

### Thermoelectric power of some high- $T_c$ oxides

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Thermoelectric power ( $S$ ) measurements are reported in some  $\text{La}_2\text{CuO}_{4-x}$  oxides with Ba and Sr doping.  $S$  gradually decreases with increasing dopant concentration  $x$ , and for small concentration the trend can be described by assuming strong correlations. While  $S$  is small for high  $x$ , the temperature dependences found indicate that the materials are not simple, uncorrelated wide-band metals.

There is considerable recent activity<sup>1-3</sup> on certain oxides which show transitions to a superconducting state at high temperatures. While the electromagnetic properties of the superconducting state presently appear to be similar to those expected from BCS theory,<sup>3</sup> the high transition temperatures are surprising in the light of the small carrier densities. The samples are typically prepared in the form of sintered powder making the interpretation of certain measurements, like the electrical resistivity in the normal state or flux expulsion in the superconducting state, somewhat uncertain because of the possible influence of high-resistance contacts between metallic or superconducting particles.

Thermoelectric power ( $S$ ) measurements have some advantages for such granular and sometimes multiphase materials. The electrical resistance between grains will have less effect on  $S$  than on the electrical conductivity because the temperature drop between grains will usually be much less significant than the voltage drop. (In other words, the relative contributions to  $S$  from two materials in series is determined by their relative thermal resistivities.) On the other hand, if there are several conducting paths in parallel, as in multiphase materials, both the thermoelectric power and the electrical conductivity will be dominated by the most highly conducting path. Also, the thermoelectric power is a zero-current property and should be zero in the superconducting state. The above points have been confirmed by measurements on a number of different high- $T_c$  oxides. However, those reported here only refer to sintered materials which have been characterized as single phase by x-ray powder diffraction.

We find that  $S$  is large, positive, and temperature independent in the pure  $\text{La}_2\text{CuO}_4$  compound, in agreement with earlier work.<sup>4,5</sup> However,  $S$  invariably starts to fall below 80 K. In some samples  $S$  and the resistivity are zero below 20 K.<sup>6</sup> So it is tempting to also ascribe the fall in  $S$  below 80 K to incipient superconductivity.

$S$  is reduced in the doped compounds, in agreement with Ref. 5 for Sr doping, and is also weakly temperature dependent, with  $S=0$  in the superconducting state. The latter is consistent with that of a ground-state condensate. In the normal state,  $S$  is not characteristic of a simple metal, but suggests that correlation effects or unusual entropy carrying excitations may be important.

For the work reported here the samples were prepared

as follows. Weighed amounts of the appropriate starting materials such as  $\text{La}_2\text{O}_3$  and  $\text{BaCO}_3$  were finely ground with an agate pestle and mortar. The mixture was fired in air at  $900^\circ\text{C}$  for 4–5 h, reground, and refired for 8–9 h. After this second heat treatment, the mixture was pulverized and pressed into pellets at 10000 lb/in.<sup>2</sup>, sintered in air for 17 h at  $1050^\circ\text{C}$ , and cooled to room temperature in about 4 h. We used a platinum crucible and a quartz tube for processing. The volume shrinkage after the first firing was  $\sim 22\text{--}25\%$  and  $12\text{--}13\%$  in the final sintering.

All the alloys and pure  $\text{La}_2\text{CuO}_4$  showed excellent overall agreement with the x-ray powder pattern obtained recently<sup>7</sup> for the tetragonal  $\text{K}_2\text{NiF}_4$ -type phase of Ba- or Sr-doped  $\text{La}_2\text{CuO}_4$  and there are no extra lines corresponding to additional phases. Our undoped sample clearly showed the splitting near  $2\theta=33^\circ$  which is a sign of the orthorhombic distortion,<sup>7</sup> and this splitting was not detected for Ba/La ratios near 0.1, indicating that the distortion is reduced on alloying. Superconducting transition temperatures, defined as the midpoint of the resistive transition, were 29 K for  $(\text{La}_{0.9}\text{Ba}_{0.1})_2\text{CuO}_4$  and 36 K for  $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_4$ , respectively.

