Enhancement of T_c of $C_yCu_{1-y}Ba_2Ca_2Cu_3O_x$ from 67 K to 120 K by reduction treatments

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Abstract

The T_c of the $C_yCu_{1-y}Ba_2Ca_2Cu_3O_{8+\delta}$ ($y \approx 0.5$) phase, synthesized under high pressure, has been raised from 67 K to about 120 K by heat-treatments under reducing conditions. An increase of both a and c lattice parameters occurs concomitantly with that of T_c (before: $a = 3.858$ (1), $c = 14.766$ (9) Å, after: $a \approx 3.862(1)$, $c \approx 14.825$ (3) Å). Subsequent heat-treatments under oxygen atmosphere lead, reversibly, to a decrease of T_c and of the lattice parameters. Consequently, the increase of T_c has been associated with an oxygen loss. Measurements of the resistivity under high pressure indicate that after reduction the overdoped as-prepared samples go towards the optimal doping. A structural model is proposed about the position of the mobile oxygen in the basal plane of the structure.

1. Introduction

In 1994, a new superconducting family in the Ba–Ca–Cu–O system was synthesized [1–3], at high temperature and high pressure generated in a belt-type apparatus. Subsequently, the presence of carbon, forming CO_3 groups, was reported from high-resolution electron microscopy [4] or EELS [5] experiments. The general formula $C_yCu_{1-y}Ba_2Ca_{n-1}Cu_n$-$O_x$ was thus proposed for this family.

The $n = 3$ and $n = 4$ members were obtained as bulk phases and characterized from the structural and physical properties point of view. Superconducting transition temperatures around 67 K and 117 K were reported for the $n = 3$ and $n = 4$ terms, respectively.

It should be pointed out that, for the first time among the high-T_c's families, the $n = 4$ member seemed to exhibit the highest T_c. Powder X-ray diffraction patterns were indexed on a tetragonal cell with parameters $a = b \approx 3.86$ Å and $c \approx 14.75$ and 18.0 Å for $n = 3$ and $n = 4$, respectively. However, a superstructure corresponding to the doubling of both a and c axes was evidenced by electron diffraction and attributed to the ordering of C and Cu atoms in a 1/1 ratio in the basal plane of the structure. By analogy with $YBa_2Cu_3O_{6+x}$, the Cu atoms of this plane, Cu1, may have a dumbbell coordination as in $YBa_2Cu_3O_6$, or a square coordination as in $YBa_2Cu_3O_7$. But one could also envisage that oxygen atoms are present at the center of the (3.86–3.86) mesh as in Hg-based cuprates. Shimakawa et al. [6] published the result of a structural refinement, based

on powder neutron diffraction data, for the $n = 4$ member using the subcell. They found that extra oxygen atoms were present around the Cu1 atoms, as in $YBa_2Cu_3O_7$. A phase with a higher T_c (126 K) was also reported to exist in some samples [7]; but it was not identified, owing to its very small superconducting volume.

Recently, Jaime et al. [8] studied the influence of pressure on the superconducting transition temperatures of $n = 4$ and $n = 3$ samples. For the former, dT_c/dP was small indicating that the $n = 4$ member is close to optimal doping. Attempts to change the Cu/C ratio as well as the oxygen stoichiometry of this member were made [8], but no significant variation of T_c was measured. On the other hand, for the $n = 3$ member a strong decrease of T_c with pressure was observed, indicating that this phase may be in an overdoped state. This result motivated us to study the possibility of changing the oxygen stoichiometry of the $n = 3$ member by appropriate heat-treatments under reducing atmospheres. These experiments together with the related modifications of the structural and physical properties are reported herein.

2. Experimental

Samples were synthesized by using a high pressure-high temperature technique in a belt-type apparatus. First, a precursor with nominal composition $Ba_2Ca_2Cu_4O_x$ was prepared by mixing BaO_2 [Aldrich, > 99%], CaO [Aldrich, 99,9%] and CuO [Aldrich, > 99%] in an alumina mortar. The mixture was heated at 910°C in an oxygen flow for 48 h with two intermediate grindings. The XRD analysis showed that two main phases were present in this as-prepared precursor, noted (I), namely $BaCuO_2$ and Ca_2CuO_3. Traces of CuO were detected, but not those of $BaCO_3$, $CaCO_3$, or $CuCO_3$. This precursor was very similar to those used for the synthesis of the Hg-based superconductors [9]. The second step of the synthesis consisted in mixing two moles of AgO and one mole of the precursor and placing this mixture in a gold capsule. AgO was added as an in-situ oxidizing agent. A graphite furnace was used to reach high temperatures. Our optimized experimental conditions for the $n = 3$ compound were: $P = 8$ GPa, $T = 1100°C$, time 0.5 h.

