Mater.Phys.Mech.3 (2001) 108-112

PHYSICAL MECHANISMS OF REDUCTION OF CRITICAL CURRENT DENSITY ACROSS GRAIN BOUNDARIES IN HIGH-T_c SUPERCONDUCTORS*

Ilya A.Ovid'ko

Institute of Problems of Mechanical Engineering, Russian Academy of Sciences,
Bolshoj 61, Vas.Ostrov, St.Petersburg 199178, Russia

Received: December 11, 2000

Abstract. The combined effects of dilatation stresses, stoichiometric and electric-charge inhomogeneities, $d_{x^2-y^2}$ symmetry of the superconducting order parameter and the faceted microstructure of grain boundaries are theoretically examined here as those causing the experimentally observed (see, e.g., Dimos et al, Phys.Rev. B 41 (1990) 4038) reduction of the critical current density J_c across grain boundaries in high-T_c cuprates. The enhancement of J_c across high-quality twist and doped grain boundaries in high-T_c cuprates is briefly discussed.

Grain boundaries (GBs) in polycrystalline high-T_c superconductors are the subject of intensive studies motivated by unremitting attention to both the fundamentals of high-T_c superconductivity and its applications. Polycrystalline high-T_c superconductors are characterized by the transport critical-current density (J_c) whose values are essentially lower (commonly by orders) than those of their single crystalline counterparts, see, e.g., [1-4]. This property plaques high-current applications of high-T_c superconductors, that potentially are capable of being extremely wide in electrical engineering. Though there are many experimentally documented facts concerning the suppression of J_c across GBs in high-T_c cuprates, its physical mechanism(s) is (are) not unambiguously recognized yet [5-7].

Several mechanisms have been proposed relating the GB-induced reduction of J_c in high-T_c cuprates to the following factors:

(i) stress fields of GBs [8-10];

(ii) deviations from bulk stoichiometry in vicinities of GBs [11,12];

(ii) the combined effects of d-wave type symmetry of the superconducting order parameter and the faceted microstructure of GBs [13];

(iv) electric-charge inhomogeneities (band banding) [9,14-16].

However, each of these mechanisms explains only a part of experimental data, if it is treated as the sole physical mechanism responsible for suppression of high-T_c superconductivity. The main aims of this paper are to theoretically describe the effect of GBs on high-T_c superconductivity with all factors, (i) to (iv), being taken into consideration, and to analyse the J_c enhancement across high-quality twist and doped GBs in cuprates.

The key points of the suggested model are as follows: (a) GB cores (layer-like cores of high-angle boundaries and cylinder-like cores of lattice dislocations composing low-angle boundaries (Fig. 1)) are characterized by a low atomic density compared to the bulk [17,18] and, therefore, by high positive values of dilatation. Tensile dilatation stresses associated with GB cores induce weak stoichiometric inhomogeneities within GB cores, because atoms of different types in polyatomic high-T_c cuprates exhibit different behaviors in response to the dilatation stresses. More precisely, relatively large cations (e.g., Y, Ba, Cu in YBaCuO and Bi, Sr, Ca, Cu in

* This paper is based on presentation given at the International Workshop on Interface Controlled Materials: Research and Design (ICMRD), St.Petersburg, Russia, June 7-9, 2000.

Corresponding author: I.A. Ovid'ko, e-mail: ovidko@def.ipme.ru

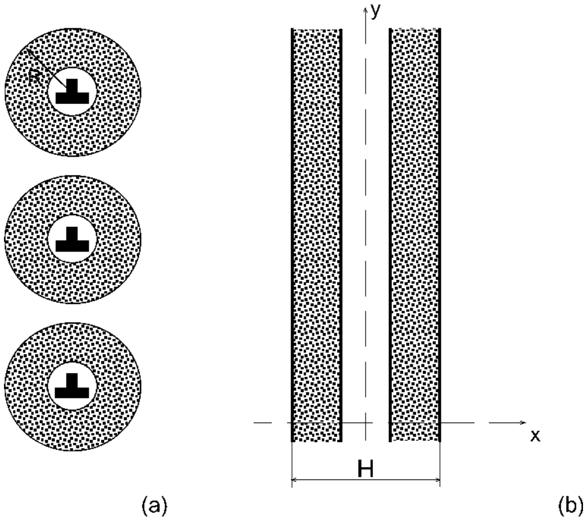

Fig. 1. Stoichiometric and electric-charge inhomogeneties within and near tilt boundaries. (a) Cores of lattice dislocations (composing low-angle boundaries) and (b) cores of high-angle boundaries are characterized by deviations from bulk stoichiometry and an excess positive charge density Q_{gb}. Their vicinities (dotted regions) are hole depletion zones.

