THERMODYNAMICS OF OXYGEN ORDERING IN $YBa_2Cu_3O_{6+x}$

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We have calculated the x-T phase diagram of the CuO_x planes assuming screened-Coulomb repulsions between O ions up to the 5^{th} nearest neighbors. The repulsion between 2^{nd} neighbors with a Cu in between is reduced by charge-transfer effects. We used the 3x3-point approximation of the cluster variation method (CVM). We show that this approximation fails for low temperature (T) and $1/3<x<1/2$. The region of failure enlarges for smaller basic clusters. Except inside this zone or very low T, all phase boundaries are continuous. Except at very high T the tetragonal phase is short range ordered.

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The oxygen ordering in $YBa_2Cu_3O_{6+x}$ and its relation to electronic and superconducting properties remains one of the most interesting and studied problems raised by the new superconducting perovskites. It is known that there are at least three different stable phases which differ by the arrangement of O atoms in the CuO_x planes (those which bisect the shortest Ba-Ba distance): tetragonal[1] (T), simple orthorhombic[1] (OI) and double- cell orthorhombic[2] (OII). For $x \sim 1/8$ and $x \sim 7/8$, there is evidence[3] of structures, whose unit cell is a multiple of $2\sqrt{2} \times 2\sqrt{2}$. Other experiments[4,5] suggest the existence of structures with unit cell $(1 \times n)$ with $n = 3,4,5$ and probably 8. However, the results of Ref.5 seem to indicate that these phases are actually metastable. In any case it is interesting to note that all observed diffraction patterns can be explained as arising from theoretically expected ground state structures[6,7], which were deduced assuming screened-Coulomb interactions V_i between any two i-th nearest-neighbor O ions of the CuO_x planes, but reduced for 2nd nearest neighbors if a Cu ion is in between ($V_{2Cu} = fV_2$, $f \leq 1$). In this letter we consider this model, but cut off the interactions beyond a distance $2a$ (the difference between the lattice parameters a and b is neglected). The thermodynamics is obtained using the cluster variation method (CVM), taking as a basic cluster a square of size $\sqrt{2}a \times \sqrt{2}a$ containing 9 possible O positions (see Fig.1). Similar studies have already been carried out[8-12]. In particular Wille et al.[9] were the first to include the

OII phase in the phase diagram. However, as explained below, our study differs from the previous ones in several important respects: the nature, magnitude and range of the interactions, the larger size of the basic cluster and the wider range of temperatures studied[11], which allowed us to discuss the validity of the method. Our results are also different.

Since $YBa_2Cu_3O_{6+x}$ is an insulator for $x \tilde{<} 0.5$ and the number of carriers for any x is very low, the importance of interatomic Coulomb repulsions is apparent[7]. The extended Hubbard model including these correlations, was used to obtain an excitonic pairing mechanism[13]. The same model provides an explanation of the metal insulator transition, the hole count, the x dependence of Cu^+ and also the reduction of the repulsion V_{2Cu} (Refs. 6, 14). Thus, a consistent electronic explanation of the O-O interactions is provided. The existence of $2\sqrt{2}$ x $2\sqrt{2}$ structures[3], even if metastable, suggests that the interactions extend to distances $2\sqrt{2}$ a ~ 11Å. In the explanation of Khachaturyan and Morris[15] of the split diffraction peaks[4] at $q = (2\pi/a)(1/2 \pm \epsilon, 0, 0)$ in terms of disordered Magneli phases, it is essential to avoid sequences of three or more consecutive parallel CuO chains. Otherwise the peak does not split[16]. Therefore it seems that interactions at distances of at least $2a$ are important. In order to include these in a CVM calculation, the smallest possible basic cluster is the one used here (Fig. 1). We derived the expression for the entropy of the different phases using the group theoretical methods

developed in Ref.17. This is the highest accurate CVM approximation used so far in this type of problems. However, it would be almost impossible in practice to use it, if it were not for one fact: the OII-T transition temperature at $x = 0.5$, T_o, is expected (and turns out to be[6]) much smaller than the nearest-neighbor O-O Coulomb repulsion V_1. Since we are interested in temperatures of the order of T_o and smaller, the configurations with nearest-neighbor O ions can safely be neglected. In this way the number of different configurational probabilities for the OII phase reduce to 100, related by 34 conditions imposed by symmetry and normalization.

