Nature of superconductivity in $BaPb_{1-x}Bi_xO_3$ solid solutions with perovskite structure. Role of dielectrization of the electron spectrum

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The electric resistance R of a set of $BaPb_{1-x}Bi_xO_3$ solutions of varying compositions is measured as a function of the temperature T. A negative temperature resistance coefficient is observed for superconducting samples with $x = 0.25$ and $T_c \approx 10$ K; this is an indication of the dielectrization of the electron spectrum. The experimentally observed absence of a heat-capacity jump at $T = T_c$ is explained on the basis of the theory of superconductors with a dielectric gap on a part of the Fermi surface.

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1. Ever increasing attention is being paid of late to the superconducting system of solid solutions $BaPb_{1-x}Bi_xO_3$, which has at a relatively low carrier density the highest critical temperature $T_c \lesssim 13$ K of all the substances that do not contain transition-element atoms.[1–15] As shown in Ref. 1, $BaPb_{1-x}Bi_xO_3$ crystallizes at all x into a structure of perovskite type. One of the most interesting and characteristic properties of the superconducting oxide ceramic $BaPb_{1-x}Bi_xO_3$ is the nonmonotonic (with a maximum) dependence of T_c on the Bi content[3,6] and on the carrier density.[11,13] This dependence is due to transition of the system from the metallic to the semiconducting state. This composition transition is accompanied by the appearance of a negative temperature resistance coefficient (TRC), which is possessed even by samples having $T_c \approx 10$ K (Refs. 5, 7, 11, and 13).

Another feature of the substance investigated is that the superconducting properties are extremely sensitive to the macrostructure of the synthesized solid solutions.[7,14] In particular, an effect was observed wherein the superconducting transition as revealed by inductive and resistive measurements vanishes when the ceramic is pulverized. It can be assumed that this effect is due to a change of the electronic states near the developed free surface, whose properties can differ from the bulk properties as a result of the surface reconstruction. The cause of this dielectrization is apparently the restructuring of the valence states of the bismuth, namely, to the surroundings-induced Bi^{4+} configuration to the states Bi^{3+} and Bi^{2+} characteristic of the semiconducting compound $Ba_2Bi^{3+}Bi^{5+}O_6$ (Ref. 18). It must be emphasized that the electron-spectrum tendency to dielectrization manifests itself not only on the surface but also in the bulk of the substance, as is evidenced by the decrease of the fraction of the superconducting phase as the composition with $x = 0.4$ is approached,[6] by the increase of the resistivity ρ, and by the appearance of a negative temperature expansion coefficient,[5–7,11,13] but also by the structural composition transition observed near $x = 0.35$ with the aid of slow-neutron scattering.

Despite the partial dielectrization of the electron spectrum, the superconductivity of $BaPb_{1-x}Bi_xO_3$ is observed in a wide range $0 \leqslant x \lesssim 0.4$ by both the inductive and the resistive method, regardless of the synthesis method and of the purity of the initial materials. In a recent paper, however,[12] doubts are expressed concerning the very existence of superconductivty in the bulk of a perovskite phase and it is assumed that the observed diamagnetism can be due to superconductivity of impurities. The basis for this statement were measurements[12] of the low-temperature heat capacity $C(T)$, which have shown the absence of any anomaly whatever near T_c. Without denying the validity of the experimental data of Ref. 12, obtained for two groups of samples, we do not agree, however, with the assumption made there that the superconductivity observed is of impurity origin. Evidence to the contrary is provided both by the dependence of T_c on x (Refs. 3 and 6), which is reproducible for samples of varying purity, and the vanishing, observed by us,[7] of the superconducting properties following crushing of samples of a given composition. Another interpretation of the results of Ref. 12, proposed in Ref. 15, is that this is a two-phase system with a small ratio of the volume of the metallic and semiconducting phases. A high T_c can be ensured in this case by superconducting pairing on the interface of the two phases,[20] or by the exciton mechanism,[21] or else because of the presence of $(-U)$ centers on the grain boundaries.[22] Unfortunately, such a simple model is refuted by the recently observed[23] effect of multiple Josephson tunneling in three-dimensional samples of the $BaPb_{1-x}Bi_xO_3$ ceramic, which is evidence of dielectrization rather than metalization of the grain boundaries. (The Josephson effect was also observed in $BaPb_{0.7}Bi_{0.3}O_3$ films.[24])

