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Monte Carlo study of oxygen ordering processes in $YBa_2Cu_3O_{7-x}$

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Abstract. The order–disorder phase transition which occurs in $YBa_2Cu_3O_{7-x}$ is studied by the Monte Carlo method. The results are in agreement with those obtained by the modified cluster variation method. At $x < 0.5$ and low temperatures the phase described by the reduced wavevector $(\frac{1}{3}, 0, 0)$ is obtained on the phase diagram. The problem of establishing thermodynamic equilibrium in this system is also discussed.

In $YBa_2Cu_3O_{7-x}$, one of three phases can be observed to depend on x and temperature T: a tetragonal (TG) phase with the oxygen disordered in the CuO plane or orthorhombic (O_I or O_{II}) phases in which oxygen is ordered in O–Cu–O chains parallel to the b axis (Jorgenson *et al* 1987, Cava *et al* 1987). The phenomena related to oxygen atom ordering are usually described by the lattice gas model with competing nearest-neighbour interactions V_1, V_2 and V_3 taken into account (see, e.g., Wille *et al* 1988, Berera and de Fontaine 1989, Zubkus *et al* 1989). The calculation of the $(t = 4T/V_1, x)$ phase diagram was performed by Zubkus *et al* (1989) at $V_2/V_1 = -0.5$, $V_3/V_1 = 0.5$, by the modified cluster variation method (Zubkus and Lapinskas 1990). The method allowed the low temperature $t \simeq 0.08$ ($T \simeq 60$ K) to be attained. Zubkus *et al* (1989) also showed that the mixed phases TG + O_I and O_I + O_{II} do not exist in $YBa_2Cu_3O_{7-x}$ at low temperatures. On the other hand, the microscopic regions of phases described by reduced wavevectors $(\frac{1}{3}, 0, 0)$ and $(\frac{2}{3}, 0, 0)$ have been observed by Werder *et al* (1988) at a certain x. It was proposed by Zubkus *et al* (1989) that an introduction of the interaction constant V_4 between the next-nearest O–Cu–O chains is necessary for the occurrence of these phases (hereafter denoted as O_{III} and O_V, respectively).

In present work the (t, x) phase diagram is studied by the Monte Carlo (MC) method. It should be noted that the MC method has already been applied to study of the TG–O_I phase transition (PT) (Zhi-Xiong and Mahanti 1988, 1989, Ota and Chandraskhev 1988).

The lattice-gas Hamiltonian used in our study has the form

$$H = V_1 \sum_{ij} n_i n_j + V_2 \sum_{ij} n_i n_j + V_3 \sum_{ij} n_i n_j + V_4 \sum_{ij} n_i n_j - \mu \sum_i n_i \qquad (1)$$

where μ is the chemical potential of the system, n_i is the occupation number which is equal to unity if the ith site is occupied by oxygen and to zero in the opposite case. The first sum in (1) is taken over nearest-neighbour oxygen atoms in the CuO plane (see

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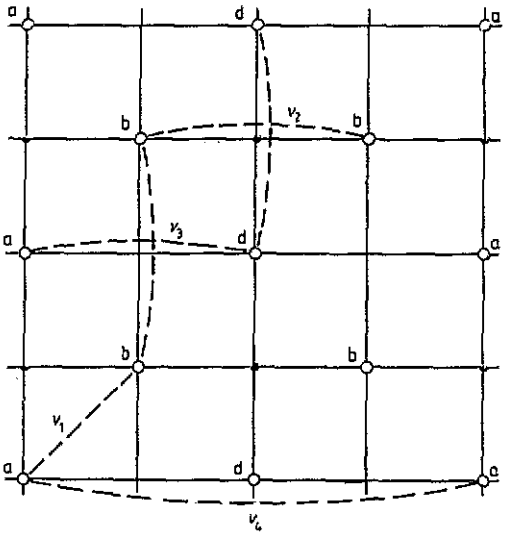

Figure 1. The schematic structure of $YBa_2Cu_3O_{7-x}$ CuO plane: ●, positions of Cu ions; O, positions of oxygen. V_1, V_2, V_3 and V_4 are the pair interaction constants between oxygen ions (see the text).

figure 1). The second and third sums are taken over next-nearest oxygen atoms depending on whether a copper atom is between these two oxygen atoms or not. The fourth sum is taken over the next-nearest O–Cu–O chains.

