Electrical Characterization of $La_{2-x}Sr_xCuO_{4-y}$ Superconductors

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The electrical behaviour of $La_{2-x}Sr_xCuO_{4-y}$ solid solutions (with $x = 0$, $x = 0.025$, $x = 0.05$, and $x = 0.15$) at temperatures between 10 and 900 K and under different oxygen partial pressure $p_{O_2} = 1 \div 10^{-6}$ atm) has been investigated. The samples prepared and measured under an O_2 flux (i.e., with $y = 0$) show a superconducting transition with $T_c = 46$, 29, 37 K for $x = 0$, 0.05 and 0.15, respectively. The samples with $x = 0.025$, $y = 0$, and $x = 0$, $y \neq 0$ exhibit no sign of superconductivity. In the temperature range 100–900 K, La_2CuO_4 is semiconducting, whereas the electrical resistivity is independent of temperature for the $x = 0.025$ sample, and the $x = 0.05$ and $x = 0.15$ are metallic.

Key words: Superconductors, electrical properties, defects.

Over the last months the search for oxides with higher and higher superconducting transition temperature (T_c) has been accompanied by systematic investigations of two families of high T_c superconductors; viz., $La_{2-x}Sr_xCuO_{4-y}$ and $YBa_2Cu_3O_{7-y}$.

In particular, a recent report [1] provided a semiquantitative picture of the temperature-concentration (T, x) phase diagram for $La_{2-x}Sr_xCuO_{4-y}$ $(0<x<0.2)$. Other authors investigated the various transitions: structural (tetragonal (T) – orthorhombic (O) [2]), insulator-metal [3], and antiferromagnetic [4], which are exhibited by these substances in addition to the superconducting transition, and which are related to the latter.

The properties of the La–Cu oxides depend strongly on the presence of impurities in the original oxides, on defects, and on the oxygen non-stoichiometry. As a consequence published data are often contradictory. For example, La_2CuO_4 at room temperature (r.t.) is a semiconductor according to some authors [5], and a metal according to others [6]. Moreover, the existence of bulk superconductivity [7], of grain-surface superconductivity [8], and the absence of superconductivity [3] has been claimed for La_2CuO_4.

This communication reports a study of the electrical properties of the $La_{2-x}Sr_xCuO_{4-y}$ superconducting solid solutions in the 10–900 K temperature range and 1–1.10^{-6} atm oxygen partial pressure (p_{O_2}) range. Most samples have been prepared under $p_{O_2} =$ 1 atm, which ensures a negligible oxygen vacancy concentration [9]. Resistivity measurements have been performed also above r.t. in order to study the reactions and equilibria of these materials with gaseous oxygen and to determine the relationships among O_2 exchange, electrical properties, and the T–O transition in pure and doped La_2CuO_4.

$La_{2-x}Sr_xCuO_{4-y}$ samples in four compositions ($x = 0$, $x = 0.025$, $x = 0.05$, and $x = 0.15$) were prepared from CuO and $SrCO_3$ (both Fluka puriss.) and La_2O_3 (Fluka purum p.a.). The powders were wet mixed, pressed into disks (diameter 8 mm, height 1–3 mm), calcinated under an oxygen flow at 1400 K for 48 h, and then slowly (5 K/min) cooled to r.t. under oxygen. A La_2CuO_{4-y} sample was also prepared in air with the same thermal treatment. Powder X-ray diffraction analyses confirmed that the conversion was complete and that all samples consisted of a single phase.

The electrical resistivity was measured with an a.c. four-point method and silver painted contacts, using two different cells for the low (10–300 K) and the high temperature (300–900 K) ranges. All experiments were carried out at 1 atm total pressure.

Figure 1 reports the resistivity data for the temperature range 300–900 K of the four samples prepared under $p_{O_2} = 1$ atm. La_2CuO_4 displays a semiconducting behaviour, the samples with $x = 0.05$ and 0.15 are metallic, whereas the $x = 0.025$ sample shows a practically constant resistivity over the whole high temperature range. The data for the samples with $x = 0$, 0.05 and 0.15 proved to be well reproducible over several thermal cycles. On the contrary, the $x = 0.025$ sample

