

Metallic, but Not Superconducting, La-Ba (and La-Sr) Copper Oxides

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New measurements are reported on three La-Ba (and La-Sr) copper-oxide compounds, including one new compound. These materials have metallic conductivities, comparable to those of the high- T_c copper oxides in the normal state, but they are *not* superconducting down to 5 K. Their magnetic susceptibility and structural features are also similar. These data provide a new challenge and test for the numerous theories of high T_c to account also for its absence in these three closely related materials.

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The discovery¹ of superconductivity near 40 K in a copper-oxide system by Bednorz and Müller was followed by the discovery² of a second class of copper oxides with T_c near 90 K. Since then, scientists all over the world have exerted an unprecedented effort to try to understand the phenomenon of high T_c by studying these two systems and trying to generalize from them. Based on different assumptions as to what features might be critical in these two systems, more than twenty different theories of high T_c have been proposed. Definitive progress in confirmation of these theories or stimulation of new ones has been severely restricted by our having a data base with only two structural types. The purpose of this Letter is to report new measurements on three La-Ba (and La-Sr) copper-oxide systems which are metallic, but *not* superconducting down to 5 K. Comparison of these apparently nonsuperconducting copper oxides with those having high T_c provides a critical test for the understanding of the origin of superconductivity in these materials. That is, we must account for why some copper oxides have such a high T_c , while other closely related compounds are not even superconducting above 5 K.

Before their recent renaissance, the La-Sr- and La-Ba-Cu-O systems had been studied extensively by Raveau and co-workers.³⁻⁶ A few of the compounds in this system were found to be metallic down to 100 K, the lowest temperature they examined. Two of these compounds were recently cooled further and found^{1,7} to be high- T_c superconductors: $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (at 30 K) and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (at 40 K) for $x \approx 0.15$. We have prepared⁸ one of the remaining metals, $\text{La}_4\text{BaCu}_5\text{O}_{13}$, and report here its electrical conductivity and magnetic-susceptibility behavior down to 5 K. In addition, we have further oxidized the compound $\text{La}_2\text{SrCu}_2\text{O}_{6+\delta}$ to make it metallic, and have discovered⁹ a new metallic compound, $\text{La}_5\text{SrCu}_6\text{O}_{15}$. The conductivity data¹⁰ for these three compounds are shown in Fig. 1, together with the data^{7,11} for the high- T_c superconductors $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ (dash-dotted) and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (dashed). It is clear that above T_c the approximate magnitudes of the conductivities of these five compounds

are comparable (especially when we recognize the variability in the conductivities of such sintered ceramic powders). Thus, the three materials reported here are all good metals, showing as high a conductivity as the best superconductors, but they are *not* superconducting¹² down to 5 K. The anomalies evident near 40 K in $\text{La}_5\text{SrCu}_6\text{O}_{15}$ and $\text{La}_2\text{SrCu}_2\text{O}_{6.2}$ are caused by small amounts of second phase of superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, estimated from magnetic-susceptibility measurements as less than 2% (consistent with its extreme weak intensity in the x-ray powder pattern).

It was found¹³ early that the superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is very sensitive to processing conditions which strongly affect the oxygen content. We have attempted to modify these three materials by changing the processing conditions. The compound $\text{La}_2\text{SrCu}_2\text{O}_{6+\delta}$, if prepared⁶ in air at 1130°C and quenched, is a semiconductor with $\delta=0$. If these samples are annealed for 3 h at 430°C in 1 bar of O_2 , they become⁶ semimetallic.

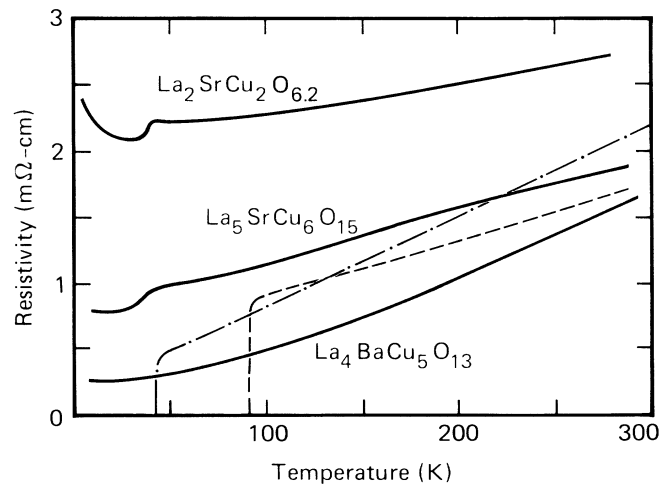


FIG. 1. Resistivity vs temperature for three nonsuperconductors compared with that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (dashed) and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ (dash-dotted). Weak anomaly near 40 K in two samples is caused by a small amount of superconducting second phase.

