The atomic structure of large-angle grain boundaries Σ5 and Σ13 in YBa$_2$Cu$_3$O$_{7-δ}$ and their transport properties

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ABSTRACT

We present the results of a computer simulation of the atomic structures of large-angle symmetrical tilt grain boundaries (GBs) Σ5 (misorientation angles 36.87° and 53.13°), Σ13 (misorientation angles 22.62° and 67.38°). The critical strain level $\varepsilon_{crit}$ criterion (phenomenological criterion) of Chisholm and Pennycook is applied to the computer simulation data to estimate the thickness of the nonsuperconducting layer $h_n$ enveloping the grain boundaries. The $h_n$ is estimated also by a bond-valence-sum analysis. We propose that the phenomenological criterion is caused by the change of the bond lengths and valence of atoms in the GB structure on the atomic level. The macro- and micro- approaches become consistent if the $\varepsilon_{crit}$ is greater than in earlier papers. It is predicted that the symmetrical tilt GB Σ5 $\theta = 53.13^\circ$ should demonstrate a largest critical current across the boundary.

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The major problem in the applications of YBa$_2$Cu$_3$O$_{7-δ}$ (YBCO) crystals is their low critical current density $J_c$ caused by poor current transmission at the grain boundaries (GBs). The first studies of this phenomenon, starting with [1], showed that $J_c$ across the GBs decreases drastically with increasing misorientations angle $\theta$ between grains. Subsequent studies have indicated that certain specific large-angle GBs (near-$\Sigma 1$ 90° [010] GBs) do not show this sharp decrease (for details see [2]). Several mechanisms have been suggested to explain the GBs influence on superconducting properties of YBCO (see for details [3, 4]). We will examine the explanations based on the reduction of the order parameter caused by strain. Chisholm and Pennycook [5] suggested that cores of dislocations forming low-angle GB are nontransparent for the supercurrent because superconductivity is suppressed in the region of the crystal lattice where strains achieve some critical value $\varepsilon_{crit}$. Based
on this idea and using experimental data they derived the radius of non-supercconducting region surrounding dislocation \( r_n^d \) as \( r_n^d \approx 2.9|b| \) (there \(|b|\) is the magnitude of the Burgers vector of the dislocation). On this point the authors of [3] left the semi-microscopical approach and used a strain of 1\(^\circ\) as the cut off between YBCO being superconducting and non-superconducting. This cut-off value was taken from macroscopic consideration: from the fact that, as it is noticed in [6], a 1\(^\circ\) strain causes YBCO to be tetragonal and so nonsuperconductive. This phenomenological criterion allows one to estimate the thickness of the non-superconducting layer enveloping the GB if the distribution of the strain in the vicinity of it is known. These type of estimates were used for low-angle grain boundaries within the dislocation model (see, for example, [4]).

A precise physical meaning of the phenomenological criterion of suppression of the superconductivity by strain is not well understood. Within the approach [5] the strain shifts the chemical potential of the Josephson junction (JJ) barrier at GB, and this may strongly affect the Josephson coupling, as long as the barrier is characterized by the proximity to the metal-insulator transition. Many properties of the low-angle GB JJ have been successfully explained by this model [5]. It has been pointed out in [4] that small changes of the local structure, existing in the vicinity of the GB on the microscopic level, should induce large variations of the valence of the copper ions, which control the transport properties. This may give a plausible microscopic explanation for the exponential drop in the critical current with grain boundary misorientation [1].

We propose that the phenomenological criterion of suppression of the superconductivity by strain [5] is caused by the change of the bond lengths, valence of atoms, and the number of charge carriers present in the GB structure on the atomic level. Therefore we will try to relate directly the bond-valence-sum analysis to the phenomenological strain criterion of suppression of the superconductivity. We use a very simple model and assume that all the atomic bonds in the given point of the strained lattice experience the same change of length irrespective of their orientation. Let us now consider the strain of the interatomic bonds in the vicinity of the GB and corresponding change of valence caused by it. Each bond between atoms \( i \) and \( j \) is associated with the bond valence \( s_{ij} \) that can be determined accordingly to [9] by the expression:

\[
  s_{ij} = \exp\left[\frac{(r_0 - r_{ij})}{B}\right],
\]

where \( r_{ij} \) is the bond length, \( r_0 \) and \( B \) are empirical constants. The oxidation state of atom \( i \) (atom’s valence) can be written as \( V_i = \sum_j s_{ij} \). If there is the average strain \( \varepsilon \) in the region
of lattice in question, the bond length changes and can roughly be estimated as \( r_{ij}^s \approx r_{ij}(1 + \varepsilon) \). The atom valence also changes to \( V_i^s \). It is easy to show that \( \varepsilon, V_i, \) and \( V_i^s \) are related by the following approximate relationship:

\[
\varepsilon \approx -\frac{B}{r_{ij}} \ln \frac{V_i^s}{V_i}
\] (1)

