

Pressure dependence of thermopower in $\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$

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Measurements of the temperature dependencies of the thermopower $\alpha(T)$ and the resistivity $\rho(T)$ of polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$ under different hydrostatic pressures are reported. They are interpreted to reveal an increase with pressure in the superconductive-condensate density n_s of the chains. A literature report of $dT_c/dP=0.25$ K/kbar for optimally doped $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Ba}_2\text{Cu}_4\text{O}_8$ is argued to be due to an increase in the elastic coupling between the CuO_2 sheets of the double Cu-O chains as a result of the increase in chain n_s . A c -axis in-phase A_g vibration of the oxygen atoms of the CuO_2 sheets is identified as a participant in the underlying physical mechanism responsible not only for high- T_c superconductivity, but also for the pressure dependencies of T_c and $\alpha(T)$. [S0163-1829(96)51518-3]

The anisotropic conductivity of the fully oxidized copper oxide superconductors $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Y-123) (Refs. 1 and 2) and naturally stoichiometric $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y-124) (Ref. 3) have demonstrated that the Cu-O chains running parallel to the orthorhombic b axis are metallic conductors having a normal-state conductivity competitive with the metallic conductivity of the CuO_2 sheets. These observations have stimulated considerable interest in the role of the chains in these materials not only as charge reservoirs for the CuO_2 sheets, but also as structural components exhibiting a superconductivity induced by proximity to the superconductive sheets. Optimal spectroscopy on single crystals⁴ and muon-spin relaxation (μSR) studies on polycrystals⁵ have provided convincing evidence for involvement of the charge carriers of the chains in superconductive condensation. The μSR data provide a measure of the ratio of the superconductive-condensate density to the charge-carrier effective mass n_s/m^* through the muon-spin depolarization rate σ , which is proportional to the inverse square of the London penetration depth $\lambda^{-2} = \mu_0 e^2 n_s / m^*$. Uemura *et al.*⁶ showed that the superconductive critical temperature T_c associated with underdoped superconductive CuO_2 sheets follows a universal linear increase with the low-temperature depolarization rate $\sigma(0)$. Tallon *et al.*⁵ showed that this linear relationship does not hold where the chains are also superconductive. The depolarization rate $\sigma(0)$ is proportional to the sum of the sheet and chain contributions $(n_s/m^*)_{\text{sh}} + (n_s/m^*)_{\text{ch}}$.

The chain contribution to the temperature-dependent thermopower $\alpha(T)$ is negative and competitive over all temperatures $T_c < T < 300$ K with the positive contribution from the sheets in fully oxidized $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$; moreover, the chain contribution exhibits the same anomalous low-temperature enhancement of the magnitude of the thermopower that is found to be a peculiar characteristic of the normal state of the superconductive CuO_2 sheets.⁷ This enhancement has a maximum at $T_{\text{max}} \approx 140$ K, which is too high to be associated with acoustic phonons; we have suggested it is associated with vibronic coupling to an optical-mode site deformation⁸ and hence that elastic coupling between the sheets and the chains may be responsible for inducing superconductivity in the chains. We have also established a relationship between dT_c/dP and $d\alpha(T)/dP$ in the system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, which

contains only CuO_2 sheets.⁹ In this paper we report on the pressure dependence of both $\alpha(T)$ and the temperature-dependent resistivity $\rho(T)$ for fully oxidized $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$. These measurements (a) answer to what extent pressure-induced charge transfer between Cu-O chains and CuO_2 sheets influences T_c in these compounds, (b) reveal an important enhancement with pressure of the superconductive-condensate density n_s of the chains, and (c) address the identification of an underlying physical mechanism that relates dT_c/dP to changes with pressure of the normal-state properties.