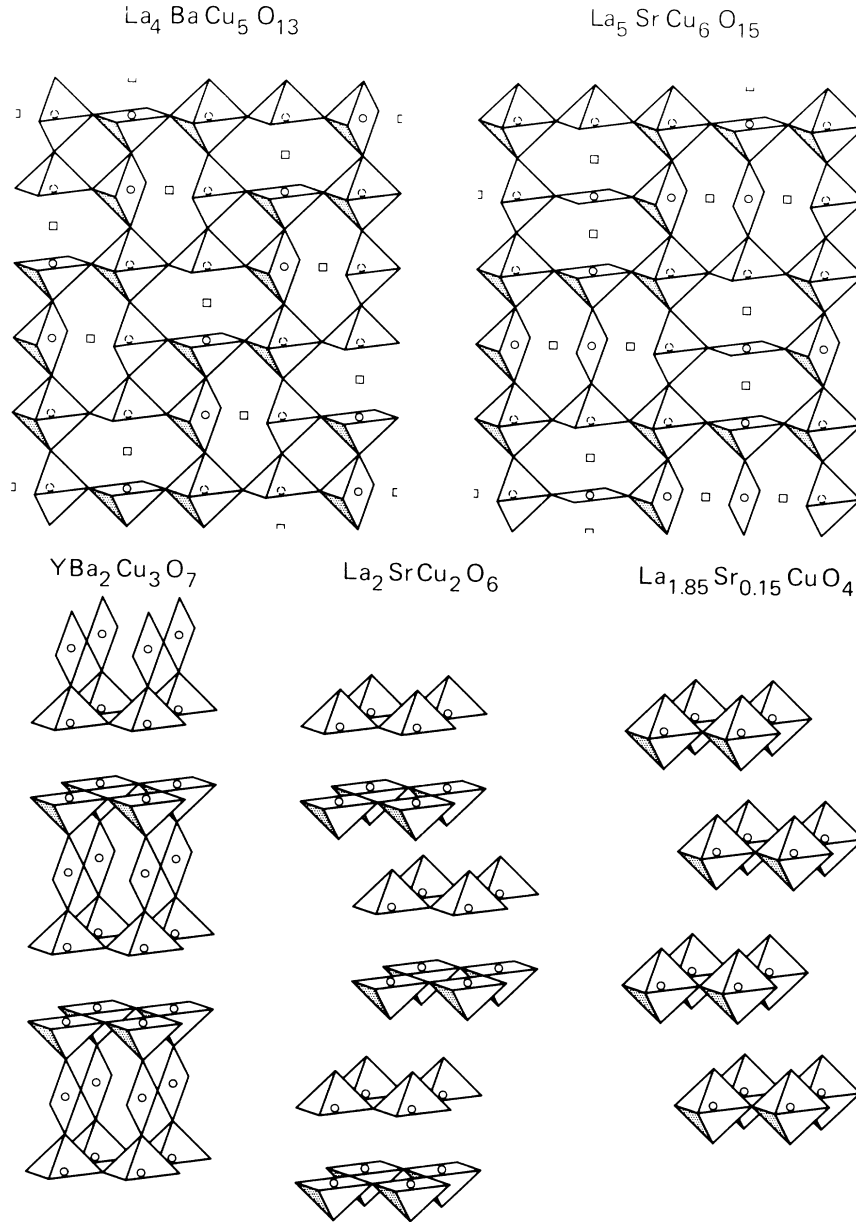


FIG. 2. Schematic comparison of the structures of the five metals discussed in an attempt to recognize the structural features responsible for high T_c (see Refs. 5, 6, and 14).

We have found that annealing for 16 h at 650°C in 6.5 bars of O_2 increases δ to 0.2 and the compound becomes metallic (Fig. 1). On the other hand, $\text{La}_4\text{BaCu}_5\text{O}_{13}$ is very sensitive to processing conditions,⁴ as is the new compound $\text{La}_5\text{SrCu}_6\text{O}_{15}$. By further varying the conditions, we have not been able to make any of these three compounds superconducting, nor those in the solid solution $\text{La}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_y$ which we have extended to $0 < x < 0.5$.

