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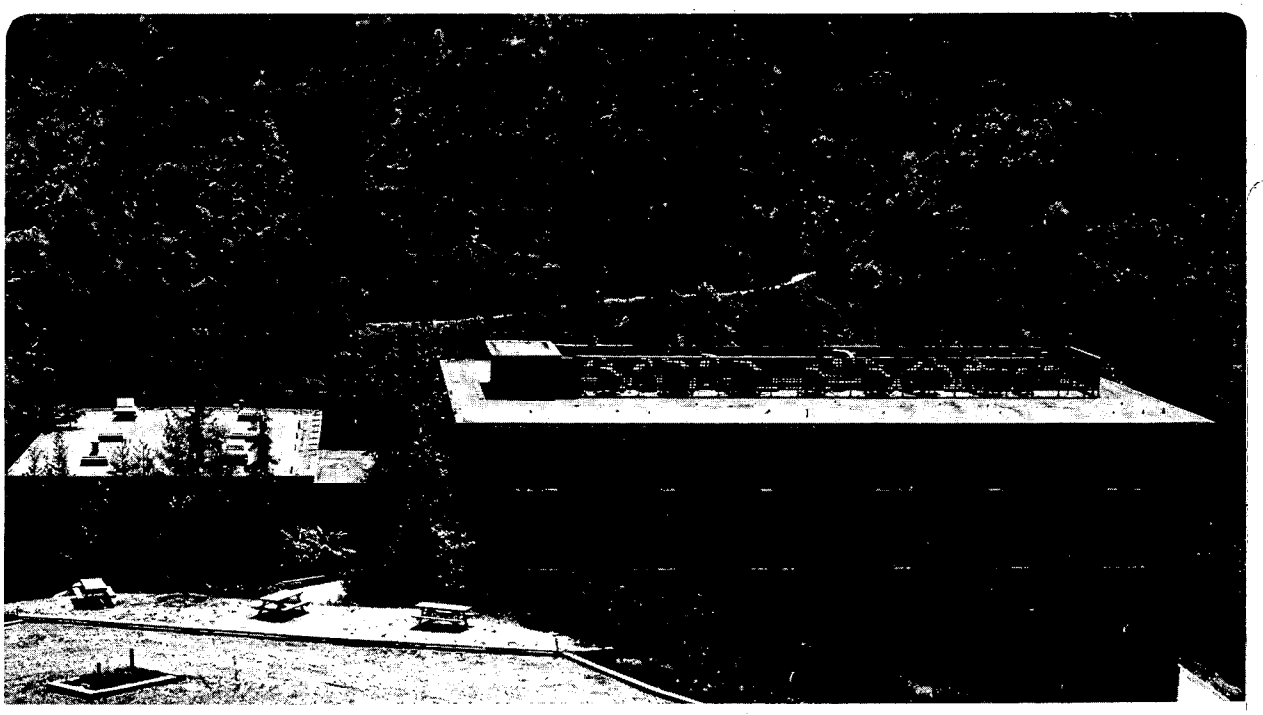

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OXYGEN CONFIGURATIONS AND THEIR EFFECT ON CHARGE TRANSFER IN $YBa_2Cu_3O_z$

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ABSTRACT

The relationship between oxygen structure, charge transfer (hole count), and oxygen content in the $YBa_2Cu_3O_z$ superconductor is studied by combining Monte-Carlo simulation with existing electronic structure calculations. The present model proposes an expansion of the hole count in terms of oxygen configuration variables for states of an arbitrary degree of order. Calculations of hole count as a function of oxygen content suggest that oxygen ordering is, at least in part, responsible for the observed plateau structure of T_c vs. oxygen content z.