Now we can estimate \( \varepsilon_{\text{crit}} \). If we take according to [6] a valence corresponding to the superconducting state as \( V_i = 2.2 \), and a valence corresponding to the non-superconducting state as \( V_i^s = 1.8 \), according to [3] take \( B = 0.37 \), and bond length between atoms Cu1 and O4 as \( r_{ij} \approx 1.96 \text{A} \), we will get the following approximate estimation \( \varepsilon_{\text{crit}} \approx 0.038 \), that is, several times greater than the value of the phenomenological criterion derived from the macroscopical consideration. Nevertheless these two approaches become consistent if we will come back to the semi-microscopical level of consideration. The strain field of dislocation can be estimated accordingly to [10] as \( \varepsilon \sim \frac{|b|}{4\pi r} \) where \( r \) is a distance from geometrical center of dislocation. If we take \( r = r_d \approx 2.9|b| \), we would get \( \varepsilon_{\text{crit}} \approx 0.027 \). Thus we can deduce that the phenomenological criterion for the suppression of superconductivity by strain at lattice level in YBCO should be approximately 3% – 4%. The approach described above can be used to estimate the nonsuperconducting region in the vicinity of any type of the crystal lattice defects whose strain field is known. Therefore it is important to know the precise number of the \( \varepsilon_{\text{crit}} \).

At the misorientations where the dislocation cores begin to overlap, the dislocation model of GBs becomes inapplicable (the concept of individual dislocations in the boundary becomes meaningless [11]). Attempts to use the dislocation models to describe large-angle regime are not justified [7]. Therefore there is no analytical method that allows a consistent calculation of the strain field for the large-angle GBs and then to estimate analytically the thickness of the nonsuperconducting layer at GB.

In this work we apply the approach of Chisholm and Pennycook [5] for the most perfect large-angle GBs with smallest \( \Sigma \) (\( \Sigma \) is inverse of the density of coincident sites if lattices of neighboring grains are assumed to fill all space). Specifically, we get quantitative information about the atomic structure of these GBs by performing their computer simulation and determining the distribution of the strain in the vicinity of GBs. Then we use the
phenomenological criterion to determine the thickness of the nonsuperconducting region enveloping large-angle GBs. The thickness of this region is estimated also by another method: determination of valences of atoms Cu1 at the vicinity of GBs by analogy to [6].

An inter-atomic potential for YBa$_2$Cu$_3$O$_7$ based on an unscreened rigid-ion model has been developed in [12]. This potential was used for computer simulation of twin boundary (TB) [13] and TB and GB [14] in YBa$_2$Cu$_3$O$_7$. In [15], the empirical interatomic potential model for YBa$_2$Cu$_3$O$_7$ was proposed. We employ this potential [15] in this study as well as the Ewald method of calculation.

We will characterize GBs by the direction of the axis of misorientation, the angle of misorientation relatively to this axis and the geometrical plane of GB which is chosen coinciding with some simple crystal lattice plane. In this article we present results of the computer simulation of the atomic structures of the symmetrical large-angle tilt GBs with the misorientation axes [001]: \(\Sigma 5\ (310)_1/(310)_2, \ \theta = 36.87^\circ; \ \Sigma 5\ (210)_1/(210)_2 \ \theta = 53.13^\circ; \ \Sigma 13\ (510)_1/(510)_2 \ \theta = 22.62^\circ; \ \Sigma 13\ (320)_1/(320)_2 \ \theta = 67.38^\circ; \ \Sigma 29\ (520)_1/(520)_2 \ \theta = 43.60^\circ.\) Boundary planes common for the two grains are given in parenthesis. The indices 1 and 2 refer to the two neighboring crystals of bicrystal. In general, the plane which is shared by the two crystals can be described by specifying the planes in each of the two crystals which is parallel with the common boundary plane [16]. The GBs \(\Sigma 5\) and \(\Sigma 13\) were chosen as the most perfect tilt GBs that cover wide range of misorientation angles and are experimentally observable [17, 16]. The \(\Sigma 29\) GB is chosen as an example of GB close to the GBs of common type.

