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Increase of T_c in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ due to an atomic ordering transition within the orthorhombic phase

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Résumé. — Nous avons récemment montré qu'on peut attendre une transition d'ordre atomique à longue distance dans $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ à une température T'_0 bien en dessous de la transition tétragonal-orthorhombic T_0 . En supposant que le désordre lié à l'existence de T'_0 agit comme paramètre de pair-breaking, nous examinons la variation ΔT_c qui en résulte pour la température de supraconductivité à δ variable. En comparaison avec les T_c mesurés jusqu'à présent et correspondant à un état d'ordre trempé depuis $T > T'_0$, l'accroissement prévu pour T_c , ΔT_c , quand $T < T'_0$, devrait être maximum autour de $\delta \sim 0,4$.

Abstract. — We recently showed that a long-range atomic ordering transition may be expected in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0 \leq \delta \leq 0.5$) at a temperature T'_0 much below the orthorhombic-tetragonal one T_0 . Assuming that the disordering linked to the occurrence of T'_0 acts as a pair breaking parameter, we examine the resulting variation ΔT_c of the superconducting temperature for varying δ . Compared to the so far measured T_c corresponding to a state of order quenched from $T > T'_0$, the increase of T_c , when $T < T'_0$, ΔT_c is expected to be maximum around $\delta \sim 0.4$.

1. Introduction.

A new feature recently arose in the interesting field of high T_c superconductors: an increase of T_c of about 50% [1] was observed in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, possibly linked, according to the authors of reference [1], to a structural transition around 240 K, i.e. at a temperature T'_0 much lower than the ortho-tetra transition T_0 . Motivated by these findings, we showed [2] that, indeed, a second atomic ordering transition T'_0 may be expected below the T_0 one, when $0 \leq \delta \leq 0.5$, in the two-dimensional (2d) oxygen-vacancy system in the basal Cu-O planes located between the Ba ones. Our model was directly translated from the well known order-disorder theories of 3d b.c.c. metallic alloys. Our conjecture of a « super » order within the orthorhombic phase took support in experiments exhibiting at room temperature (i.e. also below T_0) a regular ordering of the oxygen vacancies [3], when $\delta \neq 0$.

In this paper, assuming that T'_0 does exist, we examine the main result of reference [1], i.e. how T_c may be affected by the existence of T'_0 .

The origin of high T_c values in the new superconductors is not yet fully understood despite a considerable amount of theoretical effort [4]. In the present paper we do not answer that question either. We take for granted the high T_c values measured so far, obtained for samples prepared by rapid quenching from high temperatures. We then examine whether T_c is increased, and how much, when the samples are slowly annealed, as was the case in reference [1], in such a way that the long range atomic rearrangement occurring at T'_0 can be achieved (as well known, equilibrium is very long to be reached at ordering transition temperatures).

In usual BCS type superconductors, the Anderson theorem [5] tells us that disorder due to non-magnetic impurities cannot change the value of T_c . More generally, quoting Maki [6]: « if a static external perturbation does not break the time reversal symmetry and does not cause a long range spatial variation of the (superconducting) order parameter... the thermodynamic properties of the superconductor remain unchanged in the presence of the perturbation ». Therefore the theorem does not hold anymore if either one of the above conditions is not fulfilled. This happens not only when a

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time reversal symmetry breaking is involved [6], or for a spatially varying superconducting order parameter [6], but also when the energy gap is anisotropic due to the anisotropy of the crystal itself (see Refs. [15] to [17] of Ref. [6]). It also happens in the case of a vector pairing [7] (as opposed to the usual scalar one), or a triplet pairing [7] (as opposed to the usual isotropic singlet one), or any unconventional pairing [8] (p wave or d wave type); for instance a recent paper [9] examined the effect of magnetic as well as non magnetic impurities on anisotropic singlet superconductors, as possibly being the case in the YBaCuO family. In all of these cases, the T_c of the unperturbed system, called $(T_c)_{\text{pure}}$, is related to the one in presence of the perturbation $(T_c)_{\text{perturb.}}$ through the relation :

$$\ln \left[\frac{(T_c)_{\text{pure}}}{(T_c)_{\text{perturb.}}} \right] = \psi \left(\frac{1}{2} + \alpha_{\text{perturb.}} \right) - \psi \left(\frac{1}{2} \right) \quad (1)$$