If it is recognized that the accuracy of the calorimetric measurements is of the order of 1–2%, two possible explanations can be proposed for the heat-capacity jump ΔC at $T = T_c$.

First, if the ceramic is freely sintered, a nonporous crust is produced on the sample surface (the so-called external sintering[25]), to which a decisive role in the onset of superconductivity could be ascribed. The inductive and resistive method could then yield an affirmative result in the registration of the superconducting transition, whereas no anomalies whatever would be observed in calorimetric measure-

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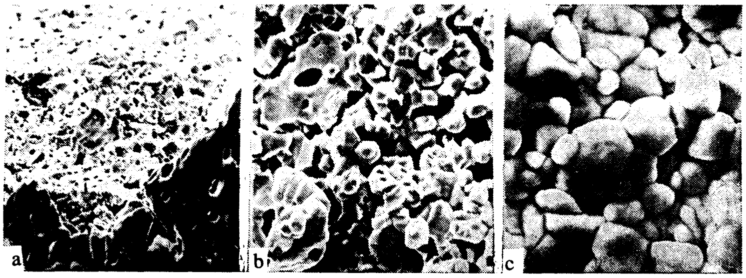

FIG. 1. Microgram of the structure of a chip of the superconducting ceramic $BaPb_{0.75}Bi_{0.25}O_3$ (a); the same in magnified scale for the inner regions of the sample (b) and for the surface crust (c).

ments. Pulverizing the samples, which breaks up the current paths, would lead to the appearance of a finite resistance and to the vanishing of the Meissner effect. It will be shown below, however, that this possibility should be rejected.

Second, as shown in the present paper, the experiments of Ref. 12 are explained on the basis of a superconductor with partial dielectrization of the electron spectrum.[26,27] This dielectrization is confirmed for the $BaPbO_3$–$BaBiO_3$ system by the set of facts described above.

2. The ceramic $BaPb_{1-x}Bi_xO_3$ samples synthesized by us from powders were porous blanks (see, e.g., Ref. 14). Owing to the successive dissolution of the pores by the vacancies and the emergence of the excess vacancies through the grid of intergrain boundaries, as well as through the gaps and cracks on the sample surface, a nonporous crust evolves near the surface.[25] The presence of such a practically pore-free layer of pores in the investigated superconducting samples is illustrated in Fig. 1, which shows the bulk structure of a chip of the ceramic blank (*a*) with composition $x = 0.25$, obtained with a scanning electron microscope. The macrostructures of the internal regions (*b*) and of the surface (*c*) are substantially different.

To verify the assumption that superconductivity might be realized for some reason near the dense nonporous region on the surface, a sample with the same composition as in Ref. 12 ($x = 0.25$) was tested for superconductivity by the resistive method immediately after the synthesis and after the surface crust was mechanically removed to a depth significantly larger than the nonporous region. The measurement results show (Fig. 2) that both the temperature dependence of the resistance and the values of T_c are exactly the same. Thus, the fact that superconductivity is present, the value of T_c, and the width ΔT_c of the transition are all determined by the entire volume of the sample and by its macrostructure, and the results of Ref. 12 cannot be attributed to special properties of the surface.

