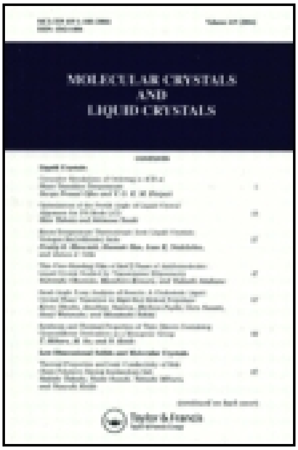

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ANIONIC INTERCALATION IN La_2CuO_4 OXIDE BY FLUORINE OR CHLORINE TREATMENT.

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Abstract - The influence of a halogen-gas (Cl_2 or F_2) treatment on both structural and physical properties of La_2CuO_4 has been studied. In all cases, the resulting product contains an excess of anionic species and shows superconducting properties below 32K and 40K respectively for the chlorine- or fluorine-treated sample. But these treatments have a different influence on the evolution of the structural properties comparatively to those observed for the starting oxide : after chlorination a decrease of the orthorhombic distortion is detected, whereas an opposite trend is shown after fluorination. The Cl_2-gas treatment leads to an oxygen-excess phase $La_2CuO_{4.08}$, whereas the fluorination yields an oxyfluoride $La_2Cu(O,F)_{4.17}$.

INTRODUCTION

It was well established that the incorporation of oxygen atoms in the semiconducting antiferromagnetic La_2CuO_4 leads to a superconducting compound having a critical temperature around 33K[1,2]. This interesting result has stimulated the investigation of intercalation of other anionic species into the La_2CuO_4 lattice. In this scope, the starting oxide has been treated under F_2- or Cl_2-gas at low temperature. In this paper are discussed the structural and physical properties of the resulting products determined by microprobe analysis, X-ray and neutron powder diffraction, ESR and EXAFS investigations, magnetic and electrical measurements.

La_2CuO_4 as starting compound was prepared by a heating cycle at high temperature under a flow of oxygen gas, as previously described[3], from stoichiometric mixtures of La_2O_3 and CuO powders. The halogenation experiments were carried out in metallic containers with the help of a "gas-line" described elsewhere[3]. The investigation of the fluorination process was studied under 1.3 bar of either pure or diluted F_2-gas for temperature T_{F_2} between room temperature and 300°C. The chlorination experiments were performed from 20°C up to 400°C under a chlorine pressure ranging from 1 to 20 bar.

RESULTS AND DISCUSSION

Halogenation process

The chlorination conditions of La_2CuO_4 powder are critical[4] : for lower chlorination temperatures (T_{Cl_2} < 200°C) no noticeable reaction occurs, whereas for higher T_{Cl_2} (350°C ≤ T_{Cl_2}) the starting oxide is mainly decomposed into LaOCl and $CuCl_2$. On the other hand, the microprobe and X-ray diffraction analyses of the Cl_2-treated samples for 200°C ≤ T_{Cl_2} ≤ 300°C reveals the presence of a decomposition phase coexisting with the main component that crystallizes as the starting oxide in the K_2NiF_4-type structure. This parasitic phase which contains chlorine species is easily removed after a washing of the product in bi-distilled water. The reaction mecanism can be explained by a partial decomposition of La_2CuO_4 into (oxy)chlorides, in particular at the surface of the grains, and the removed oxygen further reacts with the bulk (non-chlorinated) part of the grains. A modification of the unit-cell parameters of La_2CuO_4 is observed after Cl_2-treatment (Fig.1). It can be pointed out that there is a trend toward tetragonal symmetry with increasing T_{Cl_2}; this result corroborates the formation of a phase similar to that obtained during high O_2-pressure treatments[5].
Moreover, when this Cl_2-treated sample is annealed in Ar at temperatures T≥200°C, the resulting compounds correspond to stoichiometric La_2CuO_4. Similar behaviour has been detected for La_2CuO_{4+y} oxide[5].
Several reaction stages occur in the F_2-gas treatment of La_2CuO_4 depending on the fluorination temperature T_{F_2} [3].:
- for 150°C ≤ T_{F_2} ≤ 200°C, the resulting product $La_2Cu(O,F)_{4+y}$ crystallizes in an orthorhombic distortion of the K_2NiF_4-type structure (Fig.1), but an enhancement of both the orthorhombic distortion (b-a) and of the c parameter is observed ;

- for 200°C < T_{F_2} ≤ 230°C, the resulting product is a mixture of two major compounds : $La_2Cu(O,F)_{4+y}$ and a new phase "X" which can be indexed in a tetragonal unit cell with a = 5.7Å and c = 13.07 Å ;
- for T_{F_2} ≥ 250°C, the starting oxide is completely decomposed into a mixture of LaF_3 and CuF_2.

