Experimental demonstration of bulk superconductivity in the perovskite system $BaPb_{1-x}Bi_xO_3$

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The specific heat C_p of the superconducting ceramic $BaPb_{0.75}Bi_{0.25}O_3$ has been measured in the temperature range $2.5\ K \leqslant T \leqslant 300\ K$. At $T = T_c \approx 6.3$ K there is an anomaly in $C_p(T)$, corresponding to the transition into the superconducting state, as detected by induction measurements. This anomaly is observed to disappear after the samples are stored for a long time. The experimental data are analyzed on the basis of a theory of superconductors having a dielectric gap at part of the Fermi surface.

INTRODUCTION

The superconductivity of solid solutions $BaPb_{1-x}Bi_xO_3$ (BPB), discovered in 1974 by Sleight,[1] has been studied thoroughly both experimentally [2–14] and theoretically.[9,15,16] It has been shown that in spite of the small current carrier density[5] the critical temperature T_c for the superconducting transition is quite high, reaching 13.4 K.[13]

However, until now there has been no unambiguous resolution of the question as to whether the superconductivity of $BaPb_{1-x}Bi_xO_3$ is of an impurity or of a bulk nature. Thus, in Ref. 4 no observable jump ΔC_p in the specific heat C_p near T_c was detected by the induction method. This result was corroborated by experimental measurements of the thermal relaxation time in $BaPb_{1-x}Bi_xO_3$ samples of the same composition ($x = 0.25$).[14] Assuming that the superconductivity of the ceramic is a bulk effect and at the same time not contradicting the experimental data,[4] the authors of Refs. 9 and 10 attributed the failure to observe of the specific-heat anomaly near T_c to a decrease in ΔC_p resulting from a partial dielectrization of the electron spectrum of the material studied. We note that the possible existence of a dielectric gap Σ of a collective nature at congruent parts of the Fermi surface in $BaBiO_3$ follows from band-structure calculations carried out recently.[16] On the other hand, a decrease in ΔC_p at $T = T_c$ has been observed in the low temperature quenching of samples of the quasi-one-dimensional superconductor $(TMTSF)_2ClO_4$, which has a triplet dielectric gap at the Fermi surface.[17]

The reason for the bulk dielectrization of the ceramic $BaPb_{1-x}Bi_xO_3$ may be an oxygen deficiency[12] which changes the valence state of the bismuth to 3^+ and, as a consequence, causes a loss of superconductivity. In this case it was shown that the superconducting properties were restored when the samples were annealed in oxygen at a temperature below $T = 500$ °C.

1. EXPERIMENT

In order to confirm the bulk nature of the superconductivity in $BaPb_{1-x}Bi_xO_3$, the samples for this investigation were prepared so as to have the minimal degree of dielectrization, and the phase transition of these samples into the superconducting state was studied by the calorimetric method.

Twelve samples, of total mass $M = 15$ g and composition $x = 0.25$, were synthesized. The transition into the superconducting state was detected by the induction method. For the different samples, the transition curves practically coincided. One of these curves is shown in Fig. 1 by the solid triangles. The beginning of the transition corresponds to a temperature $T \approx 10$ K, and the maximum slope to a temperature $T_{\text{grad}} \approx 6.8$ K.

The specific-heat measurements were carried out in a vacuum adiabatic calorimeter, which has been described in detail in Ref. 18. The calorimetric apparatus was calibrated using brand K-1 benzoic acid (C_6H_5COOH) produced by the All-Union Research Institute of Metrology. The mass of the standard sample was 6.2914 g. The specific heat of the empty calorimetric ampoule, of volume $V = 10\ cm^3$ and mass $M = 12.7777$ g, was measured at 176 experimental points, and the relative deviation δ of these measurements from a smooth curve was: $\delta(1.9–4.2\ K) = \pm 2.06\%$, $\delta(4.2–25\ K) = \pm 0.56\%$, $\delta(25–100\ K) = \pm 0.09\%$, and $\delta(100–320\ K) = \pm 0.05\%$.