$\psi(z)$ is the digamma function [10] and $\alpha_{\text{perturb.}}$ is the pair breaking parameter related to the transport rate $\tau_{\text{perturb.}}^{-1}$ by :

$$\alpha_{\text{perturb.}} = [4 \pi (T_c)_{\text{perturb.}} (\tau)_{\text{perturb.}}]^{-1}. \quad (2)$$

We intend here to adapt the above concepts to the YBa₂Cu₃O_{7- δ} case on either side of the atomic ordering transition T'_0 .

2. Pair-breaking parameter due to atomic disordering.

We suppose that, for reasons linked to the nature of the unconventional superconductivity on this system (as was done in Ref. [9]), the Anderson theorem does not apply. More precisely, we suppose that the disappearance of atomic long-range order at T'_0 acts as a pair breaker. Then (1) should be read as follows : what plays the role of the « pure » system is the perfectly ordered phase for which the atomic long range order S is maximum, $S = S_{\text{max}}$; the « perturbed » system is the one where only a partial order $S < S_{\text{max}}$ exists. Then formula (1) is expected to read :

$$\ln \left[\frac{T_c(S_{\text{max}})}{T_c(S)} \right] = \psi \left(\frac{1}{2} + \alpha(S) \right) - \psi \left(\frac{1}{2} \right) \quad (3)$$

with :

$$\alpha(S) = [4 \pi T_c(S) \tau(S)]^{-1}. \quad (4)$$

In formula (4), $\tau^{-1}(S)$ is the variation of the transport rate due to the degree of long range atomic order S , normalized in such a way that $\tau^{-1}(S_{\text{max}}) = 0$.

According to the simple model of atomic ordering given in reference [2] for $0 \leq \delta \leq 0.5$, the 2d

oxygen-vacancy binary system is expected to be described by two atomic ordering parameters, S_{11} and S_{31} , as was done [11] in the order-disorder transformations of 3d b.c.c. Fe_{1-x}Al_x metallic alloys. S_{11} and S_{31} are both functions of the temperature T and the concentrations c and $(1-c)$ of respectively the oxygens and the vacancies (or the empty sites); c is linked to δ by $2c = 1 - \delta$. $S_{11}(T, c)$ and $S_{31}(T, c)$ have been computed in 2d in reference [2] following the simple model of reference [11] for 3d, using a mean-field approximation and interactions between first and second neighbours. S_{11} vanishes at T_0 and S_{31} vanishes at T'_0 . We have drawn, in figure 1, S_{11} and S_{31} as functions of T for $c = 0.3$ and the ratio between the second to the first neighbour interactions $\lambda = 0.315$; then with reference [2] using reference [12], one gets $T_0 = 1000.1$ K and $T'_0 = 526.6$ K, in that case.

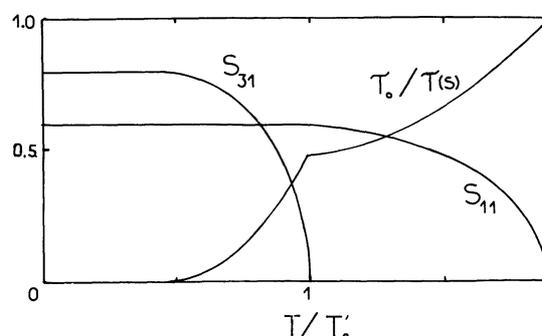


Fig. 1. — The order parameters S_{31} and S_{11} (computed in Ref. [2]) plotted versus T/T'_0 for $c = 0.3$ and the ratio between second to first neighbour interactions $\lambda = 0.315$; also plotted is the corresponding function $\tau_0/\tau(S)$ given in the text as formula (8). ($S_{11} = 0$ at $T = T_0$ with $T_0/T'_0 = 1.9$ and $T'_0 = 525.6$ K).