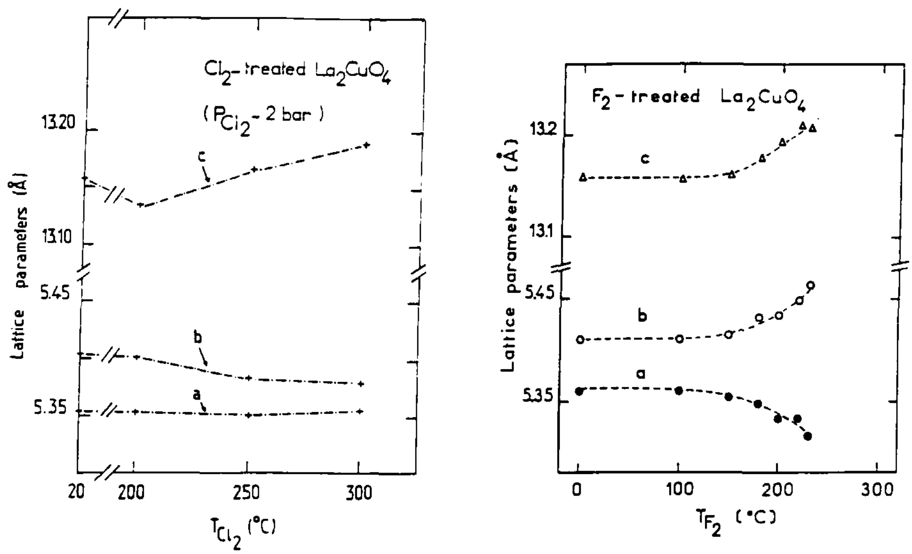

FIGURE 1 - Variation with the halogenation temperature of the unit cell parameters of Cl_2 and F_2-treated La_2CuO_4.

The fluorine analysis in $La_2Cu(O,F)_{4+y}$ deduced from Auger electron spectroscopy shows that noticeable amounts of this element can be observed at a depth of 1000 Å to 4000 Å from the surface of the grain (Fig.2). Also, after annealing at 250-300°C under vacuum or argon atmosphere, the $La_2Cu(O,F)_{4+y}$ oxyfluoride looses small amounts of oxygen and exhibits an irreversible orthorhombic → orthorhombic structural transition. After annealing at higher temperatures (500-600°C), the oxyfluoride is further decomposed into stoichiometric La_2CuO_4, LaOF and CuO. The appearance of LaOF at high temperature corroborates the presence of fluorine atoms into the structural lattice of the phases resulting from the F_2-gas treatment of La_2CuO_4.

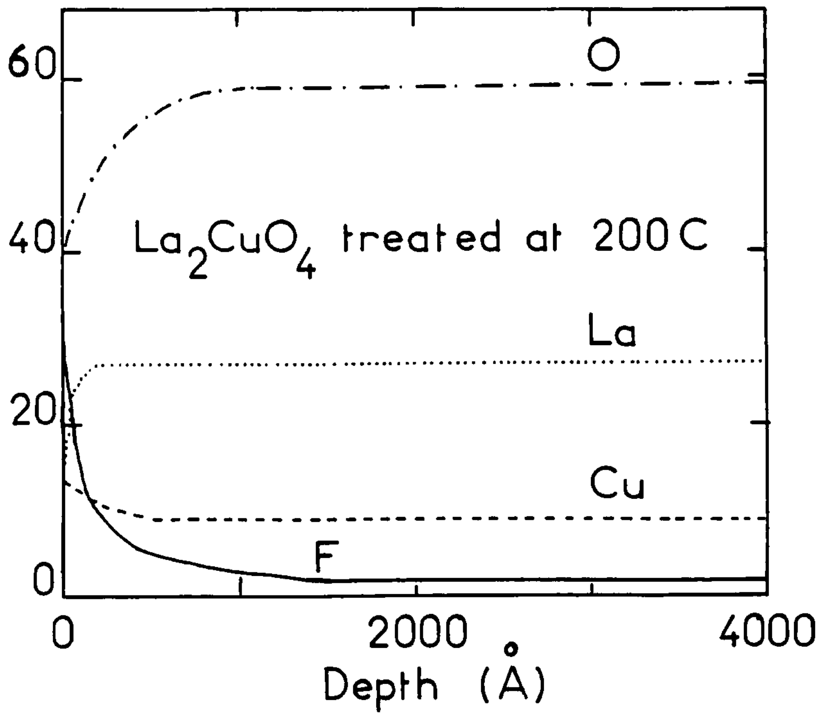

FIGURE 2 - Concentration profiles of La, Cu, O and F in F_2-treated La_2CuO_4 at $T_{F2} = 200°C$.

