Journal of Low Temperature Physics, Vol. 100, Nos. 3/4, 1995

Reentrant Superconducting Transport Behavior of Single Grain Boundary Josephson Junction in $BaPb_{1-X}Bi_XO_3$ Bicrystals

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(Received December 21, 1994; revised April 22, 1995)

Critical current and resistance of a single grain boundary in bulk bicrystals of the oxide superconductor $BaPb_{1-X}Bi_XO_3$ show a reentrant behavior in the temperature region below critical temperature of single crystal blocks. We established that the reentrant behavior is related to intrinsic properties of a barrier of single grain boundary Josephson junctions in the bicrystals. Origin and structure of the tunneling barrier in the bicrystals under study are discussed.

1. INTRODUCTION

The problem of grain boundary effects on the transport properties of high-T_c superconducting oxide materials is very exciting from the two aspects: practical applications and studies of fundamentals of the physics of planar defects in the oxide superconductors. Investigations of bicrystals with well defined single grain boundaries (GB) is a very useful method to solve both problems mentioned above. For the first time this method was successfully applied to bicrystals of the oxide superconductor $BaPb_{1-X}Bi_XO_3$[1] before the invention of high-T_c materials. Now, after

0022-2291/95/0800-0229$07.50/0

excellent series of studies of high-T_c bicrystals,[2–5] the investigation of grain boundary properties in the $BaPb_{1-X}Bi_XO_3$ seems to be complementary for extracting of common features of the whole class of oxide superconductors.

2. EXPERIMENTAL DETAILS

Bicrystals were grown by crystallization in a melt of Bi_2O_3, PbO and $BaCO_3$. Details of growth technique, chemical analysis, and sample preparation were published earlier.[6] A few bicrystals with chemical composition corresponded to the formula $BaPb_{1-X}Bi_XO_3$ and with the three values of the concentration parameter $x = 0.21 \pm 0.03$, $x = 0.27 \pm 0.03$, and $x = 0.29 \pm 0.03$ were synthesized. The structural properties were similar for the bicrystals of all the chemical compounds: each block was a single domain crystal with a well defined structural order and a typical geometrical size of 0.511 mm^3. Three characteristic components θ, δ, σ of the misorientation angles of the samples were determined using the Laue patterns according to the procedure described in Ref. 7. Our findings for the effect of misorientation angle on Josephson properties were similar to ones published for bicrystals of superconducting cuprates.[5] In particular, Josephson properties were found for bicrystals with large misorientation angles, i.e., for every angle component larger than 10–15°. The bicrystals with smaller misorientation angles demonstrated flux flow limitation of critical current and are not considered in this paper. Summary of the normal state, superconducting, Josephson, and structural properties of the studied samples is presented in Table I. Reentrant transport properties discussed further in this paper were found for all bicrystals, which demonstrated the Josephson properties. It is necessary to note that the reentrant behavior of critical current was found to be a universal feature of the Josephson junctions in the $BaPb_{1-X}Bi_XO_{3-Y}$ bicrystals for all the concentration parameters and misorientations shown in the Table. Due to this fact we will report general qualitative properties of the bicrystals without detailed quantitative analysis of the chemical content, and structural parameters.

The grain boundaries were determined by scanning electron microscopy from the angles of entry and constituted a plane with a typical size 0.51 mm^2.

The transport properties of the single grain boundary were measured with the current flowing between single crystal blocks in the direction perpendicular to the grain boundary plane. Two pairs of current and potential leads were installed in each of the two single crystal blocks using a silver paste. Superconducting properties of the bicrystals were determined by measuring temperature dependences of magnetic moment, resistivity, and I–V characteristics. Magnetic moment measurements were performed with

TABLE I

Normal State, Superconducting, Josephson and Structural Parameters of the $BaPb_{1-X}Bi_XO_3$ Bicrystals

