# Anomalies in the temperature dependences, resistance, critical current, and critical magnetic field in $Ba_{1-x}K_xBiO_3$

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The galvanomagnetic properties of the superconducting ceramic $Ba_{1-x}K_xBiO_3$ were investigated. The resistances and the current–voltage characteristics were measured in the temperature interval 2–300 K and in magnetic fields up to 8 T. An anomalous nonlinear behavior of the resistance was observed at temperatures lower than $T_c$. The dielectric growth of the resistance, observed for "large" currents at $t > T_c$, exceeds by several orders of magnitude the resistance in the normal phase and is suppressed by a magnetic field equal to the critical magnetic field that destroys the superconductivity when "small" currents flow through the sample. The temperature dependence of the critical current is nonmonotonic and "reentrant" superconductivity is observed. The temperature dependence of the critical magnetic field has a positive curvature in the entire temperature range below $T_c$, down to (0.06–0.08) $T_c$, and no saturation of $H_{c2}(T)$ as $T \to 0$ is observed. It is proposed to explain the observed effect by using the inhomogeneous superconductor–insulator state as a model.

The recently discovered[1] new high-temperature superconductor (HTSC) $Ba_{1-x}K_xBiO_3$ with $T_c = 30$ K offers new opportunities for investigating the nature of high-temperature superconductivity. This system is also of additional interest because, unlike other HTSC, $Ba_{1-x}K_xBiO_3$ is not a layered compound, has a simple cubic perovskite structure, and contains no magnetic ions. The structure and chemical properties of the $Ba_{1-x}K_xBiO_3$ system are very close to those of the known superconducting ceramic $BaPb_{1-x}Bi_xO_3$.

The superconducting system $Ba_{1-x}K_xBiO_3$ has been the subject of many investigations of its structure,[2-4] electric and optical characteristics,[2-5] critical magnetic field,[6] and other properties. We report here investigations of the temperature dependence of the resistance, of the critical current, and of the critical magnetic field in the $Ba_{1-x}K_xBiO_3$ system. The anomalous behavior of these properties in $Ba_{1-x}K_xBiO_3$ is similar to that of the corresponding characteristics of $BaPb_{1-x}Bi_xO_3$.[7-15] In the entire temperature interval below $T_c$, down to 0.06 $T_c$, there are observed in $Ba_{1-x}K_xBiO_3$ an anomalous $H_{c2}(t)$ dependence with positive curvature, "reentrant" superconductivity resistance, a decrease of the critical current when the temperature is lowered, a dependence on the critical current of the sample resistance when the superconducting state is destroyed, hysteresis of the current–voltage characteristics, and others.

Analogous anomalous properties of the $BaPb_{1-x}Bi_xO_3$ system were attributed in Refs. 6–10, using a granular superconductor as a model, to the semiconducting or dielectric properties of the boundaries through which Josephson coupling of the superconducting regions within the grains occurred. By virtue of their morphology, ceramic samples are granular structures whose properties can be influenced by the grain boundaries. The temperature dependence of the resistance in the region above $T_c$, the decrease of the critical current with temperature, and the reentrant superconductivity resistance can be attributed to the granular structure of the samples and to the influence of the grain boundaries. It is impossible to explain, however, within the framework of the granular superconductor model, all the above anomalies of the $Ba_{1-x}K_xBiO_3$ system, particularly the suppression by the magnetic field of the resistance as a function of temperature for $T < T_c$. From our point of view the aggregate of the experimental data can be more fully interpreted in terms of a model of the spatially inhomogeneous superconductor–insulator state, a model proposed by A. A. Gorbatsevich, E. V. Zhukovskiĭ, Yu. V. Kopaev, and I. V. Tokatly.

## SAMPLES

We investigated ceramic samples of $Ba_{1-x}K_xBiO_3$ with $x = 0.32$, 0.39, and 0.40, obtained using nitrate technology by sintering $Bi_2O_3$, $KNO_3$ and $Ba(NO_3)_2$ in an $N_2$ atmosphere at $T = 715$ °C, and then in an $O_2$ stream at $T = 450$ °C, followed by cooling to 150 °C. The operation is repeated 5–6 times, regrinding the mixture. Typical sample dimensions were $2 \times 5 \times 10$ mm. In the experiment we measured the sample resistance as a function of temperature in the interval 2–300 K and of the magnetic field up to 8 T. The measurements were made by the four-point method with direct and alternating (23 Hz) current. The magnetic field was perpendicular to the current and parallel to the broad face of the sample. X-ray structure analysis showed the samples to be single-phased.