INTRODUCTION

Despite the great effort expended towards an understanding of the mechanisms of high-temperature superconductivity, an all-encompassing theory does not yet exist. Several issues have been clarified with respect to $YBa_2Cu_3O_z$, namely that T_c is strongly correlated to carrier concentration and that the superconducting current consists of holes [1]. In addition, superconductivity is believed to occur in the CuO_2 sheets, with the rest of the structure acting as a charge reservoir [2]. It is generally accepted that off-stoichiometry is accommodated primarily in the basal plane of the structure [3]. Oxygen-Vacancy (O-V) ordering within this plane leads to the formation of long O-Cu-O or V-Cu-V chains (O=oxygen, V=Vacancy), which have been observed in numerous experimental and theoretical studies [4-7]. The pseudo-binary phase diagram of this system shows a high-termperature orthorhombic-tetragonal phase transition, with the existence of chain superstructures at low temperature [5]. Two primary ordered structures are the "Ortho-I" (OI) structure with stoichiometry z=7, and the cell-doubled "Ortho-II" (OII) phase with stoichiometry z=6.5 [5]. Superstructure combinations of these two phases should also exist at equilibrium [8], although the driving force for the formation of these so-called *branching phases* is not nearly as large as that for the formation of OI and OII.

One feature of $YBa_2Cu_3O_z$ which is of special interest is the non-linear variation of T_c as a function of oxygen off-stoichiometry, z. Several groups have shown[4,9] that in annealed samples there are two distinct "plateau" regions around O_7 and $O_{6.5}$ at 90 K and 60 K, respectively. Numerous investigators have attempted to correlate the observed plateau behavior with the variation of hole count (number of holes in CuO_2 plane / Unit Cell) as a function of oxygen content (see list in Ref. [10]). This is also the objective of the present investigation.

It has been demonstrated experimentally that there is a large difference between annealed and quenched samples of $YBa_2Cu_3O_z$; Veal et al. [11] and Claus et al. [12] have shown that T_c increases by as much as 30 K during room-temperature aging of quenched samples. Monte-Carlo simulations of these aging experiments [13,14] has shown that the increase in T_c at constant oxygen content is correlated with the occurrence of time-dependent oxygen ordering. Hence, the formation of ordered superstructures has a definite influence on the superconducting behavior of this system. Yet, despite the clear correlation between structure and electronic properties in $YBa_2Cu_3O_z$, many theoretical studies seem to make unjustified simplifications in one subject area or another.

Electronic structure calculations by numerous investigators [15-17] have produced interesting results for the hole count as a function of oxygen content, but the statistical models for oxygen ordering that these studies have used are quite artificial. It has been shown [8,16] that the results of these calculations are a direct result of unrealistic oxygen defect structures. However, one basic conclusion can be drawn from the studies of several investigators [16-19]: there is a large difference between assuming ordered and random distributions of vacancies, and the choice of the ordered arrangement is crucial. In general, electronic structure calculations treat the electronic

behavior of the system very accurately, but use oxygen defect statistics which are inaccurate and do not take into account states of *partial* order.

Phenomenological studies are not as rigorous concerning electronic effects, but treat oxygen defect structures in a realistic way. In general, these methods postulate the existence of some fundamental structure which gives rise to charge transfer. The simplest structure to study is the local oxygen environment around copper in the basal plane, where it has been shown [8,13] that Cu ions in the basal plane are either two-, three-, or fourfold coordinated by oxygen. If it assumed, as is generally done [3], that the apical oxygen sites are always occupied, then these three coordinations correspond to V-Cu-V, V-Cu-O, and O-Cu-O chain segments, respectively. CVM calculations [8], performed in conjunction with studies [16,20] on the oxidation states of copper in different oxygen environments, have demonstrated (using a simple model) that for $6.5<z<7$, the hole count should decrease approximately linearly with oxygen content as 7-z. Hence, this model, by itself, would not predict the existence of any plateaus in hole count for $6.5<z<7$.

In the "Minimal Size Cluster" (MSC) model proposed by Poulsen et al. [21], only ordered OI or OII domains exceeding a certain critical size can contribute to charge transfer; one defect is tolerated in each cluster to allow for thermal relaxation. Simulation on the ASYNNNI model by Poulsen et al., along with some assumptions concerning T_c and charge transfer, yield results for T_c vs. z which are in almost exact agreement with the experimental data of Cava et al.[22]. Unfortunately, a detailed study by one of the authors [23] revealed several shortcomings of the MSC model: 1) Charge transfer from other ordered structures is neglected and 2) the results obtained for T_c vs. z are very sensitive to MSC size and defect tolerance.