Usually, the formulation of the CVM in terms of correlation functions[18] suffers from convergence problems at low temperatures. This is presumably due to the fact that at low T not all correlation functions are independent, for example if the pair correlation function for 2nd neighbors along a CuO chain is maximum, all other pair correlation functions along the chain are also maximum. In Ref.9 the phase diagram for $T \tilde{<} 0.8\ T_o$ was speculated[11]. Other methods[12] also have problems at low T. Instead, the formulation of the CVM in terms of probabilities p_i of configurations i of the basic clusters[19] should become simpler at low T, since an increasing number of these p_i become vanishingly small. However, this method has the disadvantage that symmetry relations between the p_i have to be imposed. The "minor iterations" proposed by Kikuchi[19] to obtain the corresponding

Lagrange multipliers did not converge in our case. We solved these equations, ordering them according to the magnitude of the p_i involved: starting from initial approximation values of the Lagrange multipliers, a new value for the first few of them in this hierarchy is obtained solving the corresponding equations using numerical subroutines. The procedure is repeated considering a larger number of equations until all of them are included. This modified version of the natural iteration method converged at all temperatures. The numerical program was too slow for points near phase boundaries at $T \sim T_o$. Thus, the details of the phase diagram near the tricritical point were obtained from the change in sign of the lowest eigenvalue of the Hessian matrix[20].

The cluster configurations i for which $p_i \neq 0$ at $T = 0$ can be used to determine the ground state in a way similar to the cluster method developed by Allen and Cahn[21]. However, this method is not always efficient, giving rise to "impossible" structures with energy less than the true ground state. In our case, this happens for $1/3 < x < 1/2$. To see this, let us take parameters ($V_{2Cu} \leq 0$ in our case) for which at $x = 1/3$, the ground state structure has every third CuO chain full of O and no O ions elsewhere. The CVM for the T phase correctly gives only 6 cluster configurations with non vanishing $p_i = 1/6$ at $T = 0$. The occupied positions of this configurations (see Fig.1) are: (1,5,9), (2,4), (6,8), (3), (7) and (none).

The latter configuration, without any O atom, is not related

to others by symmetry conditions in the T phase. When the O chemical potential μ increases, its probability p_0 decreases and no new configurations appear, something that is impossible in the real structure. The situation is the worst when $p_0 = 0$ ($x = 2/5$). For larger values of x or T, new configurations appear and the illness heals rapidly. For all $x \geq 1/2$ or $x \leq 1/3$, the CVM correctly gives the ground state energy obtained independiently using direct enumeration and group theoretical methods[6,7]. When we start from the OII phase at $T \to 0$, $x = 1/2$ and decrease μ, at a given point the system suddenly "drops" into the spurious T phase and a first-order transition is predicted by the method. Since the failure just described is a consequence of the finite size of the clusters, the zone of failure enlarges and shifts to higher x for smaller basic clusters. Using a similar reasoning as before, it is straighforward to check that for a 4-point approximation and $V_{2Cu} < 0$, the ground state is ill described for $x > 1/2$. The 9-point cluster is the smallest one for which the ground state is decribed correctly in the interesting superconducting region $x \geq 1/2$.

In Fig.2 we show the x-T phase diagram for a screening-length $\lambda = a_o$ where $a_o = a/\sqrt{2}$ is the lattice parameter of the O sublattice. We considered $V_{2Cu} = 0$ and $V_{2Cu} = -0.1\ V_2$. These parameters are close to the ones for which a correspondence between the ground state structures and all diffraction patterns exists[6,7]. However, the ground state as a function of x loses much

of it richness when interactions beyond 5th nearest neighbors are cut off. For $V_{2Cu} = 0$ in addition to the T, OI and OII phases, structures with unit cell $2\sqrt{2} \times 2\sqrt{2}$ of the type proposed in Ref.3 are stable for $x = 1/4$ and $x = 3/4$. They have one pair of second-neighbor O ions (or vacancies added to the x=1 phase) with a Cu in between per unit cell. We call them PS[6,7]. The structures with unit cell 1x3 consisting of full and empty chains for $x = 1/3$ and $x = 2/3$ are marginally stable for $V_{2Cu} = 0$ and stable for $V_{2Cu} < 0$. We call them OIII. Since the numerical calculation of the thermodynamical potential of all these phases would be a formidable task, we have limited ourselves to the main T, OI and OII structures. The boundary between PS and OI for $V_{2Cu} = 0$ was calculated neglecting the entropy of the former. The high-T part of the phase diagram is similar to that obtained previously[9,10]. The T-OI boundary is steeper in our case, the critical x being almost T independent, as experimentally observed[1]. For $T \sim T_o$ all transitions are continuous in agreement with recent transfer-matrix calculations[12]. The only first order T-OII transitions obtained are spurious, because they fall in the above explained region of failure of the 9-point approximation. We believe that this is also the case in other CVM treatments which used smaller clusters[9,10]. The OI-OII transition line is continuous for $V_{2Cu} = 0$ and all $T > 0$, although the steepness of the transition increases sharply as T is decreased. Since for $T = 0$ one expects that only phases with definite stoichiometry are