## RESULTS

### Resistance

The temperature dependence of the resistance in $Ba_{1-x}K_xBiO_3$ (Fig. 1) coincides with $R(T)$ of $BaPb_{1-x}Bi_xO_3$ (Refs. 11 and 12) and differs from the analogous dependences for other HTSC, viz., the temperature coefficient of the resistance of $Ba_{1-x}K_xBiO_3$ is negative in the temperature range 100–300 K, becomes level at 30–100 K, and sometimes has a weak decreasing metallic behavior near the superconducting transition.

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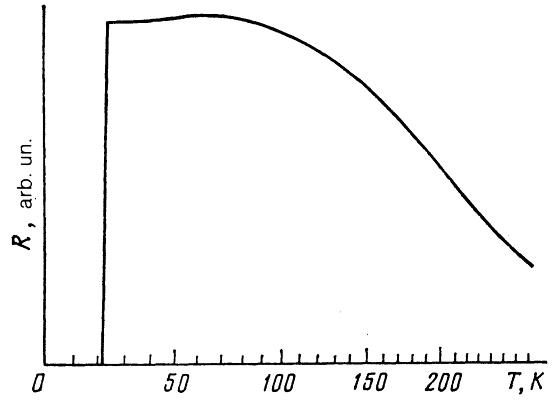


FIG. 1. Temperature dependence of the electric resistance in $Ba_{1-x}K_xBiO_3$ ceramic ($x = 0.4$).

The temperature dependence of the resistance in the region below $T_c$ is strongly influenced by the current flowing through the sample (Fig. 2). First, reentrant superconductivity resistance is observed and second, at sufficiently large currents, the sample resistance increases with decreasing temperature and exceeds the resistance in the normal state by several orders of magnitude. The temperature required to restore the resistance depends on the current. Similar anomalies were observed for all sample compositions investigated. The current at which the resistive state (or the relative increase of the resistance) is restored may vary from sample to sample. When the resistance and differential magnetic susceptibility are measured simultaneously the restoration of the superconductor resistance is not accompanied by any susceptibility changes. Thus, when the resistive state is restored no destruction of the superconducting state in the interior takes place. Application of an external magnetic field suppresses the "dielectric" growth and restores the resistance to its value in the normal phase.

The authors of Ref. 6, who also observe a growth of the resistance in superconducting $Ba_{1-x}K_xBiO_3$ samples as the temperature is lowered, attribute this fact to inclusions of the dielectric phase of $Ba_{1-x}K_xBiO_3$ with smaller $K$ contents. From our point of view the observed reentrant superconductivity is a property of the superconducting phase of $Ba_{1-x}K_xBiO_3$ itself, and cannot be ascribed to the two-phase character of the samples, since the magnetic field suppresses the "dielectric" growth of the resistance at the same time that it destroys the superconducting state in the interior; this will be discussed in detail below.

Reentrant superconductivity and the growth of resistance at $T$ lower than $T_c$ in $BaPb_{1-x}Bi_xO_3$ were attributed in Refs. 8 and 9 to granularity of the sample, i.e., to breaking of the Josephson bonds for currents between grains as a result of the increased growth of the resistance of the barrier on the grain boundaries, while the superconductivity in the grains is preserved. Various mechanisms can alter the potential barrier between the grains when the temperature is lowered: filling of the surface states on the grain boundary, semiconductor-type growth of the resistance of the layer between the grains, and others. The strong "negative magnetoresistance" at $T < T_c$ observed in $Ba_{1-x}K_xBiO_3$ (Fig. 3) and $BaPb_{1-x}Bi_xO_3$, cannot be explained in terms of the granular superconductor model.[7,8] When the magnetic field is increased the "dielectric" growth of the resistance under the condition of "large" currents (see Fig. 3) first increases and is then suppressed. The resistance is then restored to the normal-phase value which is independent of the current in the normal phase. Comparison of the temperature dependences of the resistance in various magnetic fields in "strong" (1 mA, Fig. 3) and "weak" (10 mA, Fig. 4) currents shows that the "dielectrization" in a strong current and the superconducting transition in the weak one set in at the exact same temperature, while application of a magnetic field shifts the superconducting transition and the start of the "dielectric" growth of the resistance into the region of lower temperatures and restores the resistance to its value in the normal phase. Thus "dielectrization" in strong currents exists only at those temperatures and magnetic fields for which a superconducting state exists in weak currents. We note once more that the destruction of the superconductivity resistance is not accompanied by changes of the differential magnetic susceptibility, i.e., the superconductivity in the interior of the sample is not destroyed.

