

## Thermoelectric Power: A Simple, Instructive Probe of High- $T_c$ Superconductors

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The thermoelectric power  $S(T)$  is studied for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{YBa}_2\text{Cu}_4\text{O}_8$  as a function of Zn substitution and hole concentration  $p$ . A strong enhancement in  $S(T)$  is correlated with the smooth opening of an energy gap in the normal-state spectrum, as observed from NMR and heat capacity data, which appears to be responsible for the  $p$ -dependent variation in  $T_c$ . The data are consistent with the local suppression of this energy gap in the immediate neighborhood of a Zn atom. Studies of  $S(T)$  provide a simple means to explore the energy scales associated with the superconducting phase diagram and give some key insights into the origins of cuprate superconductivity.

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There is still no consensus as to the origins of superconductivity in the high- $T_c$  superconducting cuprates (HTSC). Their phase behavior and the underlying interplay between magnetism and superconductivity is rich and complex. Certain key factors have, however, emerged. Most notably the underdoped HTSC are characterized by the presence of an energy gap  $E_g$  in the normal-state excitation spectrum which decreases with increasing hole concentration  $p$ . This gap has been variously referred to as a spin gap, pseudogap, or normal-state gap. The term *spin gap* was introduced because it was first observed in both NMR [1] and inelastic neutron scattering [2] probes of the spin susceptibility and because it is a feature of spin and charge separated models of HTSC [3]. The term *pseudogap* referred to the superconducting-gap-like depression of the infrared conductivity [4] and softening of phonon mode frequencies [5]. However, unlike a superconducting gap there is no detectable transfer of spectral weight to a zero-frequency delta function [6] and, in sufficiently underdoped samples, the gap opens at a temperature  $T_g$  well above  $T_c$  because in this region  $E_g/k_B$  exceeds  $T_c$ . Recently, high-precision differential heat capacity measurements for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (123) as a function of  $\delta$  have allowed the determination of the electronic heat capacity [7,8] and the opening of the normal-state (NS) gap followed by the opening of the superconducting gap at  $T_c$  is clearly seen. There is no evidence for a phase transition at  $T_g$  which is just an energy scale for the smooth opening of the NS gap, and, because the heat capacity is determined by the full excitation spectrum, the NS gap is evidently not just confined to the spin spectrum. The NS gap appears to be intimately related to superconductivity in HTSC: It depresses the condensation energy and  $T_c$  on the underdoped side because of the loss of low-energy NS spectral weight [8] and, therefore, its  $p$  dependence governs the shape of the superconducting phase curve [9].

Associated with the appearance of the NS gap there occurs a decrease in transport scattering rate resulting

in a downturn in the temperature dependence of the resistivity [10] which has now been observed in many underdoped HTSC. In fact, all transport properties of HTSC exhibit a systematic dependence upon hole concentration including, most notably, the thermoelectric power (TEP) which has a universal dependence upon temperature, hole concentration, and the ratio  $T_c/T_{c,\text{max}}$  [11]. The room-temperature TEP  $S(290)$  can thus be used as a measure of  $p$  for any HTSC irrespective of their disparate values of  $T_{c,\text{max}}$ . Measurements of  $S(T)$  are equally valid on sintered or ceramic samples as the TEP of untextured polycrystalline samples is just the  $a$ - $b$  plane TEP [11]. In the present Letter, by investigating the temperature-dependent TEP  $S(T)$  in Zn-substituted 123 and 124 samples with different hole concentrations we show that  $S(T)$  exhibits a significant enhancement as the NS gap opens. Moreover, the data are consistent with the gap being suppressed locally near a Zn atom [12,13] and provide key insights into the pairing mechanism, the general superconducting phase behavior, and the transport properties of the HTSC.