Let us consider first that $V_4 = 0$. Our simulation was performed on a square lattice containing 40×40 sites and employing periodic boundary conditions. The standard MC technique (Binder 1979) and the set interaction constants $V_2/V_1 = -0.5$, $V_3/V_1 = 0.5$ and $V_1 > 0$ were used. We have started from at least two different random initial configurations. The thermodynamic average of the system parameters were taken over 4000–5000 Monte Carlo steps per spin (MCS/S), the first 400–500 MCS/S being omitted. The specific heat C and susceptibility χ were calculated from the fluctuation in the energy $\langle H \rangle$ and the order parameter η, respectively:

$$C = (1/T^2)(\langle H^2 \rangle - \langle H \rangle^2) \qquad \chi = (1/T)(\langle \eta^2 \rangle - \langle \eta \rangle^2). \tag{2}$$

The order parameter is defined as follows:

$$\eta = \tfrac{1}{2}[\tfrac{1}{2}(m_a + m_d) - m_b] \tag{3}$$

where m_α is the magnetization of the sublattice α related to the sublattice coverage in the following manner:

$$m_\alpha \doteq 2c_\alpha - 1. \tag{4}$$

It is convenient to take into consideration the correlation function

$$g_{\alpha\beta} = \langle n_\alpha n_\beta \rangle \tag{5}$$

which is related to the average length of the O–Cu–O chains in the corresponding sublattices (α and β denote the nearest sublattices).

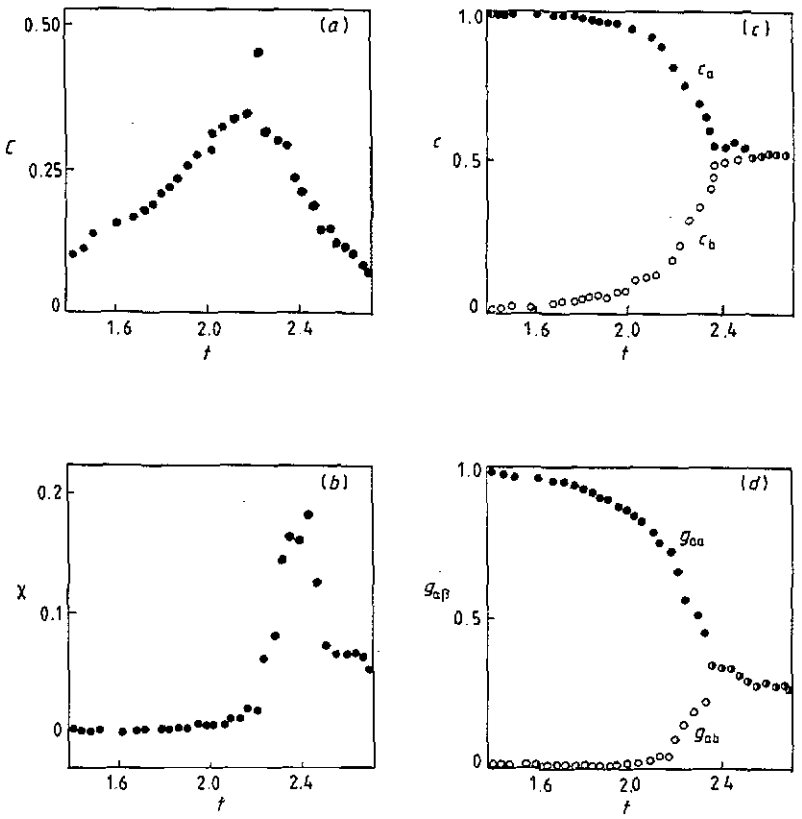

Figure 2. (*a*) The specific heat, (*b*) the susceptibility, (*c*) the partial coverage of sublattices and (*d*) the correlation factor versus temperature at $\mu/V_1 = 2.0$.

Our results can be divided into three groups depending on the μ/V_1-value. Typical results of the first group ($0.7 \leqslant \mu/V_1 \leqslant 2.0$) are presented in figure 2. The C and χ data (figures 2(*a*) and 2(*b*)) indicate a PT of second order at $t_1 \simeq 2.4$. The oxygen atoms occupy sublattice a almost completely (figure 2(*c*)) and form rather long O–Cu–O chains ($g_{aa} > 0.6$; see figure 2(*d*)) at $t < t_1$ just as the vacancy sublattice is almost empty (a and d sublattices are equivalent in this case). Note that the length of the chains increases when the temperature decreases. The oxygen atoms are equally distributed between the sublattices ($c_a = c_b$) and only short segments of the chains are formed in both a and b sublattices ($g_{aa} = g_{ab} \leqslant 0.3$) at $t > t_1$. So, a PT between the disordered TG and ordered O_I phases occurs in this case. The results of the second group ($-0.5 \leqslant \mu/V_1 \leqslant 0.3$) do not differ qualitatively from those of the first group but the PT occurs between the TG and O_{II} phases.

Figure 3 shows the results of the third group ($0.3 \leqslant \mu/V_1 \leqslant 0.7$). Two peaks of C and χ are observed at $t_1 \simeq 0.6$ and $t_2 \simeq 1.6$. As is seen from figures 3(*a*) and 3(*b*), b and d sublattices are empty at $t < t_1$ and long O–Cu–O chains are formed only in the sublattice a. All sublattices are occupied and the chains are broken at $t > t_2$. It should be noted that c_α and $g_{\alpha\beta}$ do not show the anomaly at $t = t_2$. This will be discussed below. The a and d sublattices turn out to be equilvalent at intermediate temperatures ($c_a = c_d$; see figure 3(*c*)) but the structure of the oxygen arrangement remains ordered and only

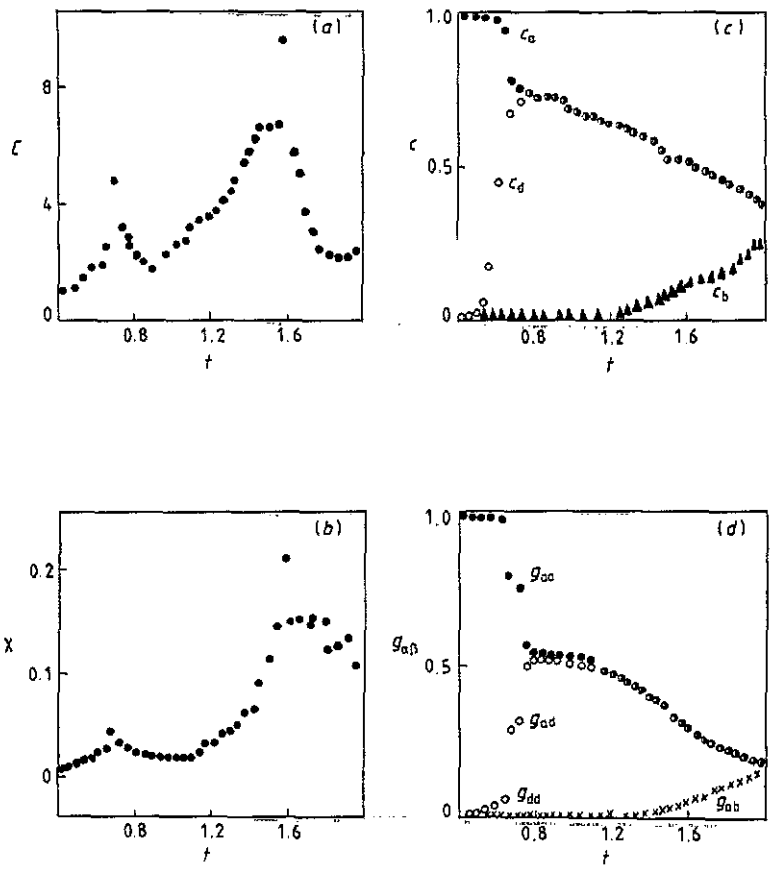

Figure 3. (*a*) The specific heat, (*b*) the susceptibility, (*c*) the partial coverage of sublattices and (*d*) the correlation factor versus temperature at $\mu/V_1 = 0.45$.

redistribution of the chain segments between a and d sublattices takes place (see figure 3(*d*)). So, the PT sequence TG $\rightarrow$ O_I $\rightarrow$ O_{II} occurs in the system in this case.

Summarizing all the results presented above, we can plot the (t, μ) phase diagram, which is shown in figure 4 together with the analytic results obtained by Zubkus *et al* (1989). Before the (t, x) phase diagram is presented, the problem of stabilizing thermodynamic equilibrium in our system has to be discussed.

It follows from symmetry of the model that $c_a = c_b = c_d$ in the TG phase. However, in our case the difference $\delta = c_a - c_b$ in the vicinity of tricritical point (according to our estimation $\mu_{tr}/V_1 \simeq 0.4$) is not equal to zero not only near the PT point but also at considerably higher temperatures (see, e.g., figure 3(*c*)). We have made attempts to increase the number of equilibrium MCS/S up to 12000 and also to take the lattice 60×60 with the same number of MCS/S, but δ remained almost unchanged. However, $\delta = 0$ at almost any $t > t_{PT}$ when the system is far from the tricritical point (see, e.g., figure 2(*c*)). We assume that $\delta \neq 0$ occurs owing to the slow stabilization of thermodynamic equilibrium of the system in the vicinity of the tricritical point. According to our estimations the region in which $\delta \neq 0$ is extended from tricritical point at distance $\Delta\mu/V_1 \simeq 0.2$–0.3.

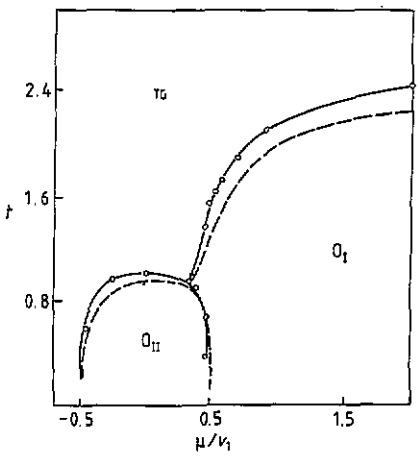

Figure 4. The (t, μ) phase diagram in the case $V_4 = 0$: – – –, results obtained by Zubkus *et al* (1989).

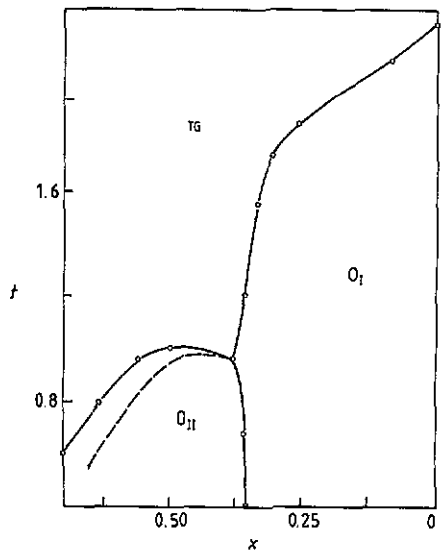

Figure 5. The (t, x) phase diagram in the case $V_4 = 0$: – – –, possible region of mixed phases from the paper by Zubkus *et al* (1989).

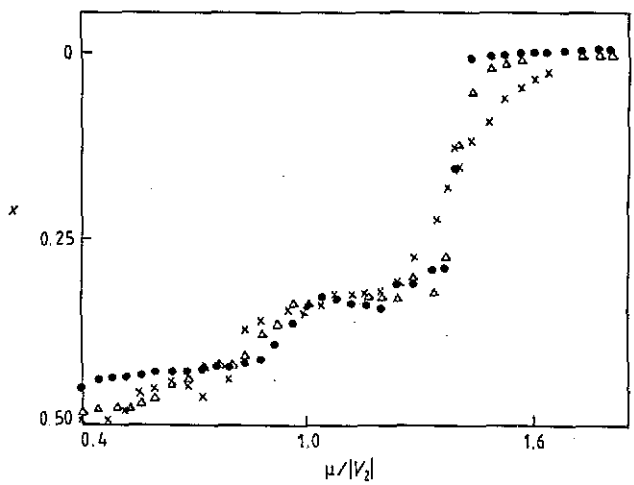

Figure 6. $\mu(x)$-dependence in the case $V_4 \neq 0$ at different values at $t' = T/|V_2|$: ●, $t' = 0.14$; △, $t' = 0.2$; ×, $t' = 0.3$.

