Oxygen Ordering in YBa$_2$Cu$_3$O$_{7-y}$ in Terms of the Landau Theory

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Abstract—Oxygen ordering in nonstoichiometric compositions of YBa$_2$Cu$_3$O$_{7-y}$ is considered in terms of the Landau theory of second-order phase transitions. It is shown that there can only be ten types of homogeneous long-range order, of which two types correspond to the OI and OII phases. The Landau theory predicts that the filling of vacant positions $2(f)D^{1}_{4b}$ by oxygen must follow a scenario that is far from forming chains but compatible with known facts. Such a scenario of filling vacancies with oxygen was not considered earlier. It is demonstrated that the predicted structures can be experimentally identified from the spectra of copper ions. In the course of identification of diffraction patterns, the symmetry-allowed displacement of copper ions from central Landau theory of second-order phase transitions. It is shown that there can only be ten types of homogeneous long-range order, of which two types correspond to the OI and OII phases. The Landau theory predicts that the filling of vacant positions $2(f)D^{1}_{4b}$ by oxygen must follow a scenario that is far from forming chains but compatible with known facts. Such a scenario of filling vacancies with oxygen was not considered earlier. It is demonstrated that the predicted structures can be experimentally identified from the spectra of copper ions. In the course of identification of diffraction patterns, the symmetry-allowed displacement of copper ions from central

It is generally accepted that oxygen ordering in YBa$_2$Cu$_3$O$_{7-y}$ compositions considerably affects their remarkable electrode properties. At least two different types of ordered distribution of oxygen and vacancies in the Cu(1)(O$_{7-1-y}$)$_2$ layer separating BaO layers in these compounds with a layered perovskite structure have been established (here, $\square$ is an oxygen vacancy). The stoichiometric composition for one of the ordered O$\square$ distributions over a system of regular points $2(f)D^{1}_{4b}$ is the YBa$_2$Cu$_3$O$_7$ composition (the OI phase with an orthorhombic symmetry). It is assumed that, in the completely ordered state of the OI structure, oxygen fills precisely half the system of regular points $2(f)D^{1}_{4b}$, thus forming the chains ...Cu(1)OCu(1)O... parallel to the direction of the larger period in the basal plane of the orthorhombic phase. It is generally agreed [1, 5–7] that the second type of the O$\square$ ordering has also been established. It corresponds to compositions close to YBa$_2$Cu$_3$O$_{6.5}$ (OII phase). In this phase, the unit cell of YBa$_2$Cu$_3$O$_7$ is doubled along the $a$ axis due to alternation of the chains ...OCu(1)OCu(1)O... and ...Cu(1)$\square$Cu(1)O... oriented along the $b$ axis. A number of experimental results were interpreted as the presence of other types of O$\square$ ordered structures that correspond to the predicted stoichiometry of the layer composition [1, 5, 6, 8–12]. However, only the conclusions concerning the difference in the oxygen population densities of regular systems of points with the coordinates (1/2 0 0) and (0 1/2 0): $\varphi$, which is averaged over the sample volume, can be regarded as reliable [1, 3, 6, 13, 14]. The difference in the occupancies of these positions can be established from the fact that diffraction patterns of YBa$_2$Cu$_3$O$_{7-y}$ contain nonoverlapping reflections with a different parity in $h$ and $k$, whose difference in intensities is proportional to $\varphi$. For this reason, the theoretical works predicting the possible fine structure of equilibrium ordered oxygen–vacancy states at given $\varphi$ and $y$ in Cu(1)(O$_{7-1-y}$)$_2$ layers are of fundamental importance.

A large number of theories have been proposed for the O$\square$ ordering in Cu(1)(O$_{7-1-y}$)$_2$ layers [7–12, 15]. Most of them are only based on the inclusion of pair interactions and only in the first three coordination spheres [8, 9, 11, 15]. As shown below, this is insufficient for establishing the stability of the OII phase to heterophase fluctuations [16, 17]. Some authors constructed phenomenological theories of oxygen–vacancy ordering [7, 8, 11, 15]. However, the starting models [7] completely disregard the presence of copper atoms in the structure. As a result, the unit cell in the models describing the structure of the Cu(1)(O$_{7-1-y}$)$_2$ layer contains, according to [7], one effective atom (O$_{7-1-y}$)$_2$ instead of two atoms, as in the real YBa$_2$Cu$_3$O$_{7-y}$ structure.

In this paper, we further develop the phenomenological Landau theory of oxygen ordering in Cu(1)(O$_{7-1-y}$)$_2$ layers, which is based on the generally accepted concepts concerning the structure of OI and OII phases. It is known that, in the Landau theory, the equilibrium energies of the phases induced by the same irreducible representation, i.e., the same order parameter (OP), differ only in the phenomenological coefficients of high (higher than second) powers of the OP [18]. Since the OP components for unlimited orderings are linear functions of the probabilities of filling certain positions in the lattice with oxygen, the components of the Landau...
potential correspond, to a high degree of accuracy, to effective interactions with three, four, or a larger number of particles [16, 17, 19]. Since many-particle interactions are weaker than pair interactions, we should admit that types of ordering with the closest energies are described by the same irreducible representation or the same OP. However, it should be emphasized that the inclusion of the second OP (if it emerges as an improper order parameter) is essential; otherwise, the relationship between the phenomenology and the microscopic theory [17] is lost.