Then the transport rate $\tau^{-1}(S)$ involved in formula (4) is easily computed as a function of S_{11} and S_{31} . According to reference [13], the residual resistivity in 3d b.c.c. alloys such as Fe_{1-x}Al_x is :

$$\rho_0 \propto \left[c(1-c) - \frac{S_{11}^2}{4} - \frac{S_{31}^2}{8} \right]. \quad (5)$$

It is easy to check that the same formula applies in our 2d case. Then the variation $\tau^{-1}(S)$ due to atomic ordering is given as usual [14] by :

$$\frac{1}{\tau(S)} = \frac{1}{\tau_0} \frac{\rho_0(S) - \rho_0(\text{order})}{\rho_0(\text{disorder}) - \rho_0(\text{order})} \quad (6)$$

$\rho_0(\text{order})$ is given by (5) with $(S_{11})_{\text{max}} = 2c$ and $(S_{31})_{\text{max}} = 2.4c$ (for $0.25 \leq c \leq 0.5$), and $\rho_0(\text{disorder})$ is also given by (5) where $S_{11} = S_{31} = 0$. We also need :

$$\tau_0^{-1} = 2 \pi N (E_F) c(1-c)(V_0 - V_v)^2 \quad (7)$$

$V_O - V_v$ is the difference between the scattering potentials of the oxygen and the vacancy, and $N(E_F)$ is the density of states at the Fermi level. The c dependence in (7) is just the Nordheim law [14]. One thus gets :

$$\frac{1}{\tau(S)} = \frac{1}{\tau_0} \left[1 - \frac{1}{4} \frac{2S_{11}^2 + S_{31}^2}{2c^2 + (1-2c)^2} \right] = \frac{1}{\tau_0} \left[1 - \frac{2S_{11}^2 + S_{31}^2}{2(S_{11 \max})^2 + (S_{31 \max})^2} \right]. \quad (8)$$

Note that if only one order parameter had been sufficient to describe the system, $S_{31} = 0$ in (5), and then $\tau^{-1}(S) = \tau_0^{-1} [1 - (S_{11}/S_{11 \max})^2]$; then with $S_{11}/S_{11 \max} = S$ one would recover, [14, 15], the usual variation in $(1 - S^2)$ of the electrical resistivity with long range atomic order, as in β brass for instance, which vanishes when $S = 1$. Note also that the short range atomic order is absent from (5). It may be of importance close to T'_0 and could be incorporated *via* an extension of the method of reference [15]. However, since the main variation of τ^{-1} arises from the long-range order and since we only aim to stress the overall effect here, we will neglect the modifications added by the short-range order. We have plotted in figure 1 $\tau_0/\tau(S)$ as a function of T for $c = 0.3$, since this case will prove in the following to be of particular importance in the YBaCuO systems.

Then back to (3) with (4) and (8) we are able to estimate the modification in T_c due to the occurrence of the ordering transition T'_0 .

3. The increase of T_c below the atomic ordering transition T'_0 .

We readily obtain :

$$\ln \left[\frac{T_c(S_{11 \max}, S_{31 \max})}{T_c(S_{11}, S_{31})} \right] = \psi \left[\frac{1}{2} + \frac{1}{4\pi\tau_0 T_c(S_{11}, S_{31})} \times \left(1 - \frac{2S_{11}^2 + S_{31}^2}{2(S_{11 \max})^2 + (S_{31 \max})^2} \right) \right] - \psi \left(\frac{1}{2} \right). \quad (9)$$

The detailed c and T dependences of S_{11} and S_{31} are given in reference [2]; we recall that $S_{11 \max} = 2c$ and $S_{31 \max} = 2 - 4c$ for $0.25 \leq c \leq 0.5$. Formula (9) expresses how the superconducting temperature is lowered when the atomic ordering of the sample is not perfect. Conversely, knowing S_{11} , S_{31} and $T_c(S_{11}, S_{31})$, we can estimate how much can be gained for T_c when the system is more ordered.

