Metal oxide superconductor $BaPb_{1-x}Bi_xO_3$: unusual properties and new applications

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This article reviews the experimental and theoretical investigations of the superconducting solid solutions $BaPb_{1-x}Bi_xO_3$ (BPB), which have critical temperatures $T_c \approx 13$ K. The crystal structure, structural phase transitions, and the electrical and optical properties are examined in detail. Methods of preparing ceramic samples, as well as thin films and single crystals, are discussed briefly. Measurements of the electron specific heat and of the upper critical magnetic field are interpreted in terms of a theory of superconductors with partial dielectrization of the electron spectrum. Particular attention is paid to those properties of BPB which are a consequence of the granularity of the ceramic macrostructure and the existence of weak Josephson links between the granules. Correlations between the composition dependences of various normal and superconducting characteristics of BPB are elucidated, and the nature of the superconducting high T_c state with a small electron density of states ($N(0) = 3 \cdot 10^{21}$ eV^{-1} cm^{-3}) at the Fermi surface is discussed.

1. INTRODUCTION

A significant advance towards the solution of the problem of high-temperature superconductivity[1,2] has been the discovery of organic superconducting compounds.[3,4] Nonetheless, the highest critical temperatures $T_c \lesssim 23.2$ K and the highest upper critical magnetic fields $H_{c2} \lesssim 600$ kOe yet obtained have been observed in inorganic materials: intermetallics with the A-15 structure and ceramic chevrel phases.[5,6] Of particular interest are the metal oxide superconductors, which are not subject to oxidation during thermal cycling and which can support large thermal loads without degradation of the critical parameters. The first superconducting oxide with $T_c > 10$ K was the compound $Li_{1+x}Ti_{2-x}O_4$, with the spinel structure.[7–9] By contrast with that material, the solid solution $BaPb_{1-x}Bi_xO_3$ (BPB), with the perovskite structure,[10,11] obtained in 1974 by Sleight, have the necessary stability in their properties, and for $x = 0.25$, have the highest critical temperature $T_c \approx 13$ K (Ref. 12) of any material not containing transition element atoms.

The purpose of this review is to summarize the investigations of the superconducting solid solutions of $BaPbO_3$–$BaBiO_3$ performed over the last decade in many laboratories in the Soviet Union, Japan, the United States, and other countries.

Interest in this system from the point of view of basic physics stems from its unique properties, which are associated with: 1) the anomalously low (for high-temperature superconductors) density of states $N(0)$ at the Fermi surface,[13] 2) the existence of a metal-insulator transition with composition,[11,14] and 3) the fact that the ceramic BPB is a multiple Josephson medium.[15,16] Although a great deal of work has been devoted to the study of the superconductivity of this material, the nature of the superconductivity is still a puzzle, and in the course of studying BPB new questions continually arise. There are, in the literature, several brief reviews of this subject,[17–20] but these lack a critical analysis of the materials then extant, and moreover, the increasing stream of information has rapidly made those reviews obsolete.

2. CRYSTAL STRUCTURE AND PHASE TRANSITIONS

The BPB solid solutions are prepared by the usual ceramic technology methods[10,11,14,17,21] or by hot pressing,[13,22,23] and if the conditions of preparation of the materials are optimized the basic superconducting properties are independent of the means used for the synthesis. The crystal structure of BPB is a slightly distorted pervoskite shown schematically in Fig. 1 (Ref. 24). The general formula is ABX_3, and it consists of connected octahedra of X-anions

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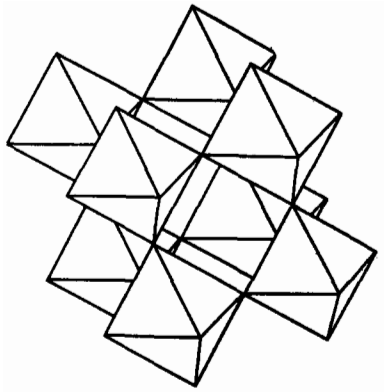

FIG. 1. Perovskite-type structure, composed of octahedra of X-anions with B-cations in the centers of the octahedra and A-cations between the octahedra (Ref. 24).

with B-cations in the centers of the octahedra and A-cations between them. Depending on the composition, some of the lead ions in the B sites may be replaced by bismuth ions of diverse valence.

The structural distortions for the limiting compositions of BPB ($x = 0$ and $x = 1$) have been determined by x-ray and neutron diffraction investigations.[25–29] Most of these investigations; confirm that the unit cell of $BaPbO_3$ at room temperature belongs to the orthorhombic system. However, in Refs. 30–32 the structure of $BaPbO_3$ is described as monoclinic. There is no consensus regarding the crystal symmetry of $BaBiO_3$ either, but from the analysis carried out in Ref. 28 we can assume that this compound is characterized by a monoclinic unit cell with an ordered arrangement of Bi^{3+} and Bi^{5+} ions.[27,33–35]

The structure of BPB solid solutions as a function of x at room temperature has been studied previously.[14,27–33,35,36] If we exclude the data of Refs. 27, 33, and 35, and the results of the x-ray diffraction studies for $x \leqslant 0.11$,[30–32,36] which have not been confirmed by other investigators, then we are led to the conclusion[14,28,29] that in the range of superconducting compositions ($0 \leqslant x \leqslant 0.4$) the lattice has orthorhombic symmetry. Results[30–32,36] obtained both for ceramic and single crystal samples also lead to this crystallographic system for $0.1 < x < 0.5$.

In addition to the phase transitions with composition, structural transitions with temperature are also observed in BPB,[28–32] from the high-temperature cubic phase to the orthorhombic-I phase and then to a low-temperature phase which, according to the data of Refs. 28 and 29, is an orthorhombic-II phase and according to Refs. 30–32 is monoclinic. Of interest are the results of Refs. 28 and 29, where, on the basis of x-ray diffraction studies of the orthorhombic-I phase it has been shown that near the composition $x = 0.25$, which corresponds to the maximum T_c,[14,21,22] the Pb and Bi ions become ordered. These conclusions were based on the measured concentration dependences of 1) the pseudomonoclinic angle β, 2) the temperature of the transition into the cubic phase, and 3) the ratio of the integrated intensities of diffraction lines with different parity of the indices (hkl). A correlation between the structural and superconducting properties follows also from measurements of the dielectric permittivity ε as a function of temperature T for ceramic and single crystal samples of BPB[30–32,36] (Fig. 2). Moreover, it has been concluded[30–32,36] that a state of spontaneous polarization exists in the low-temperature phases of BPB not only next $x = 1$,[37] but also in the range of the superconducting compositions. We note that the possible coexistence of superconductivity and ferroelectricity in this system was first pointed out in Ref. 38.

The interrelation between a structural transformation, which is accomplished by the softening of the transverse optical phonon mode, and superconductivity has been observed previously in degenerate SnTe semiconductors doped with PbTe and in GeTe,[39,40] and $SrTiO_3$.[41] However, the coexistence of ferroelectricity and superconductivity has not been demonstrated theoretically as yet,[42,43] and an unambiguous experimental verification is greatly hindered because the degenerate current carriers screen both the internal and external electric fields in the ferroelectric.

It is well known[1,3,4,6] that because of the electron-phonon interaction structural transitions are frequently accompanied by a rearrangement of the electron subsystem of the material, with the formation of a dielectric gap Σ of a collective nature at the Fermi surface. The appearance of a dielectric gap in BPB for $x > 0.4$ was first observed[14] in the absorption of optical radiation in the far infrared (Fig. 3). The metal-insulator transition has also been corroborated by electrical measurements,[14,17,22,44] as will be discussed in Section 3. The question of whether a structural instability accompanies this compositional transition remains unresolved, since the x-ray investigations that have been carried our have not detected any change in the symmetry of the

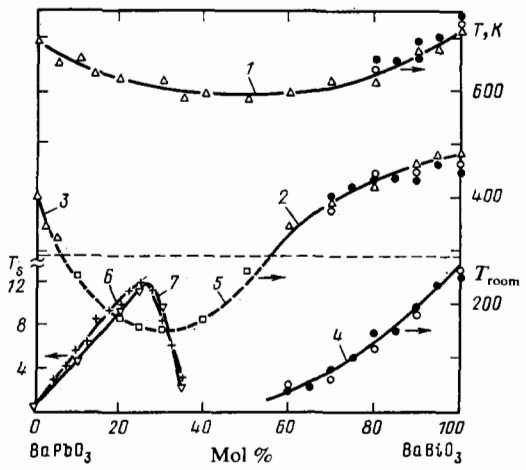

FIG. 2. Composition dependence of the temperature of the phase transition from the monoclinic lattice to the orthorhombic (curves 2, 3—△) and from the orthorhombic to the cubic (curve 1—△), determined by x-ray diffraction. Composition dependences of the maxima of $\varepsilon(T)$ (1,2,4: ●—ceramic, ○—single crystal), T_c (6-ceramic + ; 7, single crystal ▽), and the positions of the maxima of the depletion layer capacitance of single crystal samples (5—□) (the horizontal dashed lines is room temperature).[30]

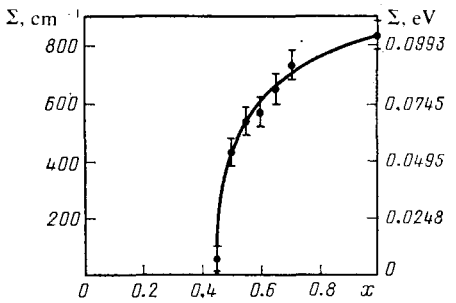

FIG. 3. Dielectric gap Σ in $BaPb_{1-x}Bi_xO_3$ as a function of composition x, as determined from the infrared absorption spectrum.[14]

crystal lattice near $x = 0.4$. Nevertheless, as can be seen from Fig. 2, extrapolation of the position of the low-temperature anomaly in $\varepsilon(T)$ along the x coordinate indicates the desirability of structural investigations at low temperatures in the neighborhood of the metal-insulator transition.