Ten samples (including those samples labeled A, B, and C) were synthesized using the precursor (I). All of them contained $C_yCu_{1-y}Ba_2Ca_2Cu_3O_x$ as the major phase. This means that it is not necessary to add carbonates to the mixtures. The amount of carbon necessary for the synthesis is incorporated during the manipulations. Barium oxide is known to be a CO_2 getter. Since several grindings were needed for the precursor preparation, the powders were exposed to air and could get the carbon atoms during these stages of the preparation. No barium carbonate was detected by X-ray diffraction. However, Aranda et al. [10] reported that $BaCuO_2$ can incorporate carbonate anions so that the true chemical composition of this phase is $Ba_{44}Cu_{48}(CO_3)_6O_{87.9}$. Different oxycarbonates have also been reported in the Ba–Ca–Cu–O–CO_2 system [11]. The infrared transmission spectroscopy revealed the presence of CO_3^{2-} groups in our precursors. We can then conclude that mixed carbonates or oxycarbonates were formed during the preparation of the precursors.

Sample D was prepared from a more oxidized precursor which was mixed with $BaCO_3$ (Johnson Matthey 99.99%) in order to obtain the approximate composition $C_{0.5}Cu_{0.5}Ba_2Ca_2Cu_3O_x$. The experimental conditions for the high pressure synthesis were the same as for samples A, B, and C.

The different samples were then heat-treated in different atmospheres and at different temperatures.

The as-prepared samples as well as the heat-treated ones were systematically characterized by powder X-ray diffraction using a D5000 Siemens diffractometer in the transmission mode and the $CuK_{\alpha 1}$ radiation. Some of the samples, either as-prepared or heat-treated, were also characterized by electron diffraction using a Philips CM300 operating at 300 kV.

The AC susceptibility or the magnetization of the as-prepared samples and heat-treated ones were measured as a function of temperature. The AC susceptibility was measured in a home-made mutual inductance bridge which was working at 119 Hz, with an applied field of 1 Oe. The sensitivity is 10^{-8} emu. The measurements were made on powders in order to avoid an overestimation of the superconducting volume due to the shielding currents which appear in ceramic samples in low fields. The magnetization was measured in a commercial SQUID magnetome-

ter operating in a 10 Oe field, either after zero-field cooling (ZFC) or in field cooling (FC) conditions. The same information is obtained in low field from both techniques of measurements (ZFC magnetization or AC susceptibility).

It was found that some of the $n = 3$ samples contained the $n = 4$ member as well as a small amount of other impurities. However, the superconducting volume and T_c of the $n = 4$ member were not found to depend on the thermal treatment, so that it was possible to follow the variations of T_c of the major $n = 3$ phase.

Electrical resistance as a function of temperature was measured for different applied pressures (P) up to 10 GPa for one heat-treated sample. The experimental set-up for these experiments has been described elsewhere [7].

3. Results

Except for the presence of the high pressure form of Ag_2O, and sometimes of a small amount of the $n = 4$ term, ten $n = 3$ samples have been prepared as almost pure phases. Their lattice parameters and T_c's were the same within one standard deviation ($a = 3.858(1)$ Å, $c = 14.766(9)$ Å, and $T_c = 66$ K). The

values are in good agreement with those given by Kawashima et al. [4] ($a = 3.859(1)$, $c = 14.766(1)$ and $T_c = 67$ K).

Four of the samples were heat-treated in argon for 10 h at 350°C, 375°C, 400°C, and 450°C, respectively. For the first two, T_c increased to ≈ 75 K, whereas for the last two, a value of ≈ 110 K was obtained. An increase of both a and c parameters occurred concomitantly with that of T_c. The superconducting volume did not change significantly. On the X-ray diffraction patterns, the reflections broadened after the heat-treatments and the presence of a small amount of $BaCO_3$ was detected; this amount increased when the heat-treatment temperature was raised. Electron diffraction patterns taken along the [010] zone axis indicated that the superstructure reflections did not change appreciably after the heat-treatments. When more reducing conditions were used (either a higher temperature, 500°C, or a flow of argon containing 5% of H_2) a partial decomposition of the sample occurred, and the appearance of Cu was detected after the use of an Ar/H_2 flow. The results concerning these samples are reported in Table 1.

