Simple solution to problems concerning oxygen ordering in $YBa_2Cu_3O_{6+x}$

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(Received 12 February 1999)

Analysis of a simple extension of the ASYNNNI model rationalizes several hitherto unexplained structural observations of the oxygen ordering in $YBa_2Cu_3O_{6+x}$: the existence of ortho-III, ortho-V, and ortho-VIII phase correlations; suppression of the ortho-I-ortho-II transition temperature relative to that of the tetragonal-ortho-I transition; no ortho-II Bragg peaks, but a crossover from Lorentzian towards Lorentzian squared line shapes; the average chain length. It yields a realistic picture of the oxygen order of importance for the understanding of the hole doping. [S0163-1829(99)02326-7]

Oxygen ordering in the incompletely filled CuO_x layers is an important feature in the high-T_c $YBa_2Cu_3O_{6+x}$ materials. Electron transfer to the superconducting CuO_2 planes depends on the local oxygen coordination of Cu ions in the neighboring CuO_x planes. Numerous experiments have aimed at determining the oxygen configurations: electron microscopy,[1] x-ray, and neutron scattering.[2–8] However, this has only yielded indirect information. Computer modeling is needed in order to give the corresponding real-space picture. Previous model studies[9–23] are unable to account for a number of pertinent details recently observed in scattering experiments. Here we demonstrate that this can be achieved by Monte Carlo simulations using a simple extension of the ASYNNNI model,[14] with a fixed and limited set of interaction parameters V_n.

Experimental investigations of $YBa_2Cu_3O_{6+x}$ have shown the existence of phases characterized by superstructures consisting of O-Cu-O chains.[1–8] These are formed along the b direction with various periodicities na in the a direction of the plane. To explain these so-called ortho-(N) structures one has to identify a Hamiltonian. The predominant interaction between occupied oxygens sites is the Coulomb repulsion directly between oxygen ions. This results in the parameters called V_1 and V_3; whereas V_2 also includes the covalent interaction across a Cu ion for oxygens along the chains. Detailed microscopic studies[9,11–13] suggest that in particular the V_2 parameter could be dependent on the structural details such as the length of formed chains, and therefore of temperature T as well as of composition x. Including this would go beyond description possible by the simple lattice model.

The ASYNNNI model has been shown[16,22] to describe the main structural transition between the tetragonal and the ortho-I structure.[8] However, a number of new and additional experimental findings[1–7] cannot be accounted for. The long-range order predicted by the ASYNNNI model in the ortho-II phase contrasts with the observed absence thereof. The ortho-II transition occurs at significantly lower temperatures than predicted by the ASYNNNI model near $x=0.5$. Also the observed trend towards an almost squared Lorentzian line shape[6] in place of a sharp Bragg peak is unaccounted for. That feature indicates the formation of a microdomain structure with finite length chains. The ASYNNNI model also falls short of explaining the observation of higher-order superstructures with periodicities of $3a$, $5a$ and of apparently incommensurate structures; see Beyers *et al.*[1] These have recently been identified as genuine bulk structures by synchrotron and neutron-scattering investigations.[7] To describe the shortcomings, extensions of the model are needed.

Long-ranged interactions between oxygens are expected[13,15,20] on the basis of the Coulomb interaction, albeit screened. However, by introducing only *one* such extra effective parameter to the ASYNNNI model we, surprisingly, found that one can account for essentially all the outstanding problems relative to the experimental electron, neutron, and x-ray-scattering data.

We have performed Monte Carlo simulations of the oxygen ordering using the extended ASYNNNI model

$$\mathcal{H}=-V_1\sum_{\langle \mathbf{r}\mathbf{r}'\rangle}^{\mathrm{NN}}\sigma(\mathbf{r})\sigma(\mathbf{r}')-V_2\sum_{\langle \mathbf{r}\mathbf{r}'\rangle}^{\mathrm{NNNCu}}\sigma(\mathbf{r})\sigma(\mathbf{r}')-V_3\sum_{\langle \mathbf{r}\mathbf{r}'\rangle}^{\mathrm{NNNV}}\sigma(\mathbf{r})\sigma(\mathbf{r}')-V_5\sum_{\langle \mathbf{r}\mathbf{r}'\rangle}^{\mathrm{NNN2V}}\sigma(\mathbf{r})\sigma(\mathbf{r}'), \quad (1)$$

where $\sigma(\mathbf{r})=1$ or 0 depending on whether the site $\mathbf{r}$ is occupied or not and the sums run over all oxygen pairs $\langle \mathbf{r},\mathbf{r}'\rangle$, which are nearest neighbors (NN), next-nearest neighbors bridged by Cu (NNNCu), and not bridged by Cu (NNNV). The corresponding interaction parameters are V_1, V_2, and V_3. The extra interaction parameter V_5 (Ref. 24) couples pairs not bridged by a Cu and $2a$ apart (NNN2V). This was previously studied[15–19] without focusing on the local structural properties.