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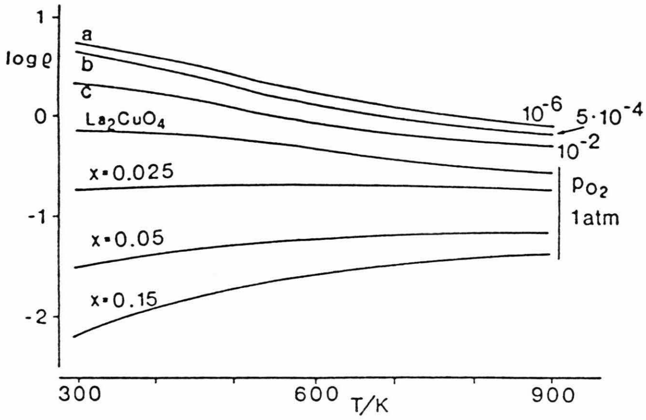

Fig. 1. Resistivity (ϱ/ohm cm) for pure and doped La_2CuO_4 in the 300–900 K temperature range and under a $p_{O_2}=$ 1 atm. Curves a, b, c are relevant to La_2CuO_4 under different partial pressures.

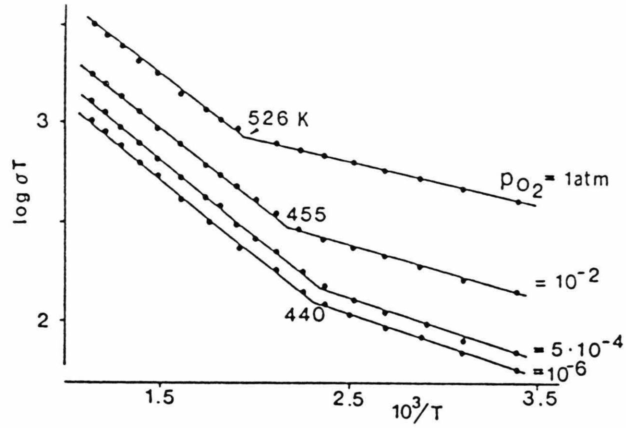

Fig. 2. Conductivity (σ/ohm^{-1} cm^{-1}) of La_2CuO_4 samples annealed and measured under different p_{O_2}.

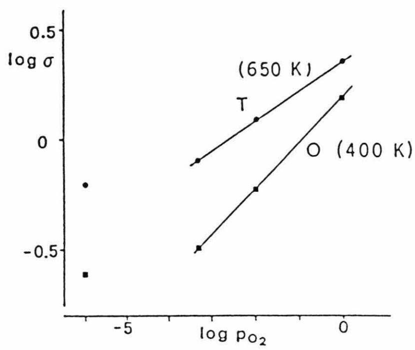

Fig. 3. Dependence of the conductivity (σ/ohm^{-1} cm^{-1}) on the oxygen partial pressure (p_{O_2}/atm) for the tetragonal ($T=650$ K) and orthorhombic ($T=400$ K) phases of La_2CuO_4.

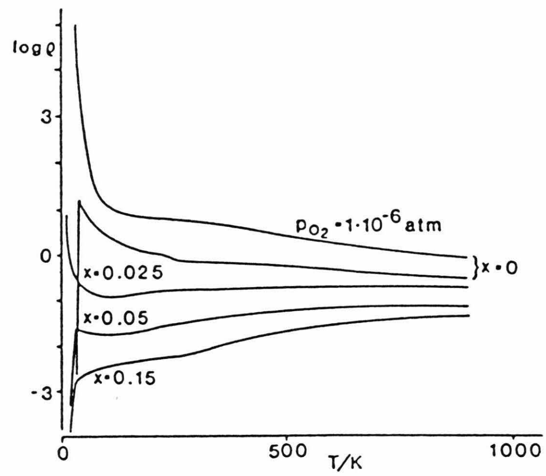

Fig. 4. Temperature dependence of the resistivity for $La_{2-x}Sr_xCuO_4$ samples with $x=0$, $x=0.025$, $x=0.05$, $x=0.15$ prepared under oxygen ($p_{O_2}=1$ atm) and for a La_2CuO_{4-y} sample annealed at 900 K with $p_{O_2}=1.10^{-6}$ atm.

in the first heating run gave ϱ values very close to those of La_2CuO_4. The curve drawn in Fig. 1 relates to data taken in subsequent cycles after an annealing of 12 h at 900 K. This indicates an instability of this solid solution at r.t., in agreement with the anomalous behaviour of samples with a composition close to $x=0.025$ reported in [8].

Measurements performed in different p_{O_2} indicated that only the resistivity of La_2CuO_4 was appreciably influenced by the oxygen partial pressure. As shown by the curves a, b, c in Fig. 1, the resistivity increases with decreasing p_{O_2}: this suggests that in La_2CuO_4 at high temperature the carriers are holes. Their presence might be due to bivalent impurities (alkaline earths), M, in our starting oxides, or to lanthanum vacancies (V_{La}''') [10].