Polycrystalline samples of Y-124 and Y-123, which were single phase to x-ray powder diffraction after slow cooling in oxygen, were cut into a rectangular shape and loaded into a self-clamped pressure cell that will be described elsewhere. The cooling rate during measurement was well-controlled to around 0.2 K/min. The pressures inside the chamber were monitored with manganin wire over the whole temperature range for each run, which allowed correction to be made to a constant pressure in the cell for all temperatures. However, we plot raw data and show, for one pressure for each compound, how the data would be modified by such a correction. The Montgomery four-probe method was used to measure resistivity. The setup for thermopower measurements under pressure was thoroughly tested; it gives the correct thermopower of Cu and Pt metal. The data are highly reproducible. The contribution from the copper leads was subtracted from all our thermopower data. The subtraction was made possible by measurement of the thermopower below $T_c = 124$ K of the Tl-2223 superconductor, which not only gave the copper-lead contribution at ambient pressure but also showed it to be essentially pressure independent. The temperature dependence of the copper-lead contribution above T_c was obtained from the literature. The systematic error to the true value of thermopower is within $\pm 0.4 \mu\text{V/K}$ in our setup. The data obtained before the application of pressure were the same as those obtained after the pressure was released, which indicates that no chemical change occurred under high pressure.

Figures 1 and 2 display the $\rho(T)$ and $\alpha(T)$ data for several hydrostatic pressures for the fully oxidized Y-123 com-

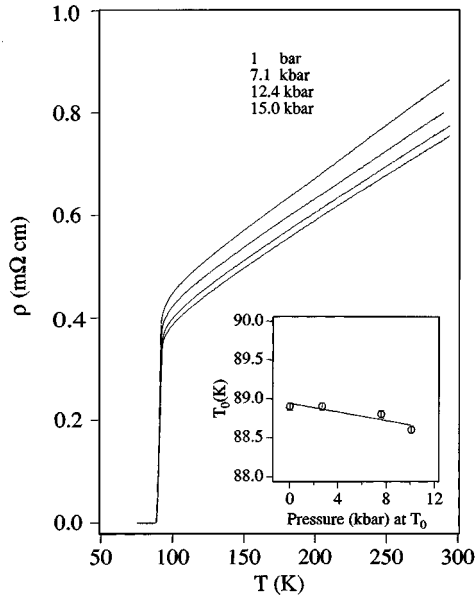


FIG. 1. Temperature dependence of the resistivity $\rho(T)$ of a polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$ sample for four different pressures.

pound ($\delta \approx 0.04$). The temperature at which $\rho(T)$ vanishes is T_0 , and a $dT_0/dP = -0.027$ K/kbar for this slightly overdoped superconductor is consistent with data reported in the literature.¹⁰ At atmospheric pressure, the $\alpha(T)$ curve in Fig. 2 is also the same as previously reported; the negative value of $\alpha(T)$ reflects a dominance of the chain contribution.⁷ Hydrostatic pressure increases the magnitude of both the negative thermopower and the negative enhancement hump.

Figures 3 and 4 show $\rho(T)$ and $\alpha(T)$ data for several hydrostatic pressures for the underdoped Y-124 sample. The measured $dT_0/dP = 0.66$ K/kbar is consistent with that re-

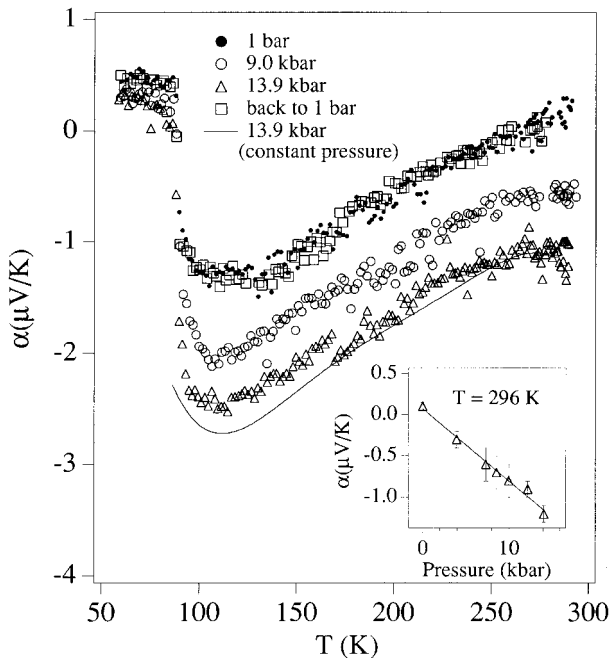


FIG. 2. Temperature dependence of the thermopower $\alpha(T)$ of polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$ obtained at different pressures.