We note that this result is not obvious beforehand. Properties of a two-dimensional superconducting metal having phonon and electron spectra different from the bulk ones are possessed, for example, by the twinning plane of a tin crystal.[28]

On the other hand, dielectrization of solid solutions at a fixed composition is confirmed by experiments on crushed ceramics.[7,14] In addition, our present experiments have shown that the temperature dependence of the resistance of a superconductor with $x = 0.25$ which was crushed, pressed, but not sintered again has at $T \lesssim 40$ K the same unusual resistance form $R = R_0 \exp(-AT^{1/4})$ as well-sintered samples of composition $x = 0.4$, which reveal no superconducting properties and have an activation conductivity at higher temperatures.[13] Figure 3 shows the temperature dependence of $\log(R/R_{300})$ of the indicated compositions. The appearance of such a dependence in a rather wide range offers also evidence that the electric conductivity and the superconductivity of $BaPb_{1-x}Bi_xO_3$ have a more complicated behavior than might be caused by uncontrollable impurities. These results, on top of the aforementioned experimental facts, favor the possibility of partial dielectrization of the electron spectrum of the samples with retention of their superconducting properties. Moreover, recent experiments[19,30] have shown that the restructuring of the valence states of Bi, which determines the character of the electric conductivity of $BaPb_{1-x}Bi_xO_3$ (the sign of the temperature coefficient of

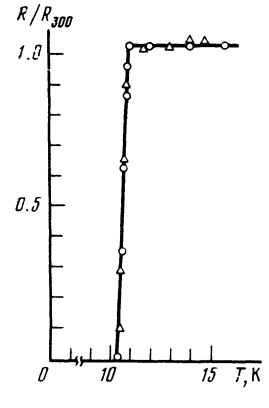

FIG. 2. Temperature dependence of the ratio of the resistance R of a $BaPb_{0.75}Bi_{0.25}O_3$ sample to its value R_{300} at $T = 300$ K before (○) and after (△) removal of the surface crust.

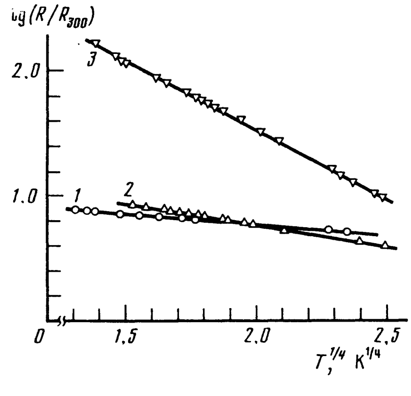

FIG. 3. Dependence of $\log(R/R_{300})$ on $T^{1/4}$ for crushed and pressed but not sintered samples with $x = 0.13$ (curve 1) and $x = 0.25$ (curve 1), as for a well-sintered sample with $x = 0.4$ (curve 3).

the resistivity) depends strongly on the oxygen content in the ceramic. The estimates made in these papers show that the loss of oxygen can lead in the upshot to a transition of all the bismuth ions into the trivalent state and to the vanishing of the superconductivity, so that the dielectrization in the system investigated is a volume effect. Multiple Josephson tunneling,[23] as well as the decrease of the diamagnetic response following the crushing,[7] are more readily due to the easier dielectrization on the sample surface and on the grain boundaries as a result of the shift of the phase equilibrium towards a lower oxygen content, and a restructuring of the electron subsystem of the bismuth.

3. To calculate the heat capacity of superconductors with partial dielectrization of the Fermi surface (FS), we use the model of an anisotropic metal whose quasiparticle spectrum contains electron $\xi_1(\mathbf{p})$, $\xi_2(\mathbf{p})$ and hole $\xi_3(\mathbf{p}) = -\xi_2(\mathbf{p})$ branches. This model was first proposed in Ref. 26 for A-15 compounds and used in Ref. 27 in an analysis of Laves phases, in which partial dielectrization of the electron spectrum was observed.[31]

