PHYSICAL REVIEW B VOLUME 46, NUMBER 22 1 DECEMBER 1992-II

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Systematics in the thermoelectric power of high-T_c oxides

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(Received 2 September 1992)

Many superconducting cuprates show a parabolic variation of T_c with hole concentration p, there being a minimum and a maximum hole concentration for superconductivity. Thermoelectric power (TEP) measurements reported here as a function of p for a number of oxides reveal several important trends: (1) close similarities in the TEP of several compounds and a change in sign of the room-temperature TEP near the maximum T_c, (2) continuity in the TEP when doping across the two superconducting-nonsuperconducting boundaries, and (3) a universal correspondence of the room-temperature TEP with p over the whole range of doping.

A wealth of experimental and theoretical work has been published on the normal-state transport properties of high-temperature superconducting (HTSC) oxides. Most HTSC systems can be continuously doped either by varying the oxygen concentration or by making suitable nonisovalent substitutions in the parent compound. Thus any complete theoretical model needs to consider the full range of doping and temperature (T) as well as the effects of isovalent substitutions. For the moment, on the experimental side, it is important to try to pick out systematic trends which may help to distinguish between different possible models.

Since the original work[1] on $La_{2-x}Sr_xCuO_4$, several HTSC cuprates have been found to show a parabolic variation of T_c with hole concentration,[2] there being a minimum and maximum value of hole concentration (p) per planar Cu atom for the occurrence of superconductivity, and an optimal value for which T_c is a maximum ($T_c^{\max}$). This range of p ($\approx 0.05 \leq p \leq \approx 0.27$) is surprisingly small,[1,2] but in some models[3] doping can lead to the screening of interactions between the Cu $3d$ electrons and their "release" as mobile carriers. We report here a number of general trends in the thermoelectric power (TEP), discussing first the overdoped region on the high p side of $T_c^{\max}$, then the underdoped, low p side of $T_c^{\max}$, and finally demonstrate a universal dependence of the room-temperature TEP on p across the entire range of doping for the cuprates investigated.

TEP measurements were made on sintered bars using a small, reversible temperature difference of 0.3–1 K; in all cases the data have been corrected for the contribution of the gold connecting leads, which was measured separately using a Pb standard.

Varying the oxygen content of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ (2:2:1:2) (Ref. 4) and $Tl_2Ba_2CuO_{6+\delta}$ (2:1:0:1) systems enables the *overdoped region* to be studied, especially for the latter where superconductivity can be suppressed.[5] In Fig. 1 are shown TEP versus temperature plots for vari-

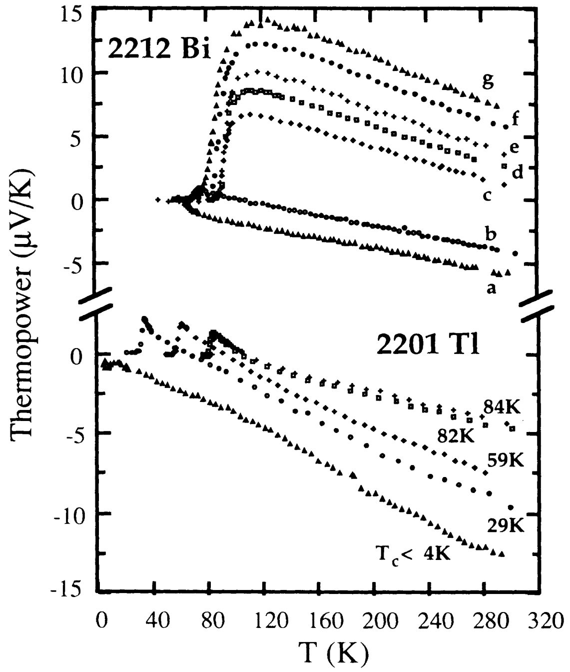

FIG. 1. Thermoelectric power vs temperature for $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $Tl_2Ba_2CuO_{6+\delta}$ at various δ. For $Bi_2Sr_2CaCu_2O_{8+\delta}$, the relative values of δ are 0.077, 0.051, 0, 0.01, −0.07, −0.025, and −0.035 (±0.005) for curves *a*, *b*, *c*, *d*, *e*, *f*, and *g*.