The crystal-gas equilibrium

$$O_O + 2\,h^{\cdot} \leftrightarrows V_O^{\cdot\cdot} + 1/2\,O_2 \tag{1}$$

is already reached at 600 K, and is achieved very fast (few minutes) at 900 K.

The Arrhenius conductivity plots (log σT vs. $1/T$) are reported in Fig. 2 for the four different p_{O_2} values. A marked knee is always apparent: when $p_{O_2}=1$ atm, it occurs at 526 K, a temperature which essentially coincides with that assigned by different authors [2, 5, 11] to a second order displacive transition from tetragonal to othorhombic. This structural transition is caused by a tilting of the CuO_6 corner-sharing octahedra (slightly elongated along the c axis) which form perovskite layers [12]. It is noteworthy that resistivity measurements allow to detect this small structural distortion. This transition temperature, T_{T-O}, decreases (remarkably at the beginning) on lowering the oxygen partial pressure, finally approaching about 440 K. A similar lowering of T_{T-O} with p_{O_2} had also been observed by Fiory et al. [13] on $YBa_2Cu_3O_{7-y}$ samples and explained by an atomic deformation-potential model.

From the data of Fig. 2, the activation energy E for the transport of holes can be evaluated as 14.2 kJ/mol for the tetragonal phase and 5.0 kJ/mol (average for the straight lines) for the orthorhombic phase. In other words, the mobility of holes is favoured by the distortion in the perovskite layers.

The trend of log σ vs. log p_{O_2} for the tetragonal (at 650 K) and the orthorhombic phase (at 400 K) is illustrated in Figure 3: concerning the three p_{O_2} values of 1, 1.10^{-2}, and 5.10^{-4} atm, the plots are practically linear with slopes of about 1/7 and 1/5 for the higher and lower temperature, respectively. From (1) follows

$$k_1 = [V_O^{\cdot\cdot}]\, p_{O_2}^{1/2} / [h^{\cdot}]^2 . \quad (2)$$

Taking into account the electroneutrality condition

$$2\,[V_O^{\cdot\cdot}] = [e'] = K/[h^{\cdot}] \quad (3)$$

one obtains

$$[h^{\cdot}] = k'\, p_{O_2}^{1/2} . \quad (4)$$

Since $\sigma \propto [h^{\cdot}]$, one can identify the experimental ratio d log σ/d log p_{O_2} with d log$[h^{\cdot}]$/d log $p_{O_2} = 1/6$. Therefore, the present data are consistent with the simple defect analysis which follows from (1).

Figure 4 reports, over the whole 10–900 K range, the resistivity data for the four samples annealed in oxygen and an La_2CuO_{4-y} sample annealed at 900 K under $p_{O_2} = 1.10^{-6}$ atm. The samples with $x = 0, 0.05, 0.15$ (annealed in oxygen) show a superconducting transition at $T_c = 46$, 29 and 37 K, respectively. Both the $x = 0.025$ sample and that of La_2CuO_{4-y} exhibit a negative temperature coefficient below 100 K without any sign of superconductivity. The same is true for the La_2CuO_{4-y} sample prepared in air (not shown).

From these results the following conclusions ca be drawn.

a) The La_2CuO_4 samples without oxygen vacancies (synthesis with $p_{O_2} = 1$ atm) are superconducting below $T_c = 46$ K and semiconducting between 46 and 900 K, with holes as majority carriers, the T_{T-O} transition occurs at 526 K.

b) The substitution of Sr^{2+} for La^{3+} with $x = 0.025$ causes the formation of a solid solution which does not have a superconducing phase above 10 K. This composition is near the limit between the insulating and metallic solids: the holes localized at the Fermi energy [11] for $0 < x < 0.025$, are mobile for $x > 0.025$ "probably because their density becomes high enough to screen the random potential introduced by the dopant atoms" [1]. With the composition $x = 0.05$ there is an increase of resistivity from about 100 K, suddenly followed at 29 K by the superconducting transition. Finally, for $x = 0.15$ the sample is a metal above $T_c = 37$ K.

c) It is accepted that in Sr doped La–Cu superconducting oxides the preservation of charge neutrality requires that the defects Sr'_{La} are compensated by holes at O^- sites in the CuO_2 planes [14]. Our data suggest that in La_2CuO_4, the presence of a small $V_O^{\cdot\cdot}$ concentration which can compensate both the M'_{La} and V'''_{La} defects, prevents the superconducting transition. In other words, observation of a superconducting phase may well depend upon the impurities of the ingredients and/or details of the preparation procedures

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