Sample	x, a.u.	θ, δ, σ, grad.	S, mm^2	T_c, K	R_N, Ω	$R_N I_c$, mV
C2-7	0.21	37°, 18°, 41°	0.6×0.8	8.5	0.7	0.1
C2-13	0.21	27°, 28°, 46°	0.5×1.0	8.1	1.5	0.05
C12-6	0.27	34°, 19°, 39°	0.9×1.0	10.7	0.3	0.1
C12-9	0.27	17°, 21°, 29°	0.9×0.7	10.9	0.8	0.28
C18-3	0.29	20°, 41°, 38°	0.4×0.9	10.3	0.6	0.03

a vibration sample magnetometer of 10^{-5} Gcm^3 sensitivity, using cooling procedure in residual external magnetic field lower than 0.2 Oe. The values of critical current were determined with the help of a computerized data acquisition system using a programmable criterion of voltage appearance between the potential leads. No significant changes were observed for the value of the criterion in the 0.1–1 μV region.

3. TRANSPORT PROPERTIES AND REENTRANT BEHAVIOR

3.1. Josephson Properties of Grain Boundary Junction in $BaPb_{1-X}Bi_XO_3$

The Josephson properties of the single grain boundary in the $BaPb_{1-X}Bi_XO_3$ bicrystals are well established now.[6,7] We have reported I–V characteristics with the evidence of the Josephson and quasi-particle tunneling[6] for these bicrystals. It was shown that critical current densities of the order of 0.01–0.1 A/cm^2 are typical for the $BaPb_{1-X}Bi_XO_3$ bicrystals, and grain boundary Josephson junctions in the bicrystals with a geometrical size of about 1 mm should be treated as "small" junctions because their size does not exceed the estimated value of the Josephson penetration depth for the above critical current densities.

Temperature evolution of the I–V characteristic for the single grain boundary for the $BaPb_{0.73}Bi_{0.27}O_3$ bicrystal is shown in Fig. 1. Josephson supercurrent is clearly seen in every characteristic in temperature region up to 9.5 K. The rounding of the I–V characteristics near the critical temperature is caused by thermally activated phase slippage (TAPS) as it has been discussed in detail for the $BaPb_{0.73}Bi_{0.27}O_3$ bicrystals recently.[7] Systems of self-excited current resonances arising in a residual magnetic field were observed. Another important evidence of the Josephson behavior in the $BaPb_{1-X}Bi_XO_{3-Y}$ bicrystals was established by observation of oscillations in their critical current vs. applied magnetic field dependences in the recent work.[7] The latter observation is the evidence that the grain

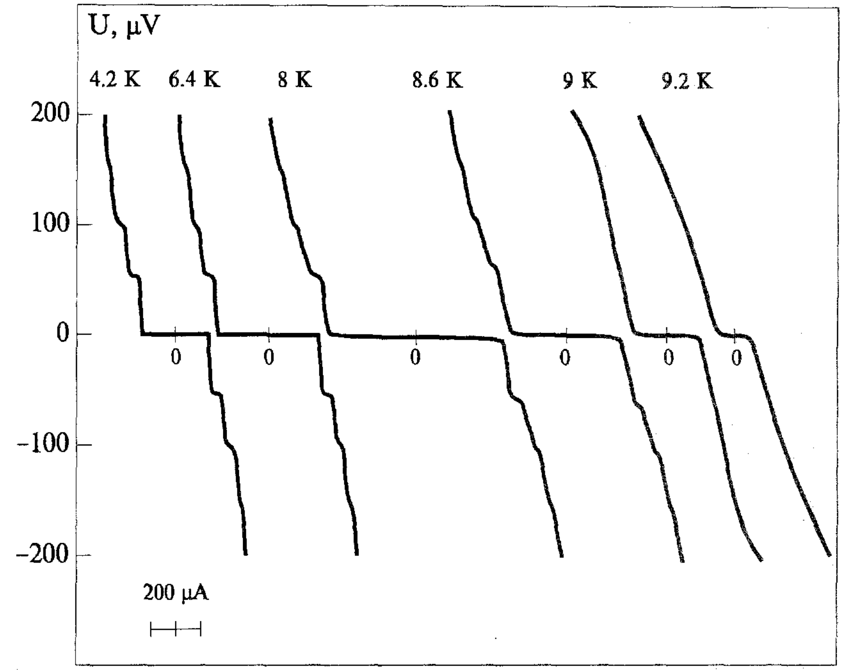

Fig. 1. Temperature evolution of the I–V characteristics of the Josephson junction in the $BaPb_{0.73}Bi_{0.27}O_3$ bicrystal.

boundary in the bicrystals under study is an unbroken and rather homogeneous Josephson barrier.