3. ELECTRICAL AND OPTICAL MEASUREMENTS

The dependence of the critical temperature of the superconducting transition on the composition of BPB has been determined by induction and resistance methods.[11,14,21,22,44] All these results are in qualitative agreement, although the absolute value of T_c at the maximum may vary. A typical curve is shown in Fig. 4 (Ref. 21), where the superconductivity of pure $BaPbO_3$, with $T_c \approx 0.46$ K, was observed in single crystals.[45] The opinion has been expressed[12,17,68] that these materials superconduct only at the compositions with $x = 0.2$ or 0.25. It is difficult to agree with this opinion, since it contradicts all previous and subsequent measurements and it can in no way account for the superconductivity of BPB at $x = 0$. The maximum value of T_c, 13.4 K was obtained[12] for the composition $x = 0.25$.

The temperature dependences of the electrical resistance R proved to be nontrivial. In particular, for compositions near the metal-insulator transition a negative coefficient of resistance was observed all the way to temperatures approaching that of the superconducting state.[22,38,46] Interpretation of this fact is complicated by the simultaneous presence of effects associated with the bulk conductivity of the material and contact phenomena caused by the granularity of the structure.

Figure 5 shows the temperature dependences of the resistivity ρ of BPB samples of various compositions prepared by hot pressing.[22] The negative coefficient of resistance and the increase in ρ with increasing x, shown in this figure, are in all probability governed by the intrinsic conductivity of the material, since the method used to prepare the samples[22] results in low porosity and large grain size $d \approx 20\ \mu$m in the ceramic. On the other hand, in samples obtained by free sintering, with considerable porosity ($\theta \approx 0.3$) and small grain size ($d \approx 1\ \mu$m), a negative temperature coefficient of resistance was observed for samples with small x, $x = 0.13$ (Ref. 38), a result that we believe is due to the determining role played by the grain boundaries. Evidence for this supposition is the value of the resistivity, $\rho \approx 5 \cdot 10^{-2}\ \Omega \cdot$cm, which is an order of magnitude greater than that reported in Ref. 22.

Interesting information was obtained in the electrical measurements on single crystals of BPB with composition $x = 0$, 0.1, 0.12, and 0.20 (Fig. 6).[47] A comparison of the data of Refs. 47 and 22 shows that for compositions that are far from the metal-insulator transition the character of the curves of $\rho(T)$ is the same in the two cases but the magnitude of ρ is greater for the polycrystalline samples. An exception is $BaPbO_3$, where, evidently there is no tunneling barrier at the grain boundaries.[56]

From Figs. 4 and 5 it can be seen that T_c is reduced long

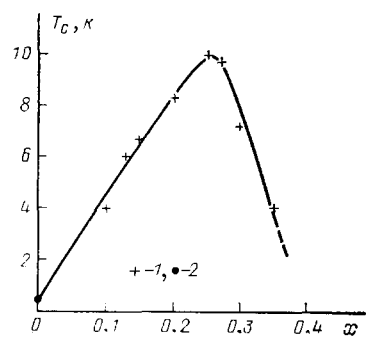

FIG. 4. 1) Critical temperature T_c of the superconducting phase transition of the ceramic as a function of x.[21] 2) The value of T_c (≈ 0.46 K) measured for single crystals.[45]

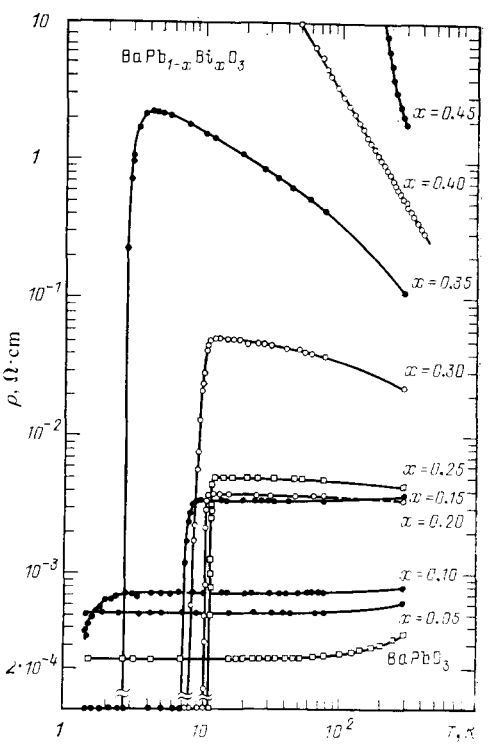

FIG. 5. Electrical resistivity ρ of $BaPb_{1-x}Bi_xO_3$ ceramic as a function of temperature T for various x.[22]

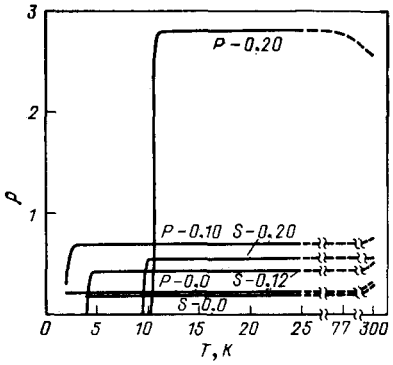

FIG. 6. Temperature dependence of the electrical resistivity ρ (measured in Ref. 47) for single crystals (S) and ceramics (P) of various composition x. $x = 0$, 0.1, 0.12, and 0.20 (vertical scale ρ in $\Omega \cdot$cm).

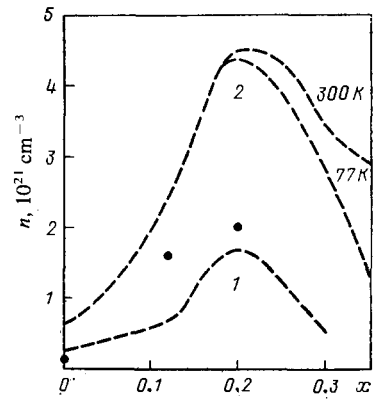

FIG. 7. Carrier concentration n determined from measurements of the Hall constant in the ceramic (curve 1, $T = 300$ K (ref. 44) and curve 2, $T = 77$ K and 300 K (Ref. 22)) and in single crystals (the solid dots[47]).

in advance of the appearance of the dielectric gap[14] observed by optical means for $x > 0.4$. To find the reason for this effect experiments were carried out in which Hall-effect measurements of the current carrier concentration n in the ceramic[22,44] and in single crystals[47] were made. The results are shown in Fig. 7, which is taken from Ref. 47. As we see, the carrier concentration is at least an order of magnitude lower than for good metals with a comparable T_c (e.g., Nb). This fact is astonishing; there is no analog among the other superconducting systems and thus far there is no satisfactory explanation of this result. The dependences $n(x)$ and $T_c(x)$ (see Fig. 4) are mutually correlated, so that the critical temperature as a function of the electron concentration is monotonic,[44] in contrast to the curve of $T_c(n)$ for the niobium-doped semiconducting superconductor $SrTiO_3$, with the perovskite structure.[48] Thus, the decrease in T_c in BPB for $x > 0.25$ is due the decrease in the electron density; hence to explain the decrease in T_c it is not necessary, as in the case of $SrTiO_3$, to invoke existing theories of the superconductivity of semiconductors and semimetals, based on the interaction of the current carriers with longitudinal optical phonons (the Gurevich-Larkin-Firsov model)[49–51] or to take into account multivalley effects.[52]

Detailed studies of the nature of the electronic states in BPB have been carried out.[13,53,54] Measurements of the thermal emf[13,53] have shown that in the region of the superconducting compositions the temperature dependence of the Seebeck coefficient S is nonmonotonic. At higher temperatures ($T > 50$ K), however, the curves of $S(T)$ have a linear part for $x \leqslant 0.3$, and the experimental data were analyzed on the basis of the formula $S = AT + S_0$, where, in the opinion of the authors, the first term corresponds to the free electrons and the second term to current carriers with low mobility. Assuming a parabolic dispersion law and electron scattering by impurities nonmonotonic dependences on x were obtained[13,53] for the effective mass $m^* \approx (1\text{–}1.5)m_e$ and for the density of states at the Fermi surface, $N(0) \approx (3\text{–}9) \cdot 10^{21}$ eV^{-1} cm^{-3}, where m_e is the free electron mass. On the basis of their conclusion that there are two groups of current carriers with different effective masses, and by extrapolating to low temperatures, the authors of Refs. 13 and 53 propose the possibility that the Pashitskiĭ plasma mechanism[50,55] of superconductivity is operative in BPB. However, this assumption has not been confirmed by other experimental data, and, moreover, those results[13,53] were obtained on the basis of a simplified model which does not take into account, for example, the effect of the grain boundaries, with a semiconducting conductivity mechanism,[56] or the effects of disorder.[57]

