

Occurrence of superconductivity in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($0 \leq x \leq 0.04$) and $\text{La}_{2-x}\text{Nd}_x\text{CuO}_4$ ($0 \leq x \leq 0.3$) systems after fluorination

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Abstract

The influence of a low temperature fluorine gas treatment on structural, superconducting and transport properties of oxides with the K_2NiF_4 structure has been studied. When materials with the composition $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ where $0 \leq x \leq 0.04$ are treated under 1 bar of F_2 gas at 200°C , an increase in the orthorhombic distortion ($b - a$) is observed and the materials become superconductors. The insertion of anionic species in the lattice is confirmed by the observation of an increase in weight and in the c -parameter and by the elemental analysis. After annealing at 200 – 250°C under vacuum or argon atmosphere, $\text{La}_{2-x}\text{Ba}_x\text{Cu}(\text{O},\text{F})_{4+\delta}$ oxyfluorides lose their superconducting properties. This change is accompanied by a structural orthorhombic-to-orthorhombic transition for values of x up to 0.02 and by an orthorhombic-tetragonal-orthorhombic sequence where $x = 0.04$. Similar behaviour is also observed in the T/O solid solution in the $\text{La}_{2-x}\text{Nd}_x\text{CuO}_4$ system ($0 \leq x \leq 0.3$).

1. Introduction

At room temperature, La_2CuO_4 crystallizes with an orthorhombic distortion (T/O) of the K_2NiF_4 structure. The structural and physical properties of this material have been shown to depend strongly on the method of preparation, which suggests the presence of various types of anionic defects in the structure. When La_2CuO_4 is stoichiometric, it is semiconducting. The insertion of anionic species in the lattice, which can be achieved using oxidizing treatments, gives rise to superconducting properties [1]. Bulk superconductivity has been achieved using a low temperature fluorination process [2].

The substitution of alkaline earth elements for La also produces a superconducting phase in the $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ systems ($\text{M} = \text{Sr}, \text{Ba}$) [3, 4]. However, a minimum value of hole doping is necessary to ensure the occurrence of superconductivity. Consequently it has not been possible up to now to obtain superconducting materials in the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ system where $x \leq 0.06$ [5].

In this paper, we describe the stabilization of superconducting phases in the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ system where $0 \leq x \leq 0.04$ by the insertion of anionic species using

a low temperature F_2 gas process. Similar behaviour is also observed in the T/O solid solution in the $\text{La}_{2-x}\text{Nd}_x\text{CuO}_4$ system ($0 \leq x \leq 0.3$).

2. Experimental procedure

The starting oxides were prepared as powder or ceramics by annealing mixtures of the corresponding binary oxides or carbonates in stoichiometric proportions. The treatment was carried out under oxygen gas flow at temperatures between 1000 and 1150°C . The fluorine gas treatment was performed at temperatures not exceeding 200°C , using the experimental conditions previously described [2]. The weight uptake ($\Delta m/m$) after fluorination was measured with an accuracy of ± 0.1 mg. The materials were characterized before and after treatment using X-ray diffraction techniques, including Guinier–Simon experiments in order to follow the temperature dependence of the cell constants up to 600°C . Elemental analyses were carried out at Service Central d'Analyse-CNRS. Magnetic susceptibilities were measured between 4.2 and 60 K using a SQUID magnetometer, generally under an applied field of 100 Oe. Electrical resistivity measurements were performed using a d.c. four-probe method and thermopower measurements were carried out using a steady state technique described previously [6].

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3. Superconductivity of F_2 -treated $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with $0 \leq x \leq 0.04$

3.1. Structural and magnetic behaviour

Within the range $0 \leq x \leq 0.06$, the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ solid solution is known to have orthorhombic symmetry at room temperature [5]. It can be seen in Table 1, in which some structural parameters are collected for $x = 0, 0.02$ and 0.04 , that the symmetry remained orthorhombic after fluorination. In general a weight increase of less than 1.5% was observed. Elemental analyses showed that the total number of anions was higher than 4 and the $\text{Cu}^{3+}/\text{Cu}_{\text{total}}$ ratios, determined from iodometric titrations, were 0.07, 0.09 and 0.08 for $x = 0, 0.02$ and 0.04 respectively.