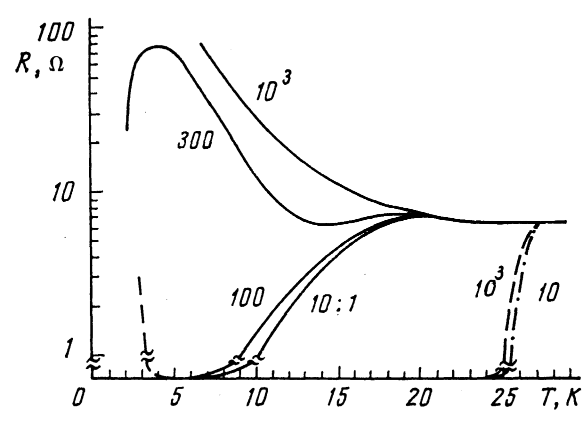


FIG. 2. Temperature dependence of the electric resistance in $Ba_{1-x}K_xBiO_3$ ceramic ($x = 0.4$) at $T < T_c$ for different measurement currents in a magnetic field $H = 1.6$ T (solid curves) and in the absence of a field (dashed and dash-dot curves). The numbers on the curves are the measurement currents in $\mu$A.

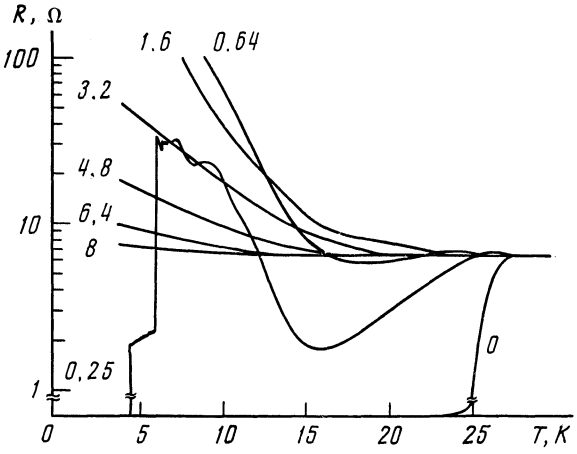


FIG. 3. Temperature dependence of the electric resistance in $Ba_{1-x}K_xBiO_3$ ceramic ($x = 0.4$) at $T < T_c$ for different magnetic fields at a "large" measurement current (1 mA). The numbers on the curves are the magnetic fields in $T$.

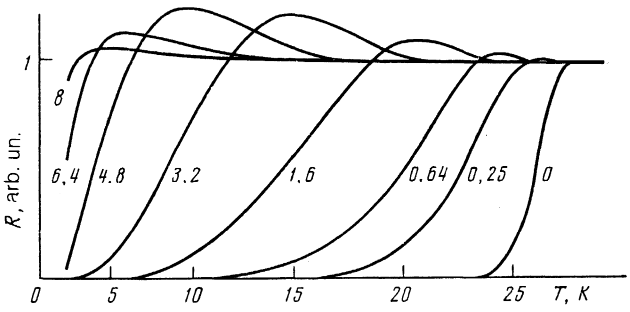


FIG. 4. Temperature dependence of electric resistance in $Ba_{1-x}K_xBiO_3$ ceramic ($x = 0.4$) for $T < T_c$ in various magnetic field at a "small" measurement current ($10\ \mu A$). The numbers on the curves are the magnetic fields in $T$.

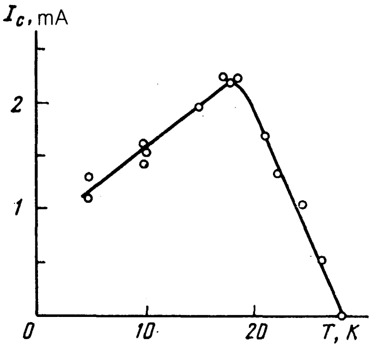


FIG. 6. Dependence of the critical current I on the temperature in the absence of a magnetic field. The values of $I_c$ are defined as in Fig. 5.