ous values of T_c (i.e., δ) for these two systems. For thallium 2:2:0:1, T_c has been varied from less than 4 K to 85 K by decreasing δ. The changes in T_c were induced by annealing treatments of the same sample and were found to be fully reversible, as was the measured room-temperature TEP. For the most strongly doped composition ($T_c \sim 3$ K) the TEP is negative and large (-12 to -15 μV/K at 300 K) and, as also shown for a second sample in Fig. 2(b), it has a linear temperature dependence extrapolating to 0 ± 1 μV/K at $T = 0$. This behavior is typical of a metal with little phonon drag. Decreasing the doping level reduces the magnitude of the TEP and increases the inversion temperature where the TEP changes sign to positive values. Except for a cusp above T_c, the temperature variation is still essentially linear (but not through the origin) with a slope varying from -0.05 to -0.02 μV/K^2. For bismuth 2:2:1:2, the most strongly doped composition again has a negative and linear TEP which extrapolates almost through the origin. The TEP is similarly displaced upwards to more positive values as the doping level is reduced, with slope varying from -0.02 to -0.043 μV/K^2. The change in sign of the room-temperature TEP occurs for hole carrier concentrations close to the maximum in T_c as found for[6,7] $YBa_2Cu_3O_{7-\delta}$ and for[8] $(Tl_{0.5}Pb_{0.5})Sr_2Ca_{1-x}Y_xCu_2O_7$ (1:2:1:2) and the same trend is evident in Fig. 1 for 2:2:0:1. For most cuprate superconductors the Hall coefficient remains positive in this overdoped region.[5,6,8]

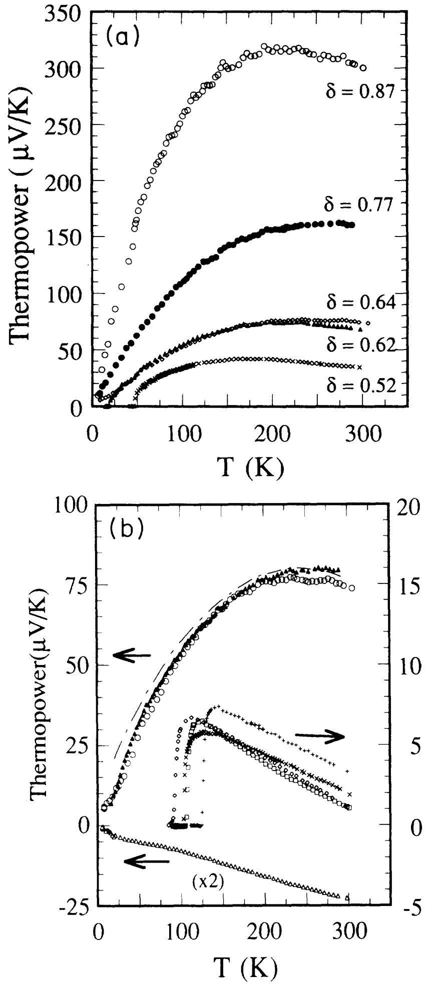

FIG. 2. (a) Thermoelectric power vs temperature for underdoped $YBa_2Cu_3O_{7-\delta}$ with $0.52 \leq \delta \leq 0.87$. For $\delta > 0.5$ the estimated uncertainty in δ relative to other preparation batches (e.g., those in Fig. 3) is ± 0.05. Superconductivity is suppressed for $\delta > \sim 0.62$. (b) Thermoelectric power vs temperature for three samples with p just less than $p_{\min}$, sintered $YBa_2Cu_3O_{6.36}$ (○), $Y_{0.6}Ca_{0.4}Sr_2(Tl_{0.5}Pb_{0.5})Cu_2O_7$ (▲), and single crystal $Bi_{2.2}Sr_2(Y_{0.47}Ca_{0.33})CuO_8$ (dashed line) (Ref. 15). Data for Bi2:2:1:2 (◇), Tl1:2:1:2 ($x = 0.2$) (×), Bi2:2:2:3 (□), Tl2:2:2:3 (+) at $T_c^{\max}$ and overdoped Tl2:2:0:1 (△) are also shown.

