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Phonon-drag thermopower correlations to T_c in superconducting $Sr_xNd_{1-x}CuO_{2-\delta}$: Evidence for phonon-mediated pairing in the high-T_c parent compounds

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The $ACuO_2$ compounds—containing only CuO_2 planes separated by A ions—are the basic "building blocks" of the more complex high-T_c superconductors. Trivalently doped $Sr_xNd_{1-x}CuO_{2-\delta}$ thin films are shown to superconduct with the appearance of a phonon-drag contribution to the thermopower at the superconducting doping threshold. A monotonic increase in this phonon-drag contribution with T_c suggests that electron-phonon interactions play an important role in the pairing mechanism. A correlation between the deduced BCS coupling constants and T_c is consistent with strong-coupling theory.

Since the discovery of high-T_c superconductivity, the nature of the pairing mechanism and, more recently, the symmetry of the order parameter, have been the source of considerable controversy. Recent experimental evidence has been put forth to support both d-wave[1–3] and s-wave[4–6] pairing symmetries, in both $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$. Various theoretical models have been invoked to explain these experiments, with spin-fluctuation-induced pairing most commonly describing the d-wave state[7] and phonon-induced pairing describing the conventional s-wave state.[8] Hence there exists an interest in devising experiments to detect systematic changes in the phonon modes as a function of the superconducting transition temperature T_c. Until now, such experiments generally utilized inelastic neutron scattering,[9] tunneling,[10] isotope shift,[11] and specific heat[12] techniques to detect changes in the phonons in the superconducting state. Although these experiments suggest significant coupling between the electrons and phonons, the experiments as a whole remain inconclusive because the phonon correlations were determined in the superconducting state where it is unclear whether superconductivity induces these correlations or vice versa. Therefore, it would be more useful to correlate the superconducting T_c to the electron-phonon coupling determined in the normal state. Unfortunately, in the high-T_c superconductors, the temperature dependence of the normal-state electrical resistivity and the Hall effect remain invariant well above and below the Debye temperature, suggesting a nonphononic normal-state electronic scattering mechanism.[13] Although it is often neglected due to theoretical complexities, the low-T thermoelectric effect is considered to be a very sensitive probe for determining the strength of the electron-phonon interaction in the normal state.[14] In this work, the low-T thermoelectric effect was used to estimate the electron-phonon coupling in 33 infinite-layer-structure thin films covering a range in compositions, five of which were ultimately found to superconduct.

To date, a variety of experimental work has been published dealing with the thermopower of high-T_c superconductors, mainly on but not limited to $YBa_2Cu_3O_{7-\delta}$.[15–18] Many experiments suggest the presence of unusually strong phonon-drag effects,[15] although no effort has so far established a pattern between any phonon-drag contributions and the respective T_c over a reasonable range of sample properties. This may be due partly to the fact that phonon-drag contributions can arise from *any* of the numerous electronic states, whereas superconductivity may be limited to only a few states, thus concealing any correlations. Therefore, to improve the chances to observe such correlations, an intensive effort has been directed recently towards fabricating infinite-layer $ACuO_2$ compounds—the basic "building blocks" of high-T_c superconductors.[19] Since these materials contain only the covalent CuO_2 sheets responsible for superconductivity separated by ions (A), they should be ideal for thermopower transport measurements.[20] It already has been shown that partial substitution of strontium ions ($A=Sr$) with trivalent cations ($A=Nd$, etc.) leads to superconducting films.[21] In this work, we demonstrate a correlation of the superconducting transition temperatures T_c from a series of such films with the phonon-drag contributions observed in the thermoelectric effect. The results suggest that phonon-mediated coupling is responsible for the superconducting state. Moreover, the relative coupling constants deduced from simple data analysis are consistent with the strong-coupling theory of Allen and Dynes.[22]

High-quality epitaxial thin films of $Sr_xR_{1-x}CuO_{2-\delta}$ (R = Sr, Ca, and Nd) were obtained by pulsed laser ablation[19,21] (~2500 Å thick) or laser molecular beam epitaxy (~300 Å thick).[23] Four-circle x-ray-diffraction data, published elsewhere,[19,23] reveal the infinite layers to be very high-quality single-crystal-like films with extremely narrow diffraction peaks, and virtually no impurity peaks present. In addition, the trivalent-doped films ($R=Nd$) have a solubility limit of $x=0.9$, which is the point at which the highest transition temperatures were obtained in these films.[21] Briefly, to facilitate the thermopower measurements, copper voltage leads and type E thermocouple junctions were attached near each end of each film with silver paste. An external heater generated a small temperature difference across the films (about 3 K). The Seebeck coefficient with respect to copper