BiSrCaCuO superconductors) substitute small anions O^{-2} in strained GB cores. The substitution processes are mediated by enhanced GB diffusion and give rise to creation of an excess positive charge density Q_{gb} (>0) of GB cores. The concentration of cations within GB cores, resulted from the substitution processes in question, weakly deviates from the bulk concentration. Actually, if the substitution does not occur, the concentration of cations within GB cores is lower than that in the bulk phase due to a low atomic density inherent to the GB phase. The subsitution of small oxygen anions by relatively large cations of other elements of a cuprate results in an increase of the initially low concentration of cations up to value close to the bulk concentration of cations. This is why experiments often do not reveal deviations from the bulk concentration of cations within GB cores. At the same time, in accordance with our model, GB cores should be deficient in oxygen, giving rise to the excess positive charge density Q_{gb}. The oxygen concentration is experimentally measured with large errors (due to low atomic weight of oxygen) [5], in which case deviations from bulk concentration of oxygen within GB cores can be not detectable in experiments.

In order to screen the excess positive charge density Q_{gb}, hole depletion zones characterized by an excess negative charge density Q_z (<0) are formed in vicinities of GB cores (Fig. 1). Such hole depletion zones have been detected in electron energy loss spectroscopy experiments [7,19,20]. Due to high sensitivity of high- T_c superconductivity to stoichiometry and hole concentration [5,7], it is natural to treat the GB cores and hole depletion zones in their vicinities as non-superconducting regions responsible for suppression of critical current density J_c across GBs in cuprates.

According to the theory of electron pairs tunneling in superconductors (see, e.g. [21]), reduction of the critical-current-density across a non-superconducting layer is approximately described by factor $\exp\{-h/\zeta\}$. Here h denotes the layer thickness and ζ the characteristic decay length which can be the tunneling length for insulating GBs or the proximity length for metallic GBs (which is close to the coherence length).

Parallel with stoichiometric and electric-charge inhomogeneities, additional geometric factors are capable of affecting the critical current density across tilt boundaries. Thus, recently, the symmetry of the order parameter in many high-T_c superconductors has been experimentally recognized as being $d_{x^2-y^2}$ [22-26] or $d_{x^2-y^2}$ mixed with an s-wave component [27]. The $d_{x^2-y^2}$ symmetry causes a dependence of the critical-current density $J_c(\alpha)$ across a GB on boundary misorientation α and orientation of boundary plane relative to adjacent grains [13,28]. With this taken into consideration, the faceted microstructure of tilt boundaries, that is often detected experimentally (see, for instance, [29-32]), also influences the transport properties of tilt boundaries in high-T_c superconductors.

With description [13] of the influence of d-symmetry and GB faceting on J_c taken into account, we find that the combined effects of dilatation-induced stoichiometric and electric-charge inhomogeneities, $d_{x^2-y^2}$ symmetry and faceting cause the following angular dependence of J_c in the case of [001] tilt boundaries:

$$\frac{J_c(\alpha)}{J_c(0^\circ)} \approx \frac{1}{S} < \prod_{m=1,2} [(\sin\alpha_m)^2 - (\cos\alpha_m)^2] >_F \int_S \left\{ \exp\frac{-h(y,z)}{\xi} \right\} dydz. \qquad (1)$$

Here α_m (m=1,2) is the smallest angle between the grain boundary plane and a principal crystallographic axis (a or b) of adjacent grain m ($\alpha_1+\alpha_2=\alpha$), and $< ... >_F$ denotes the averaging that takes into account the faceted boundary microstructure (for details, see