We now concentrate on comparing these five metallic compounds in an attempt to identify which factors are responsible for the large differences in their supercon-

ducting transition temperatures. A comparison of the structures of these five metals is given in Fig. 2. In the structure⁶ of $\text{La}_2\text{SrCu}_2\text{O}_6$, each copper is coordinated by a pyramid of five oxygens. These pyramids share corner oxygens to form two-dimensional sheets that are stacked in pairs, as shown in Fig. 2. This structure may be viewed as a $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type double-layer intergrowth (having two sheets of octahedra), with an additional sheet of oxygen vacancies in between. In the compound annealed in O_2 , $\delta = 0.2$, and 20% of these vacancies are filled with oxygen. As in the structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Fig. 2), these sheets of pyramids have excellent overlap

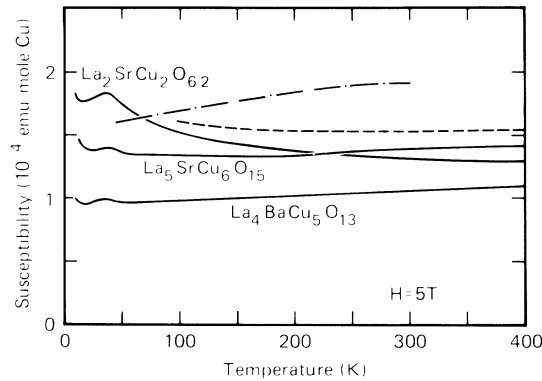


FIG. 3. Magnetic susceptibility of three nonsuperconductors together with that of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (dashed) and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ (dash-dotted). Data taken at $H=5$ T. Anomalies near 40 K are caused by small quantities of superconducting second phase.

within the sheets, but a poor overlap across the sheet of oxygen vacancies. There is an extremely weak overlap between the layers, as in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, which contains sheets of corner-sharing octahedra.

The structure⁵ of the second compound, $\text{La}_4\text{BaCu}_5\text{O}_{13}$, is also shown schematically in Fig. 2. It can be viewed as a cubic perovskite with an array of *channels* of oxygen vacancies running parallel to the *c* axis. Recent structural work¹⁴ on $\text{La}_5\text{SrCu}_6\text{O}_{15}$ indicates a similar structure, but with a different array of channels of oxygen vacancies in this material. The channels of vacancies found in these two compounds contrast with the sheets of vacancies in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{La}_2\text{SrCu}_2\text{O}_6$ and the lack¹⁵ of oxygen vacancies in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. In the case of sheets of oxygen vacancies, conduction is severely limited perpendicular to the sheets, since the overlap across the vacancies is poor, making these metals strongly two dimensional. In the case of channels of vacancies, conduction perpendicular is decreased, but the electrons can still delocalize around these channels, making these materials anisotropic three-dimensional metals, with a larger bandwidth parallel to the channels. These conclusions are confirmed by recent band-structure calculations.¹⁶

These structures may also be described in terms of sheets and chains, by our ignoring all Cu—O bonds larger than 2.1 Å (usually the bond to the apex of a CuO_5 pyramid). From this point of view, both the 40- and 95-K superconductors have CuO_2 sheets, but so do $\text{La}_2\text{SrCu}_2\text{O}_6$ and $\text{La}_5\text{SrCu}_6\text{O}_{15}$. In the latter compound, however, there are two sets of intersecting sheets, oriented perpendicular to each other. Enclosed between these intersecting sheets in $\text{La}_5\text{SrCu}_6\text{O}_{15}$ are isolated copper-oxygen chains. There are also chains in between the (nonintersecting) sheets of $\text{YBa}_2\text{Cu}_3\text{O}_7$. Neglecting the longer Cu—O bonds in $\text{La}_4\text{BaCu}_5\text{O}_{13}$ results in a structure composed solely of chains,¹⁶ not with one copper per

TABLE I. Effective copper valence (V) and T_c .

| | V | T_c (K) | Cu-O network |
|--|------|-----------|-------------------|
| $\text{La}_4\text{BaCu}_5\text{O}_{13}$ | 2.4 | < 5 | Anisotropic 3D |
| $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$ | 2.33 | 93 | Sheets and chains |
| $\text{La}_2\text{SrCu}_2\text{O}_{6.2}$ | 2.2 | < 5 | Sheets |
| $\text{La}_5\text{SrCu}_6\text{O}_{15}$ | 2.17 | < 5 | Sheets and chains |
| $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ | 2.15 | 40 | Sheets |
| $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ | 2.13 | 60 | Sheets and ?? |

repeat unit, but having a larger, x-shaped cross section with five coppers per repeat unit. We conclude that these five systems have many common structural features, with no obvious systematic differences to distinguish between the superconductors and nonsuperconductors.

In order to compare the electronic properties of these five compounds, we show in Fig. 3 the magnetic susceptibility for $H=5$ T of the three nonsuperconductors together with those of the two high- T_c compounds.^{17,18} The data for $\text{La}_4\text{BaCu}_5\text{O}_{13}$ and $\text{La}_2\text{SrCu}_2\text{O}_{6.2}$ agree with those of Raveau and co-workers^{4,6} for $T > 100$ K (where the data overlap). In order to compare meaningfully the magnitudes of χ , they have been normalized per mole copper. It is clear that the behavior of $\chi(T)$ is similar for all five compounds, i.e., only weakly temperature dependent, with a similar magnitude. We conclude that there are no major differences in $\chi(T)$ for these five compounds that would account for the large differences in their superconducting T_c 's.