stable[6,7], this and the fact that the OI phase is predicted to exist for $x \neq 1$ at $T = 0$ are noticeable. This is a consequence of the finite range of the interactions. For example, for $3/4 < x < 1$, a random configuration of $(1-x)/2$ pairs of O vacancies with a Cu in between per unit cell, added to the OI phase with $x = 1$, correlated in such a way that the distance between any two of these pairs is greater than $2a$, has the same energy as a segregated mixture of the ground state structures for $x = 3/4$ and $x = 1$. However, it has a larger entropy and is favored for $T \neq 0$. The funny curvature to the left of the OI-OII transition line for $V_{2Cu} = -0.1\ V_2$, $T < 0.02\ V$ and the first-order transition that takes place for $T < 0.004\ V$, are a consequence of the fact that the ground state for $x = 2/3$ is the OIII phase. This behaviour disappears with the repulsive interaction V_5 that stabilizes the OIII structure. Had we calculated the thermodynamic potential for this phase, the whole transition line for $T < 0.02\ V$ would probably be replaced by an OII-OIII two phase field, since a second order transition between these two phases cannot take place for symmetry reasons.

In agreement with the ground-state analysis[6,7], the low x, low T orthorhombic phase found in Ref. 10 but not in experiments[3,22], exists only for sufficiently large and negative V_{2Cu}/V_2.

In Fig. 3 we show the entropy and a pair correlation function as functions of x for $T > T_o$. Since the chosen T lies near T_o, a

"memory" of the OII phase is present in the T phase for x ~ 0.5, as can be seen in the entropy and correlation functions between 5^{th} and 2^{nd} nearest neighbors with a Cu in between. As noted earlier[6], an important difference with most other treatments of the problem is the highly correlated nature of the T phase. This justifies the low value of T_o/V_1 from the fact that the system gains considerable energy avoiding first nearest-neighbor O ions, at a comparatively low cost of entropy for x = 0.5, as seen in Fig.3(a). As a consequence, the short range order of the T phase is similar to that of the OI phase (see Fig.3(b); $p_T = x/2$ is expected for a completely disordered T phase).. This has been experimentally confirmed by perturbed - angular - correlation studies[23]. Other experiments showing the similarity between OI and T phases are the absence at the OI-T transition of discontinuities in the slope of the resistivity vs x curve[24] (a discontinuity is only observed for x = 0.5, which is probably due to the semiconductor-metal transition[14]) and in the Arrhenius plot in diffusion experiments[25]. Choi et al.[26] calculated the diffusion constant using the path-probability method. They conclude that for large V_1, this constant is related mainly to the number of O-Cu-O chainlets in the structure. Since they find that this number is significantly different in the OI and T phases, they obtain an abrupt change in the diffusion behaviour at the transition, contrary to experiments[25]. In our model, the difference in 2^{nd} neighbor O pairs with a Cu in between is minute as shown in

Fig.3(b). It was suggested that changes in the number of these pairs also correlate with corresponding observed changes in the superconducting Tc. However, our electronic structure calculations using the extended Hubbard model[6,14], show that a staircase behaviour of the number of holes and Tc is to be expected even assuming perfect CuO chains for all x.

In summary, using a higly accurate CVM and previous ground state studies, the main features of the x - T phase diagram of $YBa_2Cu_3O_{6+x}$ have been explained assuming interactions between pairs of O atoms, the order of magnitude and range of which is what is expected for a poor metal. The OII-T transition temperature at x = 0.5, T_o, is of the order of magnitude of the difference between 2^{nd} neighbor and higher order pair interactions. The transitions between T, OI and OII phases are continuous up to low temperatures determined by interactions between 5^{th} nearest neighbors or higher, for which new ordered phases succesively appear. For $T \sim T_o$, the T phase is highly correlated in agreement with experiments and early proposals, as mentioned before[6]. The value of the only interaction in the model different from a Coulomb repulsion can be understood from charge-transfer effects induced by Cu-O repulsion[6,14]. Thus, from different studies[6,13,14], one can see that the point of view of strong interatomic correlations provides an harmonious explanation of the electronic structure, oxygen ordering and pairing mechanism

of the system.