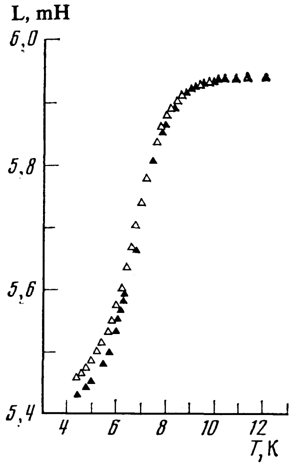

FIG. 1. Diamagnetic response of $BaPb_{0.75}Bi_{0.25}O_3$ sample as a function of temperature during superconducting transition. (▲ is immediately after preparation; △ is after 1.5 months storage in air).

TABLE I. Smoothed values of specific heat of benzoic acid.

T, K	C_p, J/mole · deg	C_{p1}, J/mole · deg	$(C_p-C_{p1})/C_{p1}$, %	C_{p2}, J/mole · deg	$(C_p-C_{p2})/C_{p2}$, %
2	0.0152	0,01527	—0.46	—	—
4	0,1233	0,1247	—1,12	0,1225	+0,65
6	0.4275	0,4443	—3,78	0,4216	+1.38
8	1.058	1,093	—3,23	1,070	—1,17
10	2.074	2,096	—1,05	2.058	+0.78
12	3.440	3,452	—0.35	3,377	+1,84
14	5,053	5,063	—0,20	5.020	+0,65
16	6,888	6,883	+0,07	6.863	+0,37
18	8,910	8,853	+0,64	8.955	—0,50
20	11,02	10.95	+0.70	11,05	—0,24
22	13,21	13.13	+0.61	13,22	—0.10
24	15,49	15.36	+0,85	15.44	+0,32
26	17,65	17,60	+0,28	17,62	+0,19

Table I shows the results of the low-temperature measurements of C_p of benzoic acid standard sample in comparison with similar data C_{p1} and C_{p2} of Refs. 19 and 20, respectively. The errors Δ_c of the measurements in this range are: Δ_c (1.9–4.2 K) $= \pm 1.5\%$ and Δ_c(4.2–25 K) $= \pm 0.75\%$.

The first series of measurements were made within six days after the samples were prepared. The $C(T)$ curves in the range 2.5–300 K are shown in Fig. 2. It can be seen that at room temperature the curve approaches its asymptotic values $C_0 = 3RS$, where R is the universal gas constant and S is the number of atoms per unit cell. [As usual[21] we can neglect the difference between the specific heats at constant volume and constant pressure; therefore, we shall henceforth omit the index p). The approximate equality $C \approx C_0$ indicates that at $T \approx 300$ K all the vibrational degrees of freedom are excited, including the corresponding optical phonons. Therefore the $C(T)$ curve cannot be described by a one-parameter Debye interpolation model. Of the greatest interest is the behavior of $C(T)$ at low temperatures, where the Meissner effect indicates a transition into the superconducting state. Shown in Fig. 3 (curve 1) is the lowest part of the curve of C as a function of T shown in Fig. 2.

The most characteristic feature of this curve is an anomaly at $T = 6.3$ K, which corresponds approximately to the maximum slope of $L(T)$ (Fig. 1) in the region of the superconducting transition. Below this temperature the experimental data lie quite well on a straight line when plotted in the coordinates $\ln C$ vs $1/T$. Thus, for $T < T_c$ there is an exponential, gap-like, character to the specific heat:

$$C=A \exp(-\varepsilon/k_B T), \tag{1}$$

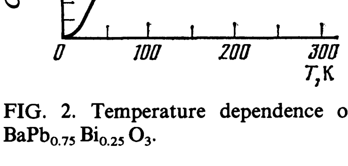

FIG. 2. Temperature dependence of specific heat of the ceramic $BaPb_{0.75}Bi_{0.25}O_3$.

where k_B is the Boltzmann constant and $\varepsilon = 6.8 \cdot 10^{-4}$ eV was found by least squares.

These facts indicate convincingly the bulk character of the superconductivity of $BaPb_{0.75}Bi_{0.25}O_3$ in spite of the suppositions of the authors of Refs. 4 and 7. The fact that the experimental points lie on an exponential curve that describes the electronic part $C_e(T)$ of the specific heat at low temperatures indicates that the crystal lattice makes a negligibly small contribution to $C(T)$ in this temperature range.