For a good conductor the TEP (S) must tend to zero as $T \to 0$. Thus if the materials in Fig. 1 did not become superconducting there would necessarily be a low characteristic temperature (or energy) at which $|S|$ has a maximum and below which S falls to zero. In metallic systems, this can correspond to a fraction of the Debye temperature (ordinary metals are influenced by phonon drag or higher-order phonon scattering processes[9]), the Kondo temperature (dilute magnetic alloys), or the spin-glass freezing temperature[10] (metallic spin glasses). Furthermore, in the absence of strong phonon drag effects (e.g., in amorphous metals), the strength of the electron-phonon coupling can be estimated from ratio of the high- and low-T slopes of S.[11]

Figure 2(a) shows typical behavior of the TEP in the underdoped region near $p \sim p_{\min}$. The TEP is now very large, varying from 30–50 μV/K for samples with $T_c \sim 50$ K to several hundred μV/K for nonsuperconducting ones. It shows a maximum at $T = T_m$ which shifts to higher temperatures as p is decreased and as a useful rule, reaches about 100 μV/K when $p \sim p_{\min}$. Since $S \approx E/(eT)$, where E is the average energy of the mobile charge carriers relative to the chemical potential, such a large value ($\approx k_B/e = 86$ μV/K) may indicate that there is a mobility edge at the Fermi level when $p \sim p_{\min}$. It can be seen that the TEP shows no qualitative change through the superconducting-nonsuperconducting boundary, apart from a change in slope of $S(290)$ vs p, visible in Fig. 3. Clearly the interactions responsible for determining the TEP persist across the range of hole concentrations from the fully localized antiferromagnetically (AF) ordered to the superconducting compositions. We note that AF correlations have been detected for the whole range of p in $YBa_2Cu_3O_{7-\delta}$.[12] It is an open question as to what extent the TEP of underdoped materials is affected by superconducting fluctuations[6] well above T_c.

The interplay of superconductivity and localization in two-dimensional systems is the subject of much current interest. For conventional superconductors in the form of ultrathin films,[13] as well as HTSC (Refs. 14 and 15), the transition from superconducting to localized behavior takes place when the sheet resistance exceeds the quantum resistance for pairs $h/4e^2$. Corresponding universal localization behavior may well occur in the TEP but we are not aware of an appropriate theoretical treatment. The $S \sim T^{1/3}$ law expected[16] for variable range hopping between well-localized states in two dimensions does not give a good fit to our data, but they do fit a $\log T$ law for $0.1 < T/T_m < 0.9$.

Figure 2(b) shows the TEP of three samples, including one single crystal,[15] which have p just less than p_{min} as well as for four compounds with $T_c = T_c^{\mathrm{max}}$. The TEP of sintered samples closely resembles the *ab* plane TEP of single crystals[15,17] and is much less sensitive to the porosity than the resistivity, probably because heat current is more efficiently transported through grain boundaries or other weak links than electric current. The similarity in the TEP of the three underdoped samples, in both magnitude and T dependence, is striking; at T_c^{min} the nature of the disorder potential appears to have little effect on the TEP. Similarly, at T_c^{max}, the magnitude and T dependence of the TEP for bismuth 2:2:1:2 (both sintered and single crystal[15,17]), bismuth 2:2:2:3, thallium 1:2:1:2, and thallium 2:2:2:3 are almost identical in the normal state. Although one should be cautious when dealing with such complicated materials this does point towards a single-band model, where the TEP is dominated by the CuO_2 planes and no significant contribution arises from the various charge reservoir layers Bi_2O_2, Tl_2O_2, or (Tl,Pb)O. The exception to this is $YBa_2Cu_3O_{7-\delta}$ near $\delta \sim 0$, where the chains also contribute.[7,18] Away from $\delta \sim 0$ the chains do not appear to be important and we believe that a single-band model does become valid.