The thermopower was measured between 4.2 and 300 K by the usual technique, and we have also measured the resistivities with four-probe methods.  $R(T)$ , normalized to the room-temperature resistivity, is shown together with  $S(T)$  for two alloys in Figs. 1 and 2. The  $T$  dependence of the resistivities of the Ba- and Sr-doped material are similar to those reported earlier by others, and we also find a similar magnitude (of the order of  $10^{-3} \Omega\text{cm}$ ). We note that  $R(T)$  decreases nearly *linearly* with decreasing temperature, down to the superconducting transition.

For the two compounds shown (which have  $x=0.1$ ),  $S$  is relatively small at room temperature. However, it increases as  $T$  is lowered, which is *not* simple metallic behavior. A positive sign is invariably observed showing that the conduction is by holes. For both compounds and the pure material<sup>6</sup> there is evidence for possible precursor superconducting effects in the thermoelectric power at 80–90 K. The small residual values of  $S$  in the superconducting state are due to the gold reference wires.

Figure 3 shows  $S$  vs  $T$  for one sample of the pure material and two lower concentration alloys. In all three cases  $S$  is temperature independent above about 100 K.

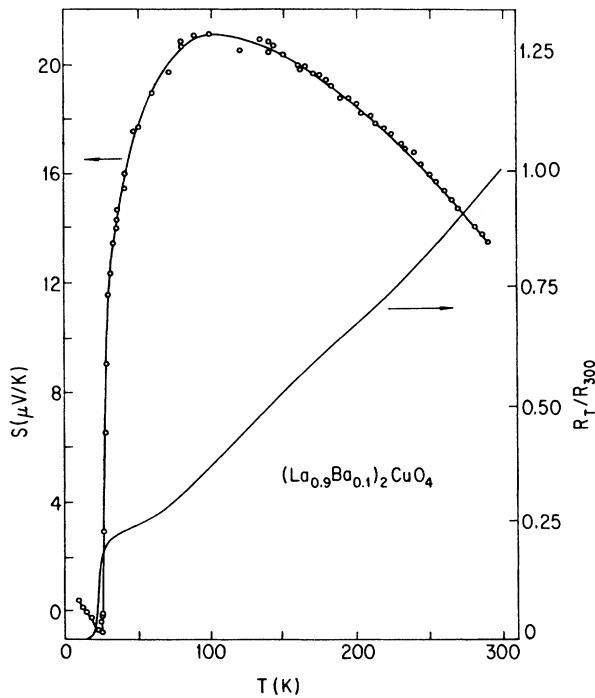


FIG. 1. Temperature dependence of the electrical resistance  $R(T)$  and thermoelectric power  $S(T)$  relative to gold, for  $(\text{La}_{0.9}\text{Ba}_{0.1})_2\text{CuO}_4$ .

The lower concentration alloys show the opposite  $T$  dependence to the higher-concentration ones in Figs. 1 and 2.

Figure 4 shows the room-temperature values of  $S$  versus dopant concentration  $x$  for all samples measured until now. Our value of  $S \approx 300 \mu\text{V/K}$  for pure  $\text{La}_2\text{CuO}_4$  is in

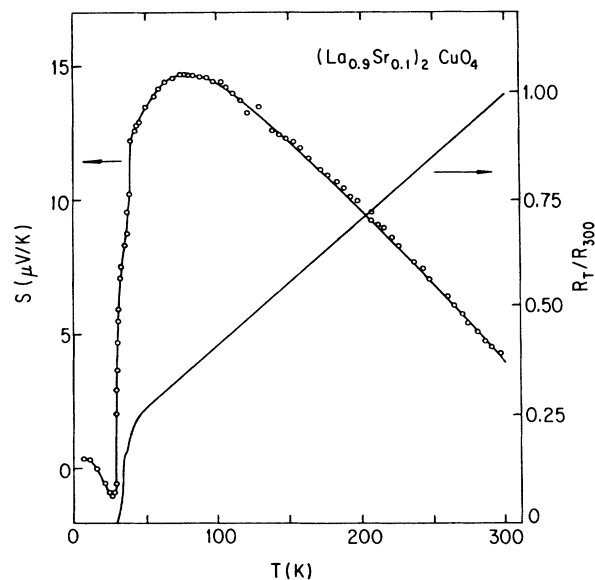


FIG. 2. Temperature dependence of the electrical resistance  $R(T)$  and thermoelectric power  $S(T)$  relative to gold, for  $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_4$ .

