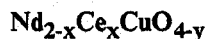




COMPOSITIONAL PROPERTIES AND THERMOELECTRIC POWER OF THE SUPERCONDUCTING CERAMIC



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We report studies on the compositional properties and subsequent thermoelectric power of ceramic samples of superconducting reduced, Ce-doped $\text{Nd}_2\text{CuO}_{4-y}$ and for the undoped parent compound as well. The synthesis of ceramic material with uniform cerium concentration is difficult, but samples can be obtained which are 20-25% superconducting by volume. For such material we find the sign of the Seebeck coefficient to be negative at all temperatures above its superconducting transition at $T = 22$ K and zero below, consistent with, but not proving purely "n-type" normal state transport and pairing. We also obtain a negative room temperature thermopower for the parent $\text{Nd}_2\text{CuO}_{4-y}$ compound, but with a change to positive sign at lower temperature. We review these findings against thermopower data reported for the "p-type" high- T_c compounds where a negative Seebeck coefficient is also observed under certain conditions, and conclude that separation of carriers into specific negative or positive entities in the spirit of the effective mass approximation is in general not possible in copper oxide perovskite superconductors.

Introduction. Until very recently, all CuO high- T_c compounds following on the initial discovery by Bednorz and Mueller¹ have contained net excess positive charge compared to the expected nominal ionic charges of their constituents. Now, it has been shown² that it is possible to obtain high temperature superconductivity near 24 K in a class of materials closely related to the original La_2CuO_4 compounds but where this compensating unit cell charge appears to be negative. It is natural to assume under these conditions, that superconductivity might be due to pairing of holes in the former and electrons in the latter. The compounds initially investigated² were cerium doped $\text{Ln}_2\text{CuO}_{4-y}$ with $\text{Ln} = \text{Nd}, \text{Pr}$ and Sm . One should note that a strong argument for the presence and pairing of electrons is the occurrence of superconductivity in the Pr member of these compounds, since Pr is believed to inhibit the formation and transport of holes in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$. The number of these "n-type" superconductors has been extended³ to include thorium doped $(\text{Nd}, \text{Pr})_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ with properties similar to their cerium predecessors. Recently, even single crystals of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ have been grown and studied.^{4,5} The superconductivity in the $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ materials exists only in a narrow range around $x \approx 0.15$, and in this aspect they appear much different than the broad doping range accommodated by their alkaline earth-doped $\text{La}_2\text{CuO}_{4-y}$ relatives. Cerium is well known to be often supra-trivalent, and, taking this to be the case in $\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ on its substitution in the Ln position, one easily sees the compensating charge must be negative given Ln^{3+} , Cu^{2+} , O^{2-} and $y \approx 0$; that is, simply stated, if one of the trivalent Ln positions is substituted by Ce^{4+} , then within the unit cell the stoichiometric positive

charge is +9 and the negative charge is -8, so that to preserve charge neutrality, extra compensating negative charge, say by having the copper atom take on a Cu^{1+} ionic state, must be induced. This picture is indeed supported by the negative signs of the Hall and Seebeck coefficients⁶ well above T_c .

Interestingly, the first work on doped $\text{Nd}_2\text{CuO}_{4-y}$ and doped $\text{La}_2\text{CuO}_{4-y}$ for that matter, was done well before the advent of high- T_c .⁷ The dopants employed were primarily the alkaline earths Ca, Sr and Ba which lowered the overall resistivity of the $\text{Ln}_2\text{CuO}_{4-y}$ host by 1-2 orders of magnitude.⁸ Much of their interpretation was based on the assumption that all members of the $\text{Ln}_2\text{CuO}_{4-y}$ series possessed the K_2NiF_4 structure, even though it was by then known that this was only true for $\text{La}_2\text{CuO}_{4-y}$ and the other rare earth cuprates were subtly, but, it turns out, crucially different,⁹ lacking as they do apical oxygens tetrahedrally coordinating the planar CuO_2 squares. What, in retrospect, is now quite remarkable, was that the sign of the Seebeck effect for all *undoped* $\text{Ln}_2\text{CuO}_{4-y}$ compounds, save La, is negative!^{7,10,11} Thus, there was a strong indication in these pioneering results that the non-La $\text{Ln}_2\text{CuO}_{4-y}$ compounds might be a promising precursor system for n-type superconductivity.

The discovery of electron high temperature superconductivity could be a potentially important discriminating factor between various theoretical models. It is clear that those models in which normal transport occurs near the extrema of a bounded band where the effective mass approximation is applicable, e.g., single-band Hubbard systems, will exhibit reciprocity in the sign of the charge. For multiple band models, or those in which configuration interaction with nearby filled bands is large, the situation is not so clear, and those models restricted explicitly to hole pairing¹² may be in serious difficulty.