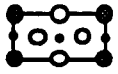
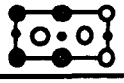
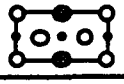
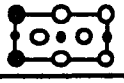
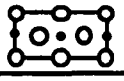
The procedure proposed here is to expand the hole concentration in the CuO_2 plane as a function of oxygen configuration variables. The values of the oxygen configuration variables are obtained from Monte-Carlo simulations on the asymmetric next-nearest-neighbor Ising (ASYNNNI) model [24] ; these results are combined with existing electronic structure calculations to calculate the hole count as a function of oxygen content.

I. CLUSTER EXPANSION OF THE HOLE COUNT

The concept of examining finite domains (within a structure) with a given configuration is extended to a more general treatment, namely that of expansion of the hole count in terms of oxygen configuration variables. Past studies have used the basic idea of cluster expansions to compute properties which are functions of configuration [25,26]; these methods have recently been shown to be rigorous when describing properties which are a function of configuration [27]. The general method is to expand a given property of configuration in a complete set of basis functions which can describe any configuration of the system. The coefficients in the expansion are then calculated for the chosen basis. Since charge transfer (hole count) is clearly dependent on the oxygen configurations around copper atoms within the basal plane, the hole count at oxygen stoichiometry z can thus be written as an expansion using a given set of configurations (Eqn. 1).The sum extends over the number of configurations (N) being used in the expansion; f_i

$$h(z) = \sum_{i=1}^{N} h_i f_i(z) \qquad (1)$$

represents the fraction of *copper* sites surrounded by the *oxygen/vacancy configuration* i (cluster probability), and h_i is what will be referred to as the "hole coefficient" for that configuration. This study uses a cluster figure which consists of two unit cells in the basal plane, and contains 8 oxygen and 3 copper sites. The number of configurations (N) considered on this cluster is 14: 6 ordered and 8 disordered. In the context of this study, "ordered" clusters are considered to be the clusters distinct by symmetry which are composed of only O-Cu-O and/or V-Cu-V chains; "disordered" clusters are all other configurations on the chosen 8 point cluster figure. This distinction between ordered and disordered clusters is not essential to the method, it is only used for simplicity. The configurations used are shown in Fig. 1, and will be referred to hereafter using

1	2	3	4
	3 Chains	C_1	0.25
	2 Chains	C_2	0.18
	2 Chains	C_3	0.16
	1 Chain	C_4	0.096
	1 Chain	C_5	-0.010
	0 Chains	C_6	-0.02

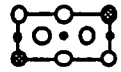
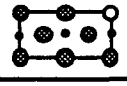
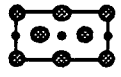
1	2	3	4
	Disord. (1)	D_1	-0.12
	Disord. (2)	D_2	-0.29
	Disord. (3)	D_3	-0.15
	Disord. (4)	D_4	0.094
	Disord. (5)	D_5	0.19
	Disord. (6)	D_6	0.48
	Disord. (7)	D_7	-1.25
	Disord. (8)	D_8	0.046

Fig. 1: Details for various configurations used in the cluster expansion. Column: (1) Configuration on cluster figure (2) Description of configuration (3) Label for configuration (4) Hole coefficient for configuration in cluster expansion.

the designations given in column three. In Fig. 1, Clusters C_1 to C_6 are the ordered clusters and D_1 to D_8 are the disordered clusters. The copper atom which is examined in the given configuration is the central Cu atom in the cluster figure.