The appropriate value of V_5 makes it play a role only at temperatures where the O-Cu-O chains are already formed. By choosing the strength of V_5 relative to the other interaction parameters it is possible to stabilize the ortho-III phase ''by construction,'' but as the introduction of V_5 explains more than what was meant to by its design. One could request inclusion of all interactions of a screened Coulomb potential. To be consistent one should then also include other

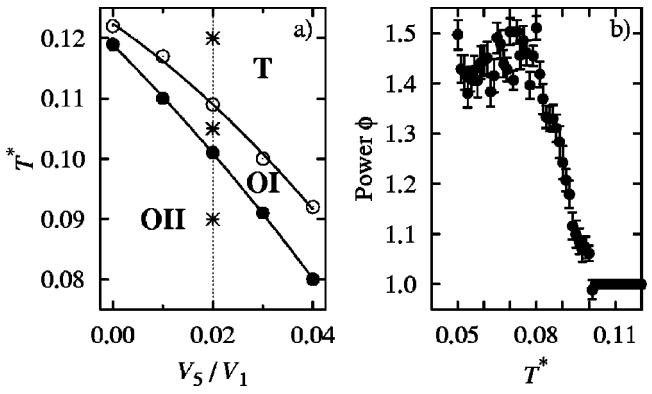

FIG. 1. (a) The variation of the transition temperatures as a function of the additional parameter V_5, for $x=0.5$. T, OI, and OII indicate the tetragonal, ortho-I and ortho-II phases. (○) and (●) are data points, lines are guides to the eye, (*) see the caption of Fig. 2. (b) Plot of the fitted Lorentzian power ϕ of the ortho-II peaks $\sim 1/(q^2+\kappa^2)^{\phi}$ for a 128×128 system with $V_5=0.02\,V_1$.

long-range interactions such as strain effects. This has been done using mean-field-like simulations[21] yielding the ortho-III, but not any ortho-V or ortho-VIII structures. A discussion of strain effects, and other mesoscopic features as twin formation,[21] is beyond the present goal. Our simulations are more accurate with respect to the phase diagram and the local structures. Due to the reciprocal space method used in Ref. 21 a wavelike structure with very short chains is proposed. This is not found in any real-space simulations.

From previous studies of the ASYNNNI model[22] where simulations have been compared to experimental data the parameters have been determined as $V_1/k_B=-5430$ K, $V_2/V_1=-0.36$, and $V_3/V_1=0.12$, where k_B is Boltzmann's constant. These values are in good agreement with the results obtained by *ab initio* electron band-structure calculations[25] and this is not violated by the small scaling of V_1 needed when including a small nonzero V_5.

Monte Carlo simulations were performed mainly at $x=0.5$ using a parallelized code by quenching 32 independent ensembles in a stepwise fashion from high temperatures. After each change in temperature the system was allowed to equilibrate for 5000 MCS (Monte Carlo steps per site). Then the structure factor $S(\mathbf{q})$, the specific heat, correlation length $1/\kappa$, the concentration $c_{\diagup}$, of the $\diagup$fold oxygen coordinated $\mathrm{Cu}^{(\diagup)}$ atoms, and the order parameter were determined by averaging typically a set of ten states, each separated by ten MCS. This scheme was found optimal for studying ordered phases, and is different from previously used strategies,[22,23] where a single ensemble was averaged over a long time series. In particular, the present method allows a study of the average domain structure that the system assumes. Importantly, the approach towards single domain states for low temperatures proceeds exceedingly slow in the simulations.[18] This is also observed in the experimental situation due to slow oxygen diffusion at low temperatures, which effectively freezes the structures at a temperature of ~ 400 K or at $T^*\equiv k_BT/|V_1|\sim 0.08$.