These results indicate a universal dependence of the TEP on p, and we have therefore looked for a quantitative correlation along these lines. However it is not straightforward to determine the effective value of p for many of the compounds investigated. Partial reduction of Tl^{3+} and Pb^{4+} renders standard titration techniques unusable for some compounds, and for $YBa_2Cu_3O_{7-\delta}$ the distribution of charge between the chains and the CuO_2 planes is not known. One method for estimating the hole concentration in the CuO_2 planes is to use a bond valence sum (BVS) analysis which relies on accurate knowledge of interatomic bond lengths.[19,20] The method can be applied for all types of doping and is not affected by possible hole trapping effects or variations in oxygen loading. Alternatively, Presland *et al.*[2] have found that the phase diagram for several doped cuprate systems is well described by the parabola

$$T_c / T_c^{\mathrm{max}} = 1 - 82.6(p - 0.16)^2 \tag{1}$$

(for $La_{2-x}Sr_xCuO_4$, $p = x$). This parabolic form seems to be quite general, so if suitable structural data are not yet available, Eq. (1) may even be used to estimate p if T_c^{max} is known.

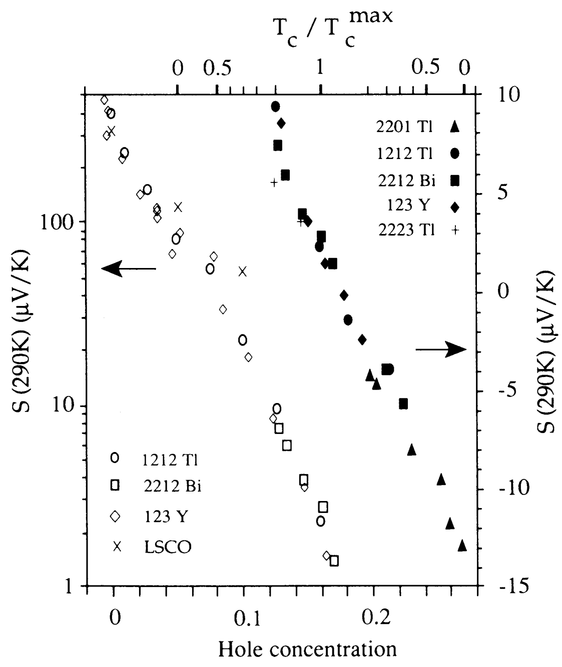

FIG. 3. Room-temperature thermoelectric power $S(290\ \mathrm{K})$ vs hole concentration (and T_c / T_c^{max}) for various high-T_c cuprates in both the underdoped (logarithmic scale) and overdoped (linear scale) regions. $La_{2-x}Sr_xCuO_4$ (LSCO) data from Ref. 33.

In Fig. 3 we have plotted the room-temperature TEP, $S(290\ \mathrm{K})$, vs p showing the underdoped and overdoped regions on logarithmic and linear scales, respectively, for a number of cuprate superconductors. For $YBa_2Cu_3O_{7-\delta}$ and the thallium 1:2:1:2 compound, we have used bond valence sums to calculate p,[19,20] while for thallium 2:2:0:1 and 2:2:2:3 and bismuth 2:2:1:2 we have used Eq. (1) with $T_c^{\mathrm{max}} = 95$,[21] 128,[22,23] and 92 K,[4] respectively (the values used for thallium 2:2:0:1 and 2:2:2:3 are the highest reported T_c's and may be lower than the intrinsic T_c^{max} for the material). We have chosen $S(290\ \mathrm{K})$ since it is well above T_c and is generally in a linear region of the curve. It can be seen that the TEP varies almost linearly with p around T_c^{max}, and that different systems lie on the same curve for a wide range of p. While we expected this behavior for low values of p, because when carriers are localized the TEP often gives a better guide to the carrier type and concentration than does the Hall coefficient,[24] we feel that the observation of a universal curve in the metallic region is an important result. As the method of determining p from BVS is not yet widely accepted, we note that there is also a clear correlation between the measured values of $S(290\ \mathrm{K})$ and T_c / T_c^{max} as shown on the alternative scale in Fig. 3.

