Transport properties of large-angle grain boundaries containing point defects in $YBa_2Cu_3O_{7-\delta}$

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The transport properties of large-angle grain boundaries (GBs) containing point defects and charges in $YBa_2Cu_3O_{7-\delta}$ (YBCO) are studied by computer simulation methods. The results of simulation of the atomic structures of large-angle symmetrical tilt GBs $\Sigma5$ (misorientation angles 36.87° and 53.13°), $\Sigma13$ (misorientation angles 22.62° and 67.38°), $\Sigma17$ (misorientation angles 28.07° and 61.93°), and $\Sigma29$ (misorientation angle 43.60°) containing point defects (neutral and charged oxygen and yttrium vacancies) are presented. The techniques of the strain analysis and the bond-valence-sum analysis are applied to determine the thicknesses of nonsuperconducting layers enveloping these GBs. Our data shows that the presence of neutral oxygen vacancies decreases the thicknesses of nonsuperconducting layers and may improve transport properties of some large-angle GBs. Adsorption capability of GBs with respect to neutral oxygen vacancies is evaluated. Its analysis demonstrates that the tilt GBs in YBCO are most probably intrinsically nonstoichiometric.

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The study of the transport properties of GBs has shown that there is a sharp decrease by orders of magnitude in the critical current density J_c across the large-angle GBs relative to the bulk. Different possible causes of this phenomenon were considered (for details see, for example, Ref. 1). The suppression of the superconductivity by strain has been well analyzed. In 1991, Chisholm and Pennycook[2] introduced the phenomenological criterion of suppression of superconductivity by strain. This criterion was successfully used by many authors for the case of low-angle GBs (see, for example, Ref. 3). In this case, the dislocation arrangement along GBs suppresses the superconductivity locally. At the large-angle regime, the dislocation model of GBs becomes inapplicable. The strain field near a large-angle GB cannot be analytically calculated. In the large-angle regime, the only reliable method for predicting the structure of a given interface is by direct modeling with appropriate interatomic potential and simulation techniques.

In Ref. 4, we carried out a computer simulation of the atomic structure of the perfect large-angle GBs (GBs without other defects on them) in the YBCO crystal lattice using the molecular dynamics method. The precise physical meaning of the phenomenological criterion of suppression of superconductivity by strain was not well understood. We suggested that it could be a direct mesoscopical revelation of the atomic level scheme:[5] small changes of the local structure in the vicinity of the GB should induce large variations of the valence of the copper ions, which control the transport properties. We related the microscopical bond-valence-sum analysis[5] to the strain analysis[6] of GBs. It was shown that the phenomenological criterion for the suppression of the superconductivity by strain at lattice level in YBCO should be approximately 3%–4%, which is several times greater than it was assumed to be when this criterion was introduced.

The relative contribution to the suppression of J_c at GBs by various mechanisms is hard to estimate. However, we would like to concentrate on another aspect of the problem. Actually, oxygen deficiency and charge presence at the GBs could substantially change the atomic structure of GBs and influence the suppression of J_c through the structural factor. The influences of the strain and oxygen deficiency at the GBs were usually considered analytically as separate causes of suppression of the superconductivity. We will try to use the computer simulation to investigate how they are related through the strain field factor. We will use the same approach to investigate the effect of the charge presence at GBs. The goal of this paper is to evaluate the influence of the real structure of GBs (presence of point defects—oxygen and yttrium vacancies and charges) on the suppression of superconductivity at these boundaries. Usually it is assumed that the presence of oxygen vacancies at GBs might increase insulating properties of GBs. It seems logical to assume that the presence of yttrium vacancies at GBs increases their ability to adsorb Ca ions (the presence of Ca at GBs essentially enhances the supercurrent[7]).

Below we present the results of the computer simulation of the symmetrical large-angle tilt GBs containing point defects with the misorientation axes [001]: $\Sigma5$ $(310)_1/(310)_2$, misorientation angle $\theta=36.87°$; $\Sigma5$ $(210)_1/(210)_2$ $\theta=53.13°$; $\Sigma13$ $(510)_1/(510)_2$ $\theta=22.62°$; $\Sigma13$ $(320)_1/(320)_2$ $\theta=67.38°$; $\Sigma17$ $(410)_1/(410)_2$ $\theta=28.07°$; $\Sigma17$ $(530)_1/(530)_2$ $\theta=61.93°$; $\Sigma29$ $(520)_1/(520)_2$ $\theta=43.60°$. Boundary planes common for the two grains are given in parenthesis. The indexes 1 and 2 refer to the two neighboring crystals of a bicrystal. The $\Sigma29$ GB is chosen as an example of a GB close to the GBs of common type. The GBs $\Sigma5$, $\Sigma13$, and $\Sigma17$ were chosen as examples of the special GBs that cover a wide range of misorientation angles and are experimentally observable in YBCO. In particular, the symmetric GBs $\Sigma5$, $\Sigma13$, and $\Sigma17$ have been observed as facets at the GBs of common type (see, for example, Ref. 8).