It must be pointed out that the Josephson supercurrent in the I–V characteristics, presented in Fig. 1 is not increasing monotonously when the temperature is decreasing. The maximal values of the critical current densities were found in the region of 0.06–0.14 A/cm^2 for different bicrystals, but the temperature at which the maxima were situated was the same for all bicrystals with the given chemical compound: 5.4 K for $BaPb_{0.79}Bi_{0.21}O_3$, 7.9 K for $BaPb_{0.73}Bi_{0.27}O_3$ and $BaPb_{0.71}Bi_{0.29}O_3$.

To conclude this section we should note that the $BaPb_{1-X}Bi_XO_3$ bicrystals clearly show properties of the Josephson junction with relatively low transparency. The described non-monotonous temperature evolution of the critical current looks anomalous and will be discussed in detail below.

3.2. Reentrant Resistivity Transitions

The temperature dependence of the resistance of the single grain boundary for one of the investigated $BaPb_{0.73}Bi_{0.27}O_3$ bicrystals is presented in Fig. 2.

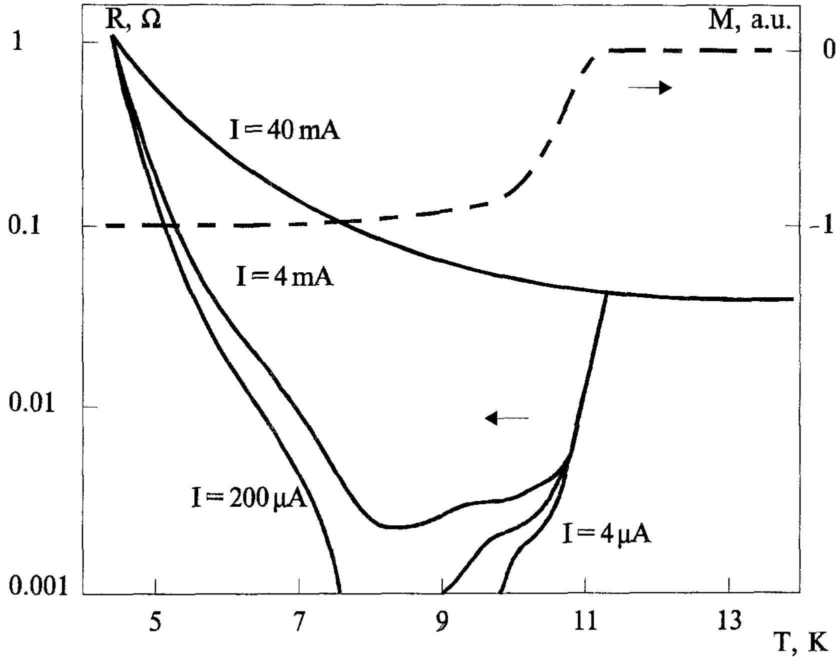

Fig. 2. Temperature dependence of the resistance and the magnetic moment of the single grain boundary of one of the $BaPb_{0.73}Bi_{0.27}O_3$ bicrystal.

