# STABILIZATION OF A NEW SUPERCONDUCTING PHASE BY LOW TEMPERATURE FLUORINATION OF La<sub>2</sub>CuO<sub>4</sub>

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When La<sub>2</sub>CuO<sub>4</sub> is treated with pure F<sub>2</sub> gas at 200°C, the X-ray diffraction pattern of the resulting product is characteristic of a new single phase derived from the K<sub>2</sub>NiF<sub>4</sub>-type structure. An enhancement of the orthorhombic distortion relative to the starting oxide is observed with: a = 5.342 Å; b = 5.436 Å and c = 13.192 Å. Both weight uptake and increase of the *c* unit cell constant could be consistent with an incorporation of fluorine atoms in the lattice. This new compound is superconducting at  $T_c = 40$  K with  $H_{c_1} \simeq 700$  Oe and exhibits a strong diamagnetic susceptibility ( $\chi_g = -6.13 \times 10^{-3}$  emu/g) at 6 K under an applied field of 1 Oe.

## 1. Introduction

Most reports have shown that stoichiometric  $La_2CuO_4$  generally exhibits a semiconducting behavior. However superconductivity occurs below 40 K when orthorhombic La<sub>2</sub>CuO<sub>4</sub> oxide is treated under strongly oxidizing conditions. When the samples are annealed under a flow of oxygen gas, the value of the diamagnetic susceptibility indicates that only 0.2% of the sample is superconducting [1-3]. On the other hand, according to previous work, the superconducting fraction increases when the samples are treated with rising oxygen pressures [1,4]. It was reported that below 320 K these oxygen-enriched materials consist of a mixture of two orthorhombic phases exhibiting nearly identical unit cell constants and different space groups. One of these phases has a stoichiometry close to  $La_2CuO_4$  and the other one, which could be responsible for the superconducting properties, contains an excess of oxygen:  $La_2CuO_{4+\nu}$ with y=0.13 [4]. One of the characteristics of the crystal structure of this latter phase, refined from single crystal neutron diffraction data, is the presence of short O-O distances suggesting the formation of peroxide ions  $O_2^{2-}$  [5].

Tissue et al. [6] reported that  $La_2CuO_4$  treated under diluted F<sub>2</sub>-gas at 350°C exhibited a superconducting behavior below 35 K and they claimed that no structural change was observed after fluorination. Our own experience in the fluorination treatment of the inorganic compounds led us recently to undertake a systematic study of the F<sub>2</sub>-gas treatment of high  $T_c$  superconductors at low temperatures. The first investigations were made on YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> oxides for which such a treatment yielded both an inhibition of the hydrolysis by the presence of an amorphous thin layer of fluorocompound and an improvement of the superconducting characteristics [7,8].

The influence of the fluorination treatment of  $La_2CuO_4$  ( $P_{F_2}=1.3$  bar,  $T_{F_2}=200^{\circ}C$ ) on its structural, magnetic and electrical properties are presented in this paper.

## 2. Experimental methods

La<sub>2</sub>CuO<sub>4</sub> as starting compound was prepared from stoichiometric mixtures of La<sub>2</sub>O<sub>3</sub> and CuO powders. After a 20 h heating cycle at 920°C in air, the resulting product was ground and treated again at 900°C for 14 h under a flow of oxygen gas. The sample was annealed at 450°C for 12 h in an oxygen atmosphere followed by a moderate cooling (100°C/ h). The oxide exhibited an orthorhombic symmetry, with unit cell constants: a = 5.361 Å, b = 5.416 Å and

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c=13.157 Å, values in good agreement with those previously published [9].

The fluorination process was carried out under 1.3 bar of pure  $F_2$ -gas for 20 h using the same experimental procedure already described [7,8]. The reaction temperatures  $T_{F_2}$  ranged from room temperature to 300°C.

The samples were analyzed before and after fluorination by X-ray diffraction  $(CuK_{\alpha})$ . Unit cell constants were determined by least-squares refinement using 5N-silicon as an internal standard. The magnetization of the compounds was measured using a SQUID magnetometer. Electrical resistance measurements were carried out above 4.2 K using a standard four-probe DC technique.