The dependence on the Ba content of both the unit-cell parameters and the volume of the compounds before and after F_2 treatment is compared in Fig. 1. For the treated compounds the most salient features are the following: with increasing x , the degree of "orthorhombicity", *i.e.* the $(b-a)$ value, tended to decrease as did that of the starting material, whereas there was a significant increase in the c -parameter.

The occurrence of superconductivity in the F_2 -treated powder samples is clearly established from the magnetic study, as shown in Fig. 2: diamagnetic signals of -0.75×10^{-3} and $-1.35 \times 10^{-3} \text{ emu g}^{-1}$ were observed at 6 K for $x = 0.02$ and $x = 0.04$ respectively. The corresponding critical temperatures, determined from the diamagnetic onset in each case, are 36 and 33 K.

We have previously pointed out that the superconducting properties of $\text{La}_2\text{Cu}(\text{O},\text{F})_{4+\delta}$ disappear in samples heated between 200 and 250 °C. Such behaviour may be associated with an orthorhombic-to-orthorhombic structural transition [7].

The thermal stability of the superconducting $\text{La}_{2-x}\text{Ba}_x\text{Cu}(\text{O},\text{F})_{4+\delta}$ phases was therefore investigated using the Guinier-Simon technique. The changes in the unit-cell parameters with increasing temperature are compared in Fig. 3. Below 200 °C, no noticeable

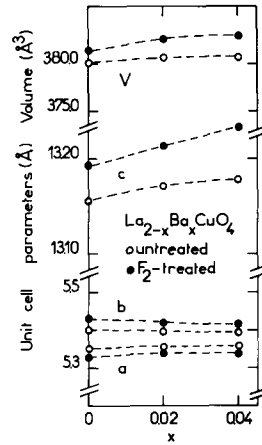


Fig. 1. $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ system ($0 \leq x \leq 0.04$): dependence of the unit cell parameters and volume on the Ba content before (open circles) and after (filled circles) fluorine treatment.

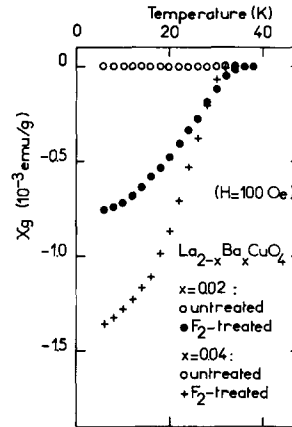


Fig. 2. Thermal dependence of the magnetic susceptibility of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with different values of x .

change occurred in either a or b , whatever the value of x . At higher temperatures ($250 < T < 350$ °C), there was a peculiar variation in the c -parameter: when $x = 0$, a sharp decrease was observed around 250 °C, whereas when $x = 0.02$ and 0.04 the intensity of the

TABLE 1. $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$: structural parameters before (a) and after (b) fluorination in F_2 diluted in N_2 in a 1/10 molar ratio for 20 h at 200 °C

x	$\Delta m/m$ (%)	Unit cell parameters (Å)				V (Å ³)	T_c (±1 K)	
		a	b	$(b-a)$	c			
0	(a)	—	5.352	5.400	0.048	13.157	380.25	—
	(b)	1.15	5.328	5.427	0.099	13.194	381.50	40
0.02	(a)	—	5.355	5.398	0.043	13.172	380.76	—
	(b)	1.2	5.342	5.421	0.079	13.214	382.66	36
0.04	(a)	—	5.356	5.394	0.038	13.178	380.71	—
	(b)	0.7	5.343	5.417	0.074	13.234	383.03	33