The hole coefficients in Eqn. 1 (h_i) are found using electronic structure parameters calculated by Lambin [19]. The results of Lambin are particularly useful in this study since he calculates hole counts for four ordered superstructures and for several disordered structures. The hole coefficients are then found by solving a system of linear equations where each equation resembles eqn. 1. For example, in the current study, 14 hole coefficients are needed, so we need at least 14 equations like eqn. 1 in order to solve the system by simple matrix inversion. In order to generate these equations, we need to know the cluster probabilities for a set of structures for which the hole count has been computed.

Computation of the cluster probabilities (f_i) of the ordered clusters in perfectly ordered structures is relatively straightforward (see Ref. [10]), and can be done by inspection for OI, OII, OIII, and the empty structure (at z=6). The hole counts for the ordered phases are then written according to eqn. 1 (see Ref. [10] for details). The values for h_{OI}, h_{OII}, h_{OIII}, and h_E are 0.25, 0.14, 0.17, and -0.02 holes/unit cell respectively [19]. In addition to these phases, Lambin also computed the hole count for a superstructure phase at z=6.875 (h_{AF} = 0.20 holes/unit cell). At this point the assumption is made that all *disordered* clusters with the same number of filled sites will have the same hole coefficient. The above information allows computation of three of the 14 coefficients needed [10]. In order to compute all 14, additional hole counts for other structures are required. These are based on the hole counts for some artificially generated structures used by Lambin; cluster probabilities for these structures are found using the same probability distributions as those that were used in [19]. A detailed description of this procedure is presented elsewhere [10].

We now have a system of equations of the form $A\mathbf{x}=\mathbf{b}$ which needs to be solved, where $\mathbf{x}$ is the vector of hole coefficients. Unfortunately, it is found that the matrix of cluster probabilities (A) is singular and hence the system cannot be solved by matrix inversion. At this point, we elect to solve the associated least-squares problem: find a vector $\mathbf{x}$ that minimizes the Euclidean length of the residual vector $\mathbf{r}=A\mathbf{x} - \mathbf{b}$. Values of the vector $\mathbf{x}$ can be computed using the singular value decomposition (SVD) of the matrix A. The least squares solution of the problem yields the hole

coefficients given in column four of Fig. 1. The details of the computations performed are rather extensive and complicated; the interested reader is referred to Ref. [10].

The expansion coefficients (h_i) to be used in eqn. 1 have now been determined. All that remains is to determine the cluster probabilities (f_i) as a function of concentration. In the previous discussion of hole coefficient computation, the cluster probabilities that were discussed were for either idealized or artificial structures; those probabilities are not to be used in the computation of the actual hole count. In order to find the hole count for a more physically realistic system, we generate cluster probabilities using Monte-Carlo simulation on the ASYNNNI model, which allows the description of states which possess an *arbitrary* degree of order.

All of the Monte-Carlo simulations are performed in the grand canonical ensemble (Glauber dynamics) using a 64 x 64 lattice (4096 sites) with periodic boundary conditions (see Ref. [10]). Simulations were performed at a temperature of 300 K for concentrations $6<z<7$; at this temperature, all of the ordered phases of interest are stable, and hence can be observed in the simulation. If the temperature of the simulations is increased, the cluster probabilities will change as some of the ordered phases become unstable (i.e. OII and OIII). At each concentration, the fraction of copper sites which exist in the configurations given in Fig. 1 are found. At each concentration, these cluster probabilities summed to 1 (correct normalization).

The ordered cluster probabilities occur in symmetric pairs: clusters which are O(1) sublattice "oxygen complements" (O(5) sites vacant) of each other have cluster probabilities which are mirror images around z=6.5. The trends illustrate exactly what one would expect: at the stoichiometry of any ordered phase (OI, OII, OIII, and the empty structure at O_6) the dominant non-zero cluster probabilities are for those clusters which are used to construct the given phase; these probabilities sum to one. The only non-zero disordered cluster probabilities are D_1, D_3, and D_5. Each of these clusters has its maximum probability when the concentration is between the stoichiometry any two of the ordered phases. All other disordered cluster probabilities (D_2, D_4, D_6, D_7, D_8) are zero across the concentration range. The fact that D_2 and D_4 vanish emphasizes the point that, at the temperatures of interest, the system prefers to form long O-Cu-O or V-Cu-V chains, with a minimum number of chain ends. Clusters D_6-D_8 have zero probability due to the highly repulsive nearest neighbor oxygen interaction. A more complete discussion is contained in Ref. [10].