The configurations of models are following. The XOY-plane coincides with the basal ab-plane of the lattice, the XOZ-plane coincides with the geometrical plane of GBs. The X-axis lies at the GBs geometrical planes. The Y-axis is perpendicular to the GBs geometrical planes. The Z-axis is directed along c-axis of crystal lattice and coincides with the misorientation axis. The extent of models along X-axis in all cases are equal to one period of coincident-site-lattice of corresponding GBs. The total number of ions in model bicrystals for GBs \(\Sigma 5\ \theta = 36.87^\circ, \ \Sigma 5\ \theta = 53.13^\circ, \ \Sigma 13\ \theta = 67.38^\circ\) is 624. For GBs \(\Sigma 13\ \theta = 22.62^\circ, \ \Sigma 29\ \theta = 43.60^\circ\) it is 650.

Periodic boundary conditions were applied at all the outer faces of the computational cell. The molecular dynamics method was used. The equations of motion were solved using the velocity form of the Verlet algorithm with the starting time step not greater than \(2.5 \cdot 10^{-15}\) s. In each of cases
of GBs simulation, we started with a sharp geometric initial configuration of the boundary. It took us 224 time steps to achieve relaxed configuration in the case of GB $\Sigma 5 \theta = 36.87^\circ$, 122 in the case of GB $\Sigma 5 \theta = 53.13^\circ$, 2471 time steps in the case of GB $\Sigma 13 \theta = 22.62^\circ$, 4331 time steps in the case of $\Sigma 13 \theta = 67.38^\circ$. In the case of GB $\Sigma 29 \theta = 43.60^\circ$ the system was far from equilibrium after 3691 time steps and there are serious doubts that the equilibrium is achievable with a sharp geometric initial configuration of the $\Sigma 29$ GB. This means that, for such a boundary, the equilibrium could be reached only if a concentration of vacancies exists at the GB.

Compared to the initial and final (relaxed) configurations, the atomic structure of GB $\Sigma 5$, $\theta = 53.13^\circ$ is represented in the Fig. 1, GB $\Sigma 13$, $\theta = 22.62^\circ$ in the Fig. 2 (all distances are expressed in angstroms). The layer representation of the YBCO lattice cell is used. All layers are parallel to the basal plane. The plane consisted of Y atoms is a reflection plane. Thus it is easy to imagine the atomic structure of rest lattice along Z-axis. Comparison of the initial and final (relaxed) configurations allowed to determine the atomic displacement vectors for the all atomic sites. They are shown as arrows in the figures. It was found that for all GBs, the $z$-components of the atomic displacement vectors are significantly smaller than $x$- and $y$-components. The maximal displacements are in the atomic plane next to the geometric plane of the GB. Especially large displacements have oxygen atoms of types O4 and O3. The magnitude of displacements drastically drops with distance from the GB geometric plane.

In order to facilitate analysis of spatial displacement distribution the average atomic displacement vector $\mathbf{u}$ was found in the each atomic plane parallel to the geometric plane of GB. The components of this vector were found by averaging of corresponding components of all the atoms at this atomic plane. For GB $\Sigma 5 \theta = 36.87^\circ$, the magnitude of the average displacement vector $u = |\mathbf{u}|$ at the plane of the GB is $1.54 \cdot 10^{-1}$ Å. At the adjacent to the GB plane, $u = 5.53 \cdot 10^{-1}$ Å, at the distance from GB $y = 4.23$ Å it drops by the order of magnitude, at the distance from GB $y = 6.64$ Å it drops by the two orders of magnitude and so on. The same character of displacement distribution is occurred for GBs $\Sigma 5 \theta = 53.13^\circ$ and $\Sigma 13$. The smallest displacements are in the vicinity of GB $\Sigma 5 \theta = 53.13^\circ$, the greatest in the vicinity of GB $\Sigma 13 \theta = 67.38^\circ$. In the case of GB $\Sigma 29$ the displacement of atoms O3 and O4 from sites adjacent to the geometrical plane of GB are extremely large $\approx 3$ Å and there is no evidence of their slowing down - configuration far from relaxed after 3691 time steps calculation. It seems that in relaxed configuration we would expect depletion of oxygen atoms at the GB.
Our results agree with experimental observations of the atomic structure GB $\Sigma 5 \theta = 36.87^\circ$ that the symmetric $\Sigma 5 \theta = 36.87^\circ$ GB demonstrates no detectable depletion zone and the lack of disordered region. The displacements of oxygen atoms outward of GBs and drastic increase of relaxation time for $\Sigma 29$ allows to suggest that the GBs with large $\Sigma$ could exist only if the oxygen depletion zone is formed in the vicinity of GBs. A presence of these zones, as it have been experimentally shown in [19, 20], may essentially influence the superconducting properties of the large-angle GBs.