#### 3. Results and discussion

When La<sub>2</sub>CuO<sub>4</sub> powders are fluorine-treated at  $T_{F_2} = 200^{\circ}$ C, a weight uptake of about 2% is observed and the resulting X-ray diffraction patterns can be completely indexed by assuming an orthorhombic unit cell derived from the K<sub>2</sub>NiF<sub>4</sub>-type structure (fig. 1). The line splitting of some pairs of reflections such as (020) and (200), (024) and (204), (133) and (313), which is more pronounced



Fig. 1. X-ray powder pattern of La<sub>2</sub>CuO<sub>4</sub> before and after fluorine gas treatment at  $T_{F2} = 200$  °C.

for the fluorinated compound than for the La<sub>2</sub>CuO<sub>4</sub> starting oxide, indicates an enhancement of the orthorhombic distortion. The values of the unit cell constants are: a=5.342 Å, b=5.436 Å and c=13.192 Å. After fluorination of La<sub>2</sub>CuO<sub>4</sub>, an enlargement of the orthorhombic cell is observed ( $\Delta V/V_0 \simeq 0.28\%$ ): c undergoes an elongation of about 0.27% whereas the product ab remains remarkably constant.

Let us note that La<sub>2</sub>CuO<sub>4</sub> is completely destroyed for  $T_{F_2} \ge 300$  °C, resulting in a mixture of LaF<sub>3</sub> and CuF<sub>2</sub>, whereas for  $T_{F_2} \le 100$  °C neither significant change in the X-ray diffraction spectra nor noticeable weight uptake are detected.

As yet, the best way to improve the superconducting properties has been achieved using oxygen high pressure treatments. This behavior has been explained in terms of additional oxygen atoms in the lattice [4,9,10]. A decrease of the orthorhombic distortion of La<sub>2</sub>CuO<sub>4</sub> toward tetragonal symmetry generally takes place and this is characterized by an elongation of the c parameter of about 0.21%. Assuming that pure stoichiometric  $La_2CuO_4$  oxide is a semiconductor, the occurrence of superconductivity in oxygen-rich compounds seems to be correlated with the additional increase of the axial elongation of the  $CuO_6$  octahedra along the c axis with respect to that already present in  $La_2CuO_4$  [4]; it can be noted that the elongation is even higher in the case of F<sub>2</sub>-treated La<sub>2</sub>CuO<sub>4</sub> samples ( $\Delta c/c=0.27\%$ ).

Both the change of the unit cell parameters and the weight uptake which are observed after the fluorinegas treatment of  $La_2CuO_4$  strongly suggest an incorporation of extra fluorine atoms in the structure, increasing thereby the separation between two layers containing corner-sharing CuO<sub>2</sub> square planes.

As shown in fig. 2, the susceptibility for a F<sub>2</sub>-treated La<sub>2</sub>CuO<sub>4</sub> sample, cooled in zero magnetic field, becomes negative just below  $40 \pm 1$  K indicating a superconducting behavior. The diamagnetic susceptibility depends strongly on the applied magnetic field. The superconducting volume fraction of the sample has been determined at 6 K from  $H = -4\pi M$  in which *M* has been calculated using the theoretical density value of La<sub>2</sub>CuO<sub>4</sub>. This fraction decreases with rising magnetic fields: 54% ( $\chi_g = -6.1 \times 10^{-3}$  emu/g) under 1 Oc, 16% ( $\chi_g = -1.8 \times 10^{-3}$  emu/g) under 20 Oe and 8% ( $\chi_g = -0.95 \times 10^{-3}$  emu/g) under 100 Oe. It is worthwhile noting that for La<sub>2</sub>CuO<sub>4</sub>, an-



Fig. 2. Magnetic susceptibility for an  $F_2$ -treated  $La_2CuO_4$  sample recorded at various applied magnetic fields.

nealed under 500 bar oxygen pressure at 500°C, bulk superconductivity is reached at 4.2 K in an applied magnetic field of 1 Oe [11]. Such a field dependence of the diamagnetic susceptibility attributed to a grainsize effect has already been observed in other oxides such as for example La<sub>1.8</sub>Sr<sub>0.2</sub>CuO<sub>4</sub> [12]. As long as the grain size is small enough, the applied field suppresses the amplitude of the order parameter within the grains, thereby reducing the coupling between the grains.