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However, that the superconductivity in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ arises from electron pairing is not yet completely settled. The evidence for an n-type normal state from core level spectroscopy is mixed. Structure has been observed¹³ in the Cu K x-ray absorption edge associated with the presence of Cu^{1+} brought about by electron donation from Ce, whereas EELS measurements¹⁴ find no indication of Cu^{1+} but in fact see loss spectra due to oxygen holes, a feature common to the p-type $\text{La}_2\text{CuO}_{4-y}$ -based superconductors. Since both near-edge x-ray absorption and electron energy loss spectroscopy are bulk measurements, these conflicting results are particularly confusing. To further confound matters, a group from Sony¹⁵ has recently reported that, although the sign of the Seebeck coefficient for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ is negative at high temperature, it becomes positive just above the superconducting transition. It may well be that in these nominally n-type systems, both holes and electrons are present with electrons the majority carrier over most of the temperature range but with the superconductivity due to hole pairing, or, because of complexities in the quasi-momentum dispersion of their band structure, it is not possible to use the effective mass approximation to separate the carriers into an identifiable charge type, thus preventing the unambiguous definition of "holes" and "electrons."

In view of the importance of ascertaining the true nature of the carrier state, we decided to undertake a study of the compositional properties of superconducting ceramic $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ with $x \approx 0.15$ and its undoped parent compound and assess the effect these properties might have on the temperature dependence of the thermoelectric power. This Communication contains our findings, and a discussion of the general interpretation of thermopower in high- T_C compounds as well.

Synthesis. Our sample synthesis followed reported methods.² Appropriate molar quantities of Nd_2O_3 (desiccated and 4N pure), CeO_2 and CuO (each 5N pure) to produce $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ were finely mixed, ground and reacted at 950 C in air for at least 24 hours. The resulting powder was reground, pressed into pellets, which were then sintered in flowing oxygen at 1050 C for 48 hours. We found that if we sintered at 1150 C, the recommended temperature,² in our furnaces the samples would partially melt. All in all, we find the margin in preparation conditions that can be tolerated is generally much tighter than for the p-type materials. After sintering, the pellets were annealed at 900 C for 24 hours in high purity flowing Ar under positive pressure with respect to ambient in a well-sealed quartz tube furnace. The samples were then rapidly quenched to room temperature in approximately 30 seconds by placing them on a massive aluminum cold plate while kept covered by flowing Ar. Essentially the same procedure was followed to prepare samples of undoped $\text{Nd}_2\text{CuO}_{4-y}$.

Microprobe and X-Ray Characterization. Scanning electron microscopy and electron beam microprobe analysis of the cerium containing samples revealed the presence of four

distinct regions, or phases. The two principal phases were nominal $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ and $\text{Nd}_2\text{CuO}_{4-y}$ with much lower ($x \approx 0.05$) Ce concentration. In addition, small regions of average composition NdCe_2O_7 and traces of Cu_2O were detected. Traces of the latter compound are evidence of the reduction of small amounts of unreacted CuO . The elemental average and standard deviation computed from six points within regions of nominal $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ are summarized in Table I. We see that the major variation is in the Ce concentration, most probably because the unreactive nature of CeO_2 retards the diffusion of cerium during the solid state reaction. This is also likely the reason for the presence of the incompletely reacted cerium-poor $\text{Nd}_2\text{CuO}_{4-y}$ and cerium-excess NdCe_2O_7 portions of the sample. With respect to the average oxygen concentration shown in Table I, it has been our experience with high- T_C compounds that difficulties arising in e-beam microprobe analysis of light elements in general result in vast overestimates of the oxygen levels, so that the number 4.78 shown is not to be taken seriously. However, it is important to note that its deviation is small, indicating that the oxygen concentration is quite uniform in the major $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ phase. To determine the absolute value of y in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ in the presence of minor phases is a difficult matter.¹⁶ Titration results imply that there is always a small amount of excess oxygen ($y \approx -0.02$) in Ar-annealed material at all Ce concentrations up to $x = 0.15$. However, since the titration technique averages over the minor phases as well, there is some concern as to the absolute value of y determined this way. On the other hand, hydrogen-reduction TGA on nitrogen-annealed $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ single crystals⁵ yields $y \approx 0.03$, and thus it is probable that the major phase in our ceramic samples in fact has an oxygen content slightly less than four.