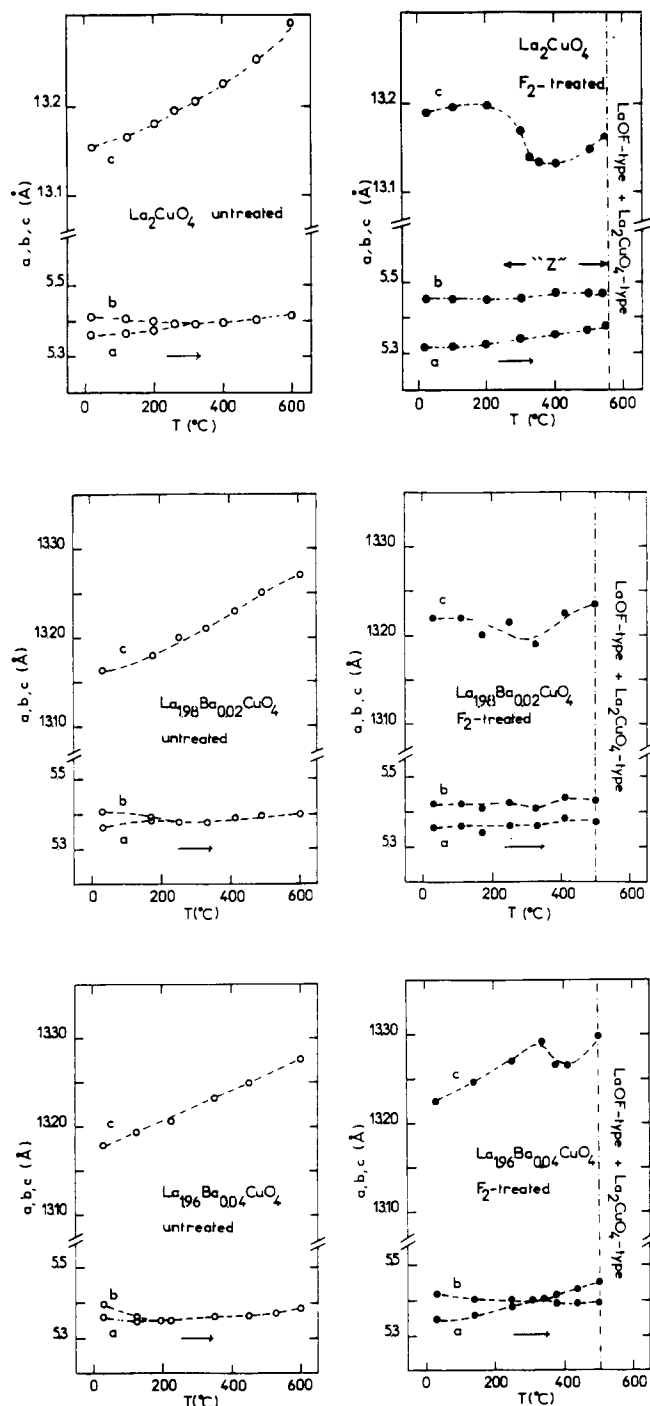


Fig. 3. Temperature dependence of the unit cell parameters in untreated (open circles) and F_2 -treated (filled circles) $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with different values of x .

phenomenon seemed to be reduced with increasing x values. Simultaneously a decrease in the degree of “orthorhombicity” ($b - a$) was observed. This property seemed to be more pronounced as the Ba content increased since it led to a tetragonal phase with $x = 0.04$. At $T = 300^\circ\text{C}$, the unit cell parameters were as follows: $a = 5.40 \text{ \AA}$ and $c = 13.285 \text{ \AA}$. The dis-

appearance of the superconductivity which occurred during this structural transition was associated for $\text{La}_2\text{Cu}(\text{O},\text{F})_{4+\delta}$ with the loss of traces of O_2 gas, observed by mass spectrometry, but without any apparent F_2 loss. The proposed mechanism could involve a structural reorganization between the anionic species which are present in the inserted sites and those directly surrounding the cations. At higher temperatures ($400 \leq T \leq 500^\circ\text{C}$), an orthorhombic non-superconducting oxyfluoride was observed whatever the Ba content, and the distortion ($b - a$) was roughly similar to that of the corresponding fluorinated material prior to annealing. Finally, above 500°C these oxyfluorides were decomposed into two main components: a La_2CuO_4 -type compound and a fluorite-type compound which could be of the LaOF type.

It should be mentioned that in $\text{La}_2\text{Cu}(\text{O},\text{F})_{4+\delta}$, the structural transition responsible for the loss of superconductivity was accompanied by the formation of an additional non-superconducting oxyfluoride (“Z”-type in ref. 7), whose composition and structure have not been clearly determined yet.