If we now wish to compare the T_c 's corresponding to two partially ordered states frozen from two

different temperatures T_1 and T_2 such that $T_1 < T_2$, we get :

$$\ln \left[\frac{T_{c(1)}}{T_{c(2)}} \right] = \psi \left(\frac{1}{2} + \alpha_{(2)} \right) - \psi \left(\frac{1}{2} + \alpha_{(1)} \right) \quad (10)$$

with :

$$\begin{cases} \alpha_{(1)} \equiv \alpha [S_{11}(T_1), S_{31}(T_1)] \\ \alpha_{(2)} \equiv \alpha [S_{11}(T_2), S_{31}(T_2)]. \end{cases} \quad (11)$$

Let us now compare the above two states on either sides of the ordering temperature T'_0 and more precisely in the case :

$$T_1 \ll T'_0 \leq T_2 \ll T_0. \quad (12)$$

The ordering parameters S_{11} and S_{31} increase very sharply (see Fig. 1) just below T_0 and T'_0 respectively, with infinite slopes at these temperatures. Therefore, in the range described by (12), we may write :

$$\begin{cases} S_{11}(T_1) \sim S_{11 \max} = 2c \\ S_{31}(T_1) \sim S_{31 \max} = 2 - 4c \end{cases} \quad T_1 \ll T'_0 \quad (13a)$$

$$\begin{cases} S_{11}(T_2) \sim S_{11 \max} = 2c \\ S_{31}(T_2) = 0 \end{cases} \quad T'_0 \leq T_2 \ll T_0 \quad (13b)$$

and then $\alpha_{(1)} \sim 0$ and we are left with :

$$\left\{ \begin{aligned} & \ln \left[\frac{T_{c(1)}}{T_{c(2)}} \right] \approx \\ & \approx \psi \left[\frac{1}{2} + \frac{1}{4\pi T_{c(2)} \tau_0} \frac{(1-2c)^2}{2c^2 + (1-c)^2} \right] - \psi \left(\frac{1}{2} \right) \end{aligned} \right. \quad T_1 \ll T'_0 \leq T_2 \ll T_0. \quad (14)$$

Then we write :

$$\tau_0^{-1} = A c (1-c) (4c-1)^{1/3} \quad (15)$$

A is a constant independent of c and determined below. On the other hand, the number of carriers is :

$$n = 1 - 2\delta = 4c - 1 \quad (16)$$

n enters in (15) insuring that there is no scattering in absence of carriers. In writing $n^{1/3}$ we have assumed that the density of states in (7) corresponds to a parabolic band of free carriers in 3d. This is a very rough approximation (see discussion below), consistent however with the experimental findings [16] that we are going to use now, in order, in particular to fix A . To do so, we suppose, as we tentatively did in reference [2], that the relative increase of T_c of ~ 0.55 observed in reference [1] corresponds to $c = 7/16$ ($\delta = 1/8$, i.e. YBa₂Cu₃O_{6.875}). Then extracting $T_{c(2)}$ from reference [16a], $T_{c(2)} \sim 84$ K for $\delta = 1/8$, and with $(T_{c(1)} - T_{c(2)})/T_{c(2)} \sim 0.55$ from

reference [1], we obtain $A/(2\pi) \sim 8.21 \times 10^2$. We may then rewrite (14) as follows :

$$\left\{ \begin{array}{l} \ln \left[\frac{T_{c(1)}}{T_{c(2)}} \right] \approx \psi \left[\frac{1}{2} + \frac{8.21 \times 10^2 y}{T_{c(2)}} \right] - \psi \left(\frac{1}{2} \right) \\ T_1 \ll T'_0 \leq T_2 \ll T_0 \end{array} \right. \quad (17a)$$

$$10^2 y = c(1-c)(4c-1)^{1/3} \frac{(1-2c)^2}{2c^2 + (1-2c)^2}. \quad (17b)$$

The function $10^2 y$ is plotted versus c in figure 2.