In the work reported in Ref. 54, reflection spectra in the near infrared were measured for ceramic samples of composition $0 \leqslant x \leqslant 0.25$. The dependence of the plasma frequency ω_p on the concentration of Bi in BPB was found to be in good correlation with the Hall data for n.[22,44,47] The values of the band effective masses were found to be $m_B^* \approx (0.5\text{–}0.8)m_e$, i.e., an order of magnitude smaller than for high-temperature superconductors, such as $Li_{1+x}Ti_{2-x}O_4$ (Ref. 8) or La_3S_4 (Refs. 18, 58), containing transition metal or rare earth ions. Agreement between the optical data for m_B^* and the values obtained from measurements of S[13,53] has been obtained[54] by introducing a correction factor $1 + \lambda$, where the electron-phonon interaction constant λ is determined in Ref. 59 on the basis of measurements of the heat capacity of BPB and the formula of McMillan for T_c.[60] We note that the validity of using this latter formula is in this case problematical, since it is not a universal formula.[1,61] In particular, the probable presence of low-frequency peaks for $\omega \lesssim 2$ meV (we take Planck's constant $\hbar = 1$) in the function $\alpha^2(\omega)F(\omega)$ for BPB with $x = 0.25$ (Ref. 68) makes simple estimates[59] unreliable.

In spite of the relatively large density of free electrons in the superconducting ceramic, measurements have been successfully carried out[62] on the wavelength dependence of the absorption of light in thin films of BPB with $T_c \approx 7$ K. From these measurements it follows that in the thin film superconductor samples the band gap is direct and has a width 2.4 eV.

The experimental data on the properties of the electron states in the $BaPbO_3$–$BaBiO_3$ solid solutions are significantly supplemented by the results of band structure calculations by Mattheiss and Hamann, who used the augmented plane wave method.[63–66] Without going into details let us note that

the calculations[63–66] basically support the picture proposed by Sleight,[10,11] according to which the electronic properties of BPB are determined by the overlap of the partly filled 6*s* bands of Pb and Bi with the filled 2*p* band of oxygen and the formation of a wide conduction band, of the order of 16 eV wide. It follows from the results of Refs. 63–65 that the monoclinic distortion of the cubic lattice in $BaBiO_3$, which brings about the formation of a semiconducting gap, is energetically favorable. Calculations for $x = 0.3$, carried out within the virtual crystal approximation[67] for the Pb and Bi atoms show that these atoms belong to a tetragonal phase,[33] whereas in fact the crystal structure of the superconducting ceramic is evidently orthorhombic (see the discussion in Section 2). Therefore, the reasons for the metal-insulator transition with composition in BPB, even after the work of Refs. 63–65, remain an open question.

The authors of Refs. 63–66 also calculated the density of states and the plasma frequencies for $0 \leqslant x \leqslant 0.3$. The results for ω_p are in satisfactory agreement with optical data;[54] however, for $N(0)$ there is a significant discrepancy between theory and experiment[13,53] which cannot be accounted for by only electron-phonon renormalization. This discrepancy may be due to the difficulties, alluded to earlier, in analyzing the data from thermal emf measurements in BPB. Nonetheless, theoretical calculations, as well as the experiments, imply a density of states $N(0) \approx 3 \cdot 10^{21}$ eV^{-1} cm^{-3} that is anomalously low for such a high-temperature superconductor.

4. ATTEMPTS TO RAISE THE CRITICAL TEMPERATURE OF BPB. PRODUCING THIN FILMS AND SINGLE CRYSTALS

When ceramics of BPB, with their high T_c, were first produced,[10,11] the natural question immediately arose as to whether it might be possible to increase further the critical temperature by complete or partial replacement of the *A* or *B* cations by other elements. The corresponding general formula can be written as $Ba_{1-y}A_yPb_{1-x}R_xO_3$. For $y = 0$, superconductivity in the ceramic above 3 K has been observed only for R = Bi,[69] although it has been possible to replace the lead by Ta, Nb, and Sb.[69,180] Replacement of Ba has proved to be more successful in this regard. For instance, in the first paper by Sleight[11] it has shown that for $y = 0.1$–0.2 the alkali metals do not reduce T_c, but they narrow the superconducting transition. However, this effect may be due simply to an increase in the amount of Pb, compared to samples with $y = 0$, that comes about during the sintering[14] or to an improvement in the sintering conditions.[73] We note that for K, Cs, and Rb the solid solutions comprise a single phase only for $y \leqslant 0.3$.[14,69]

Substituting of rare earth elements for Ba[53] leads to a rapid (Nd, Gd) or a small (La) reduction in T_c for the superconducting composition with $y = 0$ and $x = 0.25$. At the same time, for the semiconductor with $x = 0.4$ additions of La ($y = 0.1$–0.3), Nd, and Gd ($y = 0.2$) transforms the material into a superconductor with a maximum $T_c \lesssim 10.5$ K in the case of La. Incidentally, this effect provides additonal evidence against the notion[12,17,68] that there is only a narrow range of superconducting compositions around $x = 0.25$. Until now, the only element which increases T_c of BPB of the composition $x = 0.2$ is strontium,[71] in the narrow range of composition $y \lesssim 0.07$. Further increase in y results in an abrupt decrease in T_c. However, for $x \geqslant 0.25$, in both the buk samples[23,69,71] and thin films,[72] the critical temperature falls off monotonically with increasing y. We should note that solid solutions with arbitrary x with replacement of Ba by Sr are possible for any y up to $y = 1$.[69] By way of contrast with pure BPB, the symmetry of the crystal lattice is not orthorhombic except for the ranges of composition with $1 - y \ll 1$ and $y \ll 1$, and the negative temperature coefficient of resistance and superconductivity coexist.

From the above facts it is not possible to draw any definite conclusions about the causes for the increase or decrease of T_c that occurs with atom replacement because there is no unique correlation between the changes in T_c on the one hand, and changes in the lattice constant, the crystal structure, the temperature dependence of ρ, and so forth, on the other. There does exist, however, a unique correlation between T_c and the oxygen deficiency of the ceramic.[74,76,204] In accordance with Refs. 27, 34, and 35, we may assume that for fixed x, as the O^{2-} content decreases, the ratio of Bi^{3+} ions to Bi^{5+} ions changes in the direction of increased concentration of Bi^{3+}, and this ion determines the semiconducting properties of the ceramic, so that the formula for the material can be written as[74]

$$BaPb_{1-x}Bi^{3+}_{\frac{x}{2}+y}Bi^{5+}_{\frac{x}{2}-y}O_{3(1-x)}O_{\frac{5}{2}\left(\frac{x}{2}+y\right)}O_{\frac{7}{2}\left(\frac{x}{2}-y\right)},$$

where $y \leqslant x/2$.

Complete disappearance of metallic and superconducting properties for $x = 0.25$ occurs when $\approx 4\%$ of the O^{2-} is lost. In a recent investigation[204] measurements of the Hall constant of single crystal films[84] with $x = 0.3$ at various temperatures showed that oxygen vacancies lead to the formation of current carrier localization centers, so that for low T there is a localization of the remaining free carriers (Anderson localization, in the opinion of the authors of Ref. 204), and the negative temperature coefficient of resistance increases. In this process superconductivity is maintained. In this connection we should call attention to the work of Bulaevskiĭ and Sadovskiĭ,[205] who, within the framework of the Ginsberg-Landau expansion of the free energy, have studied the superconductivity of a disordered metal beyond the localization threshold.

It is well known that increases in T_c in high-temperature and structurally unstable superconductors are frequently obtained by preparing these materials in thin film form (see, e.g., Ref. 77). It is therefore not surprising that as soon as superconductivity was observed in BPB[10,11] attempts were made to prepare thin films by various methods. The principal method that has been used is a version of rf sputtering,[62,72,76,78–80] with the highest deposition rate, 400 Å/min obtained by magnetron sputtering.[81] Laser evaporation of a BPB target,[82,83] which reduces the probability of altering the composition,[79] has also been used. Immediately after deposition, the thin films are semiconducting, and only subsequent annealing in air or oxygen brings about the su-

perconducting state with the same critical temperatures as in the bulk ceramic. The critical temperature T_c falls off with decreasing film thickness for $d \lesssim 4000$ Å.[76] Similar size effects have been observed when the ceramic is finely ground.[38] For the polycrystalline films that were obtained, the critical current density did not exceed $j_c \approx 10^4$ A/cm^2 (Ref. 81). A much greater critical current density

$$j_0 \approx 2{,}5 \cdot 10^5 \text{ A/см}^2$$

is obtained in single crystal films with $T_c \approx 10$ K epitaxially deposited on a single crystal $SrTiO_3$ (100) substrate heated to 700 °C.[84]

An important advance has been the synthesis of single crystals of BPB of various compositions by many groups of investigators.[11,30,45,53,68,79,85–90,183] A detailed description of the methods of growing single crystals from a melt of the starting oxides or a melt in a KCl solvent is contained in Refs. 85–87. The maximum size of the single crystal plates has been 15×15 mm^2.[87] The critical temperatures of the superconducting transition for the single crystal samples, as in the case of the thin films, did not exceed T_c for the polycrystalline ceramics of the same composition.