The configuration of the models is as follows. The XOY-plane coincides with the basal ab-plane of the lattice.

TABLE I. Thicknesses of nonsuperconducting layers enveloping grain boundaries in $YBa_2Cu_3O_{7-\delta}$ determined by strain analysis.

Σ	θ	GB plane	Vacancy in GB	h_n(Å) ε_{crit}=1%	h_n(Å) ε_{crit}=3%	h_n(Å) ε_{crit}=4%
Σ13	22.62°	(510)		15.92	9.88	8.06
Σ13	22.62°	(510)	Neutral O4	15.31	8.87	7.20
Σ13	22.62°	(510)	Charged O4	15.47	8.94	7.22
Σ17	28.07°	(410)		15.16	9.70	8.26
Σ17	28.07°	(410)	Neutral O4	15.40	9.16	8.04
Σ17	28.07°	(410)	Charged O4	17.16	10.24	8.43
Σ5	36.87°	(310)		13.62	7.54	5.96
Σ5	36.87°	(310)	Neutral O4	11.07	4.80	3.15
Σ5	36.87°	(310)	Charged O4	13.24	6.56	4.81
Σ5	53.13°	(210)		11.16	5.70	4.16
Σ5	53.13°	(210)	Neutral O4	11.85	5.76	4.15
Σ5	53.13°	(210)	Charged O4	15.60	7.32	5.30
Σ17	61.93°	(530)		14.61	9.42	8.07
Σ17	61.93°	(530)	Neutral O4	14.60	8.84	7.31
Σ17	61.93°	(530)	Charged O4	15.14	9.72	8.31
Σ13	67.38°	(320)		19.28	11.46	9.42
Σ13	67.38°	(320)	Neutral O4	18.50	10.80	8.78
Σ13	67.38°	(320)	Charged O4	15.00	9.10	6.76
Σ29	43.60°	(520)		17.28	10.56	8.80
Σ29	43.60°	(520)	Neutral O4	16.31	9.79	8.07
Σ29	43.60°	(520)	Charged O4	16.13	9.80	8.14

The XOZ-plane coincides with the geometrical plane of the GB. The *X*-axis lies in the geometrical plane of the GB. The *Y*-axis is perpendicular to the geometrical plane of the GB. The *Z*-axis is directed along the *c*-axis of the crystal lattice and coincides with the misorientation axis. The extent of the model along the *X*-axis is equal in all cases to one period of the coincident-site-lattice of the corresponding GB. The total number of ions in model bicrystals for GBs $\Sigma5$ θ=36.87°, $\Sigma5$ θ=53.13°, $\Sigma13$ θ=67.38°, and $\Sigma17$ θ=28.07° is 624. For GBs $\Sigma13$ θ=22.62°, $\Sigma17$ θ=61.93°, and $\Sigma29$ θ=43.60° it is 650.

The molecular dynamics method was used in calculations (details are described in Ref. 4). The new substantial feature is the introduction of the point defects into models of GBs. The computer simulations of point defects in YBCO was done in a number of papers (see, for example, Ref. 9). In our case, we create the point defects (oxygen and yttrium vacancies) directly in the GB (as close as possible to the geometric plane of the GB). There are 4 different positions of oxygen atoms in the crystal lattice of $YBa_2Cu_3O_{7-\delta}$. Vacancy was created at the position of O4 in the layer Cu1–O4. In each case only one point defect at GB was created. The areas of GBs are about $(1-2)\text{nm}^2$. In order to estimate the relative contribution of charges to the suppression of the supercurrent at the GBs, we introduce them into the model in a natural way: we perform the computer simulation in the cases of presence of charged and neutral vacancies separately. The creation of charged vacancies is equivalent to the appearance of the charge $(+1.3)e$ per area of GB in the case of oxygen vacancy and charge $(-1.9)e$ per area of GB in the case of yttrium vacancy (e is the elementary charge). To create an electroneutral vacancy, we, similarly to Ref. 9, doubled the charge of the closest to the vacancy atom of the same kind as removed. When the charged vacancy was created, no such doubling of the charge was done.

In each case of GB simulation, we started with a sharp geometric initial configuration of the boundary with one vacancy created at a GB. It took us hundreds or thousands of time steps to achieve a relaxed configuration. For example, in the case of GB $\Sigma5$ θ=53.13° with neutral oxygen vacancy it took 655 time steps, in the case of GB $\Sigma13$ θ=67.38° with charged oxygen vacancy it took 3023 time steps, in the case of GB $\Sigma5$ θ=36.87° with neutral vacancy of yttrium it took 6833 time steps. For all modeled GBs stable relaxed configurations were achieved. It is interesting to note that we could not achieve a stable relaxed configuration of perfect $\Sigma29$ GB.[4] It was suggested in Ref. 4 that the GBs with large Σ could exist only if the oxygen vacancies exist at GBs. Our results now confirm this prediction, at least for the GB $\Sigma29$.