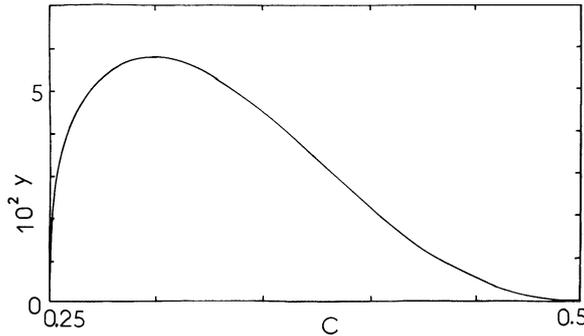


Fig. 2. — The function $10^2 y$ given in the text in formula (17b) plotted versus c .

For each value of c , the fast cooling experiments of references [16], freezing ordered states above T'_0 , give us the corresponding $T_{c(2)}$; then (17a) tells us what is the expected $T_{c(1)}$ if the sample was slowly cooled below the ordering temperature T'_0 , for instance *via* the slow temperature cycling of reference [1]. To get the highest possible $T_{c(1)}$ will thus depend on the ordering states at T_1 and T_2 through (12) and on the oxygen concentration *via* $y(c)$. There are several conflicting factors to take into account in order to optimize the effect. We would need the highest degree of order, i.e. $T_1 \rightarrow 0$; but T_1 cannot be that small since we look for the highest possible $T_{c(1)}$; since T_1 should be smaller than T'_0 , we rather search for the highest T'_0 . However, according to reference [2], T'_0 is maximum for $c = 1/4$, i.e. $\delta = 0.5$, for which the system is, in principle, not metallic anymore: following (16), there is indeed no more carrier left ($n = 0$), in which case $T_{c(1)}$ is expected to vanish as does $T_{c(2)}$ in references [16] (or very close to do so).

Clearly equation (10) ought to be solved self-consistently; for the time being and in the absence of any further experimental information (for instance what is the actual value of δ in the experiment of reference [1], which we tentatively estimate to be $1/8$), we have drawn in figure 3, for c varying between 0.25 ($\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$) and 0.5 ($\text{YBa}_2\text{Cu}_3\text{O}_7$), on one hand, the $T_{c(2)}$ values taken from reference [16a] (which we call T_c in the figure), and $T_{c(2)}$

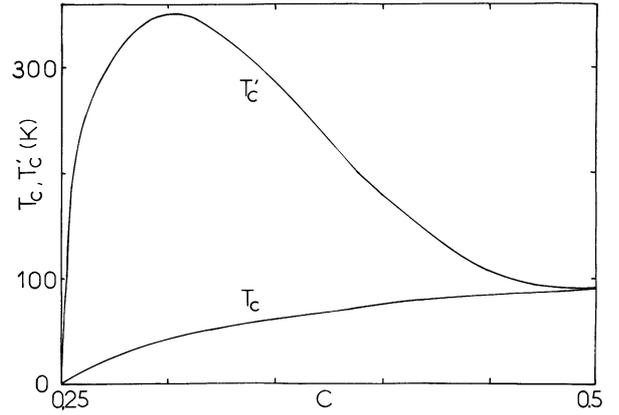


Fig. 3. — T_c and T'_c versus c for $\lambda = 0.315$ and $0.25 \leq c \leq 0.5$, i.e. $0.5 \geq \delta \geq 0$ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The superconducting temperatures T_c are extracted from the data of reference [16a] and correspond to $T_{c(2)}$ in the text; they are obtained for samples prepared by rapid cooling from high T . The superconducting temperatures T'_c correspond to $T_{c(1)}$ in the text and are calculated from formula (17a); they are expected to be the ones obtained for samples slowly annealed so that the atomic ordering, occurring below T'_0 in the oxygen-vacancy system of the CuO basal planes, has been established. T'_0 is the second ordering temperature (below the ortho-tetra one T_0) proposed in reference [2].