The existence of structural transformation and metal-insulator transitions with composition (see Sec. 2) have stimulated investigations of the conductivity and of the superconducting properties of BPB under pressure. In the nonsuperconducting ceramics with composition $x = 0.4, 0.5$ and 0.7, resistance measurements in the pressure range $P \gtrsim 50$ kbar have shown a transition into the metallic state.[91] On the other hand, in superconducting samples with $x \geqslant 0.25$ a decrease in T_c, j_c and the superconducting gap Δ has been observed as the hydrostatic pressure is increased for bulk as well as thin film samples.[92–95] Such behavior is not surprising, since in these compositions the lattice parameter decrease that occurs upon the isoelectronic substitution of Sr for Ba leads to a decrease in T_c.[23,71] At the same time, for the composition $x = 0.2$ a maximum is observed in $T_c(P)$ at $P = 4$ kbar,[93] as well as a sharp increase in the critical current I_c near $P \approx 1.5$ kbar.[95] One finds that the maximum in T_c has a good correlation with the increase in T_c and the decrease in the lattice constant by an amount of the order of 0.01 Å that occur when up to 10 at.% Sr is substituted for Ba if, in making the estimates, one uses the compressibility[71] value $6 \cdot 10^{-7}$ bar^{-1}, typical of perovskite systems. We note that this value for the compressibility has recently been obtained experimentally for $BaBiO_3$.[96]

5. GRANULAR MACROSTRUCTURE OF THE CERAMIC. JOSEPHSON EFFECTS IN BULK AND THIN FILM SAMPLES

The dependence of the conductivity and the superconducting properties on the macrostructure of BPB ceramic with fixed x was first pointed out in Refs. 21, 38, and 73. By way of example, Fig. 8 shows the structure of the internal region and of the surface layer of a sample with $x = 0.25$ prepared[97,98] by free sintering. It was observed that the superconductivity depends strongly on the presence of grain boundaries and on the properties of the electronic states at the grain boundaries, which determine, in particular, the kinetic characteristics of the material. The decisive role of the intercrystalline potential barrier in the electrical conductivity of metal oxide ceramics is well known for the case of nonlinear semiconductor varistors.[99,100] In particular, for ZnO in strong electric fields a nonlinear percolation conductivity has been observed,[101,102] in agreement with the theory of Shklovskiĭ,[103] in which surface states localized at the grain boundaries act as compensating impurities. Corroboration of the effect of surface states on the normal properties of the BPB ceramic has recently been obtained for a sample with composition $x = 0.2$ in an M–BPB–M structure,[104] (where M = Al, Cu, or Ag), where a threshold-type change in the I-V characteristic from nonlinear-symmetrical to asymmetrical was observed. The temperature dependence of the conductivity of BPB due to the grain boundaries has a complex nature,[44,97,98] since dielectrization of the electron spectrum (for instance of the type reported in Refs. 97 and 105–109 or in Ref. 110) or Anderson localization of the current carriers[57] can occur in the amorphized film. In the analysis of the electrical conductivity σ it is necessary to take into account the conducting structure characteristic of a granular composite.[111,112] Recently, for the tunneling of electrons in these systems, Shklovskiĭ has formulated a new problem in the theory of current flow—"penalized flow".[113]

Attempts have been made to determine the functional dependence of $\sigma(T)$ in BPB.[18,44,97,98,149] It was found for a

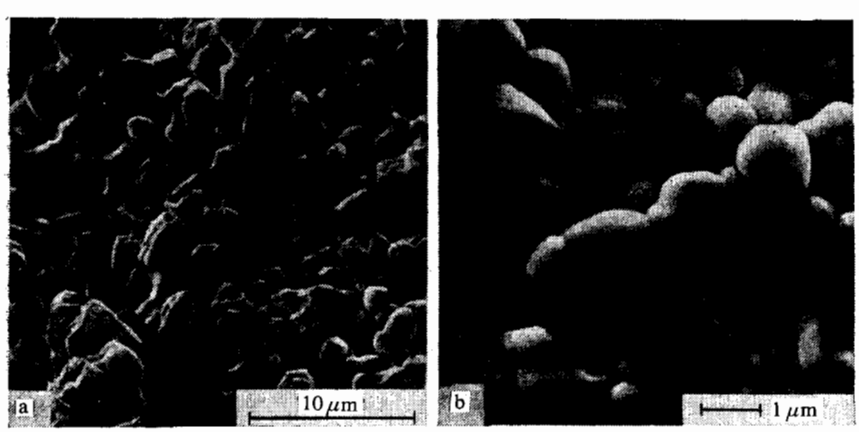

FIG. 8. Macrostructure of the inner regions of the ceramic sample with $x = 0.25$ (a) and of its surface layer (b).[97,98]

finely ground and pressed, but not re-sintered, sample of the superconducting composition $x = 0.25$ for $T \leqslant 30$ K, that $\sigma(T) = \sigma_0 \exp(AT^{1/4})$ and it coincides with $\sigma(T)$ for well-sintered samples with $x = 0.4$, that do not exhibit superconducting properties and that at higher temperatures have an activated conductivity. A similar dependence has also been observed in superconducting films of $La_{3-x}S_4$.[150] In disordered films of InO_x from 200 K to the superconducting transition the relation is $\sigma(T) = \sigma(0)(1 + T^{1/4})$ (Ref. 151), which coincides with the formula given above if one assumes that in Ref. 151 $\sigma(T) - \sigma(0) \ll \sigma(0)$. This temperature behavior of the conductivity is evidently determined both by tunneling between grains and by effects of disorder at the microscopic level.

As regards the dependence of the superconducting characteristics of BPB on the properties of the grain boundaries, the latter not only cause a smearing out of the transition into the superconducting state,[21,73] in particular because of percolation effects,[200,202] but also in some cases bring about a two-humped shape to the $R(T)$ curves near T_c.[18,44] This effect shows up most clearly in specially prepared cleaves (Fig. 9).

Thus, superconductivity exists in BPB in each individual grain at temperatures $T \leqslant \tilde{T}_{c1}$ and Josephson weak links between the grains exist for $T \leqslant \tilde{T}_{c2} < \tilde{T}_{c1}$, and this situation determines the superconducting properties of the system as a whole. This conclusion has been demonstrated correct by direct measurements of I-V curves for the bulk ceramic[15,16,95,114] and thin films.[9,56,94,115]

In a bulk sample of $BaPb_{0.75}Bi_{0.25}O_3$ of dimensions $5 \times 2 \times 1$ mm at 4.2 K and in zero magnetic field H, superconducting current due to the dc Josephson effect and switching to the single-particle tunneling branch at a critical current $I_c = 12$ mA have been observed.[15,16] The switching voltage was $U = 0.12$ V. In other samples the value of U reached the order of 1 V, i.e., generally speaking, all the different junctions involving Josephson coupling across the grain boundaries were triggered simultaneously, as a single

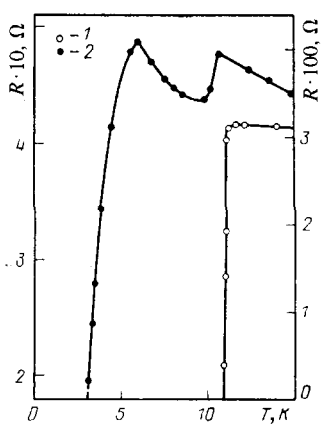

FIG. 9. Superconducting transition for the ceramic with $x = 0.2$ (Ref. 18). 1) Starting sample; 2) sample cleaved and then pressed together at the cleave.

