim 0.233$ hole/CuO₂ for the as-synthesized (Cu,C)-1223 to ~ 0.173 after annealing; and from $n \sim 0.16$ hole/CuO₂ for the as-synthesized (Cu,C)-1234 to ~ 0.12 after annealing. This suggests that the as-synthesized (Cu,C)-1223 is overdoped and (Cu,C)-1234 is nearly optimally doped, based on an optimal doping $n_0 \sim 0.16$ hole/CuO₂.² At the same time, (Cu,C)-1223 remains slightly overdoped while (Cu,C)-1234 becomes underdoped after the annealing. The dc magnetic susceptibility (χ) measured in 10 Oe in the field-cooled mode is shown in Figs. 2(a) and 2(b) for (Cu,C)-1223 and -1234, respectively. For (Cu,C)-1223, the T_c increases con-

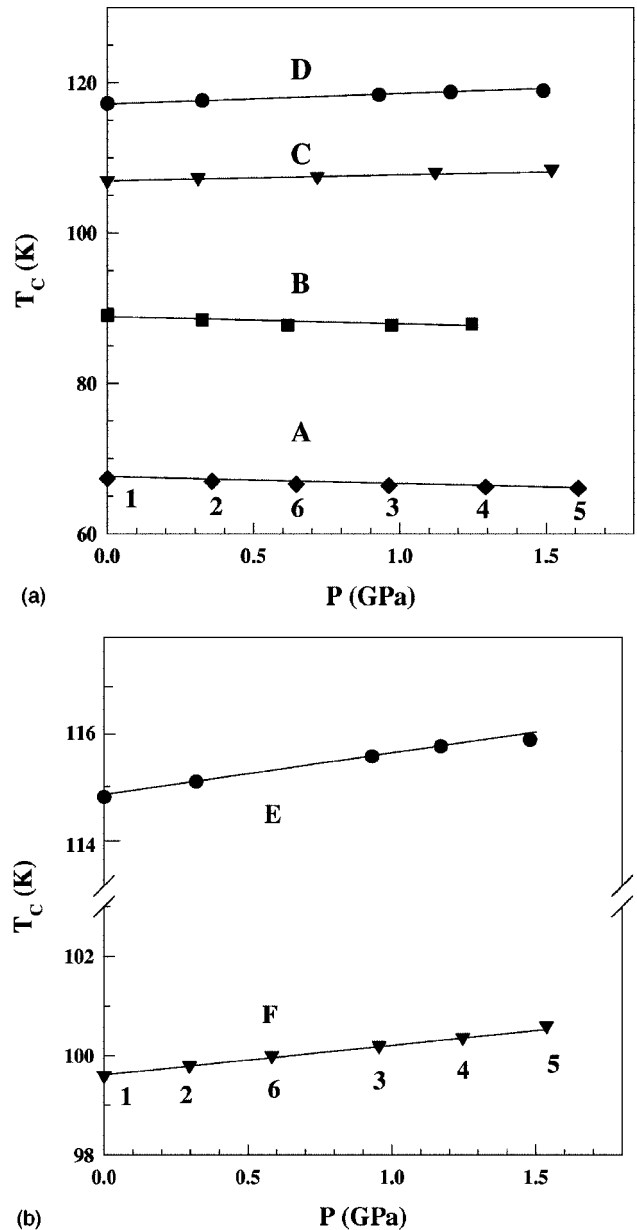


FIG. 4. T_c vs P for (Cu,C)-1223 (a) and -1234 (b) with different dopings. The number represents the sequential order of the experimental run.

tinuously from ~ 67 to ~ 118 K as the temperature of annealing in Ar increases to 550°C . The size of the Meissner effect also increases as the T_c increases for reasons not yet known. On the other hand, the T_c of (Cu,C)-1234 decreases from ~ 115 to ~ 99 K as the annealing temperature increases to 600°C in Ar. A 20% decrease in the size of the accompanying Meissner effect was also detected. The T_c variation with annealing observed confirms the doping states of the different samples before and after annealing inferred from our TEP measurements mentioned above.

We have measured the T_c of the same (Cu,C)-1223 sample, but at four different doping states, and that of the same (Cu,C)-1234 sample, but at two different doping states, after sequential annealing. Typical resistance (R) data as a function of temperature at different pressures are shown in Figs. 3(a) and 3(b) for the as-synthesized (Cu,C)-1223 and (Cu,C)-1223 annealed in Ar at 550°C , respectively. Slight