3.2. Transport properties

We also used electrical transport measurements to check that the fluorination treatment of the compounds $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ led to superconducting behaviour. For example, in Fig. 4 it can be seen that when $x = 0.04$ the fluorine treatment led to a drastic difference in the temperature dependence of the electrical resistivity. Before treatment, the resistivity first decreased with increasing temperature following a T^{-n} power law, reached a minimum, and then increased with further increase in temperature. After fluorine treatment, there was a superconducting transition at 35 K. Above the critical temperature the compound exhibited metallic behaviour with both low resistivity and low thermoelectric power in comparison with those observed for the starting oxide (Fig. 4(b)).

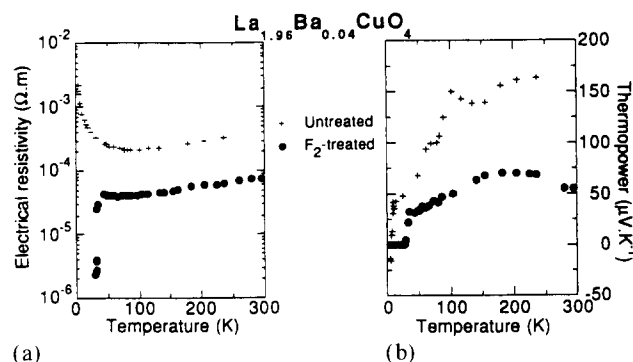


Fig. 4. Temperature dependence of (a) the electrical resistivity and (b) the thermoelectric power in $\text{La}_{1.96}\text{Ba}_{0.04}\text{CuO}_4$ when untreated and when treated with F_2 gas.

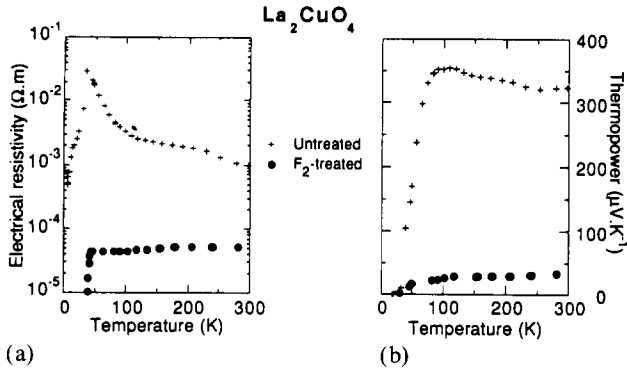


Fig. 5. Temperature dependence of (a) the electrical resistivity and (b) the thermoelectric power in La_2CuO_4 annealed in O_2 at 450°C and then treated with F_2 gas.

The case of the sample without barium ($x=0$) is even more interesting (Fig. 5). Untreated La_2CuO_4 has peculiar transport properties depending on the method of preparation and the fluorination process had a more drastic effect on these properties than on those of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ with $x=0.04$. Fluorine treatment of La_2CuO_4 led to a superconducting transition around 41 K. The effect of fluorination corresponded to a decrease of more than an order of magnitude in the room temperature electrical resistivity (Fig. 5(a)) while the thermoelectric power decreased by a factor of about ten (Fig. 5(b)).

Since the electrical resistivity and the thermoelectric power both depend on the charge carrier density, we may suppose that fluorine gas treatment drastically changes the carrier density in these ceramics. The insertion of anionic species between the CuO_2 layers could cause an increase in charge carrier density through an increase in hole doping.

4. Superconductivity of F_2 -treated $\text{La}_{2-x}\text{Nd}_x\text{CuO}_4$ with $0 \leq x \leq 0.3$

Using the same experimental conditions as described above, single phases with K_2NiF_4 -derived structure were obtained in this system for $0 \leq x \leq 0.3$. With a higher neodymium content, i.e. when $x > 0.4$, a two-phase mixture was observed containing an La_2CuO_4 -type phase and an Nd_2CuO_4 -type phase [8]. With $0 \leq x \leq 0.3$, the compounds exhibited orthorhombic symmetry at room temperature (Table 2). As shown in Fig. 6, with increasing x values the unit cell parameter c decreased and the orthorhombic distortion ($b-a$) increased slightly. This trend could be due to increasing tensile stress in the $(\text{REO})_2$ layers when La^{3+} is replaced by a smaller Nd^{3+} cation [9–11].