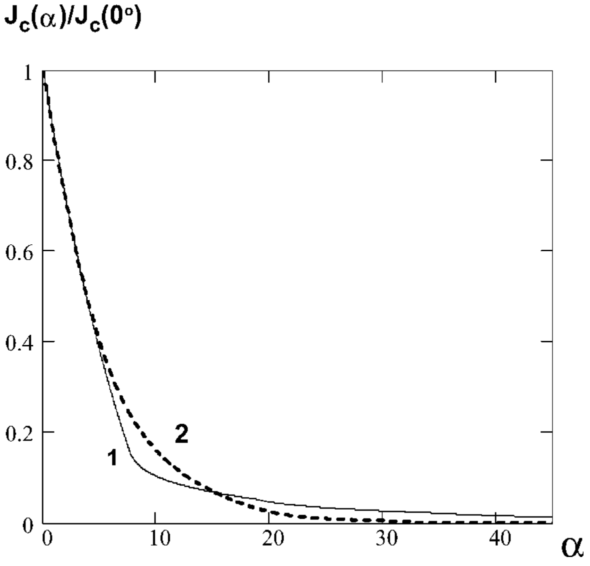

Fig. 2. Angular dependences of the critical current density J_c across [001] tilt boundaries. Solid curve 1, according to formula (1), is attributed to the combined effects of stoichiometric and electric-charge inhomogeneities, $d_{x^2-y^2}$ symmetry and the faceted microstructure of tilt boundaries. The experimentally detected [1-4] angular dependence of J_c is shown, according to [13], as dashed curve 2.

paper [13]), $h(y)$ denotes the thickness of the regions with stoichiometric and electric-charge inhomogeneities (Fig. 1), y denotes the coordinate along GB plane.

We have calculated with the help of formula (1) the angular dependence of J_c – curve 1 in Fig. 2 – attributed to the combined effects in question. In doing so, for high-angle ($\alpha \geq 20°$) boundaries, h is taken as $H \approx 3$ nm. For low-angle ($\alpha \leq 19°$) boundaries, the scale h is choosen, according to Fig. 1a, as y-dependent thickness of boundaries composed of lattice dislocation cores and their vicinities with "non-ideal" stoichiometry and charge density, that are characterized by diameters $2R \approx 3$ nm. (In this case interspacing between periodically arranged lattice dislocations composing low-angle boundaries (Fig. 1a) depends on α as [17]: $2d = b\sin(\alpha/2)$, where b is the magnitude of the dislocation Burgers vector.) In the intermediate range of α from 19° to 20°, h is taken as interpolation of corresponding values of h for low- and high-angle boundaries. Results of the averaging $< ... >_F$ are taken from paper [13] where the averaging procedure is discussed in detail. ξ is taken as 1.5 nm. (This corresponds to the coherence length in [001] planes that carry the current [5].)

The calculated dependence $J_c(\alpha)$ (curve 1 in Fig. 2) is in a satisfactory agreement with experimental data [1-4] (curve 2 in Fig. 2) for YBaCuO superconductors. This allows us to think that the idea on the combined effects of dilatation-induced stoichiometric and electric-charge inhomogeneities, $d_{x^2-y^2}$ symmetry of the superconducting order parameter and the faceted microstructure of GBs is effective in description of the dramatic distinction between the transport properties of low- and high-angle boundaries.

Now let us discuss the doping of polycrystalline high-T_c cuprates, which is capable of strongly influencing the critical current densities J_c across GBs. The remarkable experimental fact in this area is a record enhancement of J_c (by about a factor of 8) in Ca-doped YBaCuO superconductors [16].

In the framework of the suggested model, doping can decrease value of Q_{gb} and, therefore, enhance values of J_c across GBs in the following cases: (A) valency v of dopant cations is lower than that (v_k) of host cations; (B) radius r of dopant cations is larger than that (r_k) of host cations. In the case (A) the excess charge Q_{gb} decreases directly due to the doping-induced decrease of the sum charge of cations within GB core. In the case (B) the doping decreases the effect of dilatation stresses. That is, substitution of relatively small host cations by relatively large subsitute cations results in an increase of the atomic density within GB cores. As a corollary, dilatation stresses associated with GB cores are decreased, in which case so is the driving force for diffusional exchange of cations and oxygen anions within boundary cores, thus decreasing Q_{gb}. In context of the former mechanism (A) of the influence of doping on the critical current density J_c across GBs, the Ca-doping of $YBa_2Cu_3O_{7-\delta}$ bicrystals results in the experimentally detected [16] J_c enhancement due to the following. Commonly Ca^{2+} cations substitute Y^{3+} cations in YBaCuO cuprates [33]. This gives rise to a decrease of the excess positive charge density Q_{gb}, associated with $Ca^{2+} \rightarrow Y^{3+}$ substitution in GB cores, and, as a corollary, to the J_c enhancement.

In context of point (A), it is potentially interesting to experimentally test the effect of Na-doping on J_c in bi-crystalline YBaCuO. Actually, Na^{1+} cations substitute Y^{3+} cations in $YBa_2Cu_3O_{7-\delta}$ cuprates [34]. This non-isovalent doping can substantially decrease Q_{gb} and, therefore increase J_c in bi-crystalline $Y_{1-x}Na_xBa_2Cu_3O_{7-\delta}$ superconducting cuprates.