For $YBa_2Cu_3O_{7-\delta}$ we have used averages[19] of structural data from two sources[25,26] giving uncertainties in p of at least ± 0.01. The TEP data in Fig. 3 for $p \leq 0.05$ are from a total of four preparation batches, which were annealed at room temperature for several days after quenching, to allow local ordering of the oxygen atoms.[27] $S(290)$ for a freshly quenched sample can be up to 30% larger, depending on the value of δ. For $La_{2-x}Sr_xCuO_4$ $S(290)$ is higher than expected and does not change sign near $x = 0.16$. The latter may arise from the increasing concentration of oxygen vacancies for $x > 0.12$ (Ref. 28) or possible complications arising from phase separation and the orthorhombic-tetragonal transition.[29]

The universal behavior in Fig. 3 confirms that a single-band description is a good starting point for most high-T_c oxides. As mentioned, this would not be expected for $YBa_2Cu_3O_{7-\delta}$ near $\delta = 0$ due to the contribution from the CuO chains and indeed the T dependence of the TEP for values of $\delta \leq 0.2$ (Refs. 6 and 7) is different from that of all the other materials in Fig. 3. However in practice, even for this range of δ, the room-temperature TEP values still lie conveniently on the universal curve within the scatter of the data. This curve encompasses single layer ($n = 1$), double layer ($n = 2$), and triple layer ($n = 3$) CuO_2 superconductors. Despite the many different combinations of constituent atoms and different stoichiometries that are possible, the TEP (and probably other normal-state transport properties) of the cuprates seems to be determined primarily by the level of doping of the CuO_2 planes, at least for $p < 0.23$.

An example of the utility of the universal plot in Fig. 3 is shown by the comparison of the effects of Co and Zn doping on $YBa_2Cu_3O_{7-\delta}$ in Fig. 4. While the TEP shows little change up to 7% Zn, it is very sensitive to small concentrations of Co. The graph also shows the much stronger effect that Zn substitution has on T_c. These data are consistent with Zn having little effect on the CuO_2 plane carrier concentration, suppressing T_c through a strong pair-breaking effect.[30] The effect of Co substitution on the other hand is very reminiscent of that of oxygen depletion. We note that the TEP of the 4% Co sample lies nicely (not shown) on the S vs $T_c/T_c^{\max}$ curve for underdoped samples, implying Co substitution changes T_c by modifying p rather than $T_c^{\max}$. In contrast, Zn doping clearly decreases $T_c^{\max}$. For Co concentrations $x \geq \sim 4\%$, the linear TEP with negative slope at higher temperatures, and broad maximum at lower temperatures, is typical of that found[31,32] for several other high-T_c oxides near $T_c^{\max}$, indicating that the chains are no longer significant.

In summary we have reported TEP data for a variety of cuprate superconductors which all show similar behavior as a function of hole concentration. This implies that a single-band picture provides an adequate description for many high-T_c oxides. Extension of this approach to other normal-state properties as well as single crystals or oriented films should help to differentiate between the numerous theoretical models for high-temperature superconductivity. On the practical side, Fig. 3 can be used as an empirical guide for deciding whether T_c of a given material can be improved by altering the doping level.

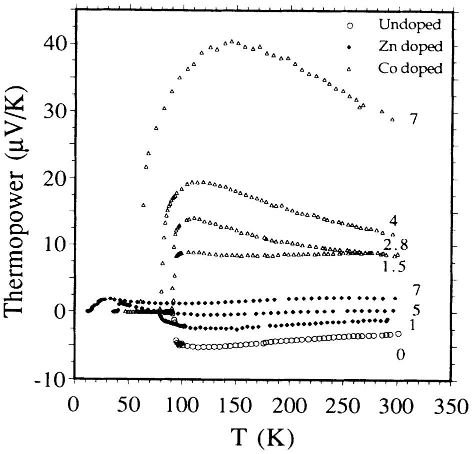

FIG. 4. Thermoelectric power vs temperature for $YBa_2(Cu_{1-x}M_x)_3O_{7-\delta}$ with M=Zn and Co for various concentrations x(%).

We are grateful to P. A. Freeman (IRC), R. S. Liu (IRC), A. R. West (University of Aberdeen), M. R. Presland (N. Z. I. I. R. D.), M. Harrison (GEC Hirst Research Centre), and E. Fung (Hong Kong Baptist College) for providing us with high-quality single-phase samples, and to W. Y. Liang and J. W. Loram for several useful discussions.

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*On leave from The Institute of Physics of the University, Zagreb, Croatia.

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