After fluorination under 1.3 bar of diluted F_2 gas at 200°C , an increase in the orthorhombic distortion was

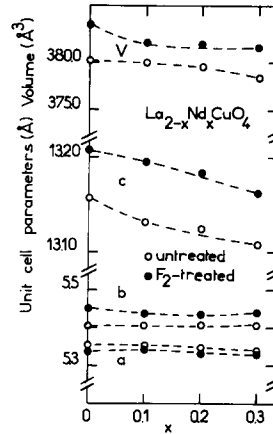


Fig. 6. $\text{La}_{2-x}\text{Nd}_x\text{CuO}_4$ system ($0 \leq x \leq 0.3$): dependence of the unit cell parameters and volume on the Nd content before and after fluorine treatment.

observed for every composition as shown in Fig. 6. The corresponding phases within the complete range of the T/O solid solution exhibited superconducting properties with $T_c \approx 33$ K, 33 K and 29 K for $x = 0.1, 0.2$ and 0.3 respectively. The thermal dependence of the magnetic susceptibility is represented in Fig. 7 for $x = 0.3$.

The paramagnetic signal from the untreated sample which was due to the presence of Nd^{3+} ions, was replaced after fluorination by a diamagnetic signal below $T_c = 29 \pm 1$ K ($\chi_g = -0.54 \times 10^{-3} \text{ emu g}^{-1}$ at 6 K), which is characteristic of the occurrence of a superconducting transition.

When the materials were heated between 200 and 250°C , the superconducting properties disappeared as already observed in the $\text{La}_{2-x}\text{Ba}_x\text{Cu}(\text{O},\text{F})_{4+\delta}$ system. This phenomenon can be attributed to an orthorhombic (superconducting phase)-to-orthorhombic (non-superconducting phase) transition. The thermal dependence

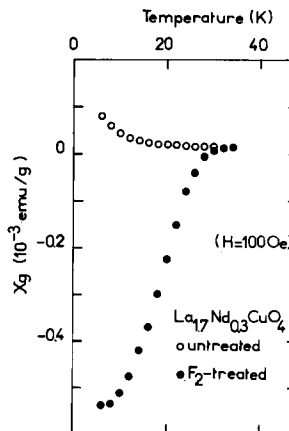
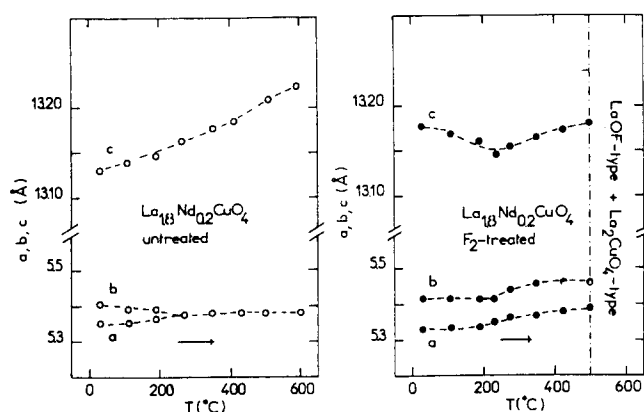


Fig. 7. Thermal dependence of the magnetic susceptibility of untreated and F_2 -treated $\text{La}_{1.7}\text{Nd}_{0.3}\text{CuO}_4$.