To find the relation of the atomic structure of GBs to their transport properties, we estimated h_n (the thickness of the nonsuperconducting layer enveloping the GB). The bond-valence-sum analysis[5] and strain analysis[6] were applied to the relaxed atomic structures of the GBs obtained by computer simulation. The results of strain analysis are represented in Table I for the cases of neutral and charged oxygen vacancies (the data for perfect GBs $\Sigma5$, $\Sigma13$, and $\Sigma29$ were presented earlier in Ref. 4). The thickness of the non-

superconducting zone h_n is determined for the various GBs using strain analysis[6] for several different values of the critical strain level: $\varepsilon_{crit}=1\%$, $\varepsilon_{crit}=3\%$, and $\varepsilon_{crit}=4\%$.

Analyzing the data presented in Table I, we can deduce that the presence of neutral oxygen vacancies reduces h_n. For $\varepsilon_{crit}=3\%$ this reduction for most GBs is around 10%. GBs $\Sigma 5$ are the two exceptions: for GB with $\theta=53.13°$, h_n changes very slightly, but, for GB with $\theta=36.87°$, h_n decreases by approximately 40%. On the one hand, one could expect that the presence of oxygen vacancies at GBs would decrease the strain in the GB region and improve superconductivity, but, on the other hand, it could substantially influence the length of the atomic bonds and spoil GB transport properties. Therefore, one could have expected that the bond-valence-sum analysis would give the opposite results as compared to the strain analysis. In fact, the data obtained by this analysis is more scattered, but for some GBs the tendency of changing h_n by the presence of neutral oxygen vacancies is revealed quite clearly. (For example, for the GB $\Sigma 13, \theta=22.62°$, containing a neutral oxygen vacancy, h_n decreases by 40%; for the GB $\Sigma 5, \theta=36.87°$, h_n decreases by 25%). Apparently, the overall contribution of the strain relaxation of the atomic structures of these GBs exceeds the effect of local change of atomic bonds lengths in the immediate vicinity of the oxygen vacancy.

The supercurrent can pass through nonsuperconducting region of GB only by some form of tunneling[10] and must therefore show an exponential drop given by $J_c \propto \exp(-2\kappa h_n)$ where κ is a decay constant determined by the barrier height Φ ($\kappa \propto \Phi^{1/2}$).[11–13] The precise calculation of $J_c(h_n)$ taking into account all aspects of the problem is a very difficult task. This is noted repeatedly in articles and reviews on this problem. The theoretical description of J_c remains incomplete, not the least because of a variety of relevant physical mechanisms.[3] Any relation between "atomistic make-up" and "tunnel conduction" across weak links suffers from clarification of relevant mechanisms and, hence, any approach is phenomenological.[13] The transport mechanisms present in GB Josephson junctions still have not been identified in detail and are discussed controversially.[12] In view of the complexity of the problem, we estimate the change of the J_c only due to the change of the h_n caused by the presence of vacancies at GBs. If only strain induced suppression of superconducting order parameter at GBs were taken into account, the decrease of h_n may substantially increase J_c. Using, similarly to Ref. 5, the approach of Ref. 11 (this approach is considered in detail also in Refs. 12 and 13), one can show that, in the considered idealized limit, the J_c would be increased for most of the analyzed GBs. For example, for the GB $\Sigma 13, \theta=22.62°$, the increase might be by 5 times, for the GB $\Sigma 5, \theta=36.87°$—by 70 times.

The presence of the neutral yttrium vacancies for some GBs increases J_c (for example, for the GB $\Sigma 13, \theta=22.62°$, the increase is by 4 times), while for some GBs J_c is slightly decreased (for example, for the GB $\Sigma 17, \theta=61.93°$, the decrease is by 12%). Comparing the data for charged and uncharged vacancies, we can estimate the influence of charges at the GBs on their transport properties. For GBs $\Sigma 5$ the presence of charge decreases J_c substantially: by 15 times for $\Sigma 5, \theta=36.87°$; by 5 times for $\Sigma 5, \theta=53.13°$. For other GBs the effect is much smaller. The presence of charged yttrium vacancies at GBs gives a similar result.