**Current-voltage characteristics**

To investigate the nonlinearity of the resistance we plotted the current-voltage characteristic (IVC) at various temperatures and in different magnetic fields [Figs. 5(a), 5(b)]. The IVC exhibits an appreciable hysteresis that is suppressed both when the temperature is raised and when the magnetic field is strengthened. There is also a maximum current $I'$ above which the IVC exhibits no hysteresis [Fig. 5(a)]. The value of $I'$ does not depend on the temperature and on the magnetic field. The IVC obtained in the hysteresis region is not fully accurate and is not strictly symmetric about the change of the current direction. We observed voltage jumps of the order of several times ten mV, which exceeds the gap permitted from the standpoint of the IVC. The character of the IVC (discontinuities, hysteresis) indicates that a bulk $Ba_{1-x}K_xBiO_3$ sample is a multiple Josephson structure. As shown in Fig. 5, the critical current $I_c$ determined from the IVC has a nonmonotonic temperature dependence (Fig. 6). A similar nonmonotonic temperature dependence of the critical field is manifested in resistance-reentrant superconductivity in this system (Fig. 2). The magnetic-field dependence of the current has not singularities: the critical current decreases monotonically

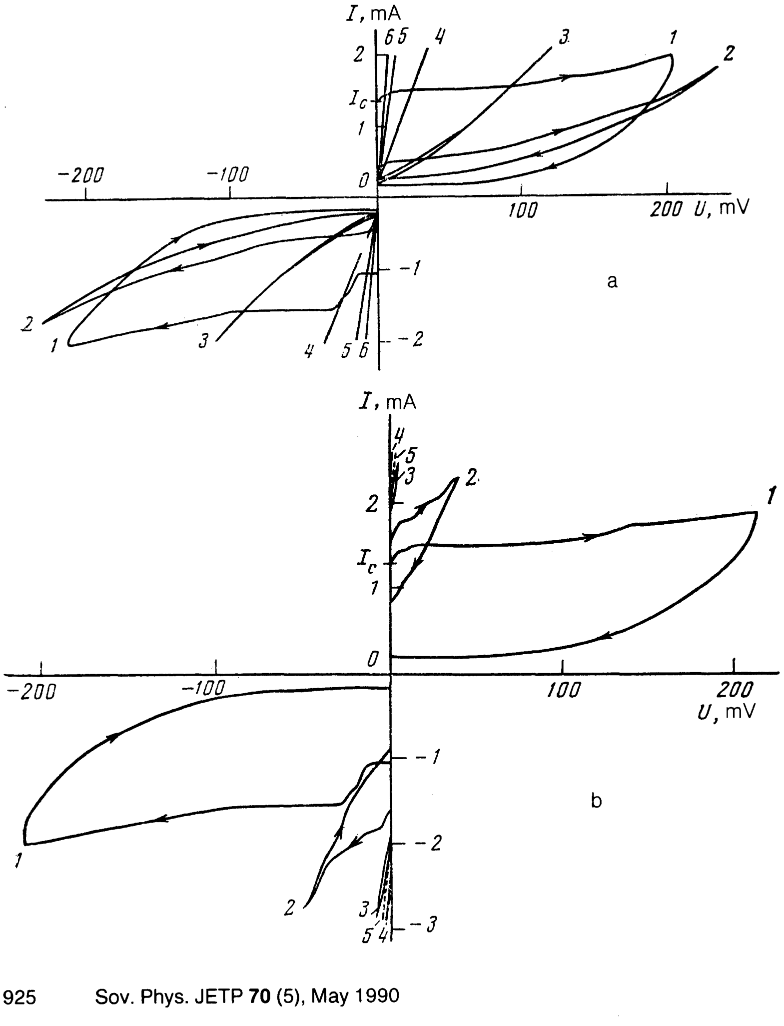


FIG. 5. Current-voltage characteristics of $Ba_{1-x}K_xBiO_3$ ($x = 0.4$) ceramic sample at different magnetic fields: a—$T = 4.8$ K; 1—$H = 0$ T, 2—0.64 T, 3—1.6 T,4—3.2 T, 5—4.8 T, 6—6.4 T; b—$H = 0$ T; 1—$T = 4.8$ K, 2—10 K, 3—15 K, 4—18 K, 5—22 K.

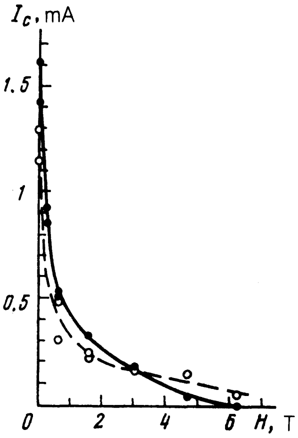


FIG. 7. Dependence of the critical current on the magnetic field at $T = 4.8$ K (O) and $T = 10$ K (●).