TABLE 2. $\text{La}_{2-x}\text{Nd}_x\text{CuO}_4$: structural parameters before (a) and after (b) fluorination in F_2 diluted in N_2 in a 1/1 molar ratio for 20 h at 200 °C

x		$\Delta m/m$ (%)	Unit cell parameters (Å)				V (Å ³)	T_c (±1 K)
			a	b	$(b-a)$	c		
0	(a)	—	5.352	5.400	0.048	13.157	380.25	—
	(b)	2.0	5.334	5.451	0.117	13.207	384.00	42
0.1	(a)	—	5.354	5.405	0.051	13.132	380.02	—
	(b)	0.7	5.332	5.430	0.092	13.195	382.03	33
0.2	(a)	—	5.347	5.407	0.060	13.125	379.46	—
	(b)	1.3	5.331	5.435	0.104	13.183	381.96	33
0.3	(a)	—	5.340	5.407	0.067	13.107	378.44	—
	(b)	1.5	5.331	5.439	0.108	13.162	381.64	29

Fig. 8. Temperature dependence of the unit cell parameters of untreated and F_2 -treated $\text{La}_{1.8}\text{Nd}_{0.2}\text{CuO}_4$.

of the unit-cell parameters was investigated using the Guinier–Simon technique. In Fig. 8, as an example, untreated and F_2 -treated samples with $x = 0.2$ are compared. Before fluorination, the compound underwent the usual $\text{T/O} \rightarrow \text{T}$ transition near 250 °C. The c -parameter was not affected by this transition and this structural change was reversible. In the F_2 -treated sample, the c -parameter decreased strongly around 200 °C whereas the orthorhombic distortion ($b - a$) diminished only slightly. The orthorhombic non-superconducting phase was found to be stable up to 500 °C. As in the other series, above 500 °C we observed the presence of two final phases: one of the La_2CuO_4 type and one of the LaOF type.

5. Conclusions

Fluorination of the systems $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and $\text{La}_{2-x}\text{Nd}_x\text{CuO}_4$ makes it possible to extend the com-

position range for superconducting phases of the K_2NiF_4 type, even for compounds crystallizing with orthorhombic symmetry at room temperature. This effect may be attributable to the incorporation of additional anions into the $(\text{La}, \text{BaO})_2$ or $(\text{La}, \text{NdO})_2$ layers of the lattice, which would relieve the tensile stress in the layer and consequently increase the value of the tolerance factor. The increase in the formal oxidation state of copper caused by the F_2 gas treatment therefore allows the stabilization of new superconductors.

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References

- 1 J. Beille, R. Cabanel, C. Chaillout, B. Chevalier, G. Demazeau, F. Deslandes, J. Etourneau, P. Lejay, C. Michel, J. Provost, B. Raveau, A. Sulpice, J. L. Tholence and R. Tournier, *C.R. Acad. Sci.*, **304** (1987) 1097.
- 2 B. Chevalier, A. Tressaud, B. Lepine, K. Amine, J. M. Dance, L. Lozano, E. Hickey and J. Etourneau, *Physica C*, **167** (1990) 97.
- 3 J. B. Bednorz and K. A. Müller, *Z. Phys. B*, **64** (1986) 189.
- 4 J. B. Torrance, A. Bezing, A. I. Nazzari, T. C. Huang, S. S. P. Parkin, D. T. Keane, S. J. La Placa, P. M. Horn and G. A. Held, *Phys. Rev. B*, **40** (1989) 8872.
- 5 T. Uemura, K. Yoshimura and K. Kosuge, *J. Phys. Soc. Jpn.*, **60** (4) (1991) 1300.
- 6 L. Piroux, P. Coopmans and J. P. Issi, *Measurements*, **5** (1987) 2.
- 7 B. Chevalier, A. Tressaud, C. Robin, B. Lepine, M. H. Tuilier,

- J. L. Soubeyrou and J. Etourneau, in B. Raveau, K. Wasa and R. Suryanaryanan (eds.), *ICMAS-91 Superconductivity: Materials, Physics and Applications*, I.I.T.T. International, Paris, 1991, p. 21.
- 8 J. B. Bringley, S. S. Trail and B. A. Scott, *J. Solid State Chem.*, 86 (1990) 310.
- 9 J. B. Goodenough and A. Manthiram, *J. Solid State Chem.*, 88 (1990) 115.
- 10 B. Chevalier, A. Tressaud, P. Caracino, C. Robin and J. Etourneau, *Physica C*, 175 (1991) 435.
- 11 F. Arrouy, A. Wattiaux, C. Cros, G. Demazeau, J. C. Grenier, M. Pouchard and J. Etourneau, *Physica C*, 175 (1991) 342..