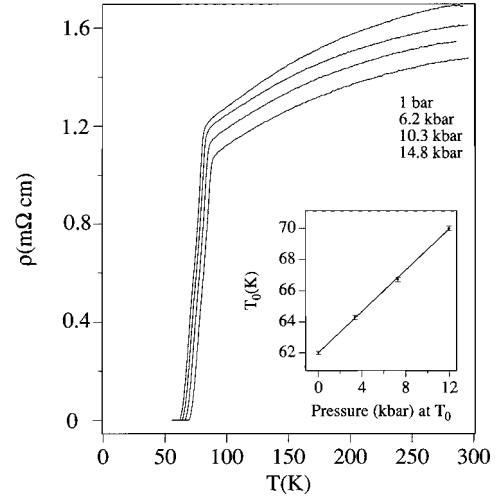


FIG. 3. Temperature dependence of the resistivity $\rho(T)$ for polycrystalline $\text{YBa}_2\text{Cu}_4\text{O}_8$ sample taken at different pressures.

ported by other workers.^{11–13} We take the pressure in the calculation of dT_0/dP at T_0 , which gives a slightly higher value of dT_0/dP than in the previously reported data. For this compound, $\alpha(T)$ is positive as in the copper oxide superconductors where the thermopower is associated with the CuO_2 sheets. However, its temperature dependence does not exhibit the positive enhancement found for the CuO_2 sheets; rather it shows a temperature dependence to be expected where there is an important negative contribution from the chains as in Fig. 2. As for Y-123 of Fig. 2, pressure decreases $\alpha(T)$, presumably by increasing the negative compo-

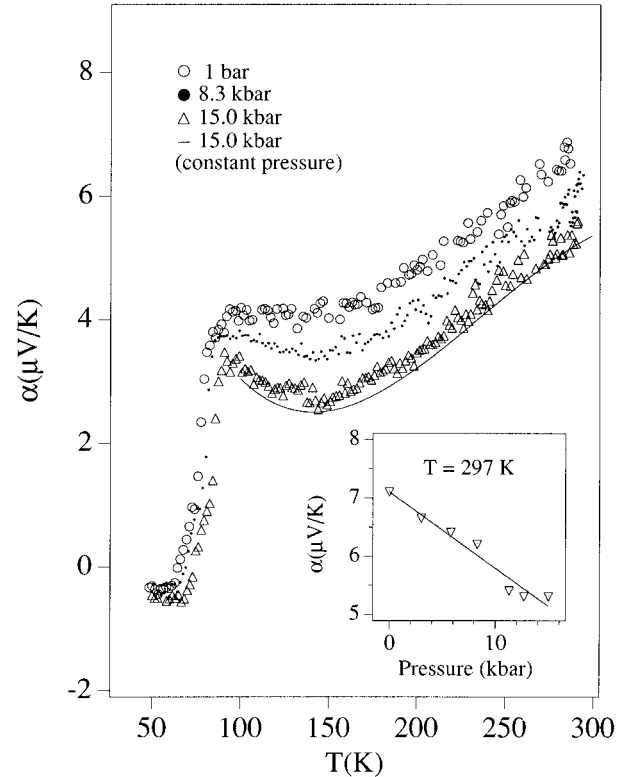


FIG. 4. Temperature dependence of the thermopower $\alpha(T)$ of polycrystalline $\text{YBa}_2\text{Cu}_4\text{O}_8$ obtained at different pressures.

nent in $\alpha(T)$ relative to the positive component. The line shown in Fig. 4 corresponds to the curve for 15 kbar at room temperature corrected to a uniform pressure for all temperatures; it shows a minimum near 140 K, the temperature where the magnitude of $\alpha(T)$ has its maximum enhancement in other copper oxide superconductors.