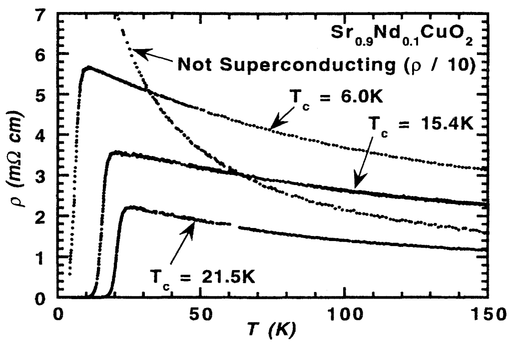

FIG. 1. Resistivity curves for four representative infinite-layer $Sr_{0.9}Nd_{0.1}CuO_{2-\delta}$ thin films. All of the infinite-layer materials show a decreasing resistivity with increasing temperature, suggesting some thermal activation of the carriers. This behavior occurs near the metal-insulator transition of $YBa_2Cu_3O_{\sim 6.4}$. The systematic decreases in the electrical resistivity with increasing T_c (midpoint values shown) are presumed to be due to slight variations in the oxygen content $2-\delta$. Hall measurements (Ref. 20) indicate that the carrier concentration is generally responsible for these effects.

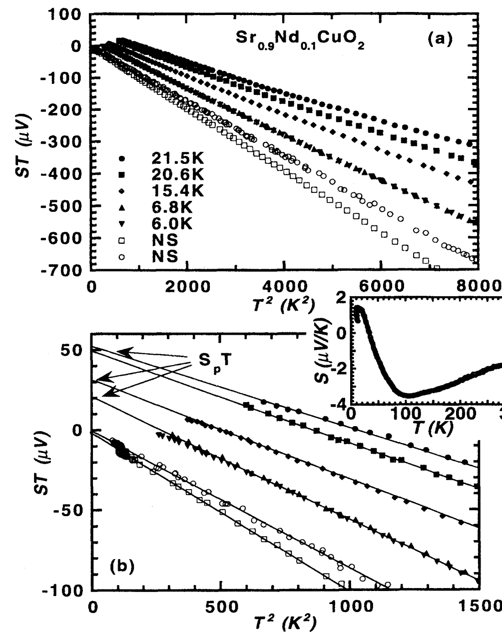

FIG. 2. (a) A plot of ST vs T^2 where S is the absolute normal-state Seebeck coefficient for seven $Sr_{0.9}Nd_{0.1}CuO_{2-\delta}$ thin films. Note that five films are superconducting with midpoint transition temperatures T_c ranging from 6.0 to 21.5 K and two films are nonsuperconducting (NS). (b) The low-T thermopower is composed of two distinct contributions $S=S_p+S_d$, where $S_p \propto 1/T$ (S_pT determined from the intercept) is characteristic of phonon drag and $S_d \propto -T$ (S_d/T determined from the slope) could arise from various mechanisms as mentioned in the text. The key finding is the monotonic scaling that exists between the "phonon-drag" voltage S_pT and the transition temperature T_c. The inset shows the thermopower for $T_c=21.5$ K plotted on a linear scale up to 300 K. All samples show the upward bend at ~ 90 K.

is equal to the measured voltage divided by the temperature difference. The absolute Seebeck coefficient of each film is then calculated by correcting for the Seebeck coefficient for copper (measured in the superconducting state of an epitaxial $YBa_2Cu_3O_7$ film). Finally, resistivity curves were obtained as a function of temperature using 1 μA dc currents; the thermal voltages were eliminated by subtracting the voltages obtained from both current polarities.

Of the 33 $Sr_xR_{1-x}CuO_{2-\delta}$ ($R=$Sr, Ca, Nd) thin films in this study, five were superconducting ($R=$Nd and $x\sim 0.9$) with transition temperatures ranging from a few degrees Kelvin through 24 K. At present, these various transitions are believed to result from either slight variations in the oxygen content $2-\delta$ or unidentified microscopic defect structures within the compounds which are controlled by the cooling rate following film growth.[23] Figure 1 illustrates systematic changes in the electrical resistivity with T_c for several representative films. Previous studies utilizing the Hall effect revealed these changes to be due to simple variations in the electron concentration.[20]