(called T'_c in the figure), given by formulas (17). Such a curve must not be taken too seriously given the approximations made above. However the qualitative behaviour is instructive: the highest value for T'_c is reached closer to $\delta = 0.5$ than to 0 although the highest T_c measured so far was obtained for $\delta = 0$. This is obviously linked to the ordering temperature T'_0 being the highest for $\delta = 0.5$. We recall here that, with $\lambda = 0.315$ and T_0 fixed thanks to the data of reference [12], it follows from our reference [2] that

$$\begin{cases} T_0 = 4762.4 c(1-c) \text{ K} \\ T'_0 = 4380 c(1-2c) \text{ K} \end{cases} \quad \lambda = 0.315 \quad (18)$$

so that for, $c = 0.3$, $T'_0 = 525.6 \text{ K}$ and $T_0 = 1000.1 \text{ K}$. Note that the value $T'_c \sim 345 \text{ K}$ reached in figure 3 for $c = 0.3$ is an overestimate since at that temperature, according to figure 1, S_{31} has not quite yet reached its maximum value, ($S_{31} \sim 0.94 S_{31 \text{ max}}$) and (13a) is not quite fulfilled. There is no need at this stage to perform a better estimate by solving (10) self-consistently, given the uncertainty of the parameters used, in particular the λ value.

In any case, the important message of figure 3 is that the neighbourhood of $\delta \sim 0.5$ may be more interesting to look at, rather than $\delta = 0$. It would thus be most interesting to repeat the slow temperature cycling experiments of reference [1] or any other method stabilizing the ordered phase below

T'_0 , for the case $\delta = 0.4$ i.e. on YBa₂Cu₃O_{6.6} samples, for instance.

4. Discussion.

Our main point in this paper is that, if T'_0 exists, then T_c may possibly be increased by quite a large amount if one allows the long range atomic order to reach its equilibrium value below T'_0 .

The existence of T'_0 may be checked by specific heat measurements. There is indeed an extra configurational contribution C to the specific heat due to the atomic ordering. It can be easily computed as the derivative with respect to T of the internal energy of configuration, $\partial E/\partial T$ in formula (8) of reference [2]. One can show straightforwardly that C increases from $T = 0$ to $T = T'_0$, then drops to very small values, to increase again when $T \rightarrow T_0$. In units of the Boltzmann constant k_B , one gets :

$$\frac{C}{N} \approx \frac{3}{2} \frac{c(1-2c)}{1-6c(1-2c)}, \quad T = T'_0 \quad 0.25 \leq c \leq 0.5$$

$$\lambda = 0.315 \quad (19)$$

(N is the number of oxygen plus vacancies), and

$$\frac{C}{N} \approx \frac{3}{2} \frac{c(1-c)}{1-3c(1-c)}, \quad T = T_0 \quad 0.25 \leq c \leq 0.5$$

$$\lambda = 0.315 \quad (20)$$

Therefore the jump at T'_0 is vanishingly small (together with the T'_0 value) when $\delta \rightarrow 0$, $c \rightarrow 0.5$, but it increases with δ to reach the value 0.75 when $\delta = 0.5$, $c = 0.25$; in the same range, the jump at T_0 decreases from 1.5 at $\delta = 0$, $c = 0.5$, to 0.64 at $\delta = 0.5$, $c = 0.25$. At $c = 0.3$, of interest here, $C/N = 0.64$ at $T = T'_0$ compared to $C/N = 0.85$ at $T = T_0$ but still with $C/N \sim 0$ just above T'_0 . These modest, although measurable, values for C/N at T'_0 rely upon the assumption made in reference [2], following reference [11], that the ordering transition at T'_0 is a second-order one. Measurements of C/N at T'_0 would thus be most interesting in several respects: the existence of T'_0 , the nature of the transition at T'_0 and the actual value of λ (supposed here to be equal to 0.315 and fixing the T_0 and T'_0 values).