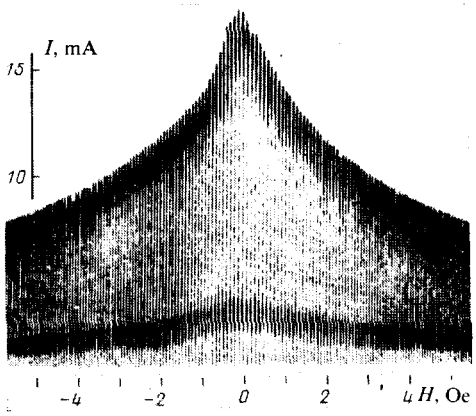

FIG. 10. Critical Josephson current I_c of a bulk ceramic sample with $x = 0.25$ as a function of the magnetic field H.[120]

junction. The reasons for this synchronization, which leads to multiple Josephson tunneling in this three-dimensional granular medium, has not been completely explained, although there are in the literature a number of models for the synchronism of several junctions by way of capacitive, inductive, or resistive coupling,[116] or through the radiation field.[117,118] An estimate of the effective number n_c of series-connected junctions, that determine the magnitude of the switching voltage U can be made[15,16] if it is assumed that this voltage is the sum of contributions $U_s \equiv 2\Delta(T)/e$ from each junction: $n_c = U/U_s \approx 40$ (here the superconducting gap $\Delta(T)$ is calculated by the BCS theory[119,124] from the measured value of T_c, and e is the electron charge).

Applying a weak magnetic field $H \lesssim 5$ Oe causes a reduction in I_c, and steps are observed in the forward branch of the I-V curves[15,16] as a result of some of the Josephson junctions, those that have a low critical current, being removed from the coherent regime of operation. Further increase in H suppresses superconducting tunneling.[120] However, the supercurrent that is evidently associated with the S-N-S junctions in the volume of the sample persists. The curves of $I_c(H)$ (Fig. 10) does not have quantum oscillations, and its envelope cannot be described by the functions $1/H$ (Ref. 121) or $1/H^2$ (Ref. 122), which are characteristic of single junctions. This same gradually sloping curve has been observed[56] in thin film samples of BPB with $x = 0.2$, 0.25, and 0.3, where I_c is the critical current of a single junction.

A detailed study of the temperature dependences $\Delta(T)$ and $I_c(T)$ was made for films with $x = 0.3$, in which, because of the weak synchronization in the quasi-two-dimensional system of grains (the film thickness was of the order of 5000 Å and the grain size was 2400 Å) switching characteristics of single Josephson junctions was obtained (Fig. 11).[115] Because of clustering the number of junctions in Fig. 11 is considerably less than the number of grains in a film of dimensions 10×10 mm. It was shown that $2\Delta(T = 4.2\ \text{K}) \approx 3.3\ T_c$ (here and subsequently we shall take the Boltzmann constant to be $k_B \equiv 1$).[115] However, in subsequent papers by this group[56,94] it was stated that for $x = 0.3$, they

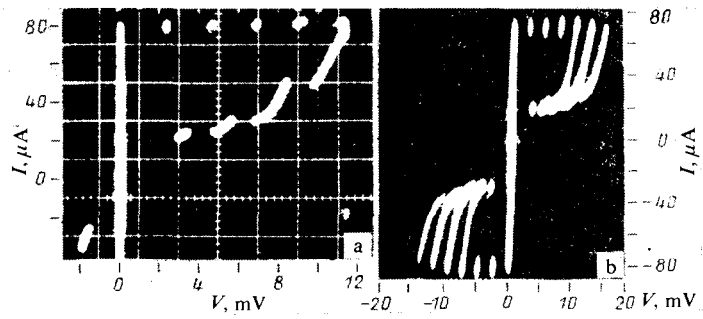

FIG. 11. a) Current-voltage (I-V) characteristic of polycrystalline films 5000 Å thick, with $x = 0.3$. The voltage jumps are 2.2 meV.[115] b) Family of I-V curves with current fluctuations resulting from external noise.[115]

found $2\Delta(0)/T_c > 2\pi/\gamma \approx 3.52$, where $\gamma = 1.78\ldots$ is the Euler constant and $2\pi/\gamma$ is the corresponding value from the BCS theory.[119] On this basis the authors of Ref. 56 made the assumption that BPB near the metal-insulator transition with composition[11,14] is a strong-coupled superconductor.[123] Nevertheless, the dependence $\Delta(T)$ obtained in Ref. 151 is in good agreement with BCS theory, while the discrepancy between the results of Ref. 94 and the curve of Mühlschlegel[124] can be explained by proximity effects.[125]

On the other hand, discrepancies have been observed[126,127,213] between the curves of $I_c(T)$ and the Ambegaokar-Baratoff formula for symmetrical S-I-S junctions[121]

$$\frac{I_c(T)}{I_c(0)} = \frac{\Delta(T)}{\Delta(0)} \operatorname{th} \frac{\Delta(T)}{2T}, \qquad (1)$$

such that the experimental points[126] for $5.5\ \text{K} < T < 8\ \text{K}$ obey the relation $[1 - (T/T_c)]^{3/2}$, which is characteristic of S-N-I-N-S junctions.[128] For the ceramic with $x = 0.2$, however, the critical current $I_c(T)$ is well described by formula (1).[95]

A sharp divergence of the curve of $I_c(T)$ from the usual tunneling dependence[121,129] has been observed[95,130] in bulk samples with $x = 0.25$ (see the insert in Fig. 12) and in measurements of $I_c(T)$ under pressure.[213] This critical current behavior leads to the appearance of reentrant superconductivity, i.e., to the collapse of the superconducting state as measured by the resistance below a certain temperature T_{c2} (Fig. 12). This effect can be explained by the breaking of the Josephson coupling by the current between the grains as a result of the increase in resistance of the barrier at the grain boundaries, while the superconductivity is preserved within the grains, a situation that is confirmed by measurements of the magnetic susceptibility.[130] The change in the characteristics of the intergrain potential barrier can occur when the temperature is lowered and is a result of the filling of the surface states at the grain boundaries,[101-102] or the semiconducting increase in the resistance of the intergranular layers.[131] Moreover, this effect may result from the dielectrization of the ceramic on account of the formation of Bi^{3+}–Bi^{5+} pairs by the mechanism of Ref. 110, a process that is more probable at the grain boundaries,[132-133] or from the transition of the grain boundary to an excitonic dielectric phase.[134]

In sum, a new phenomenon has been observed in BPB—reentrant superconductivity with respect to the resistance, which has a substantially different nature than analogous effects that have been observed experimentally in magnetic superconductors,[135,136] or that have been predicted theoretically[137-139] for granular superconductors with very fine grains, where the Coulomb energy plays an important role.

The high sensitivity of superconducting tunnel junctions to external electromagnetic radiation because of the ac Josephson effect[121,129] is, in the multiple Josephson medium presently under consideration, manifested especially clearly as a consequence of the synchronization of a large number of junctions. This has been demonstrated for both microwaves[15,16,140,144] and radiation at optical frequencies.[142,145] In particular, in thin film samples of composition $x = 0.3$ investigators have observed the appearance of a voltage $U \approx 2$ mV upon application of a microwave field of frequency 1.8 GHz, the imposition of a polarity upon U by short current pulses, and the appearance of hysteresis loops in the I-V characteristics.[140,143] In the layered structure

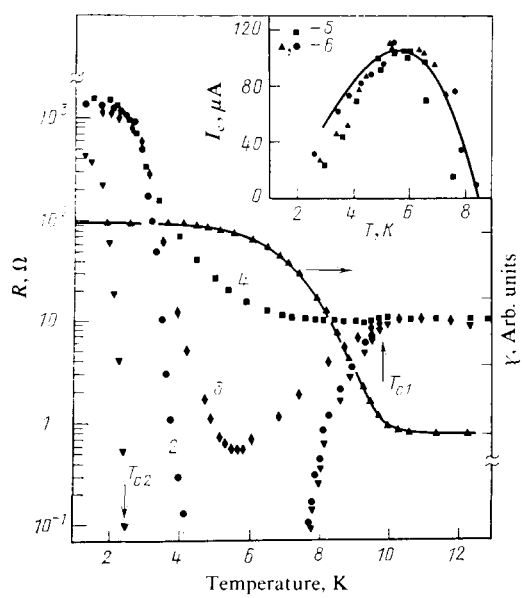

FIG. 12. Temperature dependences of the electrical resistance R and the magnetic susceptibility χ (shown by the arrows) of a bulk ceramic sample with $x = 0.25$ for various measuring currents and magnetic fields: 1) 11 μA and 0.5 Oe; 2) 72 μA and 0.5 Oe; 3) 94 μA and 2.0 Oe; 4) 72 μA and 216 Oe. The inset shows the temperatures dependence of the critical current I_c. 5) measurements at constant current; 6) in pulsed mode, with pulse length 2.0 and 0.3 ms.[130] The solid curve corresponds to a calculation[130] using the formula from the theory of Ref. 131.

BPB/Al_2O_3/BPB/sapphire, where the thickness of the BPB was 0.3–0.4 μm and that of the Al_2O_3 was 0.2–0.3 μm, the *I-V* curves of the upper receiver film[144] was found to be broadened by the Josephson superemission[70,117,118] from the lower generator film. This result is of particular interest, since in a specially prepared two-dimensional system of junctions (of lead alloys, for instance[146]), synchronous switching is observed only if the structure is sufficiently regular and uniform.

The transparency of BPB films of thickness 0.2–0.35 μm made it possible to observe the effect of light of 1–10 μm wavelength on the *I-V* characteristics in the absence of a microwave background[145,203] and to obtain switching in the hysteresis loop induced by a microwave field of frequency 2 GHz by the action of helium-neon laser light of 1 nW power (the wavelength is $\tilde{\lambda} = 632.8$ nm).[142] In this experiment the thermal action of the radiation was negligible.