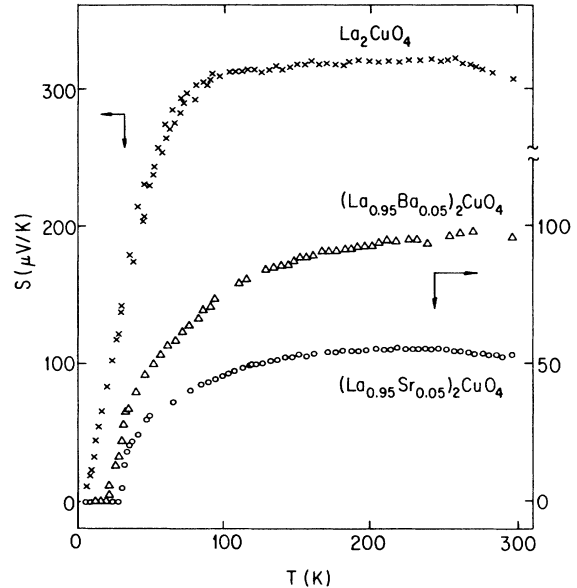


FIG. 3. Temperature dependence of thermoelectric power  $S(T)$  relative to gold for pure  $\text{La}_2\text{CuO}_4$  and two lower concentration alloys.

good agreement with earlier data.<sup>4,5</sup> Despite the fact that we are dealing with sintered oxides there are clear systematic trends in the data.  $S$  falls sharply with doping and then levels off at a small “metallic” value for  $x \geq 0.1$ .

It has been suggested<sup>8</sup> that the Hubbard model describes the basic physics of these materials. With this in

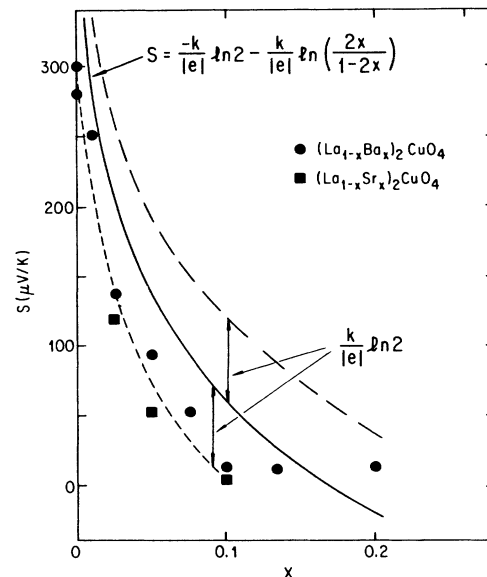


FIG. 4. Room-temperature thermopower vs dopant concentration in various oxides with high superconducting transition temperatures. The solid line shows Eq. (1) in the text with  $\rho = 1 - 2x$ . The long and short dashed lines show, respectively, the effects of removing the  $\ln 2$  term due to magnetic ordering, or adding another  $\ln 2$  term due to orbital degeneracy.

mind we have compared our data with the predictions of the Hubbard model for the thermopower<sup>9,10</sup> in the high-temperature limit,  $k_B T$  greater than the bandwidth  $W$ , but much less than the on-site Coulomb repulsion  $U$ . This type of analysis of thermopower measurements on organic conducting salts such as quinolinium (TCNQ)<sub>2</sub> forms one of the main arguments in favor of the importance of Coulomb correlations in these crystals.<sup>9,10</sup> If such a picture applies to pure La<sub>2</sub>CuO<sub>4</sub>, and if one  $d$  spin per Cu<sup>2+</sup> ion is progressively removed by replacing trivalent La or Y with divalent Sr or Ba, then at high temperatures the thermoelectric power should obey the modified Heikes formula<sup>9-11</sup>

$$S = -\frac{k}{|e|} \ln 2 - \frac{k}{|e|} \ln \frac{(1-\rho)}{\rho}. \quad (1)$$

$\rho$  is the number of electrons per Cu site, which is equal to  $1-2x$  for an alloy such as (La<sub>1-x</sub>Ba<sub>x</sub>)<sub>2</sub>CuO<sub>4</sub>.