We have estimated that $V_5/V_1=0.02\pm0.02$ should be a reasonable interval for the investigations.[19] Figure 1(a) shows that V_5 has a significant effect in opening up the gap ΔT^* between the temperatures $T^*_{\mathrm{T\text{-}I}}$ and $T^*_{\mathrm{I\text{-}II}}$ of the tetragonal

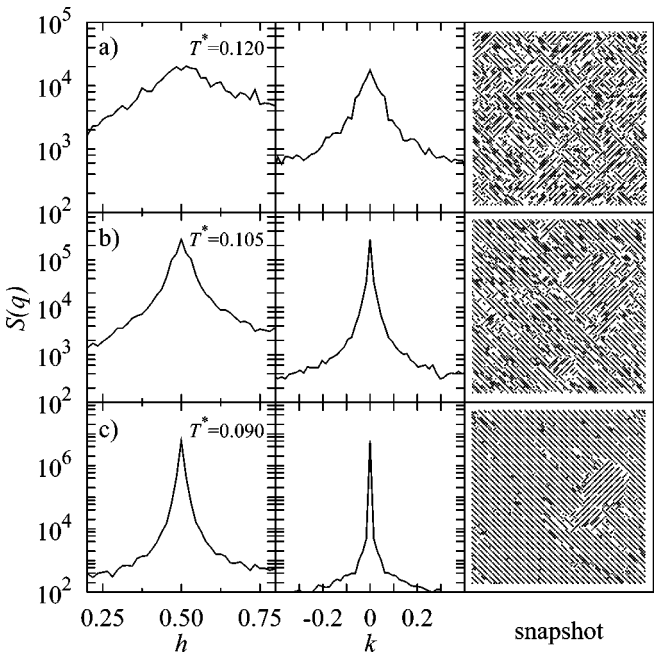

FIG. 2. Left and middle, the simulated structure factor for $x=0.5$ and $V_5=0.02V_1$ at $T^*=k_BT/|V_1|=0.12$,0.105, and 0.09 for $\mathbf{q}$ along $\{h00\}$ and $\{\frac{1}{2}k0\}$, respectively. Note the absence of a Bragg peak. Right, typical corresponding snapshots, black symbols indicate oxygen positions. Note the remaining domain structure. The chosen temperatures T^* relative to the phase diagram are indicated by (*) in Fig. 1(a).

to ortho-I and the ortho-I to ortho-II transitions. Such a gap has been observed experimentally,[5,7,8] but the size remained unexplained by the basic ASYNNNI model. A $V_5=0.02V_1$ was found optimal in explaining experimental observations and this case will be mainly discussed here. On the other hand $V_5=0.04V_1$ is too large, since it introduces ortho-III correlations in the ortho-I phase at $x=0.5$, which is not observed experimentally. For a proper estimation of the gap, we must include a small 3D coupling, V_4, between the planes.[24] This is needed to account for an observed weak correlation between the ordering in the planes. At $x=0.5$ the three-dimensional (3D) simulations[23] yields a gap $\Delta T^*=0.03$. Adding this to the gap $\Delta T^*=0.008$ found in Fig. 1 for $V_5=0.02V_1$, we obtain a total gap $\Delta T\sim170$ K, which is approaching the experimental gap $\Delta T_{\mathrm{exp}}\sim250$ K. In the simulations in Ref. 12 using a differently extended ASYNNNI model with a temperature dependent V_2 a small lowering of the ortho-II transition is discussed, but an opening of a gap is not demonstrated at $x=0.5$.

In Fig. 2 is shown the simulated structure factor $S(\mathbf{q})$ for the wave vector $\mathbf{q}$ in the $\{h00\}$ and $\{\frac{1}{2}k0\}$ directions and corresponding typical snapshots for temperatures $T^*=0.12$ in the tetragonal phase, 0.105 in the ortho-I phase and 0.09 in the ortho-II phase. It is evident and very interesting that no long-range order is developing. This has been a long-standing puzzle in experimental investigations on $YBa_2Cu_3O_{6+x}$. The temperature-dependent line shape for $\mathbf{q}$ around $\{\frac{1}{2}00\}$ shows a tendency to change towards a Lorentzian raised to a power ϕ larger than one: $S(q)\propto1/(q^2+\kappa^2)^{\phi}$. For domains with *sharp boundaries* $S(q)$ is expected to follow Porod's law, i.e., having $\phi=(d+1)/2$,