In addition to the *I-V* curves such as those shown in Fig. 11, for films with $x = 0.3$, having a small critical current and a wide voltage hysteresis, *I-V* curves with discrete current values ΔI have been observed,[147] where, for a load resistor $R_L > 1$ kΩ, the voltage jump $\Delta V = R_L \Delta I$ corresponded to a value $2\Delta \approx 2.8$ meV.

The results of the experiments described above indicate the promising potential for the use of BPB as material for elements of cryoelectronic devices such as high-sensitivity detectors of electromagnetic radiation, oscillators in the microwave range, and various types of switches. For instance,[141] when passing mutually orthogonal transport current I_x and I_y through a thin-film, an increase in I_x above the critical value $I_{cx} \approx 340\,\mu$A, produced a shift in the I_y vs V_y *I-V* curve by an amount ΔV that is a multiple of $2\Delta/e$ (Fig. 13). This structure makes it possible to develop a voltage source with zero impedance, a device that may be used as a new logic element. A device in which one current loop in a BPB ceramic controls the switching in other loops has also been proposed in Ref. 114.

6. THERMODYNAMICS AND ELECTRODYNAMICS OF THE SUPERCONDUCTING STATE

The starting point in the interpretation of the experimental results presented above was the assumption of the bulk nature of the superconductivity of BPB. A natural proof of this assumption would be the observation of a jump ΔC in the heat capacity at the temperature of the phase transition into the superconducting state. However (and in this instance the nontrivial nature of the behavior of BPB once again is manifest) measurements carried out by the adiabatic calorimetric method on samples with $x = 0.25$ (Refs. 17, 148) showed no jump ΔC in the neighborhood of $T_c \approx 10$ K, where this value for the critical temperature was clearly defined by the change in inductance. This result confirmed measurements[53] of the thermal relaxation time τ in BPB samples of the same composition, carried out by the method of Ref. 152, in which the heat capacity C is proportional to τ.

The nonobservability of an anomaly near T_c has been explained[97,98,108,109,149] by a decrease in ΔC that occurs when the electron spectrum of the material is partially dielectrized.[105] According to the model of Bilbro and McMillan[105] (see also Refs. 106, 108, 109, and 153–155), there exists parts (1 and 2) of the Fermi surface for which the condition of congruence holds:

$$\xi_1(\mathbf{p}) = -\xi_2(\mathbf{p}+\mathbf{Q}) \equiv \varepsilon(\mathbf{p}), \tag{2}$$

and this leads to an excitonic instability[156–158] and the formation of a dielectric gap Σ. Here, Σ is determined by the electron-hole pairing constant $V_{e-h} = V - 3U > 0$, where

$$\tilde{V} = V_{12,21} = V_{21,12},$$
$$\tilde{U} = V_{11,22} = V_{22,11} = V_{12,21} = V_{21,12} \tag{3}$$

are the matrix elements of the effective four-fermion interaction, constructed from the wave functions of the quasiparticles from the corresponding parts of the Fermi surface. At the same time the superconducting order parameters in the

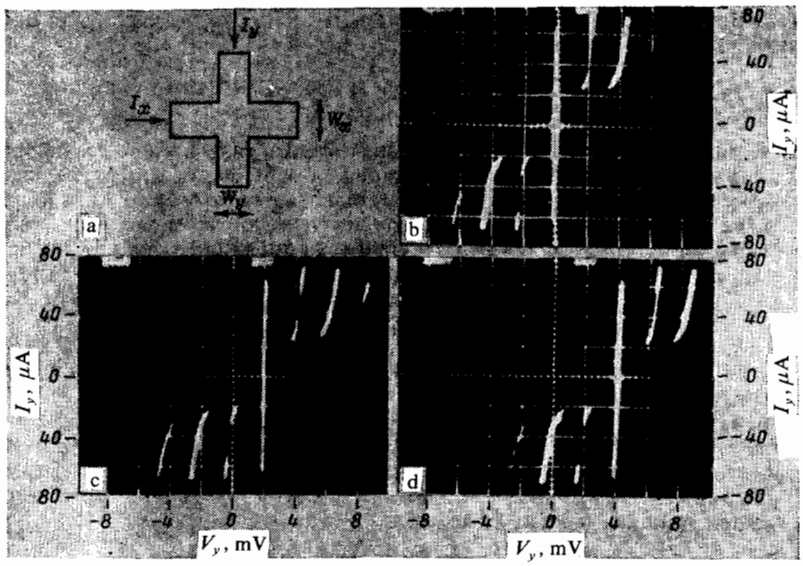

FIG. 13. Experimental arrangement for measuring the *I-V* characteristics of $BaPb_{1-x}Bi_xO_3$ films ($x = 0.3$) with mutually orthogonal currents I_x and I_y (Ref. 141). a) W_x and W_y are the electrode widths. b) I_y-V_y curves for a sample with $W_x = 20\,\mu$m, $W_y = 5\,\mu$m for $I_x = 0$. c) $I_{x1} > I_{cx} \approx 340\,\mu$A. d) $I_{x2} > I_{x1}$.

degenerate ($\Delta_{11}=\Delta_{22}\equiv\Delta_1$) and the nondegenerate ($\Delta_{33}\equiv\Delta_2$) parts of the Fermi surface, where the dielectric gap is absent, are determined by combinations of other electron-phonon interaction constants.[106] In the limit of strong mixing of the electron states from the various parts of the Fermi surface[105] all these constants have the same value and are equal to $V_{33,-3}=V_{e-e}$, with the value of V_{e-e} determining the only superconducting gap Δ in the entire Fermi surface. We note that in this case $V_{e-h}=2V_{e-e}>0$, so that in a single material there is both electron-hole pairing the Cooper pairing of quasiparticles.

Analysis of the thermodynamics of the system described above, under the assumption that $\Sigma\gg T_c$, leads to the result[97,108,109]

$$\frac{\Delta C}{C_n}=\frac{12}{7\zeta(3)}\times\frac{[\nu+(2\pi\Sigma/T_c)^{1/2}\exp(-\Sigma/T_c)]^2}{\{\nu+[4\pi^2T_c^2/7\zeta(3)\Sigma^2]\}\{\nu+[(3\sqrt{2\pi}/\pi^2)(\Sigma/T_c)^{5/2}\exp(-\Sigma/T_c)]\}}, \quad (4)$$

where C_n is the heat capacity of the normal phase at $T=T_c$, $\zeta(x)$ is the Riemann zeta function, $\nu=N_{nd}(0)/N_d(0)$ and $N_{nd}(0)$ and $N_d(0)$ are the densities of states at the nondielectricized and the dielectricized parts of the Fermi surface. The main correction term to the BCS result $(\Delta C/C_n)_{BCS}=(12/7)\zeta(3)\approx 1.43$ is contained in the first curly brackets in the denominator, and for small values of ν can lead to a ΔC that is smaller than experimental error, while T_c is quite high. The applicability of this model involving partial dielectrization[105] to BPB has been confirmed by the band structure calculations of Mattheiss and Hamann,[63-65] which showed that the condition for congruency (Eq. (2)) is exactly satisfied at $x=1$, and by experiments[90] in which a negative temperature coefficient of resistance was observed for single crystal samples with $x=0.27$. The interpretation proposed[97,98,108,109,149] for the experiments of Refs. 17, 53, and 148 is in agreement with recent adiabatic calorimeter measurements[159-161] of C. The dependence of C/T on T^2 for freshly prepared samples with $x=0.25$ is shown in Fig. 14 (curve 1). A jump ΔC is observed at $T\approx 6.3$ K, which corresponds to the point of maximum slope in the superconducting transition curve as determined by inductive measurements. The analysis made it possible to determine the parameters of the model (Ref. 105) for BPB with composition $x=0.25$: $\Sigma=46$ K and $\nu=0.9$. A repetition of the experiment on the same samples 1.5 months later showed that the jump was no longer present, while the diamagnetic Meissner properties remained practically unchanged, a result that indicates that there are some long-term relaxation processes, of an unknown nature, for the electronic states of BPB.