The dependences for $BaPb_{0.71}Bi_{0.29}O_3$ and $BaPb_{0.79}Bi_{0.21}O_3$ bicrystals were similar, and the differences between the compounds are discussed below. The dependences were measured at different fixed dc bias currents through the grain boundary junction; the values of the currents are shown near the curves. The resistivity transition measured at 4 μA bias current looks typical for a Josephson junction. The foot-like structure at the bottom of this resistivity transition is caused by the TAPS effect and was studied in detail in the framework of the RSJ model[8,9] in our previous paper.[7]

The reentrant resistivity transitions were observed at 300–600 μA bias currents. This region of currents corresponds to the values of Josephson critical current for I–V characteristics, presented in Fig. 1 in the temperature region 4.2–7.9 K. The difference between the temperature, where measured resistivity became smaller than the resistance criterion of superconducting state, and the temperature of reentrant appearance of the resistance decreases when bias current increases. Under the bias exceeding the maximum Josephson current a minimum of resistance without transition to superconducting state was observed. The temperatures of these minima were the same as the temperatures of the maxima of critical current: 5.3 K for $BaPb_{0.79}Bi_{0.21}O_3$ and 7.9 K for $BaPb_{0.73}Bi_{0.27}O_3$ and $BaPb_{0.71}Bi_{0.29}O_3$ bicrystals. No significant differences in behavior of bicrystals of both chemical compounds were observed except for the temperatures of minima and a grain boundary resistance, shown in the Table I. Thus, we conclude that the reentrant resistivity transitions should be treated as a common feature of the bicrystals under study.

We suppose that the reason of the reentrant behavior at temperatures lower than the critical temperature of the crystalline blocks is related to the decrease of the critical current and switching of the grain boundary junction in the resistive mode if the bias dc current becomes larger than the critical current at some temperature. To verify this conjecture we measured the temperature dependence of the magnetic moment of a bicrystal in the absence and in the presence of a bias current. The resulting curve is shown by the dashed line in the upper part of Fig. 2. A clear transition to the diamagnetic response below T_c without any peculiarities was observed under the bias current up to 40 mA.

The temperature dependence of the resistance described before is influenced by the Josephson and nonlinear quasi-particle tunneling in the grain boundary junction and that is the reason why this resistance cannot be treated as the intrinsic resistance of the barrier R_N. To evaluate the temperature dependence of R_N we made measurements of the grain boundary junction resistance at a bias current, high enough to obtain a voltage across junction more than the energy gap of the superconductor. The energy gap $\Delta(0) = 1.71$ meV for $BaPb_{0.73}Bi_{0.27}O_3$ was obtained in our previous paper[6] and we made the measurements of $R_N(T)$ at a bias current of 40 mA, which provided the voltage across junction greater than 10 mV. To avoid overheat of the sample by the bias current these measurements were made with the help of 1/100 duty cycle current pulses. The resulting $R_N(T)$ curve is represented by the upper solid line in Fig. 2. The R_N increases at least in one order of magnitude as the temperature changes drops T_c to 4.2 K.

The conclusion is that reentrant resistivity transition in the $BaPb_{1-X}Bi_XO_3$ superconducting bicrystals is not a bulk effect but an effect completely defined by the properties of the grain boundary Josephson junction. Transition of this junction to resistive state under a bias current due to degradation of the critical current seems to be responsible for the reentrant behavior.

3.3. Temperature Dependence of Critical Current

As it was mentioned earlier, I–V characteristics show critical current which does not increase monotonously while the temperature decreases.