The hole count as a function of concentration can now be computed from eqn. 1, using the cluster probabilities generated by Monte-Carlo and the hole coefficients from Fig. 1. The relative contribution from the ordered and disordered configurations is shown in Fig. 2(a). The total hole count, which is the sum of the two curves in Fig. 2(a), is given in Fig. 2(b) (filled circles). At

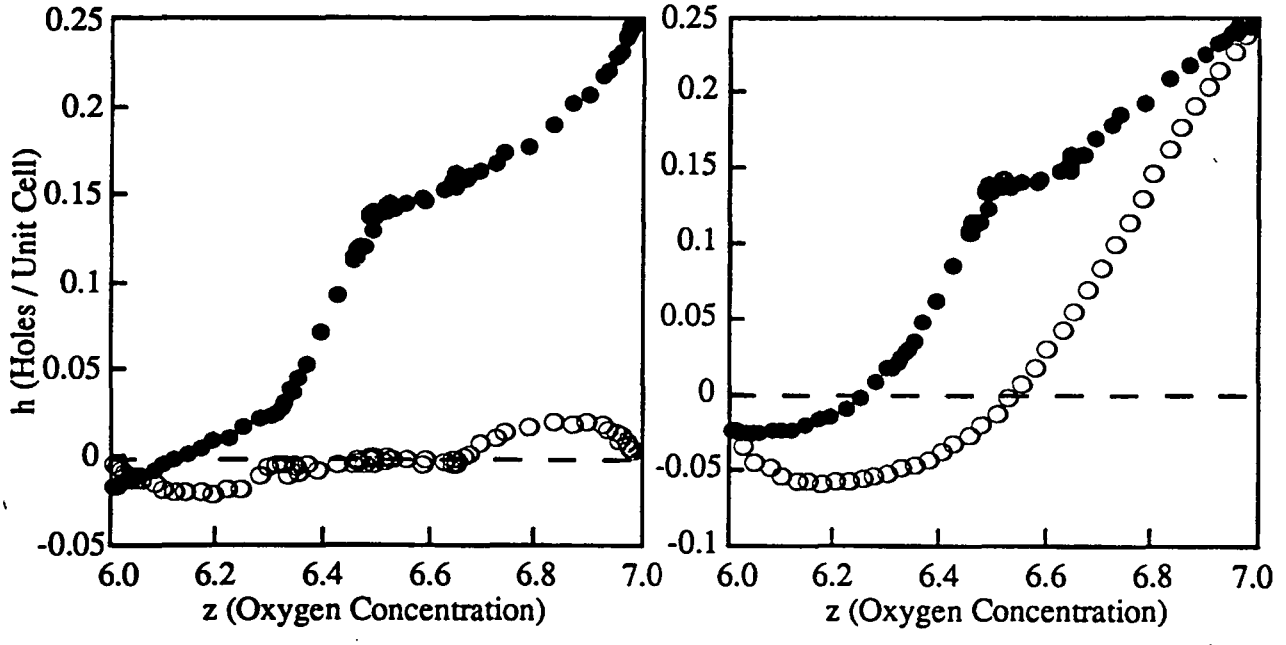


Fig. 2: Hole count (Holes/Unit Cell) as a function of oxygen content. (a) Relative contributions from ordered (filled circles) and disordered (open circles) clusters (b) Total hole count using cluster probabilities from the ASYNNNI model (filled circles). Open circles are the hole count for structures which are disordered on the O(1) sublattice.

high oxygen content, no plateau in the hole count is predicted. Rather, the hole count initially decreases almost linearly with concentration. This initial decrease is followed by a region ($6.5<z<6.75$) where the decrease is much slower, which indicates that the 60 K plateau in T_c is probably due to a relatively constant hole count. For oxygen content less than z=6.5, the hole count decreases rapidly again, and goes to zero near z=6.3. The negative final value of the hole count reflects the fact that Lambin [19] obtains a negative value for z=6.