Figure 1 summarizes the powder x-ray diffraction results on our nominally $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ samples. As pointed out above,⁹ $\text{Nd}_2\text{CuO}_{4-y}$ does not possess the K_2NiF_4 crystal structure of $\text{La}_2\text{CuO}_{4-y}$. Its unit cell is shown in the inset to Fig. 1 and differs from $\text{La}_2\text{CuO}_{4-y}$ primarily in that the oxygen atoms in apical positions relative to the CuO plane in the latter has moved to the tetragonal faces in the former. The lack of apical oxygens in $\text{Nd}_2\text{CuO}_{4-y}$ may be related to the inability to produce superconductivity by doping with alkaline earths.⁸ The diffraction pattern shown in Fig. 1 was taken under experimental conditions similar to those described elsewhere¹⁷ and most of the peak positions and intensities match very well the stick diagram computer simulation¹⁸ shown below the experimental pattern assuming direct Ce substitution on the Nd position in $\text{Nd}_2\text{CuO}_{4-y}$. Aligning the positions of the simulated 103 and 110 reflections to the measured peaks in the sample yielded values of 3.96 Å and 12.11 Å for the tetragonal cell constants a and c , respectively, in agreement with those found by most other workers for Ce concentration 0.15. The arrows indicate peaks associated with two of the impurity phases detected by microprobe; namely, Cu_2O , and then two NdCeO compounds¹⁹ which average to the NdCe_2O_7 composition. Comparing peak intensities, and using visual information from the SEM-microprobe pho-

TABLE I. Concentrations of Nd, Ce and O with respect to Cu as determined by electron beam microprobe analysis. Accuracies relative to appropriate elemental standards are Nd ($\pm 5\%$), Ce ($\pm 5\%$), Cu ($\pm 5\%$) and O ($\pm 10\%$). The numbers in the table show the average concentration at 6 random points taken over a square area approximately 200μ on side. The figures in parentheses contain the standard deviation in terms of the percentage of the average concentration.

Nd	Ce	Nd + Ce	O
1.82 (1.0%)	0.14 (17.2%)	1.96 (0.7%)	4.78 (1.1%)

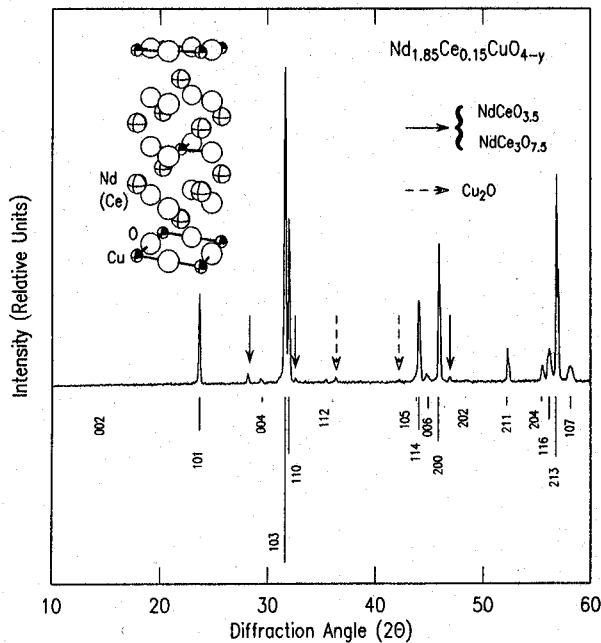


Figure 1. Powder x-ray diffraction pattern of the $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ sample whose transport measurements are reported here. The stick diagram in the bottom third of the figure is a simulation of the expected pattern using the program Lazy-Pulverix.¹⁸ The unit cell parameters obtained by matching the 103 and 110 simulated reflections to the measured pattern were $a = 3.96 \text{ \AA}$ and $c = 12.11 \text{ \AA}$. The two principal impurity phases observed are indicated by the full and open arrows. The inset contains a perspective view of the $\text{Nd}_2\text{CuO}_{4-y}$ unit cell. The various element spheres are drawn to half-scale of their ionic radii with respect to the unit cell dimensions. See text for further discussion.

tographs, we crudely estimate the volume fraction of these impurity phases to be 5% of the sample. We believe the principal source of inhomogeneity in sintered $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ ceramics to be regions of $\text{Nd}_2\text{CuO}_{4-y}$ with low amounts of cerium as determined by microprobe. These regions may comprise as much as 40-50% of the sample.