Figure 2 illustrates two components in the normal-state thermoelectric effect for a representative set of $Sr_{0.9}Nd_{0.1}CuO_{2-\delta}$ thin films. In all of our infinite-layer samples, the low-T thermoelectric effect ($\leqslant 90$ K) was found to decompose into two distinct signals: $S=S_p+S_d$, where $S_p \propto 1/T$ and $S_d \propto T$. To illustrate this decomposition, the Seebeck coefficient S is plotted as ST vs T^2 so that the intercept gives S_pT and the slope gives S_d/T. The most notable term is S_p which is inversely proportional to the temperature. Theoretical models[14] predict this T dependence to be a signature of phonon drag; therefore, we equate S_p to such effects.[24] Interestingly, note that the "phonon-drag" voltage S_pT appears just at the superconducting threshold and monotonically increases with the transition temperature T_c suggesting a connection between T_c and phonon drag. Moreover, since Ziman shows that umklapp phonon drag is highly improbable in semiconductors,[25] the positive sign of S_p strongly suggests that holes are responsible for the superconducting state in $Sr_xNd_{1-x}CuO_{2-\delta}$. The important implications of these findings are discussed in more detail below. The remaining term (denoted as S_d) could arise from several mechanisms including the vibrational energy of polarons in a variable-range-hopping model.[26] The deviations from the T-linear behavior upon approaching ~ 90 K (Fig. 2 inset) could be due to thermal broadening effects, lattice instabilities, or multicarrier-type conduction. However, we caution that the Hall coefficient does not show the anomalously small values often associated with multicarrier-type conduction.[20]

According to Bailyn, the phonon-drag thermoelectric effect derived from the variational approach is given by[14]

$$S_p \simeq \frac{2}{3ne}\sum_{\mathbf{q}} \frac{\partial N_0(\mathbf{q})}{\partial T} \sum_{\mathbf{k},\mathbf{k}'}^{\mathbf{q}} \alpha(\mathbf{q};\mathbf{k}\rightarrow\mathbf{k}') \times[m(\mathbf{k})\mathbf{v}(\mathbf{k})-m(\mathbf{k}')\mathbf{v}(\mathbf{k}')]\cdot\mathbf{V}(\mathbf{q}), \quad (1)$$

where $n[m(\mathbf{k})]$ is the concentration (mass) of the carriers, $N_0(\mathbf{q})$ is the equilibrium number of phonons having the wave vector **q**, **v**(**k**)[**V**(**q**)] is the velocity of electronic state **k** [phonon state **q**], and $\alpha(\mathbf{q};\mathbf{k}\rightarrow\mathbf{k}')$ is the probability that the phonon **q** will induce an electronic transition from state **k** to state **k**′. Referring to Fig. 2, we see that the phonon-drag contributions vanish at exactly the same point that superconductivity is suppressed. Considering the case $\alpha\neq 0$, Eq. (1) implies that S_p can vanish only when a delicate balance occurs between electron and hole competition and/or normal vs umklapp scattering. In our large sample set, it is highly unlikely that such a delicate balance can lead to the total cancellation of S_p in *all* 28 nonsuperconducting samples, especially since these samples covered a considerable range of doping. Therefore, the most plausible explanation is that the experimental S_p values simply measure the electron-lattice coupling α of the population of electronic states directly involved in superconductivity.[27] Thus the phonon-drag effect appears to be a useful tool to probe the value of α in these infinite-layer compounds. However, we point out that it is still unclear whether phonon drag can be used in this way for higher-T_c materials since S_p falls off as $1/T$, a result of increased phonon-phonon interactions.[14]