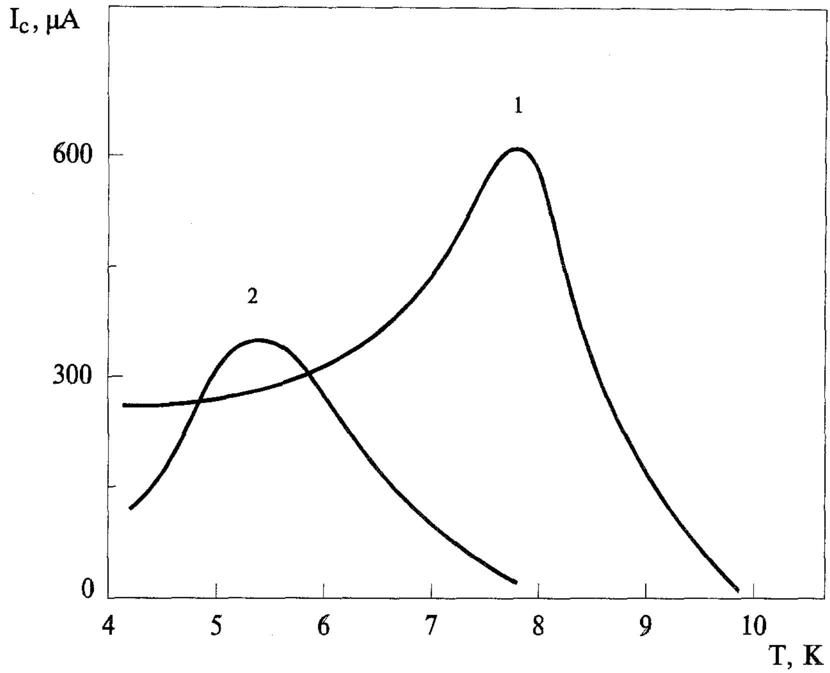

Fig. 3. Temperature dependence of the critical current for the Josephson junction in $BaPb_{0.79}Bi_{0.21}O_3$ and $BaPb_{0.73}Bi_{0.27}O_3$ bicrystals.

Detailed temperature dependences of the critical current for bicrystals of two chemical compounds $BaPb_{0.79}Bi_{0.21}O_3$ and $BaPb_{0.73}Bi_{0.27}O_3$ is shown in Fig. 3.

The common feature of the dependences is a clear maximum in the critical current at mentioned above characteristic temperature points 5.3 and 7.9 K correspondingly. We should note that the temperature position of the maxima is exactly the same as the position of minima in the temperature dependences of grain boundary resistivity described in the previous section. This fact gives us an additional strong argument for our explanation of the reentrant resistivity behavior as a result of non-monotonous critical current temperature dependences. Indeed, in our experimental procedure of resistivity measurements under a fixed current bias, temperature dependence of the resistivity follows the temperature evolution of the I–V characteristics. As we established, the I–V characteristics are nonhysteretic for all the samples. Due to this fact measured resistivity of the current biased junction must have the same peculiarity in its temperature dependence as the critical current.

The high-temperature part of the dependences clearly shows the evidence for the power-law behavior $(1 - T/T_c)$ near the critical temperature. The values of the power-law exponent were observed to be about 3/2 for the investigated bicrystals. More detailed analysis of the near-T_c behavior including the influence of the TAPS effect was reported in our paper.[7]

4. AUGER ELEMENT ANALYSIS OF THE GRAIN BOUNDARY

The anomalous Josephson properties of the single GB in $BaPb_{1-X}Bi_XO_3$ bicrystals described in the Sec. 3 of this paper lead to the conclusion that the most unusual feature of these GB Josephson junctions is the anomalous temperature dependence of the critical current. Since the GB was found to be an unbroken and rather homogeneous Josephson barrier, the anomalous behavior of the junction should be related to specific properties of the barrier, probably, the details of its internal structure. The bulk bicrystals under study provide a unique opportunity to investigate the real structure of the GB with the help of modern techniques for surface analysis. This opportunity is provided by the fact that the GB in our bicrystals has a macroscopic size and may be opened for analysis by precise splitting along the intergrowth surface, where the mechanical properties deviate appreciably from the bulk values. This analysis was performed for the C18-3, and C12-9 saples using Auger composition-profile measurements. PHI-590 Auger Microprobe was used for these experiments, and the samples were splitted and analyzed at a vacuum level of 10^{-8} Torr. Studies of profiles of chemical elements distribution were performed with the help of milling by 15 keV Ar^+ ions. Additional series of measurements were performed for the surfaces of single-crystal blocks splitted at a few thousands of microns from the intergrowth surface to test changes in the bulk chemical compositions under the ion milling.