In order to see if it is possible to increase T_c above 110 K, we chose to fix the heat-treatment temperature, but to change the treatment duration.
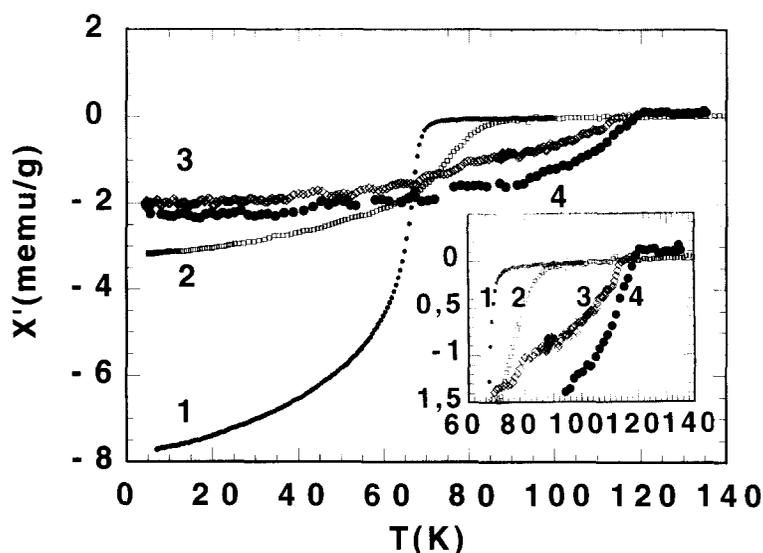
Fig. 1. χ_{AC} susceptibility as a function of temperature for sample A, as-prepared (1) and after the successive heat-treatments under Ar at 400°C (2: 2 h; 3: 4h; 4: 4.5 h).

Table 1
Lattice parameters and T_c for samples 1, 2, 3, and 4, as-prepared and after heat-treatments

Sample	a (Å)	c (Å)	T_c (K)
1	3.857(2)	14.77(1)	66
1 (after 350°C/Ar/10 h)	3.860(1)	14.81(1)	75
2	3.855(2)	14.76(2)	65
2 (after 375°C/Ar/10 h)	3.859(2)	14.80(1)	76
3	3.860(2)	14.769(9)	67
3 (after 400°C/Ar/10 h)	3.863(2)	14.82(2)	111
4	3.861(1)	14.768(8)	65
4 (after 450°C/Ar/10 h)	3.868(2)	14.82(1)	108

Two temperatures were chosen: 400°C for a sample (A), and 450°C for a (B) one. For sample A, T_c was determined from AC susceptibility measurements, whereas for sample B the magnetization was measured. In both cases, an increase of T_c was observed as the heat-treatment durations were increased. For

sample A, the AC susceptibility versus temperature after successive heat treatments (as-prepared, 2h, 4h, 4.5h) is reported in Fig. 1. After ≈ 5 h T_c seems to saturate at ≈ 120 K or higher. Fig. 2 gives the variation of T_c as a function of the lattice parameters. Fig. 3 shows the magnetization measurements after 10, 20, 30, 40, 50, and 60 h of heat-treatment of sample B. It can be seen that after 10 T_c has increased close to 110 K. For longer treatments, a small increase of T_c is observed, and a maximum of 117 K is reached after about 40 h. After that T_c doesn't change significantly. The variation of the lattice parameters was similar to that for sample A.

Starting from the point where it was the highest, the T_c of sample B was then measured as a function of applied pressure up to 10 GPa. Fig. 4a shows the superconducting transition temperature under a pressure of 2.3 GPa and the criterion used to determine T_c as a function of P. T_c as a function of P is given in Fig. 4b together with the curve from Ref. [8] obtained for an as-prepared $n = 3$ sample. It can be seen that T_c is pressure independent for the heat-treated sample whereas it was negative for the as-prepared one. As generally accepted [3], this would mean that the overdoped sample has become, by losing oxygen, close to optimal doping.