Transport and Magnetic Measurements. We also characterized our samples by measuring four-probe resistivity and a.c. susceptibility. Figure 2 contains the temperature dependence of the resistivity of the Ce-doped sample whose microprobe and x-ray properties we have just discussed. Details of the experimental technique can be found elsewhere.²⁰ The temperature dependence observed is typical of percolative conductivity characteristic of metal particles imbedded in an insulating medium. All resistivity data reported on ceramic "n-type" superconductors display this feature to some degree, even in single crystals where the source of the inhomogeneity appears to be variations in oxygen concentration or the inclusion of microcavities.^{5,4} Another signature of the percolative nature of the transport is the "tail" or "foot" below the transition temperature shown in the inset to Fig. 2. In this particular sample, zero resistance was not achieved until 14 K.

In Fig. 3 we show the temperature dependence of the a.c. susceptibility for this same sample. The data were taken using a standard compensating mutual inductance bridge

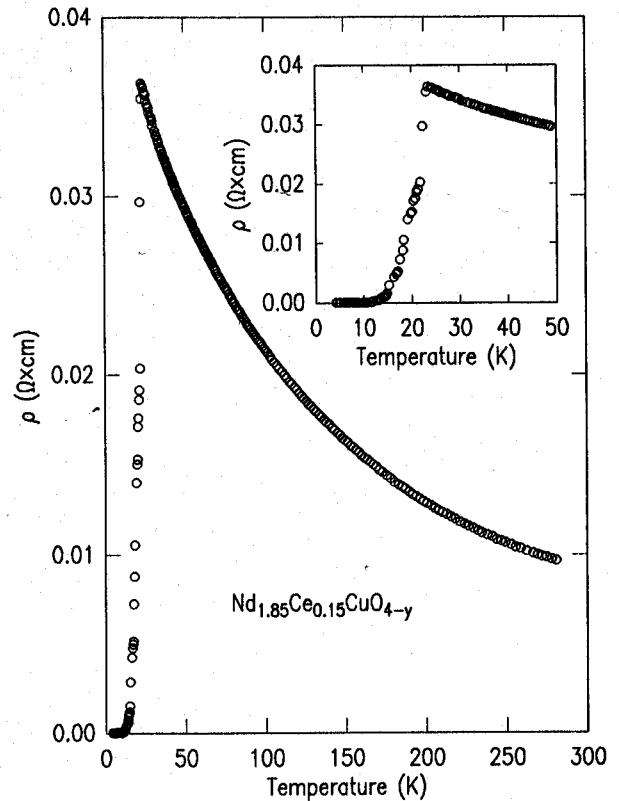


Figure 2. Resistivity of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ ceramic pellet. Inset shows region near superconducting transition. Note that the resistivity is plotted on a linear scale which tends to emphasize the upturn just above T_C .

technique.²¹ The inset shows the onset of diamagnetism at almost precisely the same temperature as the start of the drop in resistivity. Comparing the total diamagnetic shift with that from a $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ standard measured at the same time, we estimate the sample superconducting fraction to be roughly 20-25%. The volume fraction we obtain from susceptibility is consistent with the spread in Ce concentration indicated by the microprobe data.

Figure 4 displays the behavior of the thermoelectric power for our nominally $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ sample. Our experimental technique uses a low-frequency differential heat modulation method,²² which we have successfully employed on other high- T_C materials.²⁴ The magnitude of S is extremely small, typical of most metals, and vanishes to instrumental zero at almost exactly the same temperature as the onset of superconductivity in the resistivity and the diamagnetic shift in susceptibility, and is negative all the way down to T_C . There is a wide, fairly temperature independent region between 100-300 K.

Figures 5 and 6 contain the temperature dependence of the resistivity and thermopower of an undoped, reduced sample of $\text{Nd}_2\text{CuO}_{4-y}$ prepared under conditions similar to the Ce-doped runs, annealing in argon at 900 C for 24 hours and then rapidly quenched. The x-ray spectrum showed only the $\text{Nd}_2\text{CuO}_{4-y}$ pattern with no trace of unreacted CuO. It is seen that the sample is quite insulating. However, the resistivity data do not fit a simple activated energy gap model, nor do they fit any of the usual models for transport by variable range hopping. An activated model