The results of the series of measurements for the GB (1), and the surface of the splitted single crystal block (2) are presented in Fig. 4, where the ratio of amplitudes of the peaks with the Bi and Pb characteristic energies is plotted as a function of estimated depth of ion milling. Enrichment by the Bi atoms was clearly seen for all investigated GB but no significant changes in composition were observed for the surfaces of single crystal blocks before and after milling. Such a behavior may be interpreted as local changes of the value of the concentration parameter x near the intergrowth surface. This is illustrated by the recovered values of x in the right side of Fig. 4. The importance of this internal grain boundary barrier structure for the physical properties of the barrier can be understood in relation to the $BaPb_{1-X}Bi_XO_{3-Y}$ system phase diagram established in Ref. 10. In this diagram the region of superconducting compositions $0.05 < x < 0.35$ is in the neighborhood of the semiconducting region $x > 0.4$ and the semiconducting gap collapsed near $x = 0.4$. A narrow region of material with a normal metal properties is situated at $0.35 < x < 0.4$ between the superconducting and the semiconducting regions. As it was discussed in the previous section, results of the Auger analysis showed that near the GB region the concentration parameter x is greater than its bulk value. Such a local enrichment by the Bi atoms with slightly larger ion radius than for Pb might take place due to the effect of grain boundary segregation. Because the bicrystal grain boundaries form an array of uniformly spaced edge or screw dislocations[11] the concentration parameter x is expected to be equal to 0.5 in order to accommodate the mismatch between the blocks of bicrystal effectively. A characteristic length of this segregation may be taken as a few periods of the crystal lattice and estimated as 40–50 Å since the lattice period for $BaPb_{1-x}Bi_xO_3$ is at about 4.3 Å.[10] This estimate seems to be close to the observed thickness of Bi-enriched layer, as it is shown in Fig. 4. We show by the dotted lines in Fig. 4 the imaginary boundaries of the

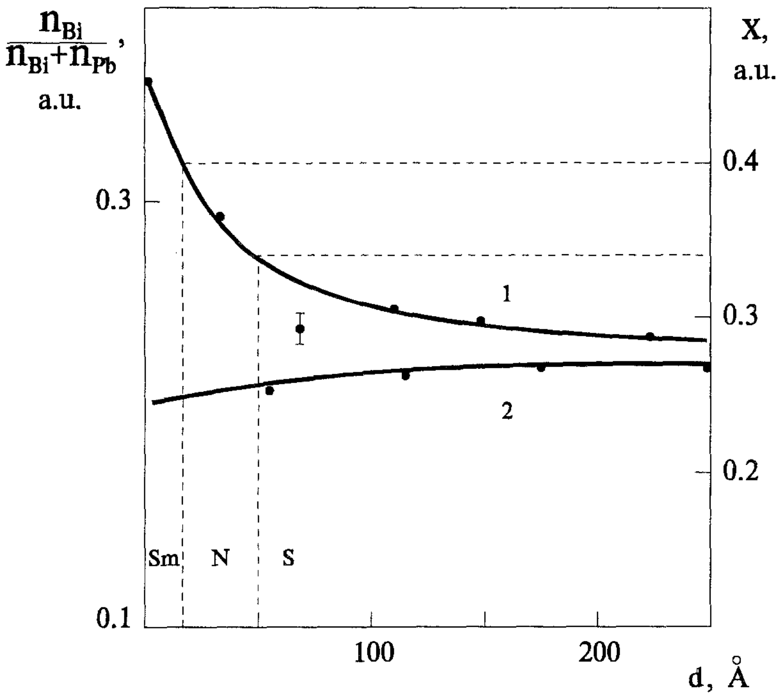

Fig. 4. Phase diagram of the physical properties of the internal grain boundary barriers with different compositions.

semiconducting Sm, normal metal N, and superconducting S regions according to the measured value of concentration parameter x and mentioned details of the $BaPb_{1-X}Bi_XO_3$ phase diagram. Thus, we can see that the structure of the barrier may be interpreted as S-N-Sm-N-S, i.e., a semiconductor barrier with normal metal layers.