In order to draw figure 3, we have chosen for $N(E_F)$ in τ_0^{-1} the density of states of free 3d carriers. As already mentioned, this is only justified by the fact that superconducting temperature values in reference [16a] (called $T_{c(2)}$ here) appeared consistent with such an assumption, although without any justification. However it has been shown [17] that in these quasi-2d systems, $N(E_F)$ is expected to exhibit Van Hove singularities [18] and would thus be quite different from the one used here. Obviously the precise value of $N(E_F)$ is a key point to determine

$T_{c(2)}$, as linked to the nature itself of the anomalous superconductivity in the YBaCuO family. Reference [17] attributed the high values of $T_{c(2)}$ to the 2d logarithmic singularities in $N(E_F)$. It is likely that these singularities, smoothed out in the disordered phase, above T_0 , would be all the more important that T is decreased below T'_0 . Related to possibly high values of $N(E_F)$ an interesting and unexplained feature appears in reference [16b] where the magnetic susceptibility χ at 100 K was also measured in the range of interest here for δ : the value of χ is about the same for $\delta < 0.25$ and $\delta > 0.45$ but is about 3 to 5 times higher for $0.25 < \delta < 0.45$, possibly linked, according to the authors of reference [16b], to the apparition of new short-range periodicities. We note that such an increase in χ , and thus in $N(E_F)$, appears for δ values including the one $\delta = 0.4$ that we propose here to be most favorable to increase T_c . Taking into account such an increase in $N(E_F)$ would all the more reinforce our proposal of T_c being the highest (below T'_0) around the composition $\delta \sim 0.4$. This brings us to another point to be discussed now.

We do not take into account in the present paper any change (once c is fixed) in $N(E_F)$ due to ordering. It has been shown in the past [19] that in V₃Au the density of states may be quite increased if one takes into account the ordering among the Au and the V atoms along the chains, which, in turn, increases the superconducting temperature of that system. Moreover it is well known [20] that, upon ordering, new Brillouin zones form and the band structure of the carriers is modified, (which react on the effective number of carriers and possibly the sign of their charge). Then, depending on the position of the Fermi level, $dN(E)/dE$ may be either increased or decreased. Interesting information could then be provided from measurements of the thermopower and the Hall coefficient.

Ordering processes react as well on other properties like elastic constants and volume changes (see Sect. II of Ref. [14] for instance) which in turn would react on the values of interactions between first, second neighbours... so that our λ 's values may not be constant when T varies. Lattice vibrations are as well influenced by the atomic ordering (see again Sect. II.8 of Ref. [14]) so that changes in the phonon spectrum should also be investigated along these lines.

We believe that a careful account of the ordering effects on the various properties of the system in its normal phase should be made before attributing the superconducting pairing to phonon or non-phonon mediated attraction. It would then be at that stage that one could check whether our assumption of the disorder acting as a pair breaker is indeed valid or not.

Finally, if interaction between atoms farther than

2nd neighbour would prove to be important, one would certainly need more than two long-range order parameters to describe the atomic ordering of the system ; in that case there would be a lot more of ordering transition temperatures with sequence $T_0 > T'_0 > T''_0 > \dots$; then, inside the parabola that we had in reference [2] for $T'_0(c)$ there would be another one for $T''_0(c)$ vanishing at $C = \frac{1}{4}$ and $C = \frac{1}{2}$ etc.

At present and given the difficulties encountered

by the experimentalists (to maintain the oxygen content constant during a given experiment for instance) and consequently the very small amount of information concerning the atomic ordering processes in the oxygen-vacancy system, the present simple model may be a sufficient starting point for more sophisticated studies.

To conclude we would like to convince the experimentalists to study the superconducting temperature in $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ samples in the atomically ordered phase below 500 K.