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Figure captions

1 - Basic cluster used in the CVM approximation. Crosses denote Cu atoms and circles the possible O positions. Even and odd numbers label inequivalent sites in the OI phase.

2 - Temperature vs composition phase diagram of YBa_2CuO_{6+x} for screening length $\lambda = a/\sqrt{2}$ ($V_1 = 0.37$, $V_2 = 0.17$, $V_3 = 0.068$, $V_4 = 0.048$ and $V_5 = 0.021$ in units of the unscreened nearest-neighbor repulsion V). Full line $V_{2Cu} = 0$, dashed line $V_{2Cu} = -0.1V_2$. Dotted line is an underestimation of the region of existence of a $2\sqrt{2} \times 2\sqrt{2}$ structure. The hatched area shows approximately the region of failure of the 9-point CVM approximation.

3 - (a) entropy (full line), and (b) probability that an O ion has a 2^{nd} neighbor with a Cu ion in between, as a function of x for T = 0.07V. Results for the T(OI) phase are indicated by full (dotted) lines. In (a) we show for comparison the entropy of totally disordered phases with (dashed line) and without (dashed-dotted line) the condition of no nearest-neighbor O ions.

Fig. 1

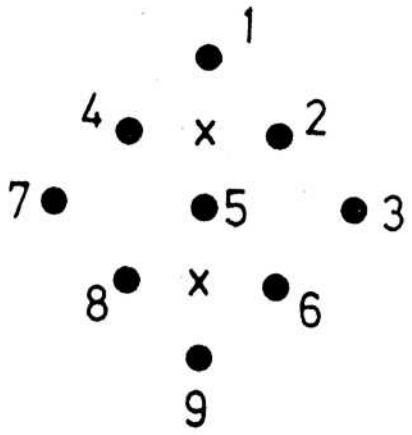
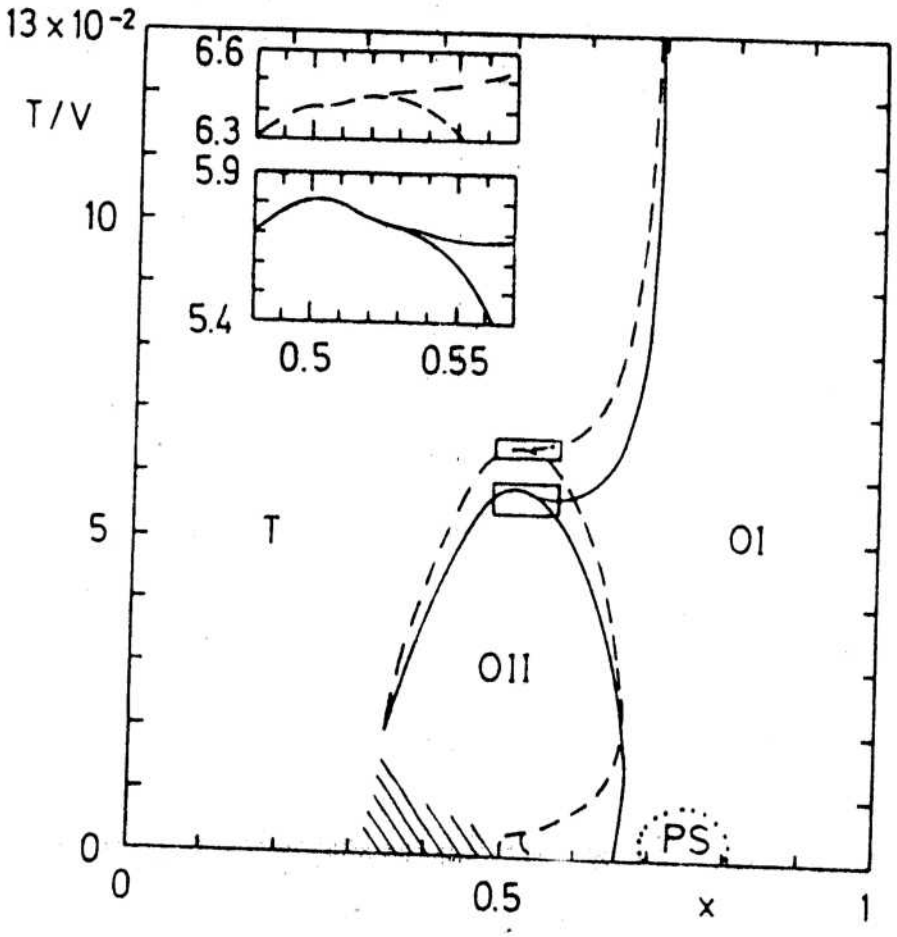