Analysis of the thermodynamic characteristics on the basis of the standard Green's-function technique leads to the following expression for the jump ΔC of the heat capacity at $T = T_c$:

$$\frac{\Delta C}{C} = 1.43\,\frac{[\nu + (2\pi\Sigma/T_c)^{1/2}\exp(-\Sigma/T_c)]^2}{[\nu + 3(2\pi\Sigma/T_c)^{5/2}\exp(-\Sigma/T_c)/\pi^2]}$$

$$\times[\nu + (2\pi T_c/\Sigma)^2]^{-1}, \qquad (1)$$

where Σ is the dielectric gap that appears on a section of the FS, $\nu = N_{nd}(0)/N_d(0)$, and $N_{nd}(0)$ and $N_d(0)$ are the densities of the electronic states on the non-dielectrized and dielectrized sections of the FS. The heat capacity C_n of the normal phase is given by

$$C_n = 2N_{nd}(0)\frac{\pi^2 T}{3} + 2N_d(0)\left(\frac{2\pi\Sigma^5}{T^3}\right)^{1/2} e^{-\Sigma/T}. \qquad (2)$$

Equations (1) and (2) explain the character of the heat-capacity temperature dependence observed in a superconducting ceramic.[12] In particular, from the $C/T = f(T^2)$ curve given in Ref. 12 follows an anomalously small Sommerfeld constant $\gamma \approx 0.15$ mJ/g · atom · K^2, which, if the usual BCS theory is valid, contradicts the high critical temperature of the samples, $T_c \approx 11$ K, which suggest a high density of single-electron states on the FS. This contradiction is readily resolved within the framework of a superconductor model with partial dielectrization of the quasiparticle spectrum. Indeed, the only contribution to the constant γ is made by the nondielectrized part of the FS, where $\Sigma = 0$ [see (2)], whereas T_c is determined by the total density of the single-electron states $N(0) = N_d(0) + N_{nd}(0)$ (Refs. 26, 27) (strong mixing of states). Comparison of γ for $BaPb_{1-x}Bi_xO_3$ and pure Nb, which has the close value $T_c \approx 0.5$ K, yields $\nu \approx 0.02$.

Another feature of the $C/T \approx f(T^2)$ curve in Ref. 12 is its nonlinearity when plotted in the indicated corrdinates. This, in our opinion, is due to the presence of an exponential contribution to the electronic part of the heat capacity both below and above T_c.

Finally, the smoothness of the $C(T)$ plot in the vicinity of T_c, which according to Ref. 12 is evidence of the absence of a phase transition in the bulk of the perovskite $BaPb_{1-x}Bi_xO_3$, is due in fact to the dielectrization of the electron spectrum, which leads to a considerable decrease of the influence of $\Delta C/C_n$. Unfortunately, it is difficult to determine directly in experiment, for superconducting ceramic samples, the value of Σ needed to calculate the jump of the heat capacity from Eq. (1). Therefore, in view of the similarity of the temperature dependences of the electric conductivity of a completely dielectrized sample with $x = 0.4$ and a crushed sample with composition $x = 0.25$ (see Fig. 3), we use as an estimate of Σ for the latter sample the activation energy of the well-sintered composition with $x = 0.4$ in the temperature region around (30–40) K, namely $\varepsilon_3' \approx 50$ K (Ref. 13). We then obtain from (1) an extremely small value, which indicates that the anomaly of the heat capacity at $T = T_c$ cannot be observed in experiment.

We note that, for a given ν, variation of Σ in a wide range does not lead to the experimentally observed value of the heat-capacity jump ΔC.

An alternate description of the dielectrization of the electron spectrum in the ceramic $BaPb_{1-x}Bi_xO_3$ is possible[32] on the basis of the concept of pairing in real space on account of the interaction of the electrons with the optical vibrations of the octahedra of oxygen in the perovskite lattice. It is stated in Ref. 32, however, that a decrease of the coordination number in the Bi-ion sublattice causes the system to go over into the metallic state. Such an analysis leads inevitably to the conclusion that metallization rather than dielectrization takes place on the surface, which is at variance with experiment.

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