Now we will try to relate atomic structure and transport properties of GBs estimating $h_n$ from computer simulation data. The results of the bond-valence-sum analysis applied to the relaxed atomic structures of the GBs obtained by the computer simulation are represented in the Table. The distance from the GB plane where bond-valence sum becomes close to the same in the “bulk” is denoted as $r_n (h_n = 2r_n)$. Then we will apply strain analysis [14]. The effect does not significantly depends on the type and sign of strain [3]. Therefore to facilitate analysis only the absolute value of the average atomic displacement $|u|$ in each atomic plane parallel to GB were used to construct approximate functions $|u(r)|$ ($r$ is the distance from the geometric plane of the GB). A measure of the lattice strain $\varepsilon$ was estimated as the derivative of the approximate function with respect to $r$. The values of $h_n$ corresponding $\varepsilon_{\text{crit}} = 3\%$ are represented in the Table. Analysis of data shows for all cases that the smallest $h_n$ has GB $\Sigma 5 \theta = 53.13^\circ$. The GB $\Sigma 5 \theta = 36.87^\circ$ has slightly greater $h_n$ though its misorientation angle is smaller. The $h_n$ of other considered GBs increases with the increasing of misorientation angles. The width of non-superconducting zone $h_n$ can be used to estimate the expected tunneling current $J_c$ that exponentially decreases with $h_n$. One can expect that the more perfect special tilt GB $\Sigma 5 \theta = 53.13^\circ$ characterized by the smallest length of the periodicity along GB should demonstrate the larger $J_c$ across boundary. We can suppose that this GB has the best transport properties in comparison with other symmetrical tilt [001] GBs. The GB $\Sigma 5 \theta = 36.87^\circ$ should have smaller $J_c$ though its misorientation angle is smaller. The two symmetrical GBs, which are complementary to each other, are different on an atomic scale and therefore, as it was pointed out in [10], the electrical measurements need to be carried out on the whole range from $0^\circ$ to $90^\circ$. $J_c$ for the other analyzed GBs should decrease with the increasing of misorientation angle in agreement with the experiment. The results show that suggestion of suppression of superconductivity at GBs by strain leads to very sharp difference in $J_c$ through special GBs with small $\Sigma$. We sug-
gest that this prediction could be tested experimentally (these results are relevant only for unfaceted GBs) and could shed light on applicability of the mechanism of suppression superconductivity by strain at the GBs in high-$T_c$ superconductors.

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| Σ  | θ     | GB Plane | $h_n(A)$ bond-valence-sum analysis | $h_n(A)$ strain analysis |
|----|-------|----------|----------------------------------|------------------------|
| Σ13| 22.62°| (510)    | 11.58                            | 9.88                   |
| Σ5 | 36.87°| (310)    | 9.48                             | 7.54                   |
| Σ5 | 53.13°| (210)    | 7.06                             | 5.70                   |
| Σ29| 43.60°| (520)    | 13.00                            | 10.56                  |
| Σ13| 67.38°| (320)    | 14.42                            | 11.46                  |

Table 1: Thicknesses of nonsuperconducting layers enveloping GBs with misorientation axis [001] in YBa$_2$Cu$_3$O$_{7-δ}$. 
Figure 1: Atomic structure of GB $\Sigma 5$, $\theta = 53.63^\circ$.

Y - +, Ba - ×, Cu1 - *, Cu2 - □, O1$^{10}$ ■, O2 - ◦, O3 - -, O4 - △.

The layer #1 (atoms Cu1 and O4) is shown in Fig. 1(b). The layers #2 (atoms O1), #3 (atoms Ba) are shown in Fig. 1(c). The layers #4 (atoms Cu2), #5 (atoms O2), #6 (atoms Y) are shown in Fig. 1(d). The projections of layers #1 – #6 are shown in Fig 1(a).
Figure 2: Atomic structure of GB $\Sigma_{13}$, $\theta = 22.62^\circ$.
The designations are the same as in Fig. 1.