Polycrystalline samples of  $\text{YBa}_2\text{Cu}_3(1-y)\text{Zn}_{3y}\text{O}_{7-\delta}$  with  $y = 0, 0.01, 0.02, 0.03, 0.05,$  and  $0.07$  were synthesized using conventional solid-state reaction of stoichiometric oxides and carbonates in air. Sets of samples with different  $y$  values were annealed together at various temperatures and oxygen partial pressures then quenched into liquid nitrogen in order to vary  $\delta$  but have the same value of  $\delta$  for each  $y$  value. Samples of  $\text{YBa}_2\text{Cu}_4(1-y)\text{Zn}_y\text{O}_8$ ,  $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Ba}_2\text{Cu}_4(1-y)\text{Zn}_y\text{O}_8$ ,  $\text{YBa}_{1.9}\text{La}_{0.1}\text{Cu}_4(1-y)\text{Zn}_y\text{O}_8$ , and  $\text{YBa}_{1.8}\text{La}_{0.2}\text{Cu}_4(1-y)\text{Zn}_y\text{O}_8$  with  $y = 0, 0.006, 0.012, 0.025,$  and  $0.037$  were synthesized using solid-state reaction of stoichiometric oxides at  $930^\circ\text{C}$  in oxygen at 60 bars pressure. All samples were free of impurity phase to the threshold of detection (2%) as determined from x-ray diffraction. Infrared reflectivity investigations of phonon-mode shifts as a function of Zn content in the 124 samples indicate that all of the Zn

substitutes in the planes rather than the chains [14]. This is also believed to be the case for 123. The TEP was measured as a function of temperature between 4 and 400 K using conventional methods [11].

We note first that the room-temperature TEP of the 123 or 124 samples is independent of Zn concentration except when the samples are heavily underdoped. This is particularly evident in the case of the oxygen-stoichiometric 124 samples for which  $S(300) = 7.0 \pm 0.1 \mu\text{V/K}$  for all Zn contents. Figure 1 shows  $S(300)$  plotted against oxygen deficiency  $\delta$  for Zn-substituted 123 and, for  $\delta < 0.4$ , the TEP is independent of Zn content. (Slight deviations for  $\delta < 0.1$  are discussed later.) Accordingly, in this doping range the TEP can still be used as a measure of the hole concentration [11] even in the presence of the strong in-plane scattering of the Zn atoms. As  $\delta$  rises above 0.4 the  $S(300)$  data "fans out" depending upon Zn concentration with the Zn-free samples showing a marked enhancement which grows with further underdoping.

A clearer picture of the origin of this Zn-dependent enhancement is obtained from the temperature dependence of the TEP for 124 shown in Fig. 2. Pairs of curves for 0% (filled symbols) and 3.7% Zn (open symbols) are shown from bottom to top for 0.1Ca:124, 0.1La:124, and 0.2La:124, i.e., showing the effects of progressive underdoping or hole filling. For pure 124  $S(T)$  is plotted for all Zn compositions giving a family of curves spreading downward for increasing Zn concentration. Data points are omitted for clarity. For each hole concentration the values of the TEP at high temperature are independent of Zn content but diverge below a characteristic temperature,  $T_g$ , which increases with decreasing  $p$ . As well as suppressing superconductivity the Zn also appears to weaken, and ultimately remove, the pretransitional enhancement in  $S(T)$ . This enhancement occurs at temperatures which are probably too high for superconducting fluctuations but are close to the temperature at which the Knight shift, spin-lattice relaxation rate, and phonon mode frequen-

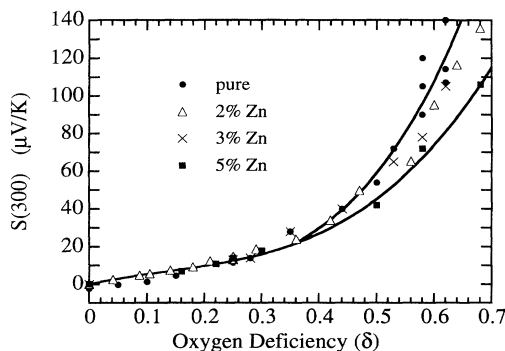


FIG. 1. The dependence of the room-temperature TEP,  $S(300)$ , on oxygen deficiency for  $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$  for  $x = 0$  (circles), 0.02 (triangles), 0.03 (crosses) and 0.05 (squares).