Structural properties

The properties of the Cl_2 and F_2-treated compounds described in Table I have been established from both Rietveld refinement of neutron powder diffraction data and analysis of the X-ray absorption spectra obtained in the La L_{III}-EXAFS region. In both cases, the extra anionic atoms occupy an interstitial site which is located between two successive (LaO) layers and which is surrounded by four La and four O atoms[6,7]. The occupancy factor of this site leads to the formulae $La_2CuO_{4.08}$ (Cl_2-treated) and $La_2Cu(O,F)_{4.18}$ (F_2-treated), in good agreement with the chemical analysis.

The comparison of the Fourier transforms of the La L_{III}-EXAFS signals (Fig.3) reveals that the local order around lanthanum is much less lowered by a Cl_2-treatment than by a F_2-treatment. For the latter compound, an increase of the amplitude of the shoulder located below 2 Å is observed. Similar behaviour has been detected at the Nd L_{III}-edge in the superoxygenated Nd_2NiO_{4+y}, for which there is an increase of the number of oxygen atoms surrounding neodymium.

Compound	Halogenation conditions	Lattice parameters				$\frac{(b-a)}{(b+a)} 10^{-4}$	T_C (K)	Ref
		a (Å)	b (Å)	c (Å)	V (Å)^3			
La_2CuO_4	-	5.352	5.400	13.157	380.2	45	-	[6]
$La_2CuO_{4.08}$ (Cl_2-treated)	P_{Cl_2} = 6 bar T_{Cl_2} = 300°C	5.355	5.378	13.185	379.7	21	32	[7]
$La_2Cu(O,F)_{4.17}$ (F_2-treated)	P_{F_2} = 1.3 bar T_{F_2} = 200°C	5.328	5.427	13.194	381.5	92	40	[6]

Table I -Crystallographic and superconducting data.

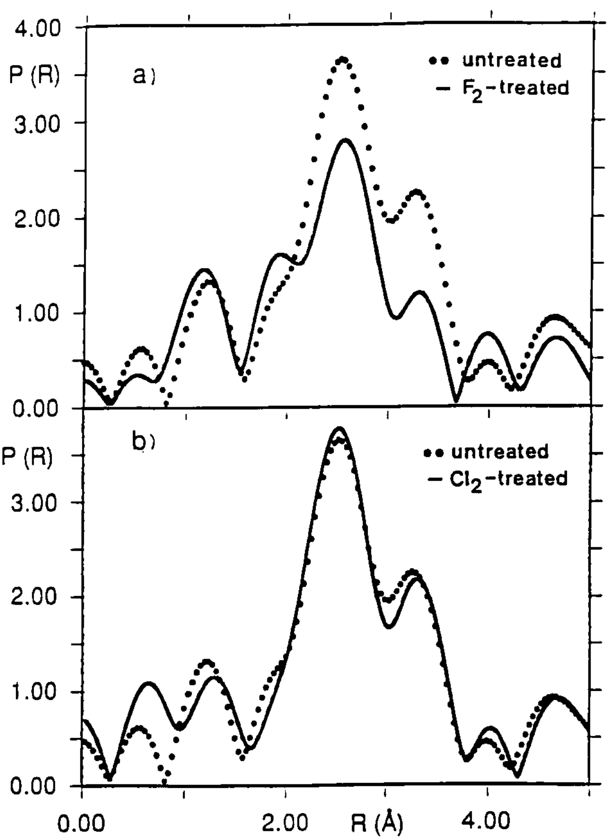

FIGURE 3 - Fourier transforms of the EXAFS spectra recorded at the La L_{III}-edge for F_2-treated (a) and Cl_2-treated (b) La_2CuO_4.

Superconducting properties

A noticeable increase of the Cu^{3+}/Cu^{2+} ratio is observed from iodometric titration experiments (Cu^{3+}/Cu^{2+} = 0.08(1)) for the Cl_2-treated compound at T_{Cl_2} = 300°C and P_{Cl_2} = 6 bar (Table I). This product shows a superconducting transition below T_c = 32K with a diamagnetic signal $\chi_g = -1.10^{-3}$ emu g^{-1} at 5K under 100Oe applied field (Fig.4). It is worthwhile noting that the superoxygenated oxide $La_2CuO_{4.08}$ prepared by electrochemical oxidation exhibits similar superconducting temperature[8].