In order to check whether the increases of T_c and of the lattice parameters were really related to a loss of oxygen, a sample (C) that had been submitted to a heat-treatment in argon at 400°C for 10 h, was

Fig. 2. Variation of T_c versus the cell parameters for sample A, as-prepared and after the successive heat-treatments under Ar at 400°C (as in Fig. 1).
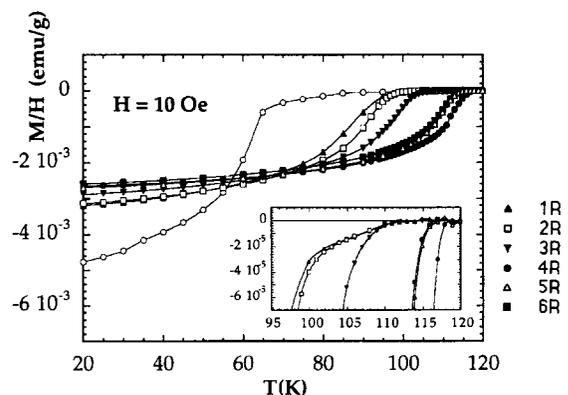
Fig. 3. Magnetization as a function of temperature for sample B: as-prepared (o), and after the successive heat-treatments under argon at 450°C. (1R: 10 h, 2R: 20 h, 3R: 30 h, 4R: 40 h, 5R: 50 h, 6R: 60 h.)
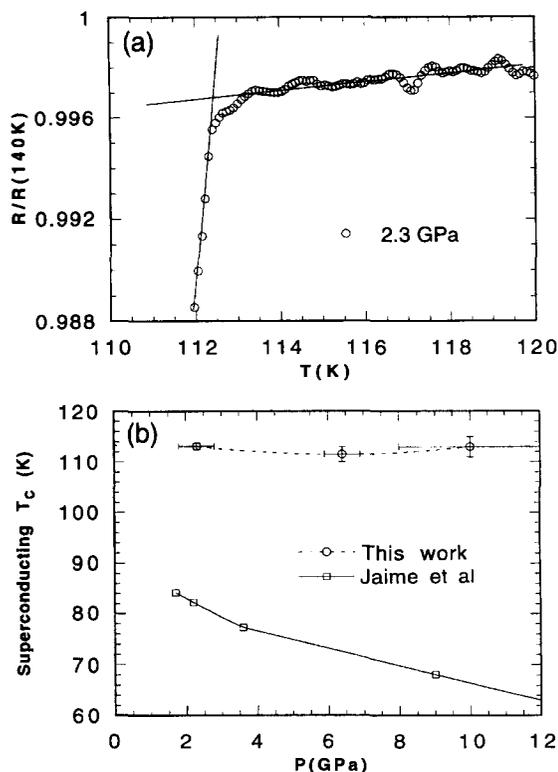
Fig. 4. a) Electrical resistance as a function of temperature for sample B (after the longest heat-treatment) at a pressure of 2.3 GPa. The criterion used to determine the superconducting transition temperature is shown. b) Dependence of T_c with the applied pressure. The results for the as prepared sample of reference [8] are also shown for comparison.

Fig. 5. T_c and c parameter for sample C: 1 as-prepared; 2 after the heat-treatment at 400°C in Ar for 10 h; 3 after the subsequent heating at 400°C in O_2 for 10 h.

The same heat-treatment as that used for sample A (400°C, argon) was applied to sample (D) prepared with an excess of carbonate. The as-prepared sample presented somewhat different lattice parameters and T_c from the other samples, namely a higher T_c (76 K) and a smaller c axis (14.713(7) Å). After about 1 h of heat-treatment T_c increases up to ≈ 105 K and then decreases for longer heat-treatments. The lattice parameters, a and c, increase as a function of the heat-treatment duration (Table 2).

4. Discussion

A common feature of the high-T_c copper oxide superconductors is that they contain CuO_2 layers. When these layers are flat as in Hg-based cuprates [12] or in the present cuprates [6,13], the value of the a parameter is almost exclusively determined by the in-plane Cu–O distance which in turn is related to the Cu valence and therefore to the oxygen stoi-

heated in oxygen at 400°C for 10 h. T_c which had increased from 67 K to 110 K after the first treatment, decreased to 80 K after the second one. The lattice parameters varied in the same fashion. This is illustrated in Fig. 5. This experiment shows the reversibility of the process and confirms that the observed changes are related to changes in oxygen stoichiometry.