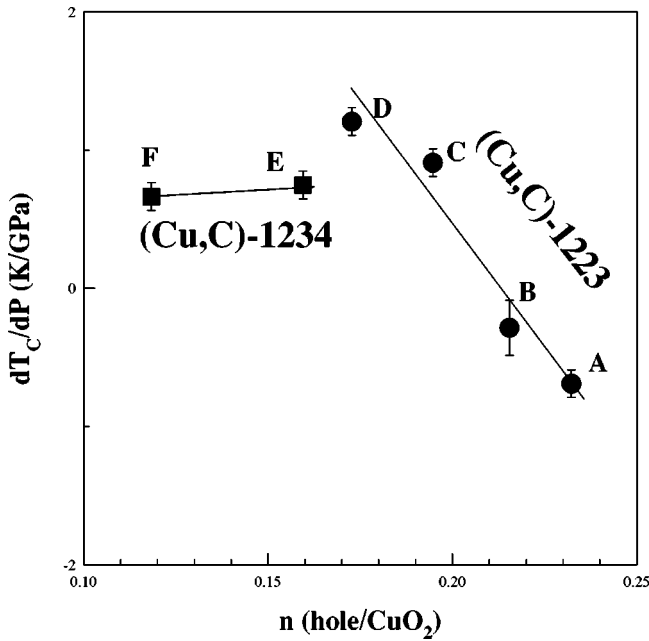


FIG. 5. dT_c/dP vs n for (Cu,C)-1223 and -1234.

sample degradation occurs after annealing as evidenced by the appearance of a long R tail below T_c . The superconducting transition is clearly shifted to lower temperatures for the as-synthesized (Cu,C)-1223 but to higher temperatures for the annealed one by pressures. The effects of pressure on the T_c 's of both samples with different dopings are summarized in Figs. 4(a) and 4(b). T_c appears to vary with pressure linearly for all samples within the pressure-range investigated. It should be noted that the pressure effect on T_c is reversible immediately after the reduction of pressure, as also evidenced in Figs. 4(a) and 4(b). The rates of T_c change induced by pressure, dT_c/dP 's, are -0.7 , -0.3 , 0.9 , and 1.2 K/GPa for (Cu,C)-1223 as-synthesized (A), and for those annealed in Ar at 350 (B), 450 (C), and 550 °C (D), respectively. The values of dT_c/dP are 0.65 and 0.75 K/GPa for (Cu,C)-1234 as-synthesized (E) and annealed in Ar at 600 °C (F), respectively. The results are summarized in Fig. 5, i.e., dT_c/dP decreases linearly with x for (Cu,C)-1223, whereas it increases slightly with x for (Cu,C)-1234.

It has been shown that O-ordering affects the T_c of cuprate HTS's and such ordering can take place even at room temperature.¹² The effect is more prominent as the sample becomes more underdoped. Fortunately, such ordering does not occur in YBCO immediately after the change in pressure, but only takes place with a long relaxation time of many hours, and the relaxation time increases rapidly with pressure.¹³ For instance, the T_c of a heavily underdoped YBCO increases from ~ 13.2 K at ambient to ~ 15.6 K measured immediately after the application of 0.79 GPa, and grows to ~ 22.4 K after consecutive annealings at 298 K for a total of 34 h. However, the complete release of the pressure at 53 K only reduces the T_c to 21.2 K, and it takes annealing at 298 K for 87 h to restore the T_c to its initial value of 13.2 K. It was therefore pointed out the important contribution of O ordering to the dT_c/dP measured. Indeed, O ordering can complicate the interpretation of the dT_c/dP data, since the sample examined can be at different O-ordering states which depend on the annealing time at or above room temperature