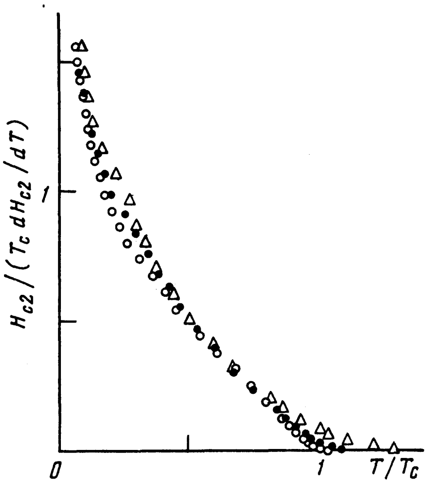


FIG. 9. Relative critical field $H_{2c}/(T_c dH_{2c}/dT)$ vs the relative temperature $T/T_c$ for different methods of determining $T_c$ from the resistance level: O—0.9 $R_{res}$, ●—0.5 $R_{res}$ and Δ—0.1 $R_{res}$.

when the field is increased. The critical current drops to zero at a lower temperature in strong fields, so that the $I_c(H)$ curves for different temperatures intersect (Fig. 7).

### Critical Magnetic Fields

The temperature dependence of the critical magnetic fields was determined by measuring the temperature of the superconducting transition in an external magnetic field (Fig. 4). The transitions are quite wide, so that $T_c$ is indeterminate. To determine the width $\Delta T_c$ of the transition at the levels 0.1 $R_{res}$ and 0.9 $R_{res}$ the value of $T_c$ varied from 1 K at $H = 0$ to 5–7 K in a magnetic field, and the width of the transition had a nonmonotonic dependence on the magnetic field (or on $\Delta T_c$ in a given magnetic field, Fig. 8). Nonetheless, in various methods of determining $T_c$, the dependence of $H_{c2}/(T_c dH_{c2}/dT)$ on $T/T_c$ has the same character (Fig. 9): a positive curvature near $T_c$, then an almost linear section, and again a positive curvature with further decrease of temperature. The dependence of $H_{c2}/(T_c dH_{c2}/dT)$ on $T/T_c$ was measured up to relative temperatures 0.06–0.08 (depending on the method used to determine $T_c$), but $H_{c2}(T)$ exhibited no tendency to saturation. A similar character of the temperature dependence of the critical magnetic fields was observed also for $BaPb_{1-x}Bi_xO_3$, both in the ceramic[11,12,14] and in single-crystal samples.[12,13,15]

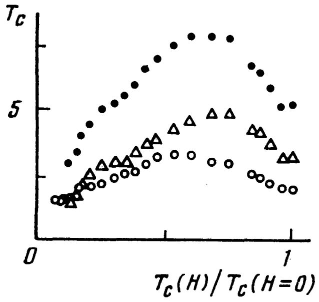


FIG. 8. Transition $\Delta T$ vs the critical temperature $T_c$ in an external magnetic field; ●—$\Delta T = T_c(0.9R) - T_c(0.1R)$, $\Delta - \Delta T = T_c(0.5R) - T_c(0.1R)$, O—$\Delta T = T_c(0.9R) - T_c(0.5R)$.

Such an $H_{c2}(T)$ dependence can hardly be explained in terms of the strong-coupling model, for this would call for assuming an unrealistically large coupling constant $\lambda$, because even for $\lambda = 30$ the positive curvature $H_{2c}(T)$ becomes negative in the temperature region $R < 0.2T_c$ (Ref. 16).

The positive curvature of $H_{c2}(T)$ follows from the bipolaron model of superconductivity,[17] and also from the theory of superconductivity of localized electrons.[18]

The temperature dependence of the critical magnetic fields was obtained in Refs. 19 and 20 for superconductors with partial dielectrization of the electron spectrum. The positive curvature of the $H_{c2}(T)$ dependence near $T_c$ is also explained by this model, but as $T \to 0$ a saturation $H_{c2}(T) \propto 1 - (T/T_c)^2$ should set in.

### DISCUSSION

These results have the following implications.