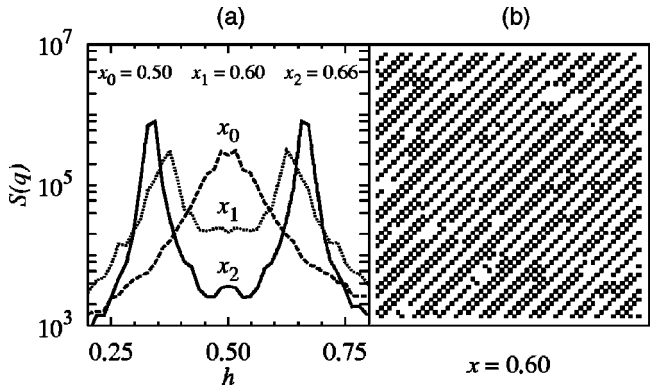

FIG. 3. (a) Left, the structure factor for a 128×128 system with oxygen stoichiometry $x=0.50,0.60,0.66$ and temperature $T^*=k_BT/|V_1|=0.08$ and $V_5=0.02V_1$. (b) Right, excerpt of snapshot showing the mixed phase. Notice the quite finite chain lengths. Similar results are obtained for $V_5=0.04V_1$.

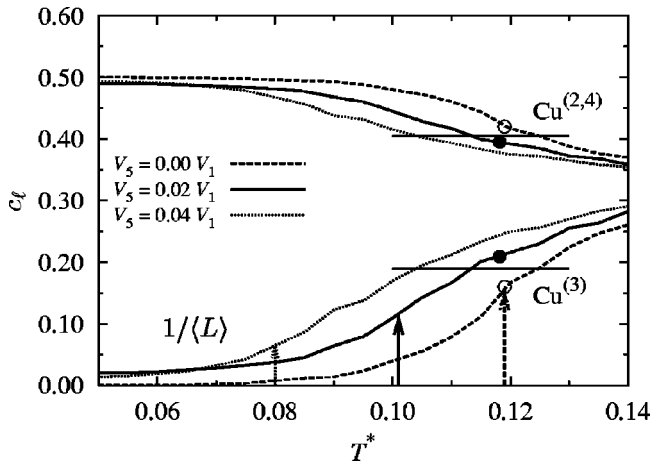

FIG. 4. The lines show the concentration c_ℓ of ℓ-coordinated $Cu^{(\ell)}$ atoms versus T^* for $x=0.5$ and various values of V_5. Thin horizontal lines represent the experimental data at $T=450$ K (Ref. 26). (○) data from the model of Ref. 12. The arrows indicate $T=450$ K obtained from the 2D OI-OII, transition, Fig. 1. (●) shows our result including both $V_5=0.02V_1$ and the 3D effect via $V_4=-0.02V_1$. Note that $\langle L\rangle$ remains finite for decreasing T^* when $V_5\neq0$.

where d is the dimensionality. It was found that the line shape is excellently fitted below the transition temperature using $\phi\neq1$. Figure 1(b). shows that ϕ approaches $\frac{3}{2}$ for $T\rightarrow0$ as expected for $d=2$, the corresponding position in the phase diagram can be read off Fig. 1(a). The actual $YBa_2Cu_3O_{6+x}$ system is having sufficient 3D interactions[24] to break the strict 2D character,[23] thus yielding $\phi=2$ for sharp boundary domains. However, in the experimental setup an integration is performed over one dimension resulting in an observed[5] line-shape power $\phi=\frac{3}{2}$ and no Bragg peaks. Hence, with 3D interactions included, our simple model is able to explain this phenomenon without resorting to an impurity based random-field effect.[5]

The presence of an ortho-III phase is indicated by peaks in the structure factor with a periodicity of 1/3. This is clearly seen in Fig. 3, which is a logarithmic plot of the structure factor for the system with oxygen stoichiometry $x=0.5$, 0.6, 0.66 at $T^*=0.08$ and with $V_5=0.02V_1$. It is by no means clear that the addition of the V_5 parameter will give rise to the ortho-V structure, as an extra even longer-range interaction might be needed to resolve a degeneracy between ortho-V and other similar phases. Nevertheless, we have observed clear indications of ortho-V domains both in the structure factor data for $x=0.6$, and in snapshots of system configurations as shown in Fig. 3. If the system had established long-range ortho-V order the peaks in the structure factor would be at $h=0.4$ and $h=0.6$, but due to the random mixture of III and V chain sequences, which one may call an ortho-VIII phase, the peaks are shifted away from these values. This is rationalizing the seemingly incommensurate phases.