Calorimetric measurements on solid solutions with $x=0.25$, carried out on single crystals[68] by the same method that was used in Refs. 48 and 159–161, permitted a determination of the Sommerfeld constant $\gamma_S=1.65\pm 0.2$ mJ/mole·K^2, but the jump ΔC was absent. In the same investigation the authors succeeded in observing a jump $\Delta C/C\approx 0.025$ by the method of calorimetry using alternating current. Indications of weak variations in the curve $C(T)$ for $T\leqslant T_c$ were also obtained for single crystal of BPB[89] by the ac heating method[162] and for samples of composition $0.2\leqslant x\leqslant 0.3$ in magnetic fields $H\leqslant 60$ kOe (Ref. 59) by the method of thermal relaxation.[152] Thus, the experiments carried out by various groups confirm the bulk character of the superconductivity of BPB. Moreover, an analysis has been carried out[53,59] on the temperature dependence $C(T)$ on the basis of the polynomial formula

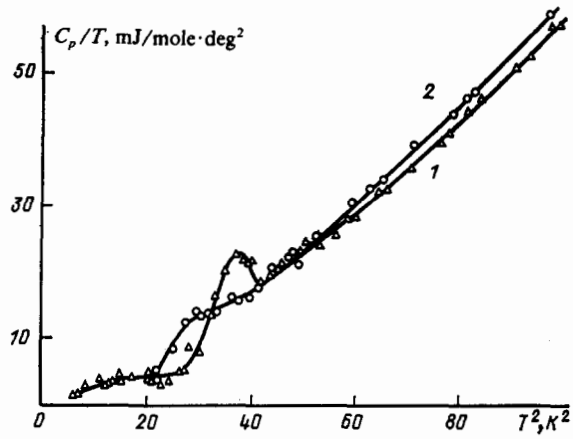

FIG. 14. Low-temperature specific heat of the ceramic with $x=0.25$ in 6 days after preparation (curve 1), and after 1.5 months storage in air (curve 2).[159-161]

$$C=\gamma_S T+aT^3+bT^5, \quad (5)$$

where a is related to the Debye temperature θ_D and the third term in (5) is introduced[59] to describe the nonlinearity of the curves of C/T vs T^2, which was also observed in other investigations.[148,159-161] The contradictory results obtained for θ_D in Refs. 53 and 59 indicate that it is not possible to describe the heat capacity of "soft" perovskite systems by a Debye interpolation model, a fact that the present authors have pointed out previously,[159-161] and which is due to the existence in BPB of low-frequency optical phonons.[63-65,68,163,164]

If the interpretation of the calorimetric measurements on BPB within the framework of a model of a superconductor with a partially dielectricized electron spectrum[105] is correct, then, as has been shown,[165,166] the temperature dependence of the upper critical field H_{c2} must be substantially different from the dependence $H_{c2}(T)$ according to the BCS theory.[6,167,168] Specifically, in the "dirty" limit where $T_c\tau_d\ll 1$, $T_c\tau_{nd}\ll 1$ and Σ is the largest energy parameter in the problem, in the limiting cases, where $T\to 0$ and $T\lesssim T_c$, we have, respectively:

$$H_{c2}=\frac{\pi cT_c}{2e\gamma D_{nd}}\left(1-\frac{\pi D_d T_c}{4\gamma\nu\Sigma^2 D_{nd}\tau_d}\right)\left[1-\frac{2}{3}\left(\frac{\gamma T}{T_c}\right)^2\right] \quad (T\to 0), \quad (6)$$

$$H_{c2}=\frac{4cT_c\,[1-(T/T_c)]}{\pi eD_{nd}\,[1+(2D_dT_c/\pi v\Sigma^2D_{nd}\tau_d)]}\left\{1-\left(1-\frac{T}{T_c}\right)\frac{(1/2)-[(28\zeta(3)/\pi^4)+2\,(D_dT_c/\pi v\Sigma^2D_{nd}\tau_d)^2]}{[1+(2D_dT_c/\pi v\Sigma^2D_{nd}\tau_d)]^2}\right\}\quad (T\leqslant T_c);\qquad (7)$$

where D_{nd}, τ_{nd}, D_d, and τ_d are the diffusion coefficients and the elastic relaxation times due to nonmagnetic admixtures of electrons from the nondegenerate and the degenerate parts of the Fermi surface, and c is the velocity of light. It can be seen from (6) and (7) that in spite of the smallness of the parameter $T_c/\tau_d\Sigma^2$, it is possible, for small v, to increase the slope $|dH_{c2}/dT|$ and thus change the sign of the curvature d^2H_{c2}/dT as compared to the BCS theory.[167-168]

At the present time there exists a great deal of experimental data on the variation of $H_{c2}(T)$, both for ceramic samples[22,47,53,82,83,164,169] and for single crystals.[47,68,90] The results of these investigations are shown in Fig. 15. It can be seen that as BPB approaches in composition to the metal-insulator transition[14] the curve of $H_{c2}(T)$ deviates from the standard curve[167-168] to the extent of changing the sign of the curvature to positive regardless of whether the sample is a ceramic or a single crystal. This result makes it possible to reject any possible explanation of the experimental data on the basis of a model of a granular, weak-coupled superconductor[170] with a characteristic intergranular distance to which, with decreasing temperature, the radius of the normal vortex core, $r\approx\xi(T)$, becomes comparable, where $\xi(T)$ is the coherence length.

On the other hand, the explanation[171] of the positive d^2H_{c2}/dT^2 in BPB on the basis of a bipolaron superconductivity mechanism does not take into account that for small x, $d^2H_{c2}/dT^2<0$ (Fig. 15). Thus, the interpretation that we have advanced for the curves of $H_{c2}(T)$ remain at present the most probable. Nevertheless, it should be borne in mind that the fact that $d^2H_{c2}/dT^2>0$ might possibly be explained on the basis of the theory[205] of the superconductivity of localized electrons if, as has been asserted,[204] a superconductor—Anderson-dielectric phase is realized in BPB.

As for the maximum value of $H_{c2}(0)$ corresponding to the composition with the highest T_c, an estimate of this quantity from the well-known formulas of the electrodynamics of superconductors in the "dirty" limit[172] is incorrect in view of the substantial deviation of $H_{c2}(T)$ from the dependence given by the BCS theory.[167,168] For instance, the value of $H_{c2}(0)$ obtained by extrapolation of the experimental curve for BPB with $x=0.27$ to $T=0$ is 44 kOe, whereas the calculation using the formula

$$H_{c2}(0)=-\frac{\pi^2T_c}{8\gamma}\left.\frac{dH_{c2}}{dT}\right|_{T=T_c}$$

yields, on the basis of the same curve, the value $H_{c2}\approx 32.5$ kOe.[90]

Of considerable interest are the measurements of the resistance of superconducting BPB, in a magnetic field, performed in a number of investigations.[46,83,173,174] For samples with $x\geqslant 0.25$ there is, at $T<T_c$, a negative magnetoresistance with two peaks, one in the region $H\leqslant 200$ Oe and the other in fields $H_{c2}<H<200$ kOe. The first of these may be explained in terms of a granular structure and Josephson links in the bulk of the material, while the negative magnetoresistance in high fields is associated by the author of Ref. 83 with the suppression of the quantum corrections to the conductivity in a magnetic field.[175-176] It should be noted, however, that the application of the theory[175,176] constructed for macroscopic homogeneous systems to a granular composite of BPB requires additional justification that takes into account percolation effects.[112]

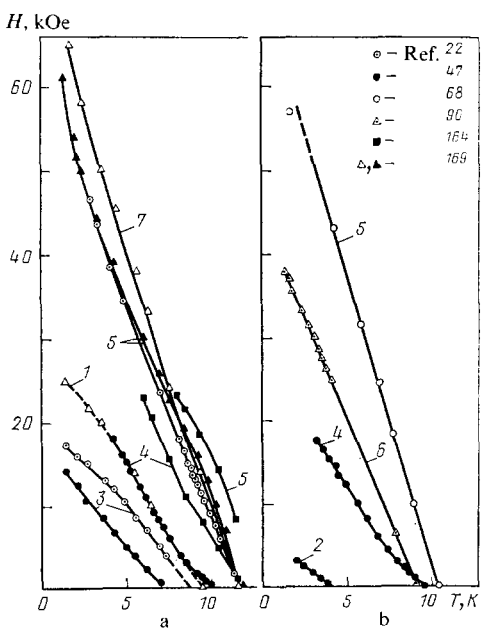

FIG. 15. Temperature dependences of the upper critical magnetic field H_{c2} for ceramic (a) and single crystal (b) samples. Curves 1–7 correspond, respectively, to composition $x=0.1$,0.12,0.15,0.20,0.25,0.27, and 0.3.

7. CORRELATION OF NORMAL AND SUPERCONDUCTING PROPERTIES. THE NATURE OF SUPERCONDUCTIVITY

In the theoretical analysis of the reasons for the appearance of superconductivity with high T_c in BPB solid solutions and the disappearance of the superconductivity with increasing Bi concentration investigators[110,171,177,178,179,184] have frequently begun with the assumption that the Bi^{3+} and Bi^{5+} ions alternate in the crystal lattice as has been shown to be the case in $BaBiO_3$.[34,35,199] Investigations have therefore been undertaken to observe directly the valence of bismuth by x-ray photoemission and resonance methods.

In the work reported in Ref. 88, for example, x-ray photoemission spectroscopy was used, but the accuracy of the methods was not sufficient to distinguish these states even for $BaBiO_3$. On the other hand, from measurements of the x-ray absorption fine structure (EXAFS) above the L_{III} series threshold for BPB with $x=0$, 0.25, 0.6, and 1.0, radial distribution functions around the Ba, Pb, and Bi ions were obtained.[182] It was found that for $BaBiO_3$ the peak correspond-

ing to the position of the oxygen ion has a doublet structure, which definitely corroborates the results of structural studies[34,35] and quantum chemical calculations.[199] Moreover, analysis of the Pb–O and Bi–O bond lengths for the compositions $x = 0.25$ and 0.6 provides indirect evidence for the possible alternation of the Bi^{3+} and Bi^{5+} ions in the solid solutions as well.