Thus, based on these estimates, we can expect that the presence of neutral oxygen vacancies at the analyzed GBs (at least, at concentrations corresponding to the conditions of our computer experiments, which show decrease in the strain level at GBs) could increase J_c. It is necessary to stress again, however, that only the influence of the strain state at GBs on superconductivity is taken into account. Actually, J_c depends on the value of the superconducting order parameter, which is a function of the oxygen concentration. The change of the barrier height Φ caused by the vacancies presence could decrease J_c. The relative contribution of these mechanisms to the change in J_c is hard to estimate theoretically and it might be revealed in experimental observations. We can assume that if experiments would show the increase of J_c at GBs with oxygen vacancies, it would be ascribed to the strain reduced factor revealed in this work. Experiments[14] demonstrated that helium irradiation at 80 keV increases J_c of the GB junction in $YBa_2Cu_3O_{7-\delta}$. It is also experimentally shown [15] that oxygen vacancies at GBs appear as a result of irradiation. Our computer simulation data might be considered as one possible explanation of these experimental observations.

Because of the substantial effect of oxygen vacancies on the transport properties of GBs, it is interesting to evaluate the adsorption capability of these boundaries with respect to oxygen vacancies. This capability can be characterized by E_b^{GB+VO}—the binding energy of an oxygen vacancy with the GB—which could be calculated by computer simulation methods. These methods were used in studies of the interaction of vacancies with twin and grain boundaries in metals (see, for example, Ref. 16). Generally, numerical values of E_b^{GB+VO} are very sensitive to the choice of the interatomic potential. We will try to avoid this complication and evaluate only comparative values of binding energies for GBs with different angles of misorientation. One could expect that this data will be more reliable than numerical values of E_b^{GB+VO} obtained by direct calculation. It can be shown that the ratio of binding energies for two different GBs, denoted by GB1 and GB2, can be estimated as follows:

$$\frac{E_b^{GB1+VO}}{E_b^{GB2+VO}} \approx \frac{E^{GB1}-E^{GB1+VO}}{E^{GB2}-E^{GB2+VO}}, \tag{1}$$

where E_b^{GB1+VO} is the binding energy of the grain boundary GB1 and oxygen vacancy VO; E_b^{GB2+VO} is the binding energy of grain boundary GB2 and oxygen vacancy VO; E^{GB1} is the energy of the microcrystallite containing the perfect grain boundary GB1; E^{GB1+VO} is the energy of the microcrystallite containing grain boundary GB1 with oxygen vacancy in it; E^{GB2} and E^{GB2+VO} are the corresponding values for the grain boundary GB2. Computer simulation data for different GBs were used to calculate relative adsorption capabilities of different GBs with respect to oxygen vacancies. The results are presented in Table II. In all cases the grain boundary $\Sigma 5, \theta=36.87°$ was taken as GB2.

We can expect that GBs with greater Σ have a greater stress level in the region of the boundary. As a result, their

TABLE II. Relative adsorption capability of grain boundaries in $YBa_2Cu_3O_{7-\delta}$ with respect to oxygen vacancies.

GB	$\Sigma 13$	$\Sigma 17$	$\Sigma 5$	$\Sigma 5$	$\Sigma 17$	$\Sigma 13$
θ	22.62°	28.07°	36.87°	53.13°	61.93°	67.38°
$E_b^{GB+VO}/E_b^{\Sigma 5+VO}$	3.26	1.22	1.00	1.48	1.72	2.52

elastic interaction with point defects should be stronger. From this point of view, one could expect that GBs $\Sigma 5$ would have smaller adsorption capabilities, which does indeed agree with the data of Table I. However, there is a surprise: the GBs $\Sigma 13$ have greater adsorption capabilities than GBs $\Sigma 17$, even though they have smaller Σ. Another surprise is that, in the case of the GBs $\Sigma 13$, the GB with a smaller angle of misorientation has greater adsorption capability than GB with a larger angle of misorientation. Thus, it is obvious that the elastic interaction of GBs with point defects in these cases is not dominant.

For all analyzed GBs, the formation of neutral oxygen vacancies is energetically favorable ($E_b^{GB+VO}>0$). The positive nonzero adsorption capability of analyzed GBs shows that they are intrinsically nonstoichiometric. Thus, the special symmetrical tilt GBs $\Sigma 5$, $\Sigma 13$, $\Sigma 17$ in YBCO are intrinsically nonstoichiometric. We can expect that tilt GBs of common type in YBCO are all the more intrinsically nonstoichiometric. Really, the GB $\Sigma 29$, that was chosen in this study as an example of a GB close to the GBs of common type, could not even achieve a stable relaxed configuration without the presence of oxygen vacancies.

The effect of nonstoichiometry has recently been shown to be important in complex oxides.[10,17] A combination of experiments and first-principles calculations in Ref. 17 reveal that the introduction of nonstoichiometry into the GBs is energetically favorable and results in structures that are observed experimentally. The assumption that there is a strong nonstoichiometry in all YBCO grain boundaries was used in Ref. 10 to explain the observed dependence of J_c on the misorientation. According to our results, at least all special and common type symmetrical tilt GBs in YBCO are most probably intrinsically nonstoichiometric.

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