In Fig. 4 is shown, for $x=0.5$, the obtained concentration c_ℓ of $Cu^{(\ell)}$ atoms with ℓ nearest oxygen neighbors (including two apical ones) for $V_5=0$, 0.02, and $0.04V_1$ as a function of T^*. For $x=0.5$ the average chain length $\langle L\rangle$ is simply[12] $\langle L\rangle=1/c_3$; it can also be found directly from the length distribution. First we notice that c_ℓ and $\langle L\rangle$ vary very smoothly through the phase transitions, see Fig. 1, indicating that $\langle L\rangle$ is not a critical variable. In order to relate T^* to a real temperature we may scale to the experimental ortho-II transition temperature $T_{\text{I-II}}$, as was done in Ref. 12. This is indicated by the arrows at the bottom line in Fig. 4. For $V_5=0$ we find c_ℓ in exact agreement with the Monte Carlo data (○) for the model in Ref. 12 in which V_2 is allowed to vary with T and x. Thus at $x=0.5$ the chain length, surprisingly, is independent of that modification of the ASYNNNI model. The introduction of V_5 has a large effect on c_ℓ. However, since $T^*_{\text{I-II}}$ decreases fast, as indicated by the arrows, the 2D simulated c_3 decreases, and hence $\langle L\rangle$ increases, as a function of V_5 at $T_{\text{I-II}}$. For $x=0.5$ the experimental data for c_ℓ at $T=450$ K[26] give $c_3=0.19$ or $\langle L\rangle=5.3$ and $c_4=0.44>c_2=0.37$, although at $x=0.5$ one would expect the latter two to be equal.[12] We have therefore plotted the average in Fig. 4 (thin horizontal lines). We have not observed any significant difference between c_2 and c_4 at $x=0.5$ in the simulations. For a proper comparison we must include the 3D coupling, the effect of which on the phase diagram can be accounted for by reducing $|V_1|$ by 17%, judged from the simulated 2D and 3D $T^*_{\text{I-II}}$ at $x=0.5$.[23] On the other hand, the effect on the ordering, and hence on c_ℓ, in adjacent planes should be negligible. Accordingly, when including V_4 the arrows on Fig. 4 moves up in T^* by up to 17%. The result for $V_5=0.02V_1$, shown as (●), gives good agreement with the experimental c_ℓ values and $\langle L\rangle=5.0$. The introduction of a finite V_5 produces a quite small $\langle L\rangle$ also for smaller T^*, see Fig. 4. This questions the validity of the infinite chain approximation used in several model studies.

With the introduction of *one* (two) extra parameter(s) the ASYNNNI model, thus extended, is able to explain several experimentally observed properties of the oxygen ordering in $YBa_2Cu_3O_{6+x}$ that the original ASYNNNI model is unable to account for. The value of the introduced extra parameter $V_5=0.02V_1$ is in accord with the estimated interaction, based on a screened Coulomb potential. Interactions to more distant neighbors are even smaller and can be neglected because their possible effects on the phase diagram occur at such low temperatures that the slowing down of the oxygen diffusion prevents a realization in $YBa_2Cu_3O_{6+x}$ as discussed by de Fontaine.[15]

The success of the present simple fixed parameter model indicates that the inherent disorder in the oxygen structure, which is always observed in $YBa_2Cu_3O_{6+x}$, may not be driven by the electron transfer between the CuO_x and CuO_2 planes. But more simply, that the variation in the copper valence is dictated by the disorder given by the oxygen interactions in $YBa_2Cu_3O_{6+x}$. This conclusion is in agreement with that no experimental evidence is found[7] for the predicted peak-splitting as a consequence of a finite chain length distribution.[11] We do not claim that the effective parameters V_n are independent of T and x, only that qualitative effects of this would be still more difficult to find in the structural data. The present study gives a more direct insight into the chain length distribution than the count of various valence Cu ions possible by NMR experiments.[26] The agreement between the simulated and measured line shapes at temperatures where oxygen diffusion becomes very slow makes it plausible that the corresponding simulated real-space snapshots represent the actual oxygen order relevant for the $YBa_2Cu_3O_{6+x}$ materials even in the superconducting phase.

We thank A. Tennant for a critical reading of the text and acknowledge SNF Grant No. 9602489 at UNI-C. D.M. would like to acknowledge the hospitality of Edinburgh Parallel Computing Center as a visitor sponsored by EU-TMR under Contract No. ERBFMGECT950051.

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