To study the electronic and lattice properties of BPB Mössbauer spectroscopy methods using the Sn nuclei have also been employed.[119,36,184,185] The nonmonotonic variation with composition of the isomeric shift δ, with the maximum for $x = 0.22$ is in good agreement with the concentration dependences of the electronic properties $T_c(x)$[11,14,21,22] and $n(x)$ of the solid solutions.[22,44,47] On the other hand, the temperature dependence of the magnitude of δ and the probability f of resonance absorption of x rays have no anomalies over a wide temperature range, and their behavior is qualitatively the same for superconducting and nonsuperconducting samples, a result that indicates the absence of any important differences in lattice dynamics.[185]

The parameters of electron-positron annihilation have also been measured for BPB of various compositions.[184] The dependences on x of the two characteristic annihilation times τ_1 (by free carriers) and τ_2 (by defects) and the annihilation intensity I_2 by the second channel are nonmonotonic: $\tau_1(x)$ and $\tau_2(x)$ have maxima and I_2 has a minimum at $x = 0.2$. The conclusion of the authors[184] that the minimum in $I_2(x)$ is due to a decrease in the defect concentration of the structure agrees with the results of Refs. 28 and 29, which were discussed in Section 2.

We should emphasize that in spite of the large amount of experimental data which has been analyzed above, the information that presently exists is not sufficient to produce a unique point of view regarding the superconductivity of BPB.

The theory of superconductivity with partial dielectrization of the electron spectrum within the framework of the Bilbro-McMillan theory[105] is phenomenological to the same degree as the BCS theory,[119,172] in that the parameters λ, Σ, and ν that enter into the theory can in principle be determined experimentally. However, to go to the limit of this phenomenological scheme, that is, to calculate these parameters from the properties of BPB in the normal state, is impossible at our present level of knowledge of this material. Therefore, the attempt[209] to calculate λ by the McMillan formula[60] or T_c appears unconvincing. Actually, as pointed out in Section 3, the formula of McMillan is not a general one.[1,61] Moreover, in Ref. 209 the material BPB was described with the use of only one simple electron band, a description that is in any case invalid near the metal-insulator transition with composition. Finally, it is obvious that the calculation of the Coulomb pseudopotential μ^* (Ref. 209) on the basis of this description claims too great a degree of accuracy, if one takes into account the approximations that were used in deriving the analytic formula for T_c (Refs. 1, 61, and 210).

On the other hand, attempts have been made to explain the properties of $BaPbO_3$–$BaBiO_3$ solid solutions in the normal and superconducting states from a more radical point of view. In one such attempt it is suggested that the superconductivity of BPB has a bulk of character, and it proposes that the superconductivity is localized at the grain boundaries and it is due to the interaction of electrons with surface excitations in an amorphized layer.[93] There is no necessity for a detailed consideration of the microscopic reasons for the pairing at the grain boundaries, since this notion is refuted in this case by the jump in the heat capacity near T[159–161] and the existence of the Josephson effect in the granular ceramic.[15,16,115]

The opinion has been expressed[13,53] that BPB has such a high T_c at such a low carrier concentration because of a plasma mechanism.[50,55] Evidence for this point of view is data that indicate the existence of two kinds of current carriers. However, as pointed out in Section 3, the analysis of the results of the Seebeck coefficient measurements for BPB,[13,53] are questionable. Furthermore, the optimistic estimates[55] of T_c for the plasma mechanism of superconductivity in semiconductors and semimetals were later called into question.[1,50,186–189] The reasons for the "lowering" of T_c in the theory have been discussed in detail in these publications.

Finally, the point of view is held[171,178,179,184,190] that BPB is an example of a superconductor in which Bose condensation of electron pairs (bipolarons) occurs.[178,191–193] The bipolaron mechanism is in fact a revival of Schafroth, Blatt, and Butler's idea[194] of the superconductivity of nonoverlapping quasimolecules. In contradistinction to the BCS theory,[119] a theory of this type requires that the inequality $V \gg E_F$ be satisfied, where V is the characteristic energy of the net attraction of the quasiparticles and E_F is the Fermi energy. We believe that this point of view (see also, Ref. 68) is refuted by band structure calculations,[63–65] from which follows the s-p character of the electron bands in BPB. Polaron band narrowing, which has been studied in connection with application to compounds with the A-15 structure,[195] is not observed here. In spite of the small density of states, the inequality $E_F \gg T_c$ is satisfied,[13,53] and optical measurements[54] lead to effective masses $m^* \approx (0.5\text{–}0.8)m_e$, so that there is no analogy with the "exotic" superconductors $CeCu_2Si_2$ (Ref. 196), UBe_{13} (Ref. 197), or UPt_3 (Ref. 198).

There is yet another version of the theory,[206] that is based, as are Refs. 171,178,179, and 190–193, on Anderson's idea[207] of the attraction between two electrons at a single bond site as a result of electron-phonon renormalization of the Coulomb repulsion. In contrast to other investigations of the material BPB (e.g., Refs. 63–65), the calculations of Ref. 206 take into account the random arrangement of the Pb and Bi atoms in a self-consistent coherent potential approximation[208] and not in the virtual crystal approximation.[67]

In this treatment the ratio between V and the band width W (the order of E_F) can be arbitrary, so that the phase diagram of the system varies depending on W/V. The authors of Ref. 206 were able to derive a dependence $T_c(x)$ that agrees qualitatively with experiment.[11,14,21,22,44]

Rice and Sneddon[110,177] have proposed a model of BPB

superconductivity that in a certain sense is alternative to that developed in Refs. 171,178, and 179. Those authors[110,177] suggest that the alternation of Bi^{3+} and Bi^{5+} in $BaBiO_3$ (Refs. 34, 35, 182, and 199) is a result of the interaction of the electrons with the displacements of the oxygen atoms, and it occurs in solid solutions up to a 65% replacement of the Bi atoms by Pb. The theory that was developed[110,177] describes the dielectrization of the electron spectrum, as does the theory of Bilbro and McMillan,[105] although it is not clear from the former[110,177] whether a version of the theory with partial dielectrization exists. The high T_c of the superconducting transition in BPB is presumed by Rice and Sneddon to be a consequence of the softening of the crystal lattice and the attendant increase in λ; here the superconductivity was discussed within the framework of BCS pairing in **k**-space.[119,172] From the calculations of Refs. 63–65 it follows that the ferroelectric shift of the Pb-Bi atoms and the oxygen breathing modes may serve the role of the phonons that are responsible for this pairing. Preliminary results of tunneling experiments[68] seem to confirm the existence of a low-frequency phonon peak of energy $\omega \lesssim 2$ meV. Phonons with somewhat higher energy $\omega \approx 6$ meV have been observed in tunneling experiments[68] for $x = 0.25$ and in Raman scattering spectra[211] in single crystals of BPB with $x = 0.3$. If one also takes into account the nonlinearity of the dependence of C/T on T^2 (Refs. 59,148, and 159–161), then it can be concluded that low-frequency optical phonons play an important role in the superconductivity of BPB.

It is interesting to note that the dependence[211] on x of the intensities of the Raman scattering peaks with frequencies 100 and 43 cm^{-1}, as well as many other characteristics of the solid solutions considered in that review, correlate well with the curve of $T_c(x)$.[11,14,21,22,44]

8. CONCLUSIONS

In conclusion we should emphasize that the uniqueness of the metal oxide superconductor $BaPb_{1-x}Bi_xO_3$ is due to the combination of a strong electron-phonon interaction and a small density of electron states at the Fermi surface. The stream of publications dealing with various aspects of the phenomena observed in the ceramic attests to the remarkable diversity of properties of this physical object. Further study of both single crystals and polycrystalline samples of BPB may prove to be very important for discovering the way to produce high-temperature superconductors, since in BPB spontaneous polarization and modification of the electron spectrum, both of which compete with Cooper pairing, play an important role, but nevertheless the critical temperature reaches 13 K.

The simplicity of producing bulk structures with Josephson tunneling and systems with symmetrical potential barriers makes the oxide ceramic a convenient model for studying synchronization in disordered Josephson media and percolation current transport through the superconducting regions in superconductor-normal metal (or semiconductor) mixtures, while taking into account the complex topological structure of an infinite cluster.[212] Investigations of nonequilibrium phenomena in superconducting tunnel junctions with natural potential contours or in ceramics of the "multiple" type or the "bicrystal" type are also of great interest. The development of modern superconductor physics along these lines, operating, upon a new level of understanding, may lead to significant progress in the applied field of low-current cryoelectronics. A variety of multifunctional devices[114] as well as fast, supersensitive radiation detectors[203] can already be made from $BaPb_{1-x}Bi_xO_3$.

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