Any correlation between the relative BCS coupling constants[27] $\lambda\propto\alpha N(\epsilon_F)$ deduced from S_p and the transition temperatures T_c in our series of superconducting $Sr_{0.9}Nd_{0.1}CuO_{2-\delta}$ cuprates would be most interesting because it would provide crucial information about the superconducting pairing mechanism. Moreover, such a correlation would allow us to test the viability of various BCS coupling theories. Unfortunately, no information is currently available for the values of $m(\mathbf{k})$, N_0, $\mathbf{v}(\mathbf{k})$, and $\mathbf{V}(\mathbf{k})$ in Eq. (1). Therefore, we can only deduce relative changes of α from our set of films. Neglecting $m(\mathbf{k})$, N_0, $\mathbf{v}(\mathbf{k})$, and $\mathbf{V}(\mathbf{k})$ for the moment, Eq. (1) states that the electron-lattice interaction is roughly proportional to S_p and to the carrier concentration, i.e., $\alpha\propto nS_p$. Recall that in a free electron gas the electronic density of states $N(E_F)$ is given by $N(E_F)=3n/2E_F$; as a result, the BCS coupling constant is given by $\lambda=\beta^2n^2S_p$, where $\beta^{-2}\propto E_F\Delta k\Omega_D^{1/2}$ and Δk is the phonon-scattering wave number. Assuming β is relatively constant, the resulting (normalized) coupling constants, determined by multiplying the square of the Hall carrier concentrations by the phonon-drag thermopower contribution coefficients, are shown in Fig. 3 as a plot of T_c versus $\lambda^{1/2}\propto nS_p^{1/2}$ (from strong-coupling BCS theory[22]) and in the inset as T_c versus $\exp(-1/\lambda)$ (from weak-coupling BCS theory). The resulting coefficients of regression, $r^2=0.985$ for strong coupling and $r^2\ll 0.84$ for weak coupling,[28] suggest that $T_c\propto\lambda^{1/2}$ in these compounds. At present, the only BCS coupling theory having this radical form was first found by Allen and Dynes,[22] who give $T_c\sim 0.15\Omega_D\lambda^{1/2}$ (here assuming a Coulomb screening $\mu^*=0.1$). Finally, estimates of the Debye temperature Ω_D from specific heat studies could facilitate the determination of specific values for λ and provide an additional test for strong coupling; unfortunately, no such studies have been performed on any infinite-layer material to date.

In summary, we studied the phonon-drag contributions in the thermoelectric effect of 33 infinite-layer $Sr_xR_{1-x}CuO_{2-\delta}$ ($R=$Sr, Ca, and Nd) thin films, the parent compounds of the high-T_c cuprate superconductors. In *all* 28 nonsuperconducting films, the low-T thermopowers were linear in T, lacking phonon-drag effects. On the other hand, *all* five superconducting samples demonstrated phonon-drag contributions $S_p\propto 1/T$ suggesting that phonon-drag effects arise from the population of electronic states involved in superconductivity. Using this phonon-drag contribution as a relative measure of the electron-lattice interaction, relative coupling constants λ were determined for a range of superconducting samples having various T_c. The resulting empirical relationship for T_c was of the form $T_c\propto\lambda^{1/2}$, which is consistent with the Allen-Dynes strong-coupling theory.[22] However, our results do not rule out a more complex pairing mechanism involving both phonons and spin fluctuations. It is plausible that all high-T_c cuprate superconductors share the same pairing mechanism but that complexities in their structures complicate the interpretation of experimental results.[29] Therefore, it is possible that other high-T_c superconductors share similar phonon-drag effects but that these cannot be observed as clearly as in the relatively simple and lower-T_c infinite layer compounds, due either to the complex structures and/or the high transition temperatures of the high-T_c materials.

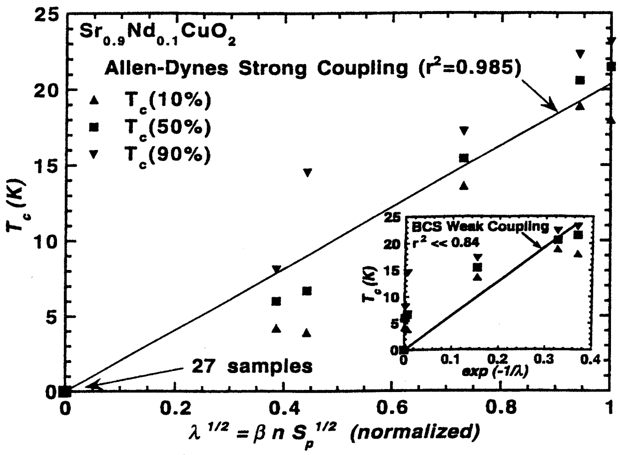

FIG. 3. Comparing the transition temperatures T_c (10%, 50%, and 90% values shown) to the relative BCS coupling constants λ indicates that the strong-coupling limit of Allen and Dynes (Ref. 22), $T_c\sim\lambda^{1/2}$, provides a better fit ($r^2=0.985$) than the weak-limit form predicted by BCS theory, $T_c\propto\exp(-1/\lambda)$. In the weak-limit case, the fit improves ($r^2\rightarrow 0.84$) as $\lambda\rightarrow 1$ for $T_c=22$ K (this case shown in the inset). As described in the text, these relative coupling constants λ are proportional to the square of the carrier concentrations, n^2, determined by Hall measurements, and the phonon-drag contributions, S_p.

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