5. DISCUSSION AND CONCLUSIONS

The single-grain boundary Josephson junction in bulk bicrystals of the oxide superconductor $BaPb_{1-X}Bi_XO_3$ shows anomalous reentrant transport characteristics. The temperature dependences of the critical current show a maximum; the temperature position of this maximum is different for bicrystals of different chemical composition. The power-law behavior of the critical current density with the exponent of about 3/2 for the investigated bicrystals was observed near T_c. Single-grain boundary junctions show reentrant resistivity transition but the bulk superconducting properties of crystalline blocks do not demonstrate any peculiarities in the temperature region below T_c. Thus, the reentrant resistivity transitions are purely grain boundary effect and are related to the anomalous temperature dependence of the critical current. The latter seems to be related to the observed increase of the barrier resistance while temperature decreases.

The experimental findings described above may be explained by assuming that the barrier in the grain boundary junction in the $BaPb_{1-X}Bi_XO_3$ bicrystal has the properties of a narrow-band semiconductor. As it is shown in Fig. 2 the resistance of the grain boundary increases as the temperature decreases and the resistance of the grain boundary Josephson junction increases by at least one order of magnitude between T_c and 4.2 K. From these data the activation energy of the semiconductor material of the barrier may be estimated as a few meV. Non-monotonous dependence of the Josephson critical current was predicted theoretically for junctions with a semiconductor barrier.[12] The general idea of this model is that two different mechanisms can be responsible for the junction critical current in different temperature regions. When the temperature is lower than the critical one, but comparable with the energy gap of semiconducting barrier, conductivity of the barrier is high enough to provide high critical currents due to superconducting pair transport with partial loss of coherence. At lower temperatures resistivity of the barrier is much higher and it behaves as a tunneling barrier with low transparency, and low critical currents. This scenario seems to be quite reasonable for our samples if we take into consideration that the expected energy gap in the semiconducting barrier is expected to be of the order of 10 K and its resistance was found to be increasing nearly exponentially at low temperatures.

According to our results described in this paper the nature of the grain boundary barrier in the $BaPb_{1-X}Bi_XO_{3-Y}$ bicrystals barrier is related to Bi ions segregation near the grain boundary, and specific properties of the phase diagram of the $BaPb_{1-X}Bi_XO_3$. We can extend the plot of the concentration profile obtained in the section to complete the diagram of the grain boundary barrier shown in Fig. 5. In this diagram the region of superconducting compositions, the semiconducting region, and a narrow region of material with normal metal properties correspond to $0.05 < x < 0.35$, $x > 0.4$, and $0.35 < x < 0.4$ correspondingly. Thus, if we accept that in the region close to the grain boundary the concentration parameter x has a value higher than its bulk value due to the effect of the grain boundary segregation, we can obtain a barrier structure similar to the one presented in Fig. 4. From this figure and the data of Auger layer-by-layer analysis described above we can estimate thickness of the barrier as 50–100 Å. Taking the value of coherence length for the $BaPb_{1-X}Bi_XO_{3-Y}$ superconductor 70–80 Å[13] into consideration we can conclude that such a thick barrier may be responsible for the properties of the low transparency Josephson junction observed in this work. The second curve in Fig. 5