Fig. 2



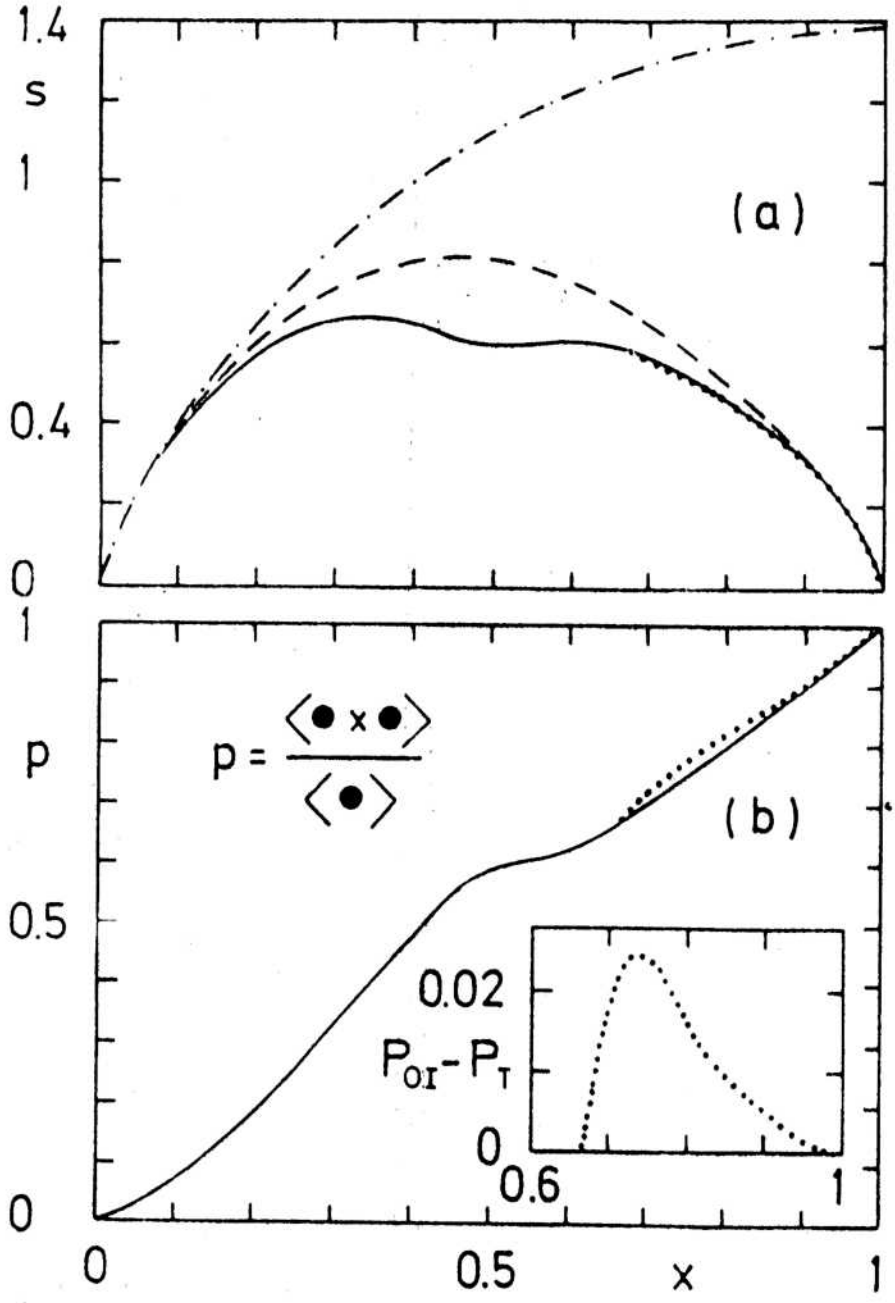

1.4
s
1
(a)
0.4
0
1
p
$p = \frac{\langle \bullet \times \bullet \rangle}{\langle \bullet \rangle}$
(b)
0.5
0.02
$P_{OI} - P_T$
0
0.6
1
0
0.5
x
1

Fig. 3