To calculate the (t, x) phase diagram the $\mu(x)$-dependence must be known. At phase separation point a continuous behaviour (second-order PT) or jump-like behaviour (first-order PT) of $\mu(x)$ can be observed. The phases are separated and temperature hysteresis of system parameters is observed when the first-order PT occurs (see, e.g., Binder and Landau 1984). In the vicinity of the tricritical point ($x > 0.5$) the existence of mixed phases is possible (Zubkus *et al* 1989). However, as was mentioned above, thermodynamic equilibrium in our system is reached very slowly just in this region and we could

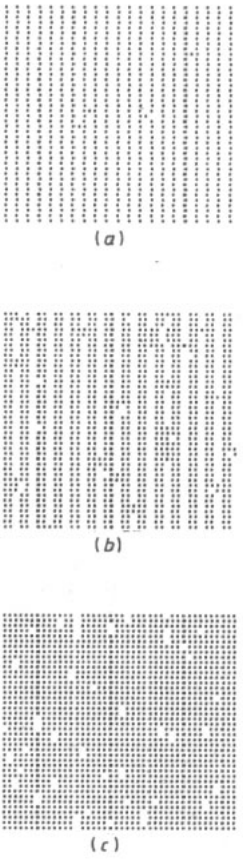

Figure 7. The distributions of empty and occupied sites of a and d sublattices (the b sublattice is not shown) obtained after 4000 equilibrium MCS/S at $\mu/|V_2|$-values of (*a*) 0.4, (*b*) 1.2 and (*c*) 1.6 and $t' = 0.2$: ●, oxygen atoms; no dot, oxygen vacancies. The sublattices are as in figure 1.

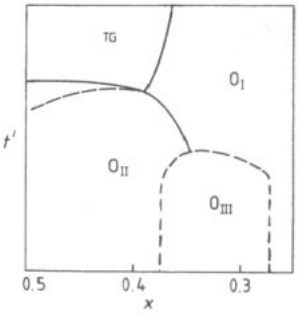

Figure 8. The schematic (t', x) phase diagram in the case $V_4 \neq 0$.

not obtain reliable data on the order of the PT. Nevertheless, it seems more reliable that only PTs of second order occur in the system in the vicinity of the tricritical point and mixed phases have not been observed in $YBa_2Cu_3O_{7-x}$ at large x and low t. The phase diagram obtained with this assumed PTs are shown in figure 5.

So the model with three interaction constants reliably describes the processes of oxygen ordering in $YBa_2Cu_3O_{7-x}$. However, there is not enough experimental data to

estimate the numerical values of the constants. For example, the estimation performed by Zubkus *et al* (1990) shows that $V_2/V_1 = -0.2$, $V_3/V_1 = 0.5$ and $V_1 = 0.54$ eV. The values differ from those used in our calculations but it was shown in their paper that the variation in V_2 does not change the phase diagram qualitatively, especially at high temperatures. Nevertheless, Horn *et al* (1987) have shown that the TG–O transition in 1:2:3 compounds is strongly influenced by the state of the carriers. The phenomena probably can be described when the interaction constant V_2 which depends on the oxygen coverage is taken into consideration. This is discussed in detail in the paper by Zubkus *et al* (1990).

When all four interaction constants V_1, V_2, V_3 and V_4 are taken into account, the thermodynamic equilibrium is reached still more slowly than in the previous case since the number of phases with similar energy increases. Therefore we have considered a simplified model. As follows from figures 2 and 3 the b sublattice is almost empty ($c_b = 0$) at $t < 0.7$ and $x < 0.5$ and therefore the sublattice has no influence on the phase diagram and we can consider the system with three interaction constants V_2, V_3 and V_4 only. This approximation is correct at $x < 0.5$ since in the opposite case the insertions of the TG phase ($c_b \neq 0$) are observed at rather low t (Zubkus *et al* 1989).

In this case we have considered the 42×42 lattice with the following set of parameters: $V_3/|V_2| = 1$, $V_4/|V_2| = 0.2$ and $V_2 < 0$. We could not obtain reliable C and χ data for this model and therefore we have estimated the PT points in a simplified way. The obtained $\mu(x)$-dependence is plotted in figure 6 at different $t' = T/|V_2|$. Three plateaux are observed in this dependence. Typical distributions of empty and occupied lattice sites are schematically shown in figure 7 at three $\mu/|V_2|$-values corresponding to plateaux in figure 6. When $\mu/|V_2| \leqslant 0.8$ (or in other terms $x \geqslant 0.4$) the phase is observed in which one empty O–Cu–O chain alternates with one occupied chain (see figure 7(*a*) at $\mu/|V_2| = 0.4$). According to the determination of phases (see, e.g., Cava *et al* 1987) this is the O_{II} phase. When $\mu/|V_2| \geqslant 1.4$ ($x \leqslant 0.2$) all O–Cu–O chains are occupied (see figure 7(*c*) at $\mu/|V_2| = 1.6$). This is the O_I phase. When $0.8 \leqslant \mu/|V_2| \leqslant 1.4$ ($0.2 \leqslant x \leqslant 0.4$) a phase is observed in which one empty O–Cu–O chain alternates with two occupied chains. In the terms proposed by Werder *et al* (1988) this is the O_{III} phase. It should be noted that in our calculation the pure O_V phase has not been obtained at any t'- and $\mu/|V_2|$-values. Because of the difficulties mentioned above we cannot obtain the exact boundaries between the O_{II}, O_{III} and O_I phases. Therefore, figure 8 shows a schematic (t', x) diagram only.

Finally we formulate the main conclusions of this work.

(i) The TG, O_I and O_{II} phase separation curves are in agreement with those obtained by the approximate analytical method (Zubkus *et al* 1989) at $x \geqslant 0.3$.

(ii) The model describes in a qualitatively correct way the oxygen ordering processes in $YBa_2Cu_3O_{7-x}$ but the quantitative characteristics of the system need separate consideration.

(iii) At $x \simeq 0.2$–0.4 the O_{III} phase in which one empty O–Cu–O chain alternates with two occupied chains may be observed in $YBa_2Cu_3O_{7-x}$.

References

Berera A and de Fontaine D 1989 *Phys. Rev.* B **39** 6727
Binder K and Landau D P 1984 *Phys. Rev.* B **30** 1477
Binder K (ed) 1979 *Monte Carlo Methods in Statistical Physics* (Berlin: Springer) section 1
Cava R J, Battlog B, Chen C H, Rietman E A, Zahurak S M and Werder D J 1987 *Phys. Rev.* B **36** 5719

Horn P M, Keane D T, Held G A, Jordan Sweet J L, Keiser D L, Holtzberg F and Rice T M 1987 *Phys. Rev. Lett.* **59** 2772
Jorgensen J D, Beno M A, Hinks D G, Soderholm L, Volin V J, Hitterman R L, Grace J D, Schuller J K, Segre C U, Zhang K and Kleefish M S 1987 *Phys. Rev.* B **36** 3608
Ota S B and Chandraskhev Rao T V 1988 *Physica* C **153–5** 257
Werder D J, Chen C H, Cava R J and Battlog B 1988 *Phys. Rev.* B **38** 5130
Wille L T, Berera A and de Fontaine D 1988 *Phys. Rev. Lett.* **60** 1065
Zhi-Xiong Cai and Mahanti S D 1988 *Solid State Commun.* **67** 287
—— 1989 *Phys. Rev.* B **40** 6558
Zubkus V E and Lapinskas S 1990 *J. Phys.: Condens. Matter* **2** 1753
Zubkus V E, Lapinskas S and Tornau E E 1989 *Physica* C **159** 501
Zubkus V E, Tornau E E, Lapinskas S and Kundrotas P J 1991 *Phys. Rev.* B **43** 13112