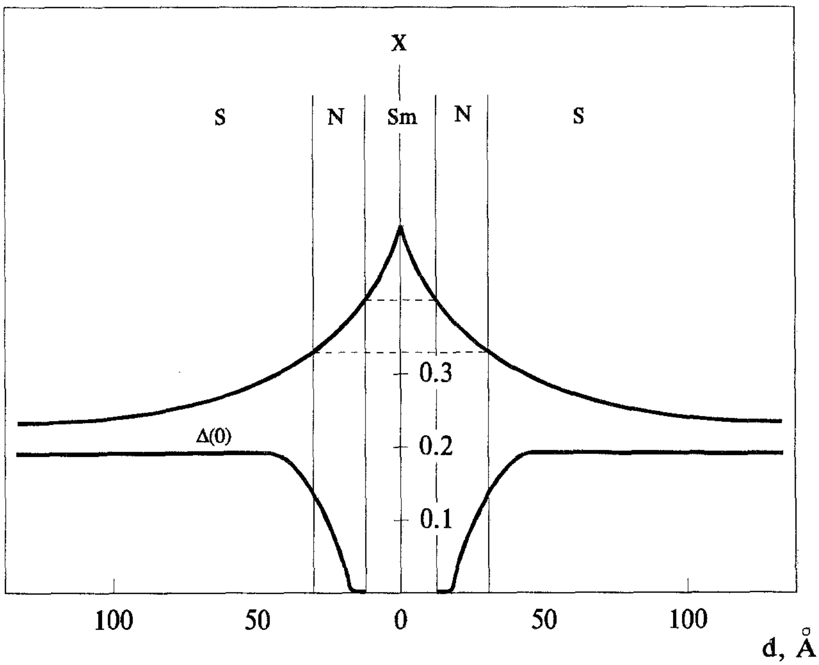

Fig. 5. Schematic diagram of chemical composition, Josephson barrier and superconducting order parameter near the single grain boundary in the bicrystal.

illustrates the behavior of the order parameter across the grain boundary in such a barrier at low temperatures. Thus, we can conclude from the diagram in Fig. 5 that the structure of the grain boundary barrier is S-N-Sm-N-S, i.e., this is a semiconducting tunneling barrier with the influence of the proximity effect in normal layers. The latter conclusion seems to be suitable to explain the power-law behavior of the critical current density with the power-law exponent at about 3/2 for investigated bicrystals near T_c. Such a behavior was theoretically predicted for tunneling junctions with the proximity effect influence.[14]

In spite of the fact that the formation of the grain boundary Josephson junction seems to be a common feature of the oxide superconductors, the origin and the properties of the barriers are possibly different for the cuprate and the copperless oxide systems. The formation of the single-grain boundary junction barrier in $BaPb_{1-x}Bi_xO_3$ with the semiconducting properties discussed here should be treated as an additional interesting feature of planar defects in the family of the oxide superconductors. More intensive studies of these phenomena are in progress.

ACKNOWLEDGMENTS

One of the authors (I.R.) wants to thank Department of Physics of the University of Illinois at Urbana-Champaign and John D. and Catherine T. MacArthur Foundation for the financial support.

REFERENCES

1. V. Stepankin *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **41**, 23 (1985).
2. D. Dimos, P. Chaudhari, and J. Mannhart, *Phys. Rev. B* **41**, 4083 (1990).
3. J. Mannhart, *Journ. of Superconductivity* **3**, 281 (1990).
4. D. Larbalestier *et al.*, *Progress in High-T_c Superconductivity*. **18** (Singapore: World Scientific, 1990).
5. R. Gross, in *Interfaces in Superconducting Systems*, S. L. Shinde and D. Rudman, eds. (New York: Springer Verlag, 1992).
6. V. Stepankin and A. Kuznetsov, *Supercond. Sci. Technol.* **5**, 34 (1992).
7. V. Stepankin and A. V. Kuznetsov, *Cryogenics* **33**, N3, 321 (1993).
8. R. Gross, P. Chaudhari, D. Dimos, A. Gupta, and G. Koren, *Phys. Rev. Lett.* **64**, 228 (1990).
9. A. Barone and G. Paterno, *Physics and Applications of the Josephson Effect* (New York: Wiley & Sons, 1982).
10. Y. Khan *et al.*, *Phys. Stat. Sol. A* **39**, 79 (1977).
11. M. F. Chisholm and D. A. Smith, *Phil. Mag. A* **59**, 181 (1989).
12. I. Itskovich and R. Shekhter, *Fiz. Tverd. Tela* **7**, 863 (1981).
13. B. Batlogg, J. P. Remeika, R. C. Dynes, and H. Barz, in *Superconductivity in d- and f-Metals*, W. Buckel and W. Weber, eds. (Kernforschungszentrum, Karlsruhe, Germany, 1982).
14. A. D. Golubov *et al.*, *Fiz. Nizkich Temp.* **10**, 799 (1984).