Recently, high-quality c-axis twist boundaries have been fabricated in BiSrCaCuO superconductors, that exhibit the enhanced transport properties

[35-37]. These twist boundaries carried critical current as high as their constituent single crystals (adjacent grains), regardless of the misorientation angle [35-37]. The specific structural feature of high-quality twist boundaries is the zero thickness of boundary core. That is, the twist boundaries are atomically intact and clean, with no detectable *c*-axis spacing increase or chemical changes between the BiO double layers [35,36]. A direct consequence of the zero thickness of high-quality twist boundary cores is the fact that there are no dilatation stresses associated with such cores. In context of our previous analysis, it means that high-quality twist boundaries should not affect the critical current density. The aforesaid is in correspondence with experimental data [35-37].

In general, GBs in high-T_c superconductors can undergo structural transformations induced by their stress fields and/or their elastic interaction with other defects (see experimental data [38-40] and theoretical models [41-43]). Such transformations dramatically change GB core structures and stress fields in vicinities of GBs, in which case, following the model suggested in this paper, they are capable of strongly influencing the critical current density across GBs. As a corollary, the transformations in question should be definitely taken into account in interpretation of experimental data on measurements of the critical currents in polycrystalline high-T_c superconductors.

In conclusion, the combined effects of dilatation-induced stoichiometric and electric-charge inhomogeneities at GBs, $d_{x^2-y^2}$ symmetry and GB faceting account for the experimentally observed [1-4] reduction of the critical current density J_c with increasing GB misorientation angle in high-T_c superconductors. The representations on these effects can be used in understanding the nature of the enhancement of J_c across high-quality twist and doped GBs in cuprates. A more detailed report of this study will be published in paper [44].

Many thanks are due to R.Masumura and C.Pande for valuable discussions. This work was supported, in part, by the Office of US Naval Research (grant N00014-99-1-0896) and RFBR (grant 01-02-16853).

REFERENCES

[1] D.Dimos, P.Chaudhari, J.Mannhart and F.K.LeGoues // *Phys.Rev.Lett.* **61** (1988) 219.

[2] D.Dimos, P.Chaudhari and J.Mannhart // *Phys.Rev.B* **41** (1990) 4038.

[3] Z.G.Ivanov, P.A.Nilsson, D.Winkler, J.A.Alarco, T.Claeson, E.A.Stepantsov and A.Ya.Tzalenchuk // *Appl.Phys.Lett.* **59** (1991) 3030.

[4] S.E.Russek, D.K.Lathrop, B.H.Moeckly, R.A.Buhrmann and D.H.Shin // *Appl.Phys.Lett.* **57** (1990) 1155.

[5] S.E.Babcock and J.L.Vargas // *Annu. Rev. Mater. Sci.* **25** (1995) 193.

[6] M.Prester // *Super. Sci. Technol.* **11** (1998) 333.

[7] N.D. Browning, E.M. James, K. Kyosuke, I. Arslan, J.P. Buban, J.A. Zaborac, S.J. Pennycook, Y. Xin and G. Duscher // *Rev. Adv. Mater. Sci.* **1** (2000) 1.

[8] M.F.Chisholm and S.J.Pennycook // *Nature* **351** (1991) 47.

[9] A.Gurevich and E.A.Pashitskii // *Phys.Rev.B* **57** (1998) 13878.

[10] D.Agassi, C.S.Pande and R.A.Masumura// *Phys. Rev. B* **52** (1995) 16237.

[11] D.M.Kroeger, A.Choudhury, J.Brynestad, R.K.Williams, R.A.Padgett and W.A.Coghlan // *J.Appl.Phys.* **64** (1988) 331.

[12] H. Betouras and R. Joynt // *Physica C* **250** (1995) 256.

[13] H.Hilgenkamp, J.Mannhart and B.Mayer // *Phys.Rev.B* **53** (1996) 14586.

[14] H.Hilgenkamp and J.Mannhart // *Appl. Phys. Lett.* **73** (1998) 265.

[15] J.Mannhart and H.Hilgenkamp // *Supercond. Sci. Technol.* **10** (1997) 880.

[16] A. Schmehl, B. Goetz, R.R. Schulz, C.W. Schneider, H. Bielefeldt, H. Hilgenkamp and J. Mannhart // *Europhys. Lett.* **47** (1999) 110.