cies all begin to fall due to the opening of the NS gap. Moreover, the sets of curves in Fig. 2 show that the enhancement onset,  $T_g$ , shifts to higher temperatures (140, 190, 230, and  $>300$  K, respectively) similar to the increase in  $E_g$  with underdoping [7,9]. The same picture is preserved for the pairs of 123 data (0% and 3% Zn) shown in Fig. 3 for  $\delta = 0.0, 0.28, 0.35$ , and 0.53. Again, a family of curves for the full range of Zn substitution is shown for the  $\delta = 0.28$  samples. Though the overall temperature dependence is rather different for 123 there is a similar enhancement in  $S(T)$  below a temperature  $T_g$  which increases with underdoping and exceeds 300 K for  $\delta = 0.53$ . [For  $\delta \approx 0$  there is an offset of  $3 \mu\text{V/K}$  between the  $S(T)$  values for 0% and 3% Zn. We find this to be common near full oxygen loading and speculate that this originates from a small oxygen deficiency in the Zn-substituted samples.] We propose, therefore, that with the opening of the pseudogap at  $T_g \sim E_g/k_B$  the transport scattering spectrum is modified in such a way that the TEP becomes significantly enhanced. Zn substitution destroys the pseudogap [15] and thus removes the pseudogap enhancement of the TEP. The onset of Zn-dependent room-temperature behavior in Fig. 1 is now clearly seen to occur at the critical hole concentration at which  $T_g$  first exceeds 300 K. For  $\delta > 0.4$  there exists a NS pseudogap in 123 at or above room temperature.

The  $S(T)$  data for 124 have a positive slope at high temperature due to the large contribution to the TEP from the double chains while that for 123 have a negative slope which is characteristic of the  $\text{CuO}_2$  planes unless  $\delta$  is close to zero when  $S(T)$  changes sign and the oxygenated single chains also contribute a positive slope [11]. This reversal in both sign and slope has been taken

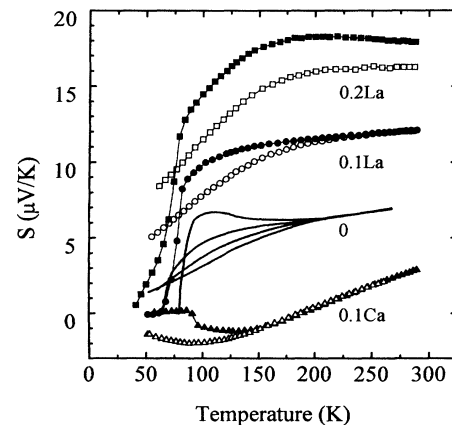


FIG. 2. The temperature dependence of the TEP for  $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Ba}_2\text{Cu}_4\text{O}_8$  (triangles),  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (solid curves),  $\text{YBa}_{1.9}\text{La}_{0.1}\text{Cu}_4\text{O}_8$  (circles), and  $\text{YBa}_{1.8}\text{La}_{0.2}\text{Cu}_4\text{O}_8$  (squares). Solid symbols denote 0% Zn and open symbols denote 3.7% Zn substitution. The family of solid curves for  $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_4\text{O}_8$  in downward order denote 0%, 0.6%, 1.2%, and 3.7% Zn substitution.

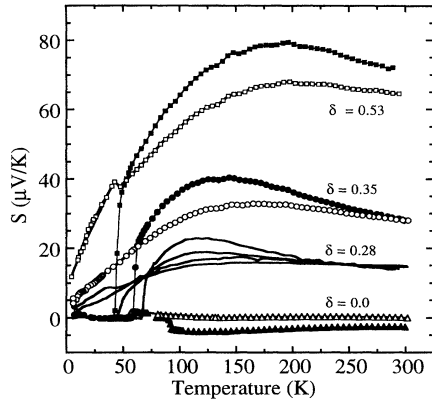


FIG. 3. The temperature dependence of the TEP for  $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$  for  $\delta = 0.0$  (triangles),  $\delta = 0.28$  (solid curves),  $\delta = 0.35$  (circles), and  $\delta = 0.53$  (squares). Solid symbols denote 0% Zn and open symbols denote 3.0% Zn substitution. The family of solid curves in downward order denote 0%, 1.0%, 3.0%, and 5.0% Zn substitution.