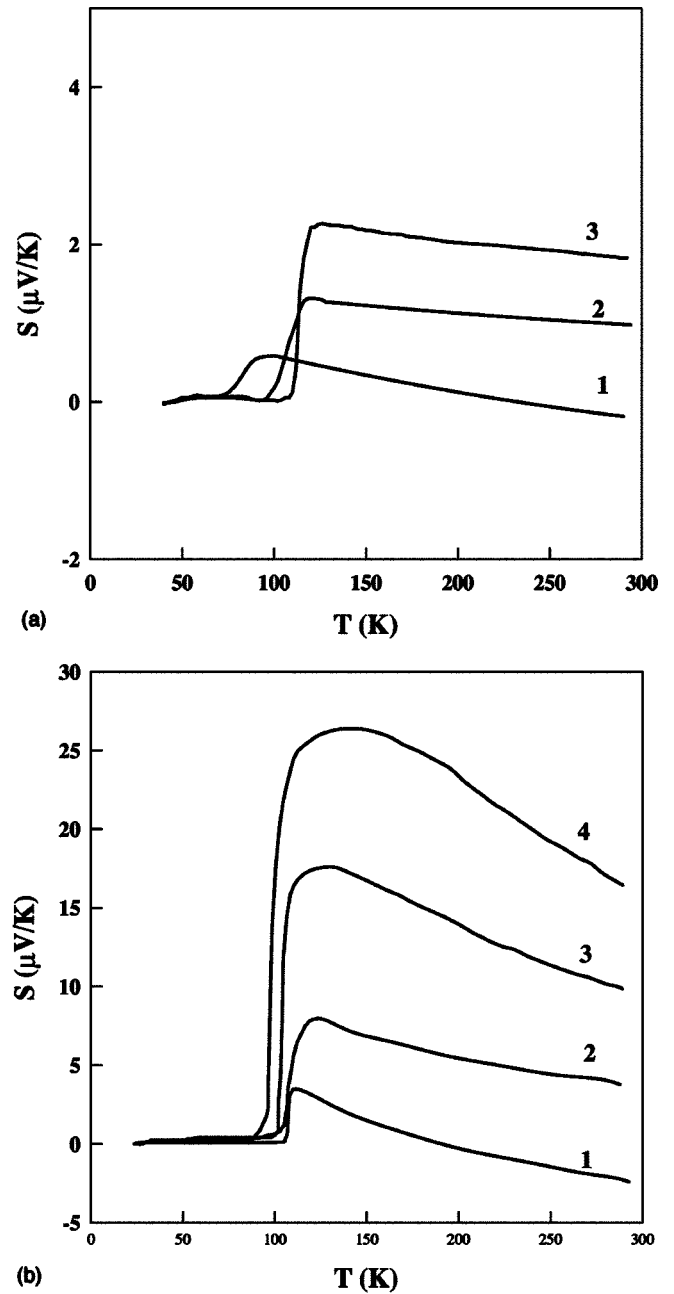


FIG. 6. TEP vs T for (Cu,C)-1223 (a) and -1234 (b): TEP increases with decreasing doping: numbers represent the sequential annealing order, upon oxygen removal.

after the application of pressure at room temperature. In our experiment, after each pressure step before the T_c was measured, the samples were held at room temperature for less than 15 min, which is very short compared to the long effective relaxation time of ~ 48 h at 0.79 GPa and ~ 6.5 h at 5 GPa for YBCO.¹³ Additionally, T_c was observed to return immediately on the reduction of pressure at room temperature to the interpolated value as shown in Figs. 4(a) and 4(b) for the overdoped (Cu,C)-1223 and the underdoped (Cu,C)-1234. All these suggest that the effect of possible pressure-induced O ordering at room temperature on dT_c/dP was negligible in the present experiment and our measurements were carried out in samples with the same O-ordering state. We therefore go ahead to compare the dT_c/dP results with predictions by the phenomenological model.^{3,4}

As pointed out earlier, dT_c/dP is expected to decrease linearly from positive to negative as n increases, according to the phenomenological model.^{3,4} Although (Cu,C)-1223 has the same structure as Hg-1223, its dT_c/dP decreases linearly with n as predicted, in contrast to that of the latter. Recent experiments⁹ show that the CuO-chains in the HTS compound provide the avenue for pressure to induce an n change and the authors suggest that the agreement between the model prediction and experimental observation on the n dependence of dT_c/dP is determined by the existence of these CuO₂ chains. Published data¹⁰ indeed show that (Cu,C)-1223 possesses the CuO-chain. Unfortunately, in spite of the similar structure reported, (Cu,C)-1234 displays a dT_c/dP that increases with n , in disagreement with the model prediction.

It has been observed that cuprate HTS's with CuO-chains, such as YBCO,¹⁴ show a TEP with a smaller temperature dependence and a smaller 295 K value than those without, such as HBCCO at the same doping levels.¹⁵ This has been ascribed to the extra contribution from the CuO-chain. We decided to measure the temperature dependences of the TEP of the two compounds at different dopings and found that they are very different. As shown in Figs. 6(a) and 6(b), the TEP's of (Cu,C)-1223 for different dopings display smaller absolute 295 K values and a smaller temperature dependence similar to YBCO, whereas those for (Cu,C)-1234 for different dopings show larger absolute values and a greater temperature dependence similar to HBCCO. It has been demonstrated that the n dependence of dT_c/dP predicted using the phenomenological model is in qualitative agreement with that observed in YBCO (Ref. 4) but not in HBCCO (Ref. 15) and that the CuO-chain configuration appears in YBCO but not in HBCCO. The present TEP observations therefore sug-

gest that the different n dependences of dT_c/dP detected in (Cu,C)-1223 and -1234 may be attributed to the different CuO-chain contributions to the electronic spectra in the two compounds. This may be related to the differences in detailed local structures, and a careful reexamination is warranted.

In summary, we have examined under hydrostatic pressures the T_c of the oxycarbonate cuprates of (Cu,C)-1223 and -1234 with different dopings. T_c was found to vary linearly with pressure up to 1.6 GPa. dT_c/dP increases linearly with n decrease for (Cu,C)-1223, which possesses the CuO-chains as the source for pressure-induced charge transfer for n variation, similar to YBCO, in agreement with the prediction by the phenomenological model. However, dT_c/dP for (Cu,C)-1234 decreases with n decrease, in spite of the reported existence of the CuO-chain in both compounds. We have also observed different temperature-dependent TEP's in the two compounds. The TEP for (Cu,C)-1223 varies only slightly with temperature, similar to YBCO, which has the CuO-chains, while that for (Cu,C)-1234 varies strongly with temperature, similar to HBCCO, which does not have the CuO chains and whose dT_c/dP does not vary with n according to the model prediction. We have therefore attributed the different n dependences of dT_c/dP to the possible different CuO₂-chain electronic contributions to the energy spectra of the two compounds.

ACKNOWLEDGMENTS

This work was supported in part by NSF Grant No. DMR 98-04325, T. L. L. Temple Foundation, John and Rebecca Moores Endowment, and the State of Texas through the Texas Center for Superconductivity at the University of Houston.

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