The  $H_{c_1}$  critical field of an F<sub>2</sub>-treated La<sub>2</sub>CuO<sub>4</sub> sample ( $H_{c_1} = 700 \pm 50$  Oe) has been estimated simply from the broad minimum occurring in the curve showing the field dependence of the magnetization at 6 K (fig. 3). Its value is clearly higher than those previously observed in other compounds having the tetragonal K<sub>2</sub>NiF<sub>4</sub>-type structure: La<sub>1.8</sub>Ba<sub>0.2</sub>CuO<sub>4</sub> ( $H_{c_1} \simeq 200$  Oe) and La<sub>1.8</sub>Sr<sub>0.2</sub>CuO<sub>4</sub> ( $H_{c_1} \simeq 300$  Oe) [12,13].

Low-temperature ESR spectra recorded for both untreated and fluorine-treated  $La_2CuO_4$  are grouped



Fig. 3. Field dependence at T=6 K of the magnetization for an  $F_2$ -treated La<sub>2</sub>CuO<sub>4</sub> sample.

in fig. 4. For the starting oxide, a weak anisotropic line appears, which is centered on  $g \simeq 2.10$ . This signal can be attributed to isolated Cu<sup>2+</sup> species arising either from small amounts of parasitic phases or from Cu<sup>2+</sup> centers not contributing to superconductivity [14]; in some cases this signal may be totally absent [15]. At low fields, an extremely weak zero-field microwave absorption is observed indicating a low amount of superconducting domains. Fluorination at 200°C has practically no effect on the intensity of the signal observed at  $g \simeq 2.10$ , but yields an abrupt and intense zero-field absorption in the ESR spectrum which can be attributed to a subsequent increase of the superconducting volume. This signal is much more field-sensitive than that previously observed in fluorine-treated YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> [16].

In order to estimate the corresponding change in electrical conductivity, similar fluorine treatments were carried out on  $La_2CuO_4$  pellets previously annealed under a flow of oxygen gas at 450°C. The electrical measurements were performed on fluorinated ceramics exhibiting the same lattice distortion as the powdered samples used for the magnetic study. The temperature dependence of the electrical resistance of the  $La_2CuO_4$  starting oxide has the classical shape already observed by many authors (fig. 5). Such an electrical behavior could be due to the simultaneous presence of superconducting and semi-



Fig. 4. ESR spectra at 4.2 K of the starting  $La_2CuO_4$  (a) and of a fluorine treated sample (b). The improvement of the zero field microwave absorption is emphasized in the inset. (Spectrometer gain conditions are noted in the figure.)

conducting phases in the sample as already claimed [9]. Once fluorinated, the sample becomes superconducting ( $T_c$  at the midpoint is between 40 K and 45 K) and shows a metallic behavior above the transition. The onset of the superconducting transition occurs at 48 K and zero resistance is observed at 32 K. Above the transition the conductivity of the fluorinated sample is larger than that found for the starting oxide. This behavior is corroborated by the value of the Seebeck coefficient at room temperature which is positive for both samples ( $\alpha \simeq 300 \ \mu V/K$  for the La<sub>2</sub>CuO<sub>4</sub> starting oxide and  $\alpha \simeq 55 \ \mu V/K$  for the F<sub>2</sub>treated compound).

# 4. Conclusions

After fluorination of  $La_2CuO_4$  at 200°C in a pure fluorine atmosphere, both a weight uptake and a pro-



Fig. 5. Temperature dependence of the electrical resistance of untreated and  $F_2$ -treated La<sub>2</sub>CuO<sub>4</sub> samples.

nounced orthorhombic distortion suggest the incorporation of fluorine inside the lattice. Some remarkable features characterize the F<sub>2</sub>-treated La<sub>2</sub>CuO<sub>4</sub> samples: (i) the superconducting transition temperature ( $T_c$ =40-45 K, determined at the midpoint from the resistivity curve) is slightly higher than those already reported for La<sub>2</sub>CuO<sub>4</sub> under oxygen atmosphere; (ii) important superconducting volume fraction; (iii) metallic behavior and large conductivity above the superconducting transition temperature. Neutron diffraction experiments are now in progress to locate the fluorine atoms in the crystal structure.

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