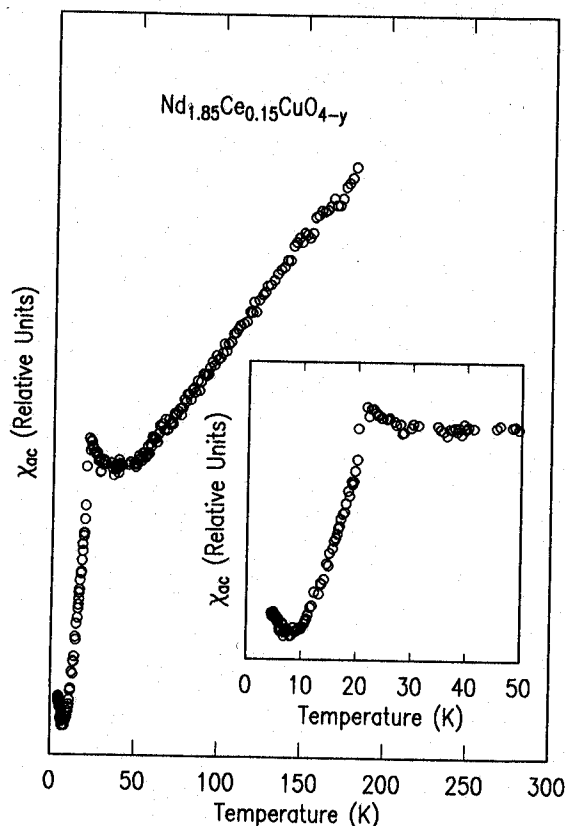


Figure 3. Raw a.c. susceptibility data for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ ceramic pellet. Insert shows region near superconducting transition. No background correction was performed.

taking into account the anisotropy of the ceramic grains may actually be more appropriate, but we did not test this conjecture. The thermopower of the sample is relatively large and negative throughout most of its temperature range as was found by the earlier workers.^{2,10,11} What was surprising is that the room temperature thermopower of an oxygen-annealed sample was also negative, whereas one might have expected holes to have been produced by the incorporation of excess oxygen.²³ Below about 70 K the magnitude of S drops sharply and changes sign. This sign change could arise from one of at least three causes: 1) Both electrons and holes are present. In the most simplistic picture, one might expect this to be the case if carriers are thermally activated across a semiconducting gap. The combined thermopower would then be given by $S = (\sigma_e S_e + \sigma_h S_h) / (\sigma_e + \sigma_h)$, where the subscripts denote the contribution to the total thermopower by electrons and holes weighted by their respective conductivities. All these quantities can have different temperature dependencies and a sign change in the net S at some given temperature is often observed in semiconductors. 2) The oxygen content is non-uniform, resulting in an inhomogeneous system containing regions of both negative and positive Seebeck coefficients. We base this on our observation that the thermoelectric power of the $\text{Nd}_2\text{CuO}_{4-y}$ sample annealed in oxygen and rapidly quenched, although negative at room temperature as mentioned above, was observed to go positive at around 150 K, considerably higher than the crossover shown in Fig. 6. Unfortunately, the sample resistance was so high as to preclude an accurate determination of the magnitude of S with our measurement technique, but the result did indicate that one can increase

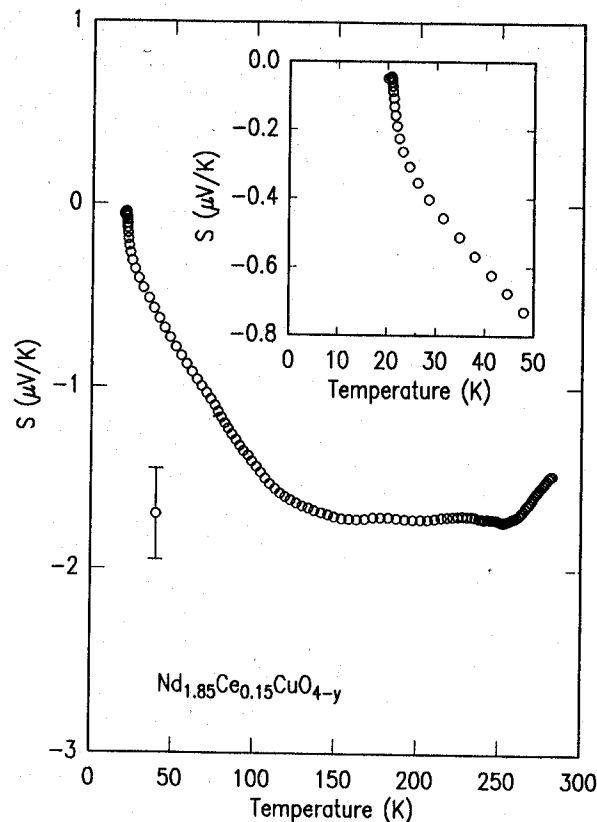


Figure 4. Thermopower of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ ceramic pellet. Insert shows region near superconducting transition. Raw data digitally smoothed -- error bar designates rms variation.

the temperature range of positive thermopower by introducing excess oxygen and therefore the crossover even in argon-annealed samples might be due to regions containing excess oxygen. 3) Finally, it could even be that some regions of the undoped sample are sufficiently devoid of oxygen as to be superconducting, leaving behind at low temperatures insulating regions of opposite thermopower sign which then dominate S . Although possible, we believe this unlikely. In undoped $\text{La}_2\text{CuO}_{4-y}$, the trace superconducting regions shorted the normal portion of the sample giving overall zero thermopower below T_C ,²⁴ with no remaining residual thermopower. Incidentally, changes in sign observed by other workers¹⁵ in the vicinity of T_C we believe may arise from the presence of undoped $\text{Nd}_2\text{CuO}_{4-y}$ which has positive thermopower at low temperature. Microprobe analysis of our Ce-doped ceramic samples definitely show that it is difficult to obtain uniform concentration of the dopant throughout the bulk volume. In passing, we remark that to our knowledge, very few, if any, models exist pertaining to the thermoelectric power of anisotropic composite media,²⁵ let alone inhomogeneous superconductors.

Discussion. The thermoelectric power is one of the most fundamental properties of condensed matter. Like the electronic specific heat, γ , S is essentially a measure of the carrier entropy in a Fermi liquid, and, also like the former, it therefore goes identically to zero in the superconducting state. Absolutely zero thermopower below a finite temperature is a unique signature of superconductivity and is displayed by no other condensed matter phenomenon. All superconductors, including the high- T_C compounds, pos-

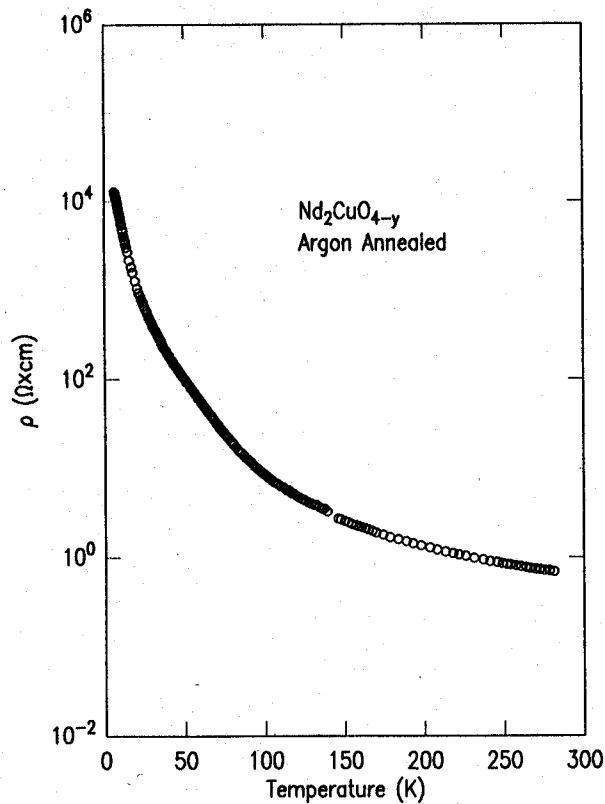


Figure 5. Resistivity of reduced $\text{Nd}_2\text{CuO}_{4-y}$.

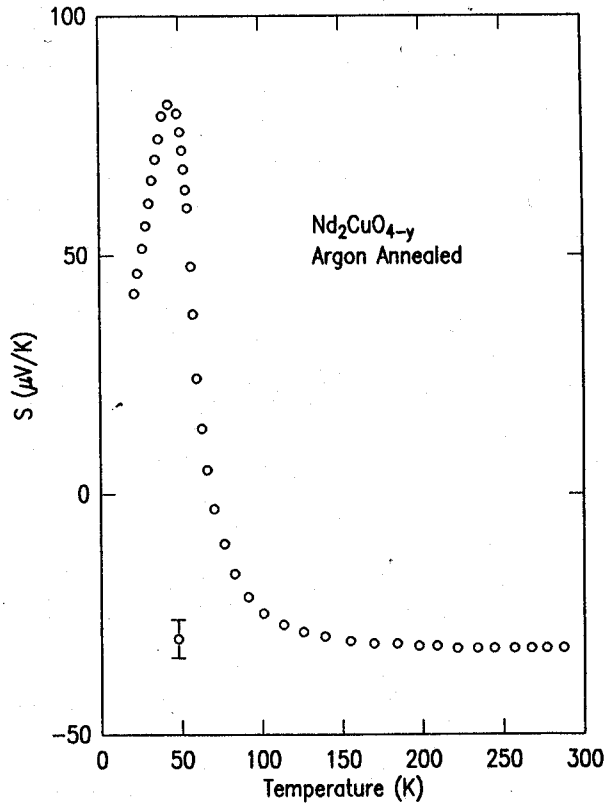


Figure 6. Thermopower of reduced $\text{Nd}_2\text{CuO}_{4-y}$. Raw data digitally smoothed -- error bar designates rms variation.