The experiments were repeated 1.5 months later. The diamagnetic properties of the sample in the transition region were essentially unchanged (Fig. 1, open triangles), whereas the dependence of C/T on T^2 had taken on a different character (Fig. 3, curve 2). As can be seen, there is a drop in the specific heat near T_c as before, but, just as in the experiments cited above,[4,14] the jump ΔC is not observed.

This result, along with a large amount of other experimental data,[2,5-11] indicates that in the material studied the electron spectrum has undergone a dielectrization, the nature of which is as yet unknown. It is difficult to account for the instability of the electronic properties with time on the basis of presently known facts, in particular, by a change of the oxygen content in the ceramic.[12] On the other hand, gas

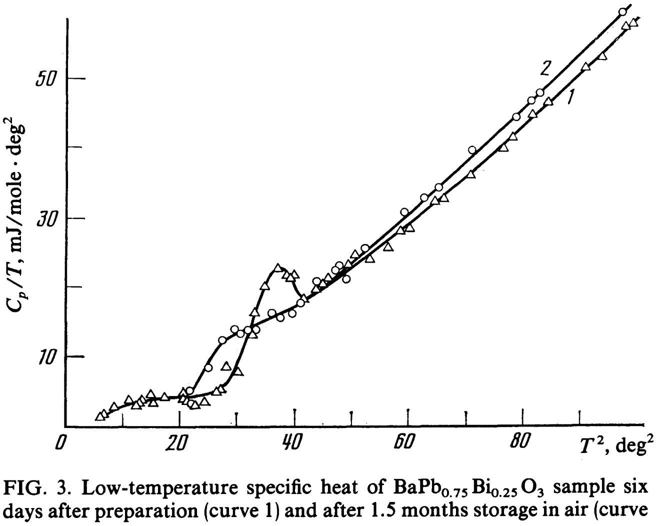

FIG. 3. Low-temperature specific heat of $BaPb_{0.75}Bi_{0.25}O_3$ sample six days after preparation (curve 1) and after 1.5 months storage in air (curve 2).

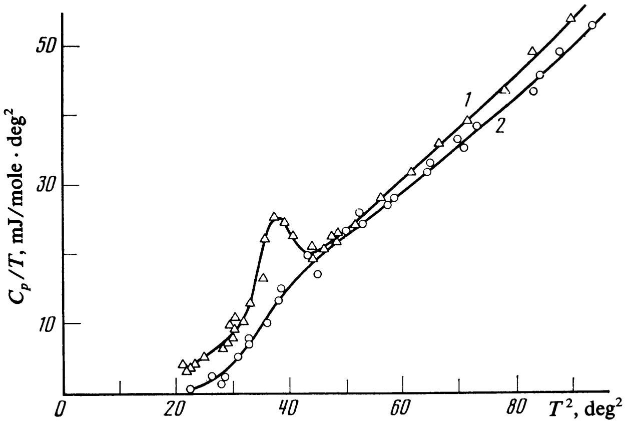

FIG. 4. Specific heat of $BaPb_{0.75}Bi_{0.25}O_3$ at low temperatures after repeated thermal treatment (curve 1) and after 1.5 months storage in the sealed calorimeter (curve 2).

adsorption might, in this case, play an important role in view of the decisive influence of the specific surface area on the electronic properties of $BaPb_{1-x}Bi_xO_3$ (the pulverization effect[2]). However, this explanation, as shown below, is not supported by the experiments.

To restore completely the superconducting properties of the material it was heated at a temperature $T \approx 400$ °C, at which temperature, according to Ref. 12, there is no loss of oxygen. Immediately after this annealing the samples were placed into the calorimeter. Figure 4, curve 1, shows the measured dependence C/T vs T^2 for a ceramic sample which has gone through a repeated heat treatment. As expected, the original shape of the temperature dependence of the specific heat, with the characteristic jump at $T = T_c$, was restored. In order to prevent contact with the atