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Oxygen evolution from $\text{YBa}_2\text{Cu}_3\text{O}_7$ compound studied by Monte Carlo simulation

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Abstract. A Monte Carlo study of oxygen thermal evolution from a basal plane of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ compound is performed. Perfectly ordered copper–oxygen chains with the imposed nearest and next-nearest neighbour oxygen–oxygen interactions and energy barriers for oxygen diffusion and desorption are the starting conditions of the simulation. The characteristic peak related to the destruction of an ordered O1 structure is found. The influence of lattice size and heating rate on the obtained results is evaluated. A qualitative comparison with the experimental results is carried out when a surface barrier is considered as rate-limiting and readsorption of oxygen is introduced.

1. Introduction

Structure and electronic properties of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (YBCO) depend critically on the amount of oxygen in the sample. This is true for the intergrain and grain surface oxygen, whose effect is not quite clear, as well as for the oxygen which forms the crystal lattice of the material. It is known that the superconducting properties of YBCO are very sensitive to the concentration x , distribution and ordering of oxygen atoms in the basal CuO planes. For example, the superconducting temperature T_c of YBCO has a strongly expressed two-plateau $T_c(x)$ dependence, most likely occurring due to the transport of superconducting carriers from the basal planes [1, 2]. This process is clearly determined by the state of oxygen ordering in these planes. Depending on the concentration, oxygen can either be randomly distributed over the CuO plane (tetragonal phase, $x < 0.3$) or arranged by the strong attractive intrachain interaction into O–Cu–O chains, constituting one of several orthorhombic phases experimentally observed in YBCO compound at $x > 0.3$ [3, 4].

Due to the importance of oxygen stoichiometry in YBCO, there is still considerable interest in the kinetic processes, which can change the oxygen amount and its ordering. Usually, oxygen thermal desorption and intercalation experiments are performed in order to evaluate oxygen bonding and structure. From these experiments the activation energy E_a is obtained. In the case of desorption this energy is the sum of all steps of oxygen evolution comprising bond breaking (or activation out of lattice site), diffusion through the lattice and along the grain boundaries to the surface, and,

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finally, the desorption to the gas phase. Analysing the desorption of oxygen from YBCO, one must take into account that oxygen desorbs in several stages. First, at temperatures above 420 K, the desorption of molecular oxygen, entrapped in the intergrain material or on the surface, is observed with $E_a = 0.75$ eV/atom [5]. At higher temperatures, $T > 700$ K, the evolution of the basal-plane oxygen takes place with the activation energy being 1.1–1.2 eV/atom [6–9]. The YBCO sample becomes unstable and decomposes during a final evolution of oxygen from other oxygen-containing planes at $T > 1100$ K ($E_a = 2.8$ eV/atom) [7]. Certainly, the desorption from the basal planes is the most interesting one owing to a dramatic influence of length, distribution and ordering of copper–oxygen chains on T_c . Transformations in these chains (orthorhombic–tetragonal phase transitions), controlled by the oxygen diffusion kinetics, are supposed to be dependent on the temperature and partial pressure as well as on the heating rate and grain size effects [10]. It should be noted that the diffusion of oxygen in YBCO can be regarded as a two-dimensional process, mostly proceeding in the CuO planes [11]. Theoretical studies of diffusion in these planes were carried out assuming the system to be in a thermodynamic equilibrium. However, the desorption in YBCO is usually a non-equilibrium process in certain stages of the experiment.

In this work we perform the simulation of desorption of oxygen atoms from the free boundaries of a basal CuO plane. Nearest- and next-nearest-neighbour oxygen interactions and the barriers for oxygen hopping and desorption are taken into account. We investigate shortening and depletion of O–Cu–O chains due to heating with subsequent evolution of oxygen as a result of its diffusion to the plane boundaries. We further examine qualitatively the oxygen evolution curves and their dependence on the heating rate and lattice size as well as on the activation energy of oxygen diffusion U_0 and the desorption energy U_{des} . We try to elucidate to what extent the investigated system can be considered to be in thermodynamic equilibrium, in order, for example, to study the transition from orthorhombic to tetragonal phase. The results of our Monte Carlo simulation including the mechanism of oxygen readsorption are compared with the experimental curves of oxygen evolution.

2. Model

To describe the evolution of oxygen from a basal plane we have chosen the ASYNNNI model proposed by de Fontaine *et al* [12] commonly used for the investigation of oxygen ordering and diffusion in YBCO compound. The Hamiltonian of the interacting oxygen atoms in the ASYNNNI model is expressed as

$$H = v_1 \sum_{NN} n_i n_j + v_2 \sum_{NNN \text{ over Cu}} n_i n_j + v_3 \sum_{NNN} n_i n_j + \epsilon \sum_i n_i \quad (1)$$

Here the site occupation number is equal to 1 or 0 and the mean value $\langle n_i \rangle = x/2$, ϵ denotes the site binding energy. In a real physical system of desorbing particles ϵ can depend on the distance from the surface boundary. We do not consider this dependence, and assume that $\epsilon = 0$ over all the lattice. The values of interaction constants are taken from the total-energy band structure calculation by Sterne and Wille [13]: $v_1 = 4356$ K, $v_2 = -1516$ K and $v_3 = 696$ K. Variation of the charge due to loss of oxygen is assumed to appear only locally and it does not influence the

interactions in the rest of the lattice. The diffusion of the chosen lattice-gas system takes place via nearest-neighbour hopping with the time measured in Monte Carlo steps per site, i.e. a particle is randomly selected N times for each step and N is the total number of particles. In accordance with our model a chosen oxygen atom jumps to one of the four neighbouring sites (if it is empty) with the probability [14]

$$\begin{aligned} P &= \exp[(U_0 + H_{\text{fin}} - H_{\text{in}})/T] & H_{\text{fin}} > H_{\text{in}} \\ P &= \exp(U_0/T) & H_{\text{fin}} < H_{\text{in}}. \end{aligned} \quad (2)$$

Here H_{in} and H_{fin} are initial and final energies before and after the jump, equation (1), U_0 is the activation energy of oxygen diffusion (energy barrier between two sites for a single oxygen atom). For simplicity the attempt frequency, which usually appears before the exponent in probability, ((2)), is taken to be equal to one, implying a time scaling of the system. We start from a rectangular lattice of ordered chains arranged in the orthorhombic O_1 structure [3] with $x = 1$. The chains are initially arranged parallel to the shorter boundary directed along the b -axis on which the periodic boundary conditions are imposed. The boundary directed along the a -axis is free and it is here that oxygen desorption takes place. Further, for the atoms evolving from a basal plane, a barrier of desorption energy U_{des} is imposed on the sites located on the free boundary. We suppose that the oxygen atoms in YBCO leave the plane in this manner, because oxygen diffusion and desorption in the direction perpendicular to the chains would require considerably higher temperatures to overcome a strong short-range attraction in the chains v_2 (the energy of one atom evolution at $x = 1$ is equal to $\Delta E_b = -v_2 - 2v_3 - U_{\text{des}}$ in the former and $\Delta E_a = -2v_2 - v_3 - U_{\text{des}}$ in the latter case). For the sites located on the lattice boundary, U_0 is substituted by U_{des} when the oxygen is going to jump out of plane, but it remains U_0 if the oxygen returns to the plane from this boundary. It should be noted that the readsorption of desorbed oxygen is not taken into account in the first stage of the calculations, but it must be included in order to obtain satisfactory agreement with the experimental results.

In the experiments [6,8] the measure of oxygen evolution is the temperature dependence of the partial pressure p of the gas phase. Therefore, instead of the dependence of the desorption rate dx/dT on T , we plot the temperature dependence of dp/dT with p related to x by the ideal-gas law. We consider the sample in a chamber of constant volume V where the change of pressure due to oxygen evolution from the sample is $\Delta p \sim \Delta(xT/V)$.

3. Results and discussion

Since oxygen desorption in many cases is a non-equilibrium process (and is always non-equilibrium in our calculations unless we consider oxygen readsorption), the results depend considerably on the heating rate dT/dt and the size of lattice. The limited rate of the desorption process results in the shift of the dp/dT curve towards higher temperature for more rapid heating. Otherwise, for a very low heating rate or isothermal conditions the desorption takes place even at low temperatures (below 500 K) provided the oxygen pressure is low enough. The lattice size determines the amount of oxygen to be desorbed. Since the surface/volume ratio decreases as the sample volume increases, the larger lattice needs more time for oxygen to escape. In

the case of constant dT/dt this should cause a widening of the peak in dp/dT . This is seen from figure 1 where we have chosen two lattice sizes, 17×2048 and 33×2048 , and fixed the values of diffusion and desorption barriers $U_0 = 500$ K and $U_{des} = 0$. In all the displayed dependences we observe one well defined peak and its satellite in lower temperatures which is related to the evolution of oxygen with very short diffusion path to the surface. The nature of the satellite peak becomes clear when the starting conditions for the oxygen chains arrangement in the OI structure are slightly changed: instead of chain ends being occupied by oxygen we leave depleted last row sites at both the free ends of the lattice. As a result, the left peak is considerably diminished. In a real physical situation with higher activation and desorption barriers this peak disappears.

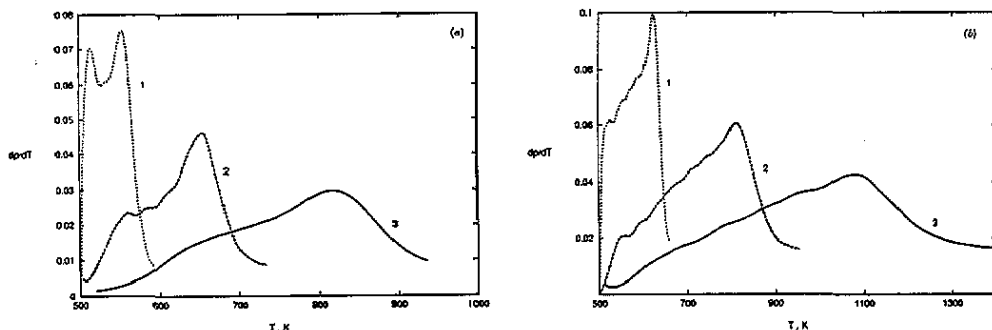


Figure 1. Temperature dependence of dp/dT at various lattice sizes and heating rates: (a) 17×2048 , (b) 33×2048 . Curve 1, $dT/dt = 0.01$; 2, 0.05; 3, 0.2 K per MC step. The values of energies $U_0 = 500$ K and $U_{des} = 0$.

One of the two rate-limiting mechanisms, namely either bulk diffusion or surface reaction (desorption), should be taken into account considering the oxygen evolution. The first one corresponds to small U_{des} and the other to large U_{des} as compared to U_0 . But it is also likely that both processes are important, and their relative significance depends on temperature.

However, if we consider marginal cases, then the first mechanism leads to the conclusion that the oxygen is inhomogeneously distributed in the lattice with almost empty regions near the edges and nearly perfect OI structure in the middle of the lattice. Oxygen evolution occurs due to depletion from the O-Cu-O chain ends and a rapid diffusion through the empty region towards the edge. Really, the initial OI phase simply melts from its borders with a constant oxygen out-diffusion rate. This situation is clearly seen in figure 2 where the influence of the activation barrier U_0 on oxygen evolution is shown for $U_{des} = 0$. The linear increase of dp/dT is due to temperature while the dx/dT remains constant during the main time of the process. The diffusion rate is controlled by U_0 and oxygen depletion from the chains is controlled by both U_0 and the oxygen-oxygen interactions. As is seen, with an increase of U_0 the low-temperature peak decreases and shifts to higher temperatures. No order-disorder transition should occur in this case and no trace of it should be observed in the $p(T)$ and dp/dT dependences.

Such a behaviour was confirmed by monitoring oxygen distribution during diffusion to the lattice boundaries. At an initial stage of oxygen evolution the OI structure

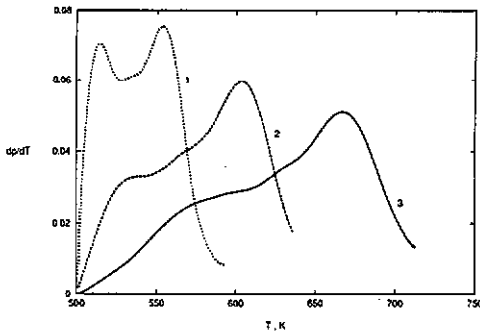


Figure 2. Temperature dependence of the oxygen evolution on the activation energy for 17×2048 lattice with $dT/dt = 0.01$ K per MC step and $U_{des} = 0$. Curve 1, $U_0 = 500$; 2, 1000; 3, 1500 K.

with the melting chain ends is observed, i.e. the decrease of oxygen concentration hardly changes the amount of 3-coordinated copper in the remaining OI structure. Other possibilities are unfavourable due to the strong intrachain interaction v_2 and the very strong nearest-neighbour repulsion v_1 which almost exclude the probability of oxygen hopping somewhere in the middle of ordered chains and, most likely, excludes other mechanisms of oxygen evolution (e.g. diffusion perpendicularly to the chains). At higher temperatures (but $T < T_{max}$) the lattice can be roughly separated in three parts: the OI chains in the middle and tetragonal-like structures with the equal occupancies of chain and vacant sites closer to the boundaries. In between these regions some kind of intermediate structure is observed. At $T = T_{max}$ the OI structure disappears, but in the centre of the sample the amount of occupied sites in the chains is slightly larger than that of the vacancies. Nevertheless, the resultant structure can be regarded as almost tetragonal, since the similarity of concentration of oxygen rows along the a -axis shows that the system is in thermodynamic equilibrium at $T > T_{max}$. The peak in figures 1–3 at T_{max} is clearly associated with the disappearing of the chain structure, since at $T > T_{max}$ oxygen diffuses and desorbs very fast.

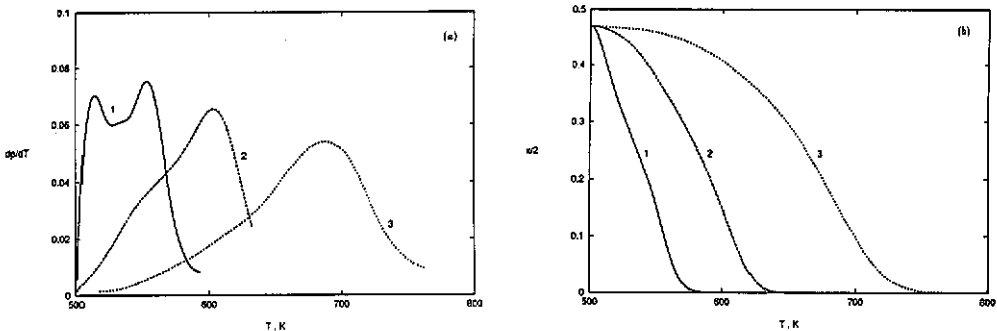


Figure 3. Temperature dependence of (a) dp/dT and (b) oxygen amount $x/2$ on desorption energy for 17×2048 lattice with $dT/dt = 0.01$ K per MC step and $U_0 = 500$ K. Curve 1, $U_{des} = 0$; 2, 2000; 3, 3000 K.

The second mechanism, specified by a large desorption barrier U_{des} , implies that the slow process of surface reaction (desorption) determines the oxygen evolution while the relatively fast bulk diffusion ensures uniform distribution of the remaining oxygen over the lattice. In figure 3(a) the dp/dT dependence on the desorption barrier U_{des} is presented. The low-temperature peak completely disappears at U_{des}

= 3000 K, i.e. at energies where the order of the ratio $U_{\text{des}}/U_0 = 6$ corresponds to that usually observed for metal surfaces [15]. The decrease in oxygen content with temperature for various values of U_{des} is depicted in figure 3(b). The robust curve with an inflection point at the high-temperature peak T_{max} is observed at $U_{\text{des}}/U_0 = 6$. One can consider the situation with the large U_{des} as a thermodynamic equilibrium of oxygen in the lattice with a uniform effective chemical potential which, however, appears to be different from that of the environment. This difference is the driving force of the desorption. In this case the behaviour of the oxygen system is the same as in a real thermodynamic equilibrium, i.e. there should exist the order-disorder phase transition between the tetragonal and orthorhombic phases at certain x and T with a kink in the concentration dependence of the effective chemical potential and a subsequent anomaly in $p(T)$ or dp/dT . We do not dare to claim that the curves 3 on figure 3(a) or 2 on figure 4 correspond to this case, because the value $U_{\text{des}} = 3000$ K is still comparable with the interaction energies v_1 , v_2 and v_3 , nevertheless they demonstrate an approach to the above-mentioned scheme. Unfortunately, our computer resources were insufficient to perform calculations with even higher U_{des} in a reasonable time. As is seen from the comparison of the curves 1 and 3 in figure 3, the out-diffusion is no longer at a constant rate, like in the first case. At $U_{\text{des}} = 3000$ K the dp/dT curve has a peak corresponding to $x \simeq 0.2$, which cannot be attributed to any phase transition but is rather a result of increasing desorption rate as the temperature increases. At temperatures above the peak there is almost no oxygen left and the dp/dT abruptly goes down. The residual dp/dT in the high-temperature limit is due to the pressure increase with the temperature according to the ideal-gas law as the total oxygen content in the chamber is constant. However, the value of residual dp/dT is much lower than that of the experiment, when the theoretical pressure was scaled (by adjusting the chamber volume) to match the experimental peak value for dp/dT . Any attempt to adjust the values U_{des} , U_0 and dT/dt in order to match both the peak and residual values of dp/dT with those of the experiment [8] failed (see e.g. curves 1 and 3 in figure 5). Moreover, the peak of the calculated dp/dT dependence corresponds to a much lower value of oxygen concentration ($x \simeq 0.2$) than that estimated from the experimental $p(T)$ dependence [8] which is approximately equal to $x \simeq 0.6$.