The open circles in Fig. 2(b) show the hole count for structures which are completely disordered on the O(1) sublattice. The cluster probabilities in this case are found as products of point probabilities (see Ref's [10,19]), since all of the pair and multisite oxygen correlations vanish in the disordered phase. As has been observed in other theoretical investigations[16,18,19], the hole count for the disordered structure is lower at all concentrations than the hole count for the ordered chain structures.

II. DISCUSSION

It has already been stated that the configuration dependence of charge transfer in this system allows us to use an expansion in oxygen configuration variables. For simplicity, this study uses a cluster figure which consists of two adjacent unit cells in the basal plane. This cluster figure is the next level above examination of basal plane copper coordination, and allows for an unambiguous description of ordered structures. This choice could be altered to allow for larger clusters, as long as the choice can be made consistent with the electronic structure calculations. The only problem with expanding the size of the cluster figure is that the number of different possible configurations on this cluster rises exponentially with its size.

The method of cluster expansion is exact up to the point where the expansion coefficients are determined. In order to find the coefficients, it was necessary to use hole counts computed for artificial disordered states. Disordered cluster probabilities are found using the same distribution that Lambin used for the computation of hole counts of disordered structures [10]. Whether or not this is a completely accurate description of the disordered state, it is consistent to use the same distribution for the cluster probabilities. The solution to the system of equations was accomplished by solving a minimal least-squares problem with the singular value decomposition (SVD) of the cluster probability matrix. This method of solution is preferred when solving a linear system which involves a rank-deficient matrix, and it provides a minimal length solution vector which is unique. The hole coefficients determined by this method are merely the expansion coefficients which best represent the electronic structure data using the chosen configurational basis.

The central result presented here is the hole count as a function of oxygen content found using the configuration expansion. The filled circles in Fig. 2(b) predict the qualitative behavior of hole count correctly: the number of holes decreases with decreasing oxygen content. Unfortunately, no plateau at 90 K is predicted, contrary to the predictions of previous methods [15,17]. The initial rapid decrease in hole count can be explained by the increase in the number of chain ends (threefold basal plane Cu atoms). As the oxygen content is further decreased, OIII followed by OII ordering stabilizes the hole count by decreasing the number of chain ends. Hence, the curvature in the hole count decreases in the region $6.5<z<6.75$, creating a weak plateau. The rapid decrease in hole count past OII stoichiometry is again due to the rapid increase in the number of chain ends. The hole count for completely disordered structures (Fig. 2(b), open circles) clearly illustrates that disordered configurations yield a much lower hole count than do ordered configurations. No "plateau" in the hole count for $6.5<z<6.75$ is observed for the disordered structures because the stabilizing influence of the ordered structures (OII and OIII) is not present.

III. CONCLUSION

The problems surrounding the understanding of the superconducting behavior of $YBa_2Cu_3O_z$ as a function of its oxygen stoichiometry are numerous, and many have attempted to come up with plausible models which correctly predict this behavior. The current method of cluster expansion produces some interesting results, but it does not yield the plateau structure in the hole count that had been anticipated. This is most likely not a failure of the present model. The cluster expansion method provides evidence to support two important conclusions: 1) the 90 K plateau is *not* due to a constant amount of charge transfer (plateau in the hole count), and 2) the 60 K plateau is a direct consequence of the formation of ordered oxygen structures (OII, OIII, etc.).

Based on the above conclusions, it is clear that any correct prediction of hole count as a function of oxygen content will probably not give the predicted plateaus in T_c. In order to explain the plateau behavior of T_c, new attempts must be made to develop a theory which correlates charge transfer (hole count) with T_c. In general, it appears that such a theory must predict a nonlinear relationship between T_c and the amount of charge transfer.

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