Attempts were also made to incorporate more oxygen in an as-prepared overdoped sample by heat-treatment under high oxygen pressure (P_{O_2} = 1250 bar, $T \approx 330$°C for about 20 h). About 2/3 of the phase decomposed and T_c of the remaining fraction remained constant. Therefore, it seems that the maximum oxygen stoichiometry is obtained in the conditions of the high pressure synthesis.

Table 2
Lattice parameters and T_c of sample D after successive heat-treatments

Treatment time (h)	a (Å)	c (Å)	T_c (K)
0	3.857(1)	14.713(7)	76
0.5	3.858(1)	14.730(9)	88
1	3.859(1)	14.752(7)	105
1.5	3.863(3)	14.755(21)	105
2	3.860(2)	14.761(1)	100
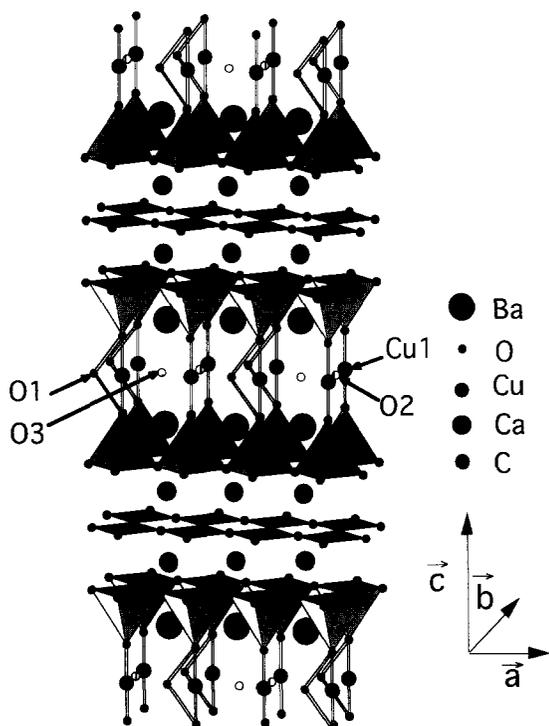
Fig. 6. Structural model for $C_{0.5}Cu_{0.5}Ba_2Ca_2Cu_3O_{8.5+x}$. The two possible positions, O2 and O3, for the mobile oxygen atoms in the basal plane are indicated.

chiometry. An increase of the a parameter, such as the one shown in Fig. 2, due to a heat-treatment under Ar, should be related to a decrease of the Cu valence. By analogy with the variation of the c parameter with oxygen stoichiometry found in $YBa_2Cu_3O_{6+x}$ [14], the decrease of c, shown in Fig. 2, can be associated to a gain of oxygen atoms located in the basal plane of the structure and linked to Cu1.

The variation of T_c with the oxygen stoichiometry of the member with $n = 3$ can be understood if one calculates the average valence of the Cu atoms in the CuO_2 planes. The formula of the $n = 3$ phase can be written as $C_yCu_{1-y}Ba_2Ca_2Cu_3O_{8+\delta}$ where δ represents the total amount of oxygen in the basal plane of the structure. Two kinds of oxygen atoms are located in this plane: one, O1, which belongs to the CO_3 group and one, either O2 or O3 in the positions as indicated in Fig. 6. The number of O1 atoms is equal to that of the C cations (y), but the number of O2 or O3, x, can vary. In any case

$\delta = x + y$. The valence of the CO_3 group is taken equal to -2. The average valence of Cu in the CuO_2 planes is then given by:

$$v(Cu) = (8 + 2x - 2y - (1 - y)v(Cu1))/3, \quad (1)$$

where $v(Cu1)$ is the average valence of the Cu atoms in the basal plane of the structure. The valence of Cu depends on both the carbon content and the oxygen stoichiometry.