The small value of $dT_0/dP = -0.027$ K/kbar in Fig. 1 shows that pressure induces little, if any, electron transfer from the CuO_2 sheets to the Cu-O chains in slightly overdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with $\delta \approx 0.04$, which is in marked contrast to the underdoped composition; for $\delta \approx 0.3$, a $dT_0/dP = 1.0$ K/kbar was found.⁹ It follows that, for $\delta \approx 0.04$, the pressure dependence of the thermopower reflects changes occurring in the sheets and the chains at essentially fixed charge-carrier concentrations in each. Measurements of the pressure dependence of $\alpha(T)$ in the system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ have shown⁹ that the overdoped $x=0.22$ composition exhibits no pressure dependence of either T_c or the thermopower of the CuO_2 sheets. The absence of any significant pressure dependence of T_0 in overdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with $\delta \approx 0.04$ is therefore consistent with an absence of charge transfer from or to the CuO_2 sheets and a T_c determined by the hole concentration in the CuO_2 sheets, as implied by the μSR data of Tallon *et al.*⁵ Therefore little, if any, pressure dependence of the thermopower from the CuO_2 sheets should be present as in overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. It follows that the changes in $\alpha(T)$ with pressure shown in Fig. 2 reflect primarily changes in the chain contribution to $\alpha(T)$, which is negative. We have pointed out elsewhere¹⁴ that the thermopower imparted by a partially filled band is a measure of the curvature of the $\varepsilon(\mathbf{k})$ dispersion curve at the Fermi energy ε_F . The increase in the magnitude of the negative $\alpha(T)$ with pressure shown in Fig. 2 indicates an increase in the curvature of the chain $\varepsilon(\mathbf{k})$ at ε_F . A flattening of the $\varepsilon(\mathbf{k})$ curve, i.e., a higher degeneracy at ε_F , allows stabilization of a greater superconductive-condensate density in the chains. The μSR data of Tallon *et al.*⁵ have shown that an increase in the chain n_s does not change T_c in the overdoped compositional range, so our deduction of an increase in the chain n_s is consistent with a $dT_0/dP \approx -0.027$ K/kbar.

The temperature dependence of the thermopower $\alpha(T)$ shown in Fig. 4 agrees, at ambient pressure, with that reported by Tallon *et al.*;¹⁵ it differs from that found for other underdoped cuprate superconductors. Underdoped CuO_2 sheets should exhibit a maximum positive enhancement at $T_{\text{max}} \approx 140$ K whereas Fig. 4 shows a minimum in $\alpha(T)$ near 140 K as does $\alpha(T)$ in Fig. 2. We conclude that the fully oxidized double chains of the Y-124 oxides make a negative contribution to the thermopower that is in opposition to a relatively large, positive thermopower from underdoped CuO_2 sheets and that, as in fully oxidized Y-123, an enhancement of the magnitude of the negative contribution is responsible for the minimum in $\alpha(T)$ at almost 140 K even though the negative contribution remains smaller than the positive contribution. Indeed, the minimum in $\alpha(T)$ near 140 K is deepened with pressure. The existence of a chain enhancement factor in the normal state with a $T_{\text{max}} \approx 140$ K signals, according to other $\alpha(T)$ data on the copper oxide superconductors, condensation in the double chains below

T_c of superconductive pairs. This deduction finds independent confirmation in the μSR data of Tallon *et al.*,⁵ which show a deviation from the universal T_c versus $\sigma(0)$ of Uemura *et al.*⁶ because of a contribution from $(n_s/m^*)_{\text{ch}}$.

In order to account for a negative contribution to the thermopower from the double chains, we note that the lower y^2-z^2 Hubbard band of the chains is split in two by the translational symmetry since the double chains have two distinguishable Cu(1) atoms. Underdoped CuO_2 sheets would have around $p \approx 0.125$ holes per Cu(2) atom in the lower x^2-y^2 Hubbard band of the CuO_2 sheets. A formula $\text{YBa}_2\text{Cu}_4\text{O}_8$ then gives 0.625 electrons per Cu(1) atom in the lower Hubbard y^2-z^2 band of the double chains; and a splitting of this y^2-z^2 band in two by the translational symmetry leaves the partially occupied band one-quarter filled, which accounts for a negative chain contribution to the thermopower.

The large $dT_0/dP = 0.66$ K/kbar observed for Y-124 has been interpreted^{11,13} to be caused by electron transfer from the CuO_2 sheets to the double chains in this underdoped material, and indeed a large electron transfer from the sheets to the chains has been confirmed for underdoped Y-123.⁹ On the other hand, the optimally doped $x=0.1$ composition of the system $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_4\text{O}_8$ retains a large $dT_0/dP = 0.25$ K/kbar.¹⁶ (T_c increases from 82 K at $x=0$ to 90 K at $x=0.1$ in this system.) At optimal doping, transfer of electrons either from or to the CuO_2 sheets can only reduce T_c , so the large $dT_0/dP = 0.25$ K/kbar can only be due to some other factors. In optimally doped $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, a $dT_0/dP = 0.1$ K/kbar is due to a straightening of the Cu-O-Cu bond angle in the CuO_2 sheets,¹⁷ but this mechanism is apparently not operative in slightly overdoped Y-123, Fig. 1. We proposed here an alternate mechanism for $dT_c/dP > 0$: the increase with pressure in superconductive-condensate density n_s in the double chains, which we deduced above, is caused by the enhancement of the elastic coupling between the CuO_2 sheets and the double chains along the c axis. An increase in the amplitude of the oxygen

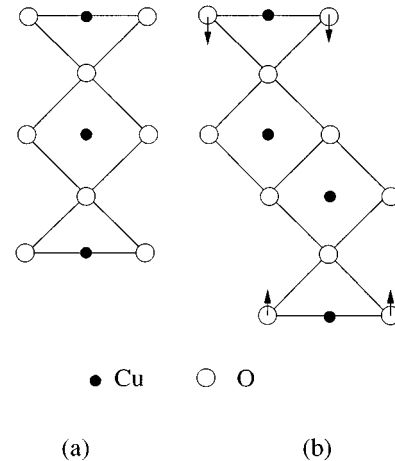


FIG. 5. Schematic plot of the coupling of CuO_2 sheets by (a) single in $\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$ and (b) double Cu-O chains in $\text{YBa}_2\text{Cu}_4\text{O}_8$.

displacements of a vibronic coupling, through cooperative elastic interactions between the chains and sheets, increases T_c for the CuO_2 sheets.

Indirect support for this proposal comes from the observation¹⁸ that all the Raman modes for Y-124 increase linearly with pressure except the in-phase O(2)-O(3) A_g vibration of the oxygen atoms of a CuO_2 sheet along the c axis—see arrows in Fig. 5(b), which saturates above 60 kbar. At the same pressure, T_c versus pressure saturates also.¹¹ Therefore, we tentatively associate this optical-mode oxygen motion with the formation of superconductive pairs. Moreover, a phonon-drag gives a low-temperature thermopower enhancement of $\alpha(T)$ due to acoustic phonons that has a $T_{\text{max}} \approx 0.2-0.3\theta_D$, where θ_D is the Debye temperature.¹⁴ The O(2)-O(3) A_g in-phase optical mode has a characteristic temperature of 672 K; and 20% of this temperature would give a $T_{\text{max}} \approx 134$ K, which is close to the $T_{\text{max}} \approx 140$ K for the enhancement term found for the normal state of the copper oxides that become superconductive. Pressure increases the enhancement maximum as well as T_c , which is a further indication that the two are related to a common underlying physical mechanism such as the optical-mode oxygen vibration that we have identified.

In conclusion, measurement of $\alpha(T)$ and $\rho(T)$ under pressure have shown that (a) pressure induces little electron

transfer between the sheets and the chains in nearly optimally doped Y-123 and that the electron transfer from sheets to chains in underdoped Y-124 cannot alone account for the magnitude of $dT_0/dP = 0.66$ K/kbar, (b) pressure increases significantly the superconductive-condensate density n_s of the chains in both Y-123 and Y-124 fully oxidized samples in a manner that is consistent with published μSR data, (c) our results establish a relation between the enhancement factor in $\alpha(T)$ and the superconductive condensate density n_s , and (d) a common underlying physical mechanism underlies T_c and both the nearly temperature-independent term α_0 and the enhancement term $\delta\alpha(T)$ of the thermopower $\alpha(T) = \alpha_0 + \delta\alpha(T)$. We tentatively identify this mechanism as an optical-mode oxygen vibration that couples vibronically to the electrons of a CuO_2 sheet and elastically along the c axis to the Cu-O chains of the Y-123 and Y-124 structures to induce a parasitic superconductivity in the chains.

Recently, several reports have appeared regarding superconductive condensation in the chains of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Refs. 19 and 20) and interplane coupling in $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$.²¹

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