References

- [1] BHARGAVA, R. N. *et al.*, *Phys. Rev. Lett.* **59** (1987) 1468, this paper mentions a number of earlier refs. finding increased T_c but with no reproducibility ; see also
MATTHEWS, D. N. *et al.*, *Nature* **328** (1987) 787.
- [2] BÉAL-MONOD, M. T., to appear in *J. Phys. France* (Janv. 1988).
- [3] ALARIO-FRANCO, M. A. *et al.*, to appear in *Mater. Res. Bull.* (1987) ;
CHAILLOUT, C. *et al.*, to appear in *Solid State Commun.* (1987).
- [4] See for instance a review in RICE, T. M., *Z. Phys.* **B 67** (1987) 141.
- [5] ANDERSON, P. W., *J. Phys. Chem. Sol.* **11** (1959) 26 ;
ABRIKOSOV, A. A. and GORKOV, L. P., *Sov. Phys. J.E.T.P.* **8** (1959) 1090.
- [6] See the review by MAKI, K., in *Superconductivity*, Ed. Parks (Marcel Dekker Inc., NY) (1969) Vol. 2, Chap. 17.
- [7] BALIAN, R. and WERTHAMER, N. R., *Phys. Rev.* **131** (1963) 1553.
FOULKES, I. F. and GYORFFY, B. L., *Phys. Rev.* **B 15** (1977) 1395 ;
LARKIN, A. I., *J.E.T.P. Lett.* **2** (1965) 130 : this is the case of triplet pairing *via* nearly ferromagnetic spin fluctuations as in liquid ^3He .
- [8] For an attractive interaction due to nearly antiferromagnetic spin fluctuations see BÉAL-MONOD, M. T. *et al.*, *Phys. Rev.* **B 34** (1986) 7716 ;
SCALAPINO, D. J. *et al.*, *Phys. Rev.* **B 34** (1986) 8190 ;
MIYAKE, K. *et al.*, *Phys. Rev.* **B 34** (1986) 6554.
- [9] MAEKAWA, S. *et al.*, *Jpn J. Appl. Phys.* **26** (1987) L771.
- [10] See, for instance, ABRAMOWITZ, M. and STEGUN, I. A., *Handbook of Mathematical functions* (Dover) 1965.
- [11] RUDMAN, P. S., *Acta Metall.* **8** (1960) 321.
- [12] JORGENSEN, J. D. *et al.*, *Phys. Rev.* **B 36** (1987) 3608.
- [13] NOSAR, A. N. and SMIRNOV, A. A., *Phys. Met. Metallogr.* **12**, 5th issue (1961) 7. Note that the ordering parameters η_1 and η_2 of this reference identify respectively to $S_{11}/2$ and $S_{31}/2$ of reference [11].
- [14] MUTO, T. and TAKAGI, Y., The theory of order disorder transitions in alloys, in *Solid State Phys.* **1** (1955) 194, section III, Ed. F. Seitz and Turnbull D. (Academic Press) ; see also
DIENES, G. J., *J. Appl. Phys.* **22** (1951) 1020.
- [15] BÉAL, M. T., *J. Phys. Chem. Sol.* **15** (1960) 72 ; this paper applies to alloys where only one long-range order parameter is needed as in $\text{CuZn}\beta$.
- [16] a) MONOD, P. *et al.*, *J. Phys. France* **48** (1987) 1369 ;
b) CAVA, R. J. *et al.*, *Nature* **329** (1987) 423 ;
c) JOHNSTON, D. C. *et al.*, Proc. Symposium « Inorganic superconducting materials », New Orleans, Aug. 31st-Sept. 4th (1987) to be published ; given the error bars, these three sets of measurements are quite compatible and show that the measured superconducting temperatures for samples rapidly cooled from high temperatures (our $T_{c(2)}$ here) decrease when δ varies from 0 to 0.5.
- [17] LABBÉ, J. and BOK, J., *Europhys. Lett.* **3** (1987) 1225.
- [18] VAN HOVE, L., *Phys. Rev.* **89** (1953) 1189.
- [19] LABBÉ, J., VAN REUTH, E. C., *Phys. Rev. Lett.* **24** (1970) 1232.
- [20] MUTO, T., *Sci. Papers Inst. Phys. Chem. Research* (Tokyo) **34** (1938) 377 quoted in reference [14] above ;
SLATER, J. C., *Phys. Rev.* **84** (1951) 179 ;
CORCIOVEI, A. and GRECU, D., *Acta Phys. Pol.* **XX**, Fasc. 3 (1961) 197.