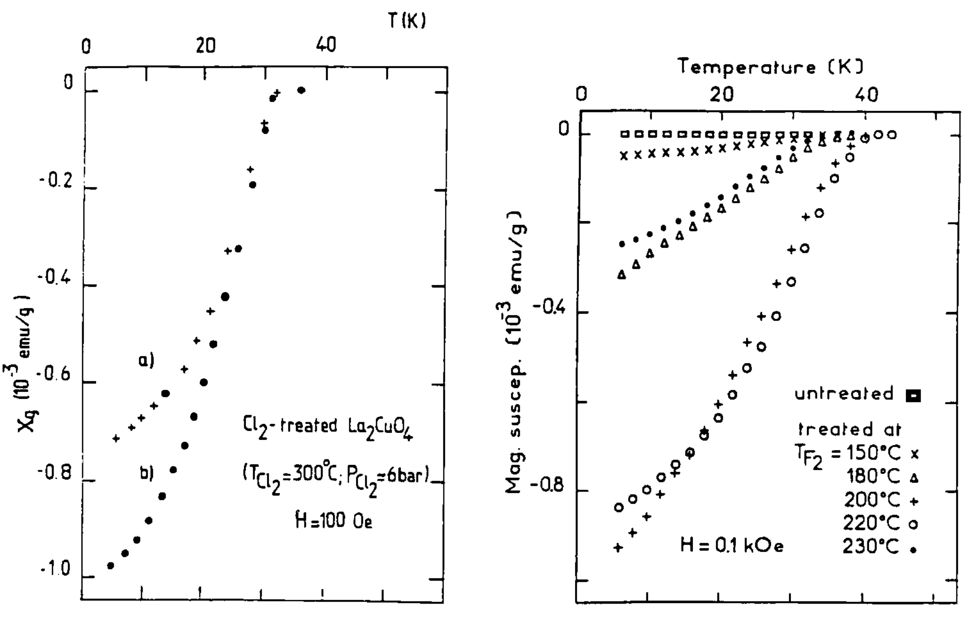

FIGURE 4 - Temperature dependence of the magnetic susceptibility of La_2CuO_4 treated in Cl_2-gas (before (a) and after (b) washing) or in F_2-gas at various T_{F_2} temperatures.

This result is in agreement with the formula $La_2CuO_{4.08}$ determined from our neutron diffraction investigation performed on the Cl_2-treated sample. On the other hand, for materials F_2-treated at 150°C ≤ T_{F_2} ≤ 230°C, the magnetic susceptibility becomes negative below 40K, confirming the superconducting behaviour of these

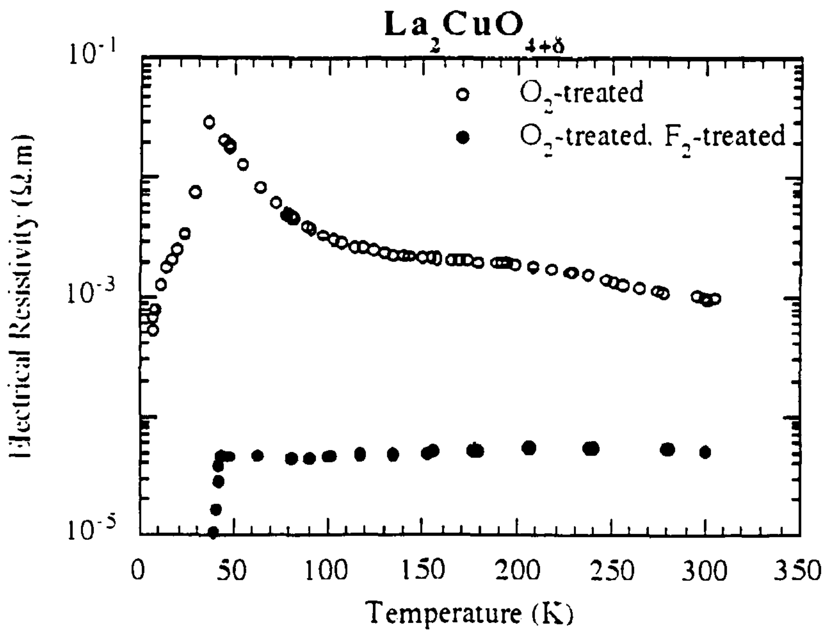

FIGURE 5 - Temperature dependence of the electrical resistivity of La_2CuO_4 before and after the F_2-treatment.

oxyfluorides (Fig.4). The 6K-susceptibility increases with increasing T_{F2} for 150°C ≤ T_{F2} ≤ 200°C, then decreases in the 200°C < T_{F2} ≤ 230°C range. This result is due to the partial decomposition of $La_2Cu(O,F)_{4+y}$ oxyfluoride into a new non superconducting oxyfluoride ('"X" phase) containing a large amount of Cu^{3+}.
The electrical resistivity of the La_2CuO_4 sample shows a decrease around 41K (Fig.5). However, neither zero electrical resistivity nor Meissner effect is observed down to liquid helium temperature. On the contrary, the F_2-treated sample exhibits a superconducting transition with a zero electrical resistance below 38K[9].

CONCLUSIONS

The chlorine or fluorine gas treatment of La_2CuO_4 oxide leads to an insertion of anionic species into the lattice, between two successive (LaO) layers. The occurrence of superconducting behaviour of the resulting products is ascribed to the increase of the formal oxidation state of copper due to this anionic intercalation.

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