We have seen that, after the maximum reduction, sample B was close to the optimal doping which should correspond to an average copper valence $v(Cu) \approx +2.15$. As can be surmised from the well defined superstructure reflections in electron diffraction patterns, the carbon content y of this sample is close to 0.5. In this case, from equation (1), x is related to $v(Cu1)$ by:

$$x \approx 1/4(v(Cu1) - 1). \quad (2)$$

As $v(Cu1)$ can vary between 1 and 2, the value of x after the last reduction treatment must be comprised between 0 and 0.25. Let us examine the two extreme values.

The case $x = 0$ and $v(Cu1) = +1$ corresponds to the absence of oxygen in O2 or O3 positions at optimal doping. It is then immediately clear that in contrast to the case of $YBa_2Cu_3O_{6+x}$ no additional oxygen is needed to introduce holes in the copper oxygen planes. Additional oxygen will thereby overdope the copper oxide planes and will induce a decrease of T_c. From a crystal chemistry point of view, this additional oxygen atom will more likely occupy the O3 rather than the O2 position, and therefore will not be bonded to Cu1. This may explain why T_c decreases rather quickly when oxygen is introduced since the additional charges would be transferred to the CuO_2 planes and would not oxidize the Cu1 atoms. The dumbbell coordination is specific for Cu^{+1} cations.

In the other extreme case, $x = 0.25$ and $v(Cu1) = +2$, since Cu1 is already in the highest valence state, the introduction of oxygen will necessarily give charges to the CuO_2 planes. However, from Eq. (1), we would have

$$v(Cu) = 2 + 2/3 \, x. \quad (3)$$

It would then be possible to reach the underdoped region ($v(Cu) \leq 2.15$) for $0 \leq x \leq 0.23$, which is not

observed experimentally. Furthermore, from a crystallochemical point of view, this model is not very satisfactory since half of the copper atoms in a $+2$ valence state would have a dumbbell coordination. There is not enough oxygen to form squares around all Cu1 atoms. From this analysis, the most probable structural model seems to be the one where oxygen exists in the O3 position in the as-prepared sample. This oxygen is lost during the reduction treatment and the highest T_c is reached when the O3 position is empty. To check the validity of this model, it is necessary to determine the positions of the oxygen atoms in the basal plane of the structure and the oxygen stoichiometry before and after the reduction treatment.

Eq. (1) shows that the optimum doping can be reached for different values of the (x, y) pair of parameters. At the maximum reduction $(x = 0$ and $v(Cu1) = +1)$,

$$v(Cu) = (7 - y)/3 \qquad (4)$$

If $y \geq 0.55$, then $v(Cu) \leq 2.15$ and the sample is underdoped. This assumption is corroborated by the behavior of sample D. The additional replacement of Cu1 atoms by carbon induces a decrease of the c parameter because the C–O bond lengths are much smaller than the Cu–O ones. The same behavior has been reported for Hg-based cuprates when Hg is partially replaced by carbon [15]. The highest T_c (optimal doping) for this sample is obtained before the maximum reduction and it is possible to attain the underdoped region. However, if we compare the highest T_c for sample A or B, and D, we observe that the increase of the carbon content induces a decrease of the maximum T_c. This has been already observed in the Hg-based cuprates when Hg is partially substituted with C [15]. One of the possible explanation is that the random replacement of some Cu1 atoms by C may induce some local distortions in the adjacent (BaO) and (CuO$_2$) layers.

We have tried to apply the same heat-treatments to the $n = 4$ phase. But no change in T_c or the lattice parameters has been observed. However, one should remember that in the Hg-based cuprates, when the number of CuO$_2$ layers increases, the range of δ variation decreases. For this phase, it appears from valence calculations that the optimum doping would

occur for an x value close to 0.05, which could already exists in the as-prepared samples.

5. Conclusion

We have been able to raise the T_c of the $C_yCu_{1-y}Ba_2Ca_2Cu_3O_{8+\delta}$ phase from 67 K to 120 K by heat-treatments under reducing conditions. This value is higher than that found for the $n = 4$ member, so that also in this family the highest T_c corresponds to $n = 3$ as for the other superconducting cuprate families. This value of T_c is very close to the one mentioned in the introduction (126 K) observed in some samples. This could indicate that the unidentified phase having a $T_c \approx 126$ K is in fact an optimized $n = 3$ phase. We could not increase δ beyond the value obtained for as-prepared samples. By varying the carbon content, y, it is possible to change the T_c value for a given δ. However, a precise structural determination is needed for understanding the doping mechanism in these phases.

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