sess this behavior. However, with regard to normal state properties, perhaps no other aspect of high temperature superconductivity is as little understood as is the thermoelectric power. In its most elementary form, S for an uncorrelated Fermi liquid can be derived directly from the charge transport Boltzmann equation and is²⁶

$$S = -(K_0^{-1}K_1)/|e|T, \quad (1)$$

where

$$K_n = \frac{1}{3} \int 2\tau_k \vec{v}_k \vec{v}_k \left(-\frac{\partial f_0}{\partial E} \right) [E(\vec{k}) - E_F]^n d^3k. \quad (2)$$

Here τ , v and E are the quasimomentum-dependent carrier scattering time, group velocity and single particle energy, respectively, and E_F is the Fermi energy. In the low temperature limit of $k_B T < E_F$, Eqs. (1) and (2) yield

$$S = -\frac{1}{3} \pi^2 \frac{k_B^2}{|e|} T \frac{\partial}{\partial E} [\ln \sigma(E)]_{E=E_F} \\ = -\frac{1}{3} \pi^2 \frac{k_B^2}{|e|} T \left[\frac{N(E_F)}{n} + \frac{\tau'(E)}{\tau} \Big|_{E=E_F} \right], \quad (3)$$

where $N(E_F)$ is the single particle density of states at the Fermi energy and n is the carrier concentration. The last term in Eq. (3) arises from application of the effective mass approximation for metals, viz., $\sigma = ne^2\tau/m^*$. Equations (1-3) describe what is called the "diffusion thermopower"; that is, the diffusion of the electron gas in the applied thermal gradient. If the carrier scattering is independent of its energy, the thermoelectric power of a well-behaved metal is simply proportional to the temper-

ature, with the negative sign denoting electron transport.²⁷ Almost all the historical superconductors, including the $\text{BaPb}_x\text{Bi}_{1-x}\text{O}_{3-y}$ system,²⁸ exhibit this linear T -dependence at sufficiently high temperature, but it appears totally absent in all the CuO high- T_C materials, where S in the normal state is essentially temperature independent, as in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$,²⁹ or even inversely proportional to temperature as observed for the Sr -doped $\text{La}_2\text{CuO}_{4-y}$ compounds.³⁰ In addition to the diffusion term, a further contribution to the thermopower can occur in metals due to phonon flow within the thermal gradient "dragging" along more carriers at temperatures well below the Debye temperature.³¹ Extreme phonon drag^{32,33} has been put forward as a possible explanation for the inverse temperature dependence, but this seems unlikely in view of the lack of conclusive evidence for strong electron-phonon coupling, such as a significant isotope shift. However, one should not rule out drag-like effects due to strong coupling to other bosonic excitations, e.g., excitons, plasmons or spin-waves. On the other hand, the weak temperature dependence, including the inverse aspect, can in principal also be explained within an extended Hubbard model in the limit of strong correlation and narrow bandwidth with respect to temperature.³⁴ Such models³⁵ have been extensively employed to interpret the thermoelectric properties of conducting organic materials. Because Hubbard-like models are thought applicable to the CuO high- T_C compounds, this picture was applied to doped- $\text{La}_2\text{CuO}_{4-y}$ data,³⁰ and qualitative agreement was obtained for the temperature and concentration dependence of S . In such a narrow band, highly correlated framework, the thermoelectric power is a measure of the entropy of the carrier spin configuration manifold, which should decrease under application of a saturating external magnetic field.

However, it was subsequently found²⁹ that S changed hardly at all, thus effectively ruling out the possibility of charge transport in high- T_C compounds via correlated hopping. This does not say Hubbard concepts can not in general apply -- the current two-band models propose that transport occurs in a fairly wide oxygen band against a background of short-range correlated Cu^{2+} spins.³⁶ In this picture, the carriers themselves need not necessarily be correlated in the normal state. On the other hand, the lack of a magnetic field dependence in S is also consistent with a high temperature paired RVB state.²⁹