In Table I we show a comparison of the nominal degree of oxidation of these materials expressed as an effective Cu oxidation valence. There is apparently no correlation between T_c and the degree of oxidation.

In conclusion, we have presented new data on three La-Ba (and La-Sr) copper-oxide compounds which are *not* superconducting down to 5 K. These materials have many chemical and structural features in common with the two high- T_c systems, including the fact that they are all copper oxides, oxidized beyond the nominal Cu^{2+} , and contain Cu-O networks, separated by ordered arrays of oxygen vacancies that reduce their dimensionality. These features may be necessary for superconductivity, but these new data show that they are clearly not sufficient. The subtle differences between these materials suggest that superconductivity in these systems is a subtle phenomenon. These data provide a much more extensive data base for our understanding of these materials and determining what is the mechanism for their spectacular behavior.

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slowly. Oxygen content was determined by iodometric titration techniques.

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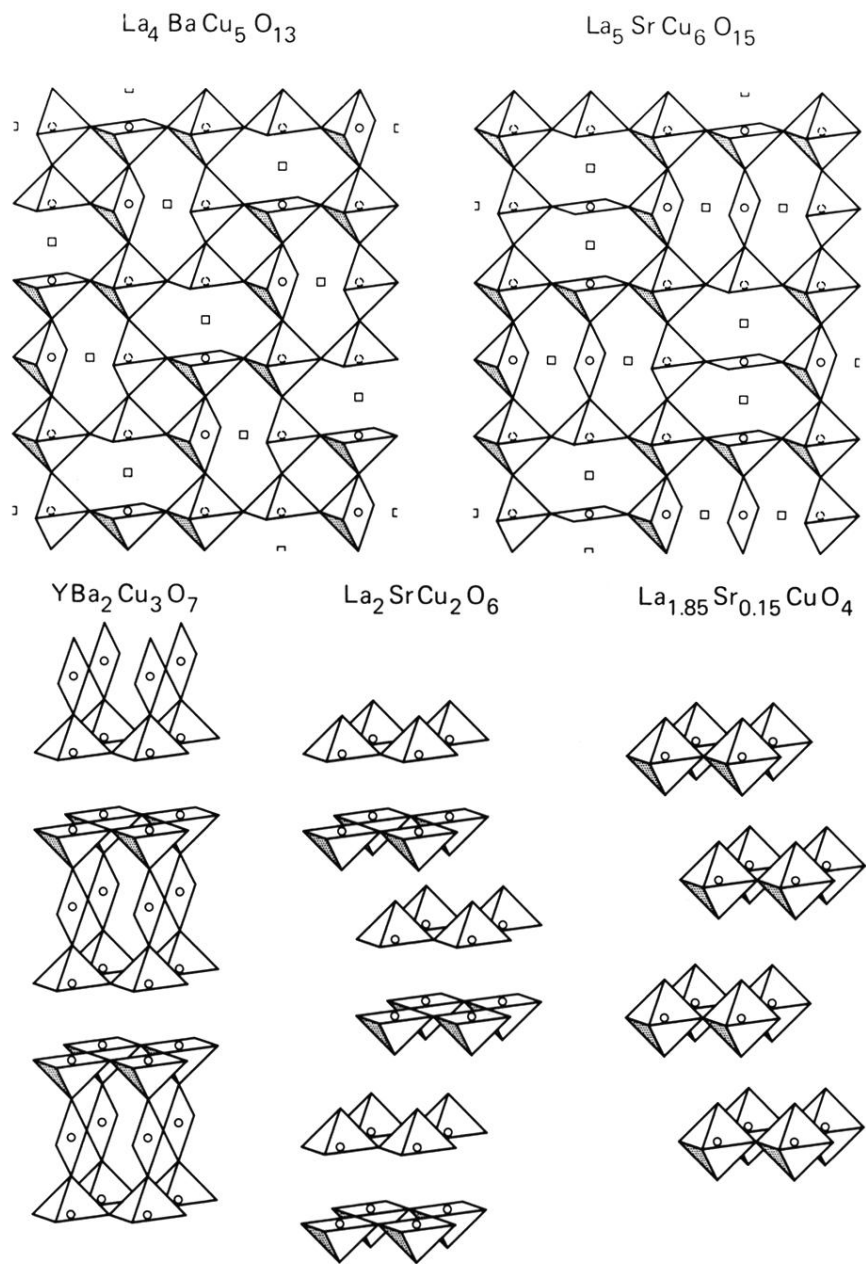


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