as evidence for a Van Hove singularity [16] but in fact is unique to 123; it originates solely in the chains and is absent for the other HTSC. In spite of their different  $T_g$  dependences for the TEP, 123 and 124 have similar  $T_g$  values for the same  $T_c/T_{c,\text{max}}$  values, i.e., for the same hole concentration. We develop this further as follows. The temperatures  $T_g$  have been read off the  $S(T)$  curves in Figs. 2 and 3 and plotted against  $p$  in Fig. 4 (solid squares). For 123  $p$  was determined from the  $S(300)$  values and its correlation with hole concentration [11] while, for 124,  $p$  was determined from the ratio of  $T_c$  to  $T_{c,\text{max}}$  ( $=93.5$  K) using the parabolic relation  $T_c/T_{c,\text{max}} = 1 - 82.6(p - 0.16)^2$ , which is conveniently satisfied for a number of, and perhaps all, HTSC [17]. Also plotted

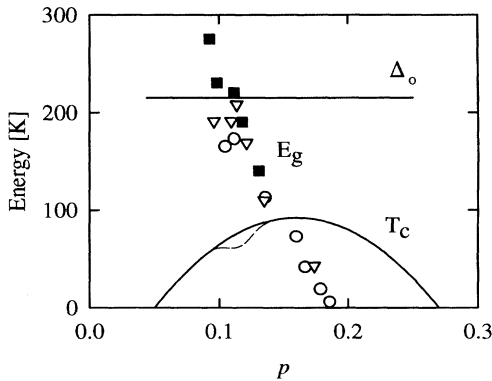


FIG. 4. The hole-concentration ( $p$ ) dependence of  $T_g$  (solid squares) from the present TEP data and  $E_g$  from NMR shifts (triangles) and from heat capacity (circles). The solid curve shows the parabolic  $p$  dependence of  $T_c$  found for many HTSC, including  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . The dotted curve shows a possible intrinsic "60 K plateau," as seen in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , which coincides with  $E_g \approx \Delta_0$ .

is this parabolic phase curve  $T_c = T_c(p)$  (solid curve) and the  $p$  dependence of  $E_g$  determined [9] from heat capacity (circles) and NMR studies (triangles). *The good correspondence among the three data sets for  $E_g$  shows that the TEP probes the same gap as does the heat capacity and the NMR.*

The present results allow a number of important conclusions to be drawn.

(i) The family of  $S(T)$  curves for the full range of Zn substitution shown in Fig. 2 for 124 and in Fig. 3 for 123 with  $\delta \approx 0.28$  provide further evidence that, although Zn substitution suppresses the pseudogap, it does not depress  $E_g$  homogeneously. In contrast to the effect of hole doping which decreases both  $E_g$  and  $T_g$  as shown in Figs. 2, 3, and 4, progressive Zn substitution for both 123 and 124 just reduces the magnitude of the TEP enhancement without altering  $T_g$ . The  $S(T)$  curves proceed to an asymptotic curve which is the apparent TEP in the absence of both a NS gap and superconductivity. The fact that  $T_g$  remains unchanged through this progression to the asymptotic curve is consistent with the NS gap being suppressed near a Zn atom [12,13] and hence the TEP enhancement due to regions remote from a Zn atom is simply diluted, rather than shifted, with increasing Zn concentration.

(ii) It is often proposed that the unusual transport properties of the HTSC, including the  $T$  and  $p$  dependence of the TEP, provide a key to understanding the pairing mechanism. Zn substitution destroys spin correlations, superconductivity, and the pseudogap but does not alter the TEP except to suppress the pseudogap enhancement in  $S(T)$ . This surely implies that the unusual  $S(T, p)$  is unrelated to either spin correlations or the pairing mechanism.

(iii) While the superconducting gap energy  $\Delta_0$  is relatively independent of  $p$ ,  $T_c$  falls on the underdoped side because the pseudogap reduces the entropy available for superconductivity [8]. The  $p$  dependence of  $T_c$  is determined by the  $p$  dependence of  $E_g$  [9] shown in Fig. 4. This model provides a simple explanation for the unusual isotope effect in HTSC (which is negligible near optimum doping but rises to around 0.5 with underdoping [18]) if the isotope effect resides in the pseudogap correlations and not in the pairing interaction. This suggests a nonphonon pairing interaction such as, e.g., spin fluctuations, together with a phonon-mediated pseudogap such as, e.g., the dynamic Jahn-Teller instability proposed by Markiewicz [19], which appears to be supported by recent neutron scattering data [20].