We now review briefly the ambiguities observed in the sign of S in both the $\text{La}_2\text{CuO}_{4-y}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ classes of materials. The conventional picture would have all materials previous to the discovery of the Ce-doped $\text{Nd}_2\text{CuO}_{4-y}$ compounds display positive S due to the excess positive compensating charge per unit cell--but this is not always the case. Both $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ with $x \geq 0.2$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ near $y = 0$ have negative thermopower at room temperature.^{32,37,38,39,29} Moreover, the Hall coefficient of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ for $x \geq 0.2$ is negative.⁴⁰ It is known that for heavily doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$, oxygen will evolve from the material unless care is taken to anneal in a high pressure oxygen ambient,⁴¹ and this may lie behind the subsequent observation of n-type behavior. In $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, the sign of S is critically dependent on how close one is to seven oxygen atoms per unit cell. Also, the sign can depend on the relative magnitudes of opposing diffusion and drag contributions.³³ Other interpretations^{29,39,33} of this unusual behavior involve recourse to subtle features in the band structure, e.g., E_F lying close to a critical point, which, on application of Eq. (2), results in an extremely small negative thermopower. In both compounds there exists some basis for this argument, given the complexity of their band structures in the energy region pertaining to charge transport.⁴² In fact, local density functional band structure calculations^{43,44} reveal that, at least in the context of single particle theory, the sign of both the Hall and Seebeck coefficients depend on the precise location of E_F , which in turn depends on the carrier concentration.

In view of the difficulties apparent in understanding the temperature dependence, magnitude and sign of the thermopower in the nominally p-type high- T_C compounds, what can be said about the results for the $\text{Nd}_2\text{CuO}_{4-y}$ system? We can say with certainty that the sign of the thermopower remains negative all the way down to T_C in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$. This is consistent with, but does not prove, a totally electron normal state and subsequent pairing of these electrons in the superconducting state. One should still remain cautious when applying the appellation "n-type" to these materials. The magnitude of the thermopower is much smaller than in optimally doped (lowest resistivity, highest T_C) $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$, and resembles $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ with $y = 0$ in this aspect. The principal

contribution of our studies on $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ is to emphasize that a consistent picture for all aspects of the thermoelectric power of high temperature superconductors has yet to be found, and to ascribe its sign as an indication of carrier charge type in the context of the effective mass approximation is a gross oversimplification. Moreover, we feel the role of the apical oxygen, that is, the presence or lack thereof, on normal state transport properties in the CuO planes is a key issue in high- T_C and needs to be much better understood, not only in the "214" compounds, but also in the "2223" bismuth and thallium high- T_C superconductors where the central CuO plane lacks the apical oxygen present in the two neighboring layers, as well as the "infinite" layer compound,⁴⁵ $\text{Ca}_{0.85}\text{Sr}_{0.14}\text{CuO}_2$. There are several theoretical indications that the apical oxygen may be central to "hole" doping. Significant contributions to $N(E_F)$ in $\text{La}_2\text{CuO}_{4-y}$ arise from hybridization of the apical O $2p_\pi$ orbitals with Cu 3d states.⁴⁶ These contributions are absent in $\text{Nd}_2\text{CuO}_{4-y}$.⁴⁷ The resulting bands of symmetry $3z^2 - r^2$ move toward the pure O 2p band on removing electrons⁴⁸ and may be where the resulting carriers reside at sufficiently high concentration levels. Band calculations⁴³ indeed show that on doping $\text{La}_2\text{CuO}_{4-y}$ with Ba, the O $2p_\pi$ states of the apical oxygens move to E_F . To have similar detailed calculations such as these for the $\text{Nd}_2\text{CuO}_{4-y}$ structure, undoped and doped, would be most useful in helping to further understand our present thermopower measurements.⁴⁹

Summary. In summary, we have measured the compositional properties and thermoelectric power of a carefully characterized ceramic sample of reduced, Ce-doped $\text{Nd}_2\text{CuO}_{4-y}$. The synthesis of single phase material with uniform cerium concentration by ordinary solid state reaction techniques is difficult, but samples can be obtained which are 20-25% superconducting by volume. We find the thermopower of these samples to be small and negative all the way to the onset of superconductivity at 22 K as determined by resistivity and a.c. susceptibility, supporting but not proving n-type transport and superconductivity. We also find the room temperature thermopower of the undoped $\text{Nd}_2\text{CuO}_{4-y}$ compound to be negative whether argon or oxygen annealed but with a sign change occurring at lowered temperatures. Comparison of these findings with those on previous "hole-like" compounds, recognizing that the latter can also display a negative Seebeck effect, leads us to conclude that the effective mass description in terms of simple "holes" and "electrons" must be applied to the copper oxide perovskites with discretion. We believe the doping chemistry involved with the presence or absence of the apical oxygen may hold the key to understanding not only the thermopower, but their general transport properties as well.

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