1. The anomalous behavior of the resistance at temperatures below $T_c$ is associated with the superconducting state. The current-dependent "dielectric" growth of the resistance when the temperature is lowered in the region $T < T_c$ is observed only if superconductivity, determined from the differential magnetic susceptibility, exists in the bulk of the sample. Destruction of the superconducting state by a magnetic field eliminates the anomaly of the resistance.

2. If the resistance in the superconducting state is destroyed by a current flowing through the sample, a resistance growth that depends on the current and on the magnetic field is observed, up to values exceeding by several orders of magnitude the sample resistance in the normal state. The increase of the resistance cannot be explained by saying that when the temperature is lowered the resistance of the barriers on the intergrain boundaries increases due to dielectrization, and hence to breaking of the Josephson bonds between the superconducting grains, since application of a magnetic field restores the resistance to a value equal to the sample resistance in the normal state.

3. A bulk $Ba_{1-x}K_xBiO_3$ sample is a multiple Josephson structure, in which the aggregate of transitions take

place simultaneously, so that the voltage discontinuities on the IVC reach values of several times ten mV, larger than the gap width possible in the BCS theory. If Josephson junctions occur in intergrain boundaries, the parameters of the transitions should be different and in this case, generally speaking, it is difficult to explain their synchronization.

4. The critical current determined from IVC has a nonmonotonic temperature dependence.

5. The plot of the critical magnetic field vs temperature has a positive curvature, and as the temperature tends to zero no tendency of $H_{c2}$ to saturate is observed down to $(0.06–0.08)T_c$.

The aggregate of the observed effects can be explained by using the following model of the spatially inhomogeneous state of a superconducting dielectric. In systems in which the Fermi level lies near the band gap, where a transition can occur at the onset of a dielectric gap on the Fermi surface or a superconducting gap in the dependence, say, on the electron density or some other parameter, a phase state characterized by formation of a structure of spatially separated superconducting and dielectric regions can set in, i.e., the superconducting order parameter and the dielectric gap turn out to be modulated in antiphase. (The "dielectric" regions are not necessarily dielectric in the standard meaning. These are region in which the width of the band gap is increased and the number of free carriers is correspondingly decreased, so that the resistance increases.) When the superconducting gap vanishes, say in a strong magnetic field, the "dielectrization" of the neighboring region vanishes simultaneously and the system turns into a homogeneous metal. The connection between the superconducting regions through the "dielectric" ones is via the Josephson tunneling mechanism. Accordingly there exists a critical Josephson current that tunnels through the "dielectric" regions.

When the temperature decreases (for $T < T_c$) the superconducting and "dielectric" regions can become redistributed both in real and momentum space, i.e., a relative change can take place in the dimensions of the "dielectric" and superconducting region, or an increase is possible in the depth of modulation of the superconducting order parameter and of the dielectric gap. The growth of the relative dimensions of the "dielectric" regions and the increase of the depth of modulation of the gap should then lead to a decrease of the critical current, and to a "dielectric" increase of the resistance in a large current as the temperature is lowered $(T < T_c)$, as was indeed observed in our experiments.

The anomalous temperature dependence of the critical magnetic field can be attributed to the same causes: a decrease of the dimensions of the superconducting regions or an increase of the superconducting gap in the superconducting region when the temperature is lower. In the first case we measure the critical magnetic field of the superconducting region, with temperature-dependent dimensions on the order of the depth of penetration of the magnetic field, i.e., the decrease of the dimensions of the superconducting region as the temperature is increased leads to an increase of the effective critical magnetic field. In the second case the increase in the depth of modulation of the superconducting order parameter, i.e., the increase of the superconducting gap in superconducting regions with decrease of temperature, means that at a lower temperature we measure the critical magnetic field of a superconductor having a larger gap and accordingly a larger value of $H_{c2}(0)$.

The properties of the sample as a multiple Josephson system are also in good agreement with the model of spatially inhomogeneous state of superconducting dielectric with Josephson bonds between the superconducting regions. The parameters of the Josephson junctions in such a system should be close, and one should not be surprised at the synchronization of several Josephson junctions, manifested by large voltage discontinuities on the IVC (up to several tens of mV), larger than the gap widths possible according to the BCS theory.

Thus, the copper-free high-temperature superconductor $Ba_{1-x}K_xBiO_3$ for $T$ lower than $T_c$ exhibits anomalous temperature dependences of the resistance, critical current, and critical magnetic field, which can be explained by using the model of a spatially inhomogeneous superconductor–dielectric state.

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