[17] A.P.Sutton and R.W.Baluffi, *Interfaces in Crystalline Materials* (Clarendon Press, Oxford, 1995).

[18] A.Seeger and P.Haasen // *Philos.Mag.* **3** (1958) 470.

[19] S.E. Babcock, X.Y. Cai, D.C. Larbalestier, D.H. Shin and N. Zhang // *Physica C* **227** (1994) 183.

[20] N.D. Browning, M.F. Chisholm, S.J. Pennycook, D.P. Norton and D.H. Lowndes // *Physica C* **212** (1993) 185.

[21] A.Barone and G.Paterno, *Physics and Applications of the Josephson Effect* (Wiley, N.Y., 1982).

[22] C.C.Tsuei, J.R.Kirtley, C.C.Chi, Lock See Yu-Jahnes, A.Gupta, T.Shaw, J.Z.Sun and M.B.Ketchen // *Phys.Rev.Lett.* **73** (1994) 593.

[23] J.H.Miller, Q.Y.Ying, Z.G.Zou, N.Q.Fan, J.H.Xu, M.F.Davis and J.C.Wolfe // *Phys.Rev.Lett.* **74** (1995) 2347.

[24] D.A.Wollman, D.J.Van Harlingen, D.J.Lee, W.C.Lee, D.M.Ginsberg and A.J.Legget // *Phys.Rev.Lett.* **71** (1993) 2134.

[25] D.J.Van Harlingen // *Rev.Mod.Phys.* **67** (1995) 515.

[26] Y.Ishimaru, J.Wen, K.Hayashi, Y.Enomoto and N.Koshizuka // *Jpn.J.Appl.Phys.* **34** (1995) L1532.

[27] K.A.Müller // *Nature* **377** (1995) 133.

[28] M.Sigrist and T.M.Rice // *Rev.Mod.Phys.* **64** (1995) 503.

[29] S.J.Rosner, K.Char and G.Zaharchuk // *Appl.Phys.Lett.* **60** (1992) 1010.

[30] C.Traeholt, J.G.Wen, H.W.Zandbergen, Y.Shen and J.W.M.Hilgenkamp // *Physica C* **230** (1994) 425.

[31] D.J.Miller, T.A.Roberts, J.H.Kang, J.Talvaccio, D.B.Buchholtz and R.P.H.Chang // *Appl.Phys.Lett.* **66** (1995) 2561.

[32] B.Kabius, J.W.Seo, T.Amrein, U.Dahne, A.Sholen and K.Urban // *Physica C* **231** (1994) 123.

[33] J.T. Kucera and J.C. Bravman // *Phys. Rev. B* **51** (1995) 8582.

[34] Y. Dalichaouch, M.S. Torikachvili, E.A. Early, B.W. Lee, C.L. Seaman, K.N. Yang, H. Zhou and M.B. Maple // *Sol. State Commun.* **65** (1988) 1001.

[35] Y. Zhu, Q. Li, Y.N. Tsay, M. Suenaga, G.D. Gu and N. Koshizuka // *Phys. Rev. B* **57** (1998) 8601.

[36] Q. Li, Y.N. Tsay, M. Suenaga, G.D. Gu and N. Koshizuka // *Supercond. Sci. Technol.* **12** (1999) 1046.

[37] Q. Li, Y.N. Tsay, M. Suenaga, R.A. Klemm, G.D. Gu and N. Koshizuka // *Phys. Rev. Lett.* **83** (1999) 4160.

[38] M.F. Chisholm and D.A. Smith // *Philos. Mag. A* **59** (1989) 181.

[39] I.-F. Tsu, S.E. Babcock and D.L. Kaiser // *J. Mater. Res.* **11** (1996) 1383.

[40]I.-F. Tsu, J.-L. Wang, D.L. Kaiser and S.E. Babcock // *Physica C* **306** (1998) 163.

[41] I.A. Ovid'ko // *J. Phys.: Condens. Matter* **13** (2001) L97.

[42] M.Yu. Gutkin and I.A. Ovid'ko // *Phys. Rev. B* **63** (2001) 064515.

[43] M.Yu. Gutkin and I.A. Ovid'ko, *Defects and Plasticity Mechanisms in Nanostructured and Non-Crystalline Materials* (St.Petersburg: Yanus, 2001), in Russian.

[44] I.A. Ovid'ko // *Mater. Sci. Eng. A* (2001), in press.