However, a third explanation seems to be the most probable for the experiments when the crystal-gas system reaches true thermodynamic equilibrium with increasing temperature well before all the oxygens leave the sample. In this case only the initial rise of the dp/dT has any relevance to the dynamics of oxygen out-diffusion or desorption. As these processes become faster at high temperature, thermodynamic equilibrium between the desorbed gas and the remaining oxygen of the lattice may be ensured even for dT/dt as high as 10 K min^{-1} [8]. Thus, from a certain temperature, as long as equilibrium is reached, the dp/dT does not depend either on both U_{des} and U_0 or on dT/dt . What should depend on dT/dt is the temperature at which the equilibrium is achieved. This temperature also depends on the ratio of the sample volume to the chamber volume. It is likely that the result [8], which we attempted to fit, is obtained under equilibrium in its high-temperature part. This assumption is supported by the results of [6] where the oxygen content x , obtained with a temperature ramp 10 K min^{-1} , coincides with that obtained in equilibrium starting at 900 K.

In order to verify this assumption, a flow of readsorbed oxygen was introduced in our system. We assumed the probability of oxygen reappearance on the free boundary

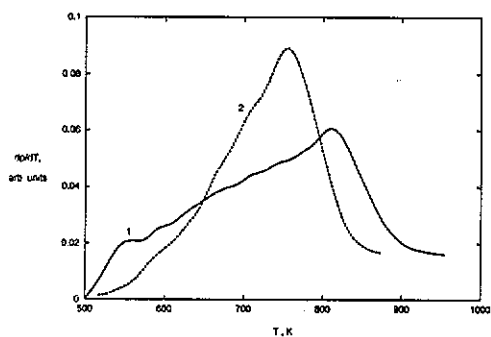


Figure 4. Comparison of two rate-limiting mechanisms of oxygen evolution for the 33×2048 lattice. Curve 1 corresponds to the parameters $U_0 = 1000$ K, $U_{des} = 0$ and $dT/dt = 0.05$ K per MC step; curve 2, $U_0 = 500$ K, $U_{des} = 3000$ K and $dT/dt = 0.01$ K per MC step.

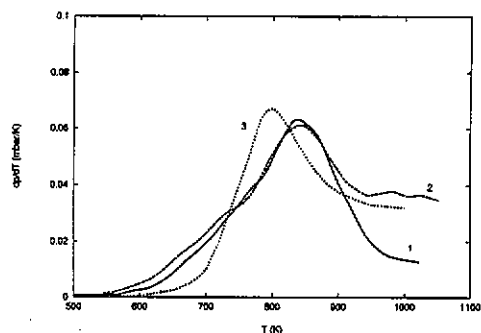


Figure 5. Oxygen evolution curves obtained for 17×2048 lattice with the parameters $dT/dt = 0.05$, $U_0 = 500$ K, $U_{des} = 3000$ K without readsorption (curve 1), $dT/dt = 0.01$, $U_0 = 1200$ K, $U_{des} = 5000$ K with readsorption (curve 2) and their comparison with the experimental results [8] (curve 3).

to be proportional to the oxygen pressure in the chamber. This modification of our model allowed us to establish thermodynamic equilibrium between the desorbed gas and the sample. The simulation of oxygen evolution with the oxygen readsorption included is presented by the curve 2 of figure 5. As is seen, the peak and residual values of the dp/dT dependence are pretty close to those of experiment [8]. The peak of dp/dT , obtained with readsorption, corresponds to the experimental value of $x \simeq 0.6$. A thorough choice of the model parameters would allow us to fit the calculated and experimental curves more closely. However, we did not seek a quantitative correspondence, since the model is anyway rather simplified.

In conclusion, we have performed a Monte Carlo simulation of oxygen evolution from a basal plane of YBCO for various rates of the surface reaction and bulk diffusion. It was pointed out that in order to explain the experimental data on oxygen evolution the surface reaction should be considered as rate-limiting. Also, the flow of readsorbed oxygen should be introduced in order to fit the experimental dp/dT dependence under the constant heating rate dT/dt . Clearly, the high-temperature part of the experiment [8] runs in the thermodynamic equilibrium and does not represent the kinetics of the oxygen. The calculations neglecting the readsorption of the oxygen could be descriptive of experiments with much larger ratio of chamber volume to the sample volume. However, one can meet the problem of accurate measurement of very low oxygen pressures. The oxygen evolution in vacuum or ambient He or N_2 [10, 11] also excludes oxygen readsorption.

Acknowledgments

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