Equation (1) is the only way we know of accounting for a temperature-independent thermoelectric power. If the conduction process involves hopping of  $d$  electrons from one Cu<sup>2+</sup> ( $d^9$ ) ion to a Cu<sup>3+</sup> ( $d^8$ ) ion, then entropy considerations<sup>9</sup> lead to the above formula with  $\rho$  equal to the ratio of Cu<sup>2+</sup> ions to the total number of Cu ions, i.e.,  $\rho = 1-2x$ . The  $\ln 2$  term comes from the spin degree of freedom and will be absent if the Cu<sup>2+</sup> ions are ordered magnetically, which is probably the case for pure La<sub>2</sub>CuO<sub>4</sub>.<sup>12</sup> On the other hand, if the Cu<sup>2+</sup> ions are not ordered, and have twofold orbital degeneracy (which occurs for strictly octahedral symmetry<sup>13</sup>), then there would be an extra  $\ln 2$  term from the orbital degrees of freedom. These various possibilities are sketched in Fig. 4.

Bearing in mind that there are no adjustable parameters in Eq. (1) (apart from the modifications discussed above), the above equation gives a good description of the effect of doping on the room-temperature thermopower up to  $x=0.1$ . Although some temperature dependence is observed, which cannot be accounted for by Eq. (1), this is less marked for concentrations below  $x=0.1$ . In this concentration region the decrease in  $S$  towards lower temperatures could perhaps arise from the fact that the bandwidth is comparable with  $T$ .<sup>10</sup> Opposite  $T$  dependence ( $S$  increasing as  $T$  decreases) can be obtained in the Hubbard model by introducing the nearest-neighbor Coulomb interaction.<sup>10</sup>

The above picture has several obvious consequences which may perhaps be tested in future experiments. It implies that conduction is via hopping of  $d$  electrons; that the

pure compound has a Cu<sup>3+</sup>/Cu<sup>2+</sup> ratio which is usually in the range 0.003–0.05 and that for  $x \leq 0.1$  possible oxygen deficiencies are not changing the Cu<sup>3+</sup> ratio significantly. Furthermore, if the Cu<sup>3+</sup> ions had spin degrees of freedom (say  $S=1$ ),<sup>13</sup> there would be an extra  $+\ln 3$  term in Eq. (1) which would reduce the agreement in Fig. 4.

We cannot fit the data to the Heikes formula for  $U=0$ , because if one considers a single  $d$  subband with room for only two electrons, then the thermopower would be zero for the pure compound due to electron-hole symmetry. If there is full orbital degeneracy (i.e., a narrow  $d$  band containing eight or nine electrons), then  $S$  would only fall very slowly with dopant concentration  $x$ .

For  $x \geq 0.1$ , Eq. (1) does not apply to our findings because  $S$  remains small and positive. However, for a simple uncorrelated metal (without phonon drag) the order of magnitude of  $S$  is given by

$$S \approx \frac{k_B^2 T}{e} n(\epsilon_F), \quad (2)$$

where  $n(\epsilon_F)$  is the density of states at the Fermi level. More precisely,  $S$  is proportional to the logarithmic derivative of the product of the electron mobility and the density of states at  $\epsilon_F$ .<sup>14</sup> The room-temperature values of  $S$  correspond to  $n(\epsilon_F)$  values a factor of 10 or so times larger than ordinary metals such as Cu. However, the observed temperature dependence (see Figs. 1 and 2) is opposite to that expected from Eq. (2).

Alternatively it is conceivable that for  $x \geq 0.1$  the number of Cu<sup>3+</sup> ions no longer rises with  $x$ , for example, because oxygen defects start to compensate for the Sr or Ba doping, and the hopping picture still applies.

In conclusion, pure La<sub>2</sub>CuO<sub>4</sub> has a large, positive, and temperature-independent thermoelectric power. Doping with Sr or Ba systematically reduces  $S$  and introduces a weak temperature dependence. However, for all concentrations  $S$  remains positive. Even though  $S$  becomes small for  $x \geq 0.1$  it does not show typical metallic behavior. We have also found that thermoelectric power measurements sometimes give indications of a tendency towards superconductivity (precursor effects) at even higher temperatures than resistance data.

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