The following order of presentation of the paper is used by us. At first, we determine all possible OP that can lead to a superstructure typical of the OII phase. Then, we establish a relation between the Landau OP and the probability of populating certain vacancies accessible for oxygen in the large unit cell in the structure of the Cu(1)(O_3)_2 layer. Then, we list all possible oxygen–vacancy orderings that can occur as second-order transitions from the disordered state.2

Then, the group-theoretical method of counting stable phases is also used to determine the phases whose equilibrium free energies differ insignificantly from the energies of phases in which a second-order transition is possible. This difference in energies only appears due to many-particle interactions. In conclusion, the possible experimental identification of phases is considered.

1. STRUCTURE OF THE ORDER PARAMETER

The symmetry of YBa_2Cu_3O_6 indicates that the oxygen ordering in the Cu(1)(O_3)_2 layer, which corresponds to the orthorhombic OII phase, is determined by the two-pronged star of the vector \( \mathbf{k}^{(1)} \) (point X of the Brillouin zone (BZ) of the \( D_{4h}^1 \) group):

\[
\mathbf{k}^{(1)} = i(\pi / |a|), \quad \mathbf{k}^{(2)} = j(\pi / |b|).
\]

Here \( a \) and \( b \) are the vectors of translations of a unit cell along \( x(i) \) and \( y(j) \). The large unit cell includes eight positions populated with equal probabilities by oxygen atoms in the tetragonal phase. According to [16, 17], expressions (1) imply that the microscopic theory, which completely reflects the symmetry of the problem, should take into account interactions in at least five coordination spheres. We choose a copper atom as the origin of the Cartesian reference frame and enumerate the \( 2f \) positions in the large unit cell of the tetragonal phase:

\[
\begin{align*}
1 & : (\tau 0 0); \\
2 & : (0 \tau 0); \\
3 & : (\tau 0 \tau); \\
4 & : (0 \tau \tau); \\
5 & : (\tau 2\tau); \\
6 & : (2\tau 0); \\
7 & : (\tau 2\tau); \\
8 & : (2\tau \tau).
\end{align*}
\]

Here and below, we use Kovalev’s notation [21]: \( |a| = |b| = 2\tau \) in the tetragonal phase. Let \( P_i \) be the probability that oxygen occupies the \( i \)th position from (2). We can establish the dependence of the Landau potential \( \Phi \) on \( P_i \) using the linear combinations of \( P_i \) (i = 1, ..., 8), which form the basis for irreducible representations of the \( D_{4h}^1 \) group. The following linear combinations of \( P_i \) form the basis for the \( T_i \) representations of the \( D_{4h}^1 \) group, which are characterized by \( k^{(1)} \) and \( k^{(2)} \) (1), \( \mathbf{k} = 0 \) and \( \mathbf{k} = 1/2(\mathbf{b}_1 + \mathbf{b}_2) \) (the \( X, F, \) and \( R \) points of the BZ [21]):

\[
\begin{align*}
\chi_1(T_1) & = (P_2 + P_4 - P_6 - P_8)/2, \\
\chi_2(T_1) & = (P_1 + P_3 - P_5 - P_7)/2, \\
\eta_1(T_2) & = (P_1 - P_3 + P_5 - P_7)/2, \\
\eta_2(T_2) & = (P_2 - P_4 + P_6 - P_8)/2, \\
\Psi_1(R) & = (P_1 - P_3 - P_5 - P_7)/2, \\
\Psi_2(R) & = (P_2 - P_4 - P_6 - P_8)/2, \\
3^{1/2} & = (P_1 + P_2 + P_3 + P_4 + P_5 + P_6 + P_7 + P_8)/3^{1/2},
\end{align*}
\]

\[
= (P_1 - P_2 + P_3 - P_4 + P_5 - P_6 + P_7 - P_8)/3^{1/2}
\]

Here, \( c = 1 - y \) is the oxygen concentration in the Cu(1)(O_3)_2 layer, and \( \phi \) is the averaged difference in the probabilities of filling the positions (0 1/2 0) and (1/2 0 0). The Landau potential depends on the seven linear combinations of \( P_i \) (3)–(5) and (7) through 19 polynomials forming the complete rational basis of vector invariants of the \( L(D_{4h}^1) \) group:

\[
\begin{align*}
\Psi_1^2 + \Psi_2^2 + \Psi_1^2 \times \Psi_2^2; & \quad (\Psi_1^2 - \Psi_2^2)\phi, \\
\chi_1^2 + \chi_2^2; & \quad \chi_1^2 \times \chi_2^2; \quad (\chi_1^2 - \chi_2^2)\phi, \\
\eta_1^2 + \eta_2^2; & \quad \eta_1^2 \times \eta_2^2; \quad (\eta_1^2 - \eta_2^2)\phi, \\
\Psi_1\chi_2\eta_1 + \Psi_2\chi_1\eta_2; & \quad \Psi_1\chi_2\eta_1 + \Psi_2\chi_1\eta_2, \\
\Psi_1\chi_3\eta_1 + \Psi_4\chi_1\eta_2; & \quad \Psi_1\chi_3\eta_1 + \Psi_4\chi_1\eta_2, \\
(\Psi_1\chi_3\eta_1 + \Psi_5\chi_1\eta_2)\phi; & \quad \Psi_1\chi_3\eta_1 + \Psi_5\chi_1\eta_2, \\
\Psi_2\chi_2^2; & \quad \Psi_1^2 \times \Psi_2^2; \\
\Psi_1^2 + \eta_2^2; & \quad \chi_1^2 + \eta_2^2; \quad \eta_1^2 + \eta_2^2; \quad \phi^2.
\end{align*}
\]

2 In the publications whose authors emphasize that experiments were made on homogeneous samples, it is stated that no indications of a first-order transition between the tetragonal and orthorhombic phases of YBa_2Cu_3O_6 are observed, both upon the attainment of the orthorhombic state due to a change in temperature [20], and upon the variation of oxygen concentration [3, 4, 6].