

Monte Carlo simulation of reorientation driven by oxygen transport in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$

György Szabó

Central Research Institute for Physics, H-1525 Budapest, P.O. Box 49, Hungary

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We studied the effect of an external field on the rearrangement of hopping particles in a quarter-filled lattice-gas model introduced to investigate the oxygen ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$. In the fourfold-degenerate, cell-doubled phase of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$, oxygen diffusion is anisotropic due to the presence of Cu-O chains. Monte Carlo simulations show that these chains prefer an orientation parallel to the applied field. In the presence of an applied field, the two possible chain directions are distinguished analytically by using a simple mean-field approximation.

Oxygen ordering leads to anisotropic oxygen diffusion in the CuO basal plane of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and related materials because the oxygen atoms prefer to move along the Cu-O chains formed in the ordered phases.¹⁻³ The arrangement of copper atoms, however, permits two Cu-O chain directions perpendicular to each other; both of them are realized in a twinned single crystal. Very recently a reorientation process driven by particle transport was observed in a two dimensional lattice-gas model exhibiting anisotropic diffusion (and ionic conduction) related to the symmetry breaking of the ordered states.⁴ In this latter model the particles form horizontal or vertical chains on a square lattice below a critical temperature. We have shown that these chains prefer the orientation parallel to the applied field. In other words, the chain direction may be modified by applying an electric field. The analogy between the two systems inspired us to investigate the effect of oxygen transport on the stable chain directions in the superconducting oxides too. This effect might be very important from the viewpoint of technology because the oxygen transport is present in the bulk when its oxygen content is changed by appropriate heat treatment.

In this work we adopt the lattice-gas model introduced by de Fontaine *et al.*⁵ to describe the oxygen ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The oxygen transport in the present Monte Carlo simulation is induced by an external field and its effect is studied at a fixed concentration. In this simple case the observed reorientation process is supported by a simple analytical calculation.

Following de Fontaine *et al.*,⁵ the lattice-gas model on a simple square lattice may be described by the Hamiltonian

$$H = \frac{1}{2} \sum_{i,j} J_{ij} n_i n_j, \tag{1}$$

where $n_i = 1$ if site i is occupied by an oxygen atom and $n_i = 0$ if it is empty. To take the role of Cu ions into consideration anisotropic second-neighbor interactions, J_2 and J_3 have been introduced as shown in Fig. 1. In our analysis a repulsive first neighbor interaction J_1 and $J_2 = -J_3 = -J_1/2$ was chosen because the ordering processes are well studied by several authors for these p parameter values.⁶⁻¹² This model possesses all the p essen-

tial features observed for oxygen ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.¹³⁻²⁰

We restrict ourselves to investigating a quarter filled lattice having an ordered, cell-doubled ground state. In this fourfold-degenerate state (called OrthoII) the particles form Cu-O chains parallel to the direction $(1,1)$ or $(1,-1)$. To describe the long-range order and the ordering processes, the lattice sites are divided into four sublattices as shown in Fig. 1. For example, in the OrthoII phase with chains parallel to the $(1,1)$ direction the particles reside dominantly in sublattice a (or c).

The dynamic behavior of the system is described by Kawasaki dynamics, i.e., the particles can jump to one of the empty nearest neighboring sites.²¹ The strength of the driving field is characterized by an electric field $\mathbf{e} = (e_1, e_2)$ measured in J_1 units; the lattice constant and the electric charge are chosen to be unity. In the presence of an electric field \mathbf{e} the jump rate from site j to k is given as

$$\Gamma(j \rightarrow k) = \frac{1}{\tau} n_j (1 - n_k) \frac{1}{1 + \exp[\beta(E_{k,j} - \mathbf{e} \cdot \mathbf{r}_{k,j})]}, \tag{2}$$

where $E_{k,j}$ is the potential energy difference between the

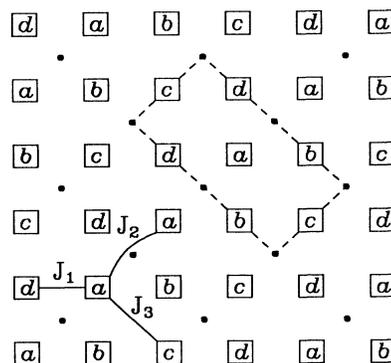


FIG. 1. Oxygen sites (squares) are divided into four sublattices labeled a, b, c, d in the CuO basal plane of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The black bullets represent copper atoms. Dashed lines display the unit cell. Pair interactions (J_n) between two oxygen sites are indicated too.

two sites, and $\mathbf{r}_{k,j}$ is the displacement vector. Here τ is an undetermined time constant which we put equal to unity when measuring times in Monte Carlo steps/particles (MCS).

The effect of electric field was studied by a standard Monte Carlo simulation on an 80×80 square lattice with 1600 particles (for details see the review by Binder and Stauffer²²). Our analysis is carried out at fixed temperature ($k_B T/J_1 = 0.22$) below the critical temperature ($k_B T_c/J_1 \approx 0.23$ at the given size) of the order-disorder phase transition for different electric fields. Each run was started from an ordered OrthoII state with a completely occupied sublattice a . Using this simulation technique we have determined the ratio of the diffusion coefficient parallel and perpendicular to the chain direction in the absence of an electric field: $D_{\parallel}/D_{\perp} \approx 1.8$.

The time evolution of the system was studied when switching on a parallel [$\mathbf{e} = e_{\parallel}(1,1)$] or perpendicular [$\mathbf{e} = e_{\perp}(1,-1)$] electric field. Following our previous work⁴ the observed process was monitored by determining $\varphi = \arctan(b_{++}/b_{+-})$ where b_{++} and b_{+-} denote the number of second-neighbor bonds along the directions (1,1) and (1,-1). The value of φ is characteristic of the dominant chain direction because $\varphi = 0^\circ$ in the initial state and $\varphi = 90^\circ$ in those OrthoII ground states having chains parallel to the (1,-1) direction. The deviation from $\varphi = 0^\circ$ (or 90°) indicates the density of defects characteristic to the state at finite temperature.

Figure 2 represents the time evolution of φ under different electric fields. In the absence of electric field (a) φ fluctuates around an average value $\varphi_0 = 9.2^\circ$. The average value of φ increases when a parallel field is switched on as shown by curve (b). A reorientation process may be observed when a perpendicular electric field is applied. Curve (c) in Fig. 2 demonstrates that the perpendicular field component e_{\perp} forces the chains to be parallel to the applied field direction. The average value of the reorientation time is about 60 000 MCS when $e_{\perp} = 0.04$. This reorientation time strongly depends on both the temperature and the magnitude of the applied field. In agreement with Ref. 4 the reorientation time decreases with increasing temperature and/or e_{\perp} . These features were observed for different sizes. Unfortunately, a more detailed numerical analysis of the reorientation time goes beyond our

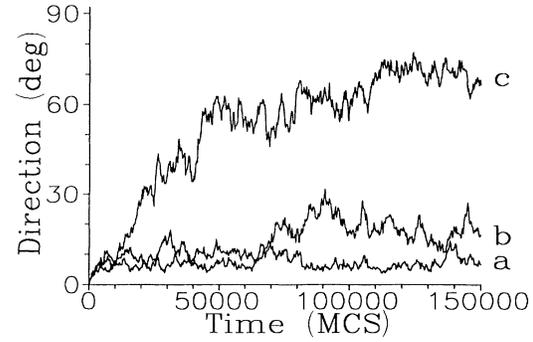


FIG. 2. Time evolution of the dominant chain direction φ at temperature $k_B T/J_1 = 0.22$ under different electrical fields: (a) no electric field, (b) parallel field with $e_{\parallel} = 0.04$, (c) perpendicular field with $e_{\perp} = 0.04$.

computer capacity in view of the long running time required. The real-time monitoring of the particle distribution visualizes that the reorientation process is analogous to the recrystallization investigated by Binder and Müller-Krumbhaar²³ in a spin system by a sudden reversal of the external magnetic field below T_c . More precisely, recrystallization is initiated by a nucleation process generated by the fluctuations and it is followed by the growth of the preferred domains. This is the reason why the reorientation process may be observed at low driving field in the vicinity of the critical temperature.

It is worth mentioning that the single-domain structure transforms into the high temperature phase when the magnitude of the parallel field exceeds a threshold value $e_{th} \approx 0.05$. This phenomenon may be interpreted as a decrease of critical temperature dependent on the applied field. A similar effect was found in a 2D lattice-gas model with repulsive first-neighbor interaction when particle transport is generated by an electric field.^{24,25}

The above results may be confirmed qualitatively by a simple analytical calculation. According to the master equation defined by Eq. (2) we can determine the time derivative of the average sublattice occupations n_{α} ($\alpha = a, b, c, d$) in mean-field approximation. The time dependence of n_{α} is determined by the equation

$$\begin{aligned} \tau \frac{dn_a}{dt} = & -n_a \{ (1-n_b)[f(E_{ba}-e_1)+f(E_{ba}+e_2)] + (1-n_d)[f(E_{da}+e_1)+f(E_{da}-e_2)] \} \\ & + (1-n_a) \{ n_b[f(E_{ab}+e_1)+f(E_{ab}-e_2)] + n_d[f(E_{ad}-e_1)+f(E_{ad}+e_2)] \} , \end{aligned} \quad (3)$$

where $f(z) = 1/[1 + \exp(\beta z)]$ and $E_{\alpha\beta}$ ($\alpha, \beta = a, b, c, d$) is the energy difference between sublattices α and β in the mean-field approximation. Further equations for the time dependence of n_b , n_c , and n_d may be derived by cyclic permutation of the indices in Eq. (3). In the absence

of an electric field the steady state ($d/dt = 0$) solution of Eqs. (3) reproduces the equation of states suggested by the Ising model (1) in a simple (Bragg-Williams) mean-field approximation. To find the solution the average sublattice occupations are parametrized as

$$\begin{aligned} n_a &= \rho + x + y, & n_b &= \rho - x + z, \\ n_c &= \rho + x - y, & n_d &= \rho - x - z, \end{aligned} \quad (4)$$

where ρ is the average concentration, x , y , and z are order parameters. The numerical solution of (3) plotted in Fig. 3 demonstrates that the system undergoes two subsequent, second-order phase transitions. On decreasing the temperature the disordered (tetragonal) phase transforms into an intermediate OrthoI phase ($k_B T_{c1}/J_1 = 0.75$) characterized by a finite x meanwhile $y = z = 0$. In this state the mean-field approximation suggests a chessboardlike spatial distribution corresponding to isotropic behavior due to the equivalence between the diagonal directions (1,1) and (1,-1). This phase transforms continuously into the OrthoII phase characterized by a finite y if $x > 0$ meanwhile z remains zero. The critical temperature of this phase transition is $k_B T_{c2}/J_1 \approx 0.50$.

The steady-state solution of Eqs. (3) may be evaluated numerically in the presence of an electric field as shown in Fig. 3. This figure demonstrates that the critical temperatures are reduced by the perpendicular field and the equivalence between sublattice occupations n_b and n_d is no longer valid in the OrthoII phase (see the insert). The application of a parallel field also reduces the critical temperatures but the symmetry of the OrthoII phase is not changed. The previous statements are supported by analytical investigation around the critical temperatures. In the equilibrium state ($e_1 = e_2 = 0$) the above critical temperatures are determined by a series expansion of Eqs. (3) with respect to x or y and z . The same method may be used to investigate the effect of the electric field on the critical temperatures. Assuming ($y = z = 0$) the series expansion with respect to x yields the following critical temperature if $e_1, e_2 \ll k_B T_{c1}(0)$:

$$T_{c1}(e_1, e_2) \approx T_{c1}(0) \left[1 - \frac{e_1^2 + e_2^2}{8(k_B T_{c1}(0))^2} \right], \quad (5)$$

where $k_B T_{c1}(0) = -(4J_1 - 2J_2 - 2J_3)\rho(1-\rho)$. In agreement with the expectation the electric field decreases the critical temperature of the tetragonal to the OrthoI phase transition independently of the field direction.

Analysis of the OrthoI-to-OrthoII phase transition is more complicated because the appearance of y results in

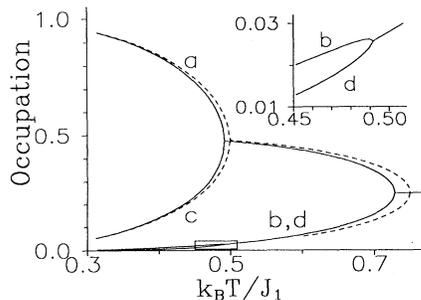


FIG. 3. Temperature dependence of sublattice occupations in the mean-field approximation for $e_1 = 0$ (dashed lines) and $e_1 = 0.2$ (solid lines). The bifurcation of n_b and n_d within the rectangle is magnified in the inset.

the anisotropy of the system. Assuming the knowledge of the value of x in the OrthoI phase the Eqs. (3) are investigated in the limit $y, z \rightarrow 0$. The leading terms of the series expansion of (3) with respect to y and z yield two equations,

$$Ay + Bz = 0, \quad Cy + Dz = 0, \quad (6)$$

where the coefficients A , B , C , and D are very complex functions. For simplicity, discussion will be concentrated on the close vicinity of the critical temperature where $A \propto (T - T_{c2}(0))$, $B, C \propto (e_1 - e_2)$, and $D = \text{const}$. The trivial ($y = z = 0$) solution of Eqs. (6) may be identified as an unstable OrthoI phase if $T < T_{c2}$. If there is no electric field ($e_1 = e_2 = 0$) or it is parallel to the chains ($e_1 = e_2$) then coefficients B and C disappear. In this case the $y \rightarrow 0$ solution can exist at the critical temperature ($T = T_{c2}(0)$) meanwhile $z = 0$. In other words, the parallel field does not affect the symmetry ($n_b = n_d$) and the decrease of the critical temperature observed by numerical solution of Eqs. (3) is not relevant. The situation is drastically modified by an electric field having a component perpendicular to the chains ($e_1 \neq e_2$) because Eqs. (6) have a nontrivial solution ($z \propto (e_1 - e_2)y$) if $AD - CB = 0$. Consequently the sublattices preceding and succeeding the occupied chains are distinguished under the particle transport. This result may be interpreted as a congestion when the particles pass through the barrier formed by the Cu-O chains in the OrthoII phase. Moreover, the decrease of the corresponding critical temperature is proportional to $(e_1 - e_2)^2$.

The above predictions of the mean-field approximation may be accepted with some criticism because mean-field theories neglect the role of fluctuations and overestimate the critical temperatures. In the present mean-field approximation the ordering process is separated into two continuous phase transitions (see Fig. 3) in contrast to the more sophisticated methods.¹³⁻²⁰ This artificial separation, however, allowed us to clarify the fact that the reorientation process is strongly related to the appearance of chains pointing out a preferred direction in the system. Here it is worth mentioning that according to the previous studies the intermediate OrthoI phase can appear at higher concentrations in agreement with the prediction of the present mean-field approximation.

In our previous model⁴ exhibiting the transport driven reorientation process the directions of elementary jump were parallel or perpendicular to the chain direction. In the present model, however, the reorientation process has been demonstrated without having elementary jumps parallel or perpendicular to the preferred direction. The common feature of these results is the existence of the transport driven reorientation observed in such models exhibiting anisotropic diffusion related to the broken symmetry of the particle distribution.

The present results suggest that the reorientation process driven by an electric field may be realized and studied experimentally in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals (or thin layers). In experimental realization, however, the magnitude of the electrical field is limited by the Joule heat produced by the dominant electron current. For-

tunately the reorientation process is not restricted to a fixed concentration because the anisotropy can appear in a wide range of concentration, and this fact implies an additional possibility for realizing the reorientation process based on particle transport driven by the variation of chemical potential. This way seems to be more suitable

with regard to technology. Very recent Monte Carlo simulations^{26,27} indicate some additional phenomena (and difficulties) when the transport is driven by a chemical-potential gradient therefore systematic analysis is required to understand this type of complex nonequilibrium phenomenon.

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