(iv) The fact that  $S(300)$  is a featureless, monotonic function of  $\delta$  as shown in Fig. 1 indicates that, across the 60 K plateau, the hole concentration  $p$  continues to increase as  $\delta$  decreases, i.e., the 60 K plateau in  $T_c$  vs  $\delta$  would be preserved in a plot of  $T_c$  vs  $p$ . We recognize the existence of oxygen ordering effects around  $\delta \approx 0.5$  but conclude that the underdoped plateau (or dip), as seen

also in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  [21], is probably a general feature of the  $T_c$  vs  $p$  phase curve and for 123 and 124 appears to coincide with  $E_g(p) = \Delta_0$  ( $=215$  K [8]) as shown in Fig. 4.

We have compared the temperature dependence of the TEP for 0% and 3.7% Zn-substituted 124 with the Knight shift [22], the  $305\text{ cm}^{-1}$  phonon-mode softening [5] and the resistivity. The enhancement in both the TEP and conductivity and the mode softening all start at the same temperature. Notably, however, the Knight shift shows that, even at the 3.7% level, the pseudogap is not fully suppressed even though superconductivity is ( $T_c = 0$ ). If one accepts that the suppression of superconductivity and of the NS gap are both local effects, then this can be understood within a picture in which superconductivity is suppressed when the mean spacing of Zn atoms falls below a coherence length [23] and the pseudogap is suppressed when the mean spacing falls below the pseudogap correlation length. At intermediate concentrations the pseudogap survives in the region between Zn atoms. This picture appears to be sustained by the present data. Superconductivity is first suppressed in the 124 compound when  $y = 3\%$ , i.e., at a  $\text{CuO}_2$  plane concentration of 6%. Here the mean spacing between Zn atoms is  $16\text{ \AA}$ , which is equal to the coherence length. Moreover, the pseudogap is suppressed when  $y = 6.3\%$  [22] or at a mean spacing of  $2.8a$ . This occurs when adjacent Zn atoms share the same next-nearest neighbor at  $1.4a$  ( $\approx$  the spin-fluctuation correlation length [2]) and implies that the pseudogap is completely suppressed at nearest-neighbor sites to a Zn atom and substantially suppressed at the next-nearest-neighbor site.

The data in Figs. 1, 2, and 3 tend to favor a theory where the transport properties are determined by the level of hole doping and, it is not obvious how to reconcile it with band theory and a large Fermi-surface picture where the scattering by Zn atoms might be expected to have an effect. It implies that the TEP is determined by the strength of electron-electron interactions, which vary strongly with doping rather than by details of any scattering process. Recently the unusual TEP of HTSC was ascribed to a large  $T$ -independent phonon-drag term [24]. Although phonon drag is usually suppressed by alloying, Zn substitution has little effect on metallic Cu because of their similar atomic weights [25]. So a phonon drag picture is not inconsistent with the present results. Generally phonon drag effects become larger for lower carrier concentrations [25], so the opening of a pseudogap would be expected to enhance the TEP as observed. Alternatively the electron diffusion TEP is given by  $S_e = \langle \epsilon \rangle / eT$ , where  $\langle \epsilon \rangle$  is the mean energy of the carriers (of charge  $e$ ) relative to the Fermi level. Provided there is a source of asymmetry about the Fermi level, the gap in the charge and spin spectrum [12] could have a strong effect on  $S_e$ . Similar substitution experiments but with a

much larger difference in atomic weights would help to distinguish between these two possibilities.

In summary, we report a marked enhancement in the thermoelectric power which correlates with the opening of a NS energy gap. In combination with a previously reported correlation between the TEP and the doping state [11] the TEP is seen to be a simple but powerful probe of the phase behavior of the HTSC. Zn substitution inhomogeneously suppresses both the NS gap and the superconducting order parameter and, at an intermediate concentration, the former survives while the latter does not. The data are consistent with a nonphonon pairing interaction and a phonon-related NS gap, and are consistent with a Van Hove singularity model where the singularity sweeps through the Fermi energy with doping. The 60 K plateau appears to be intrinsic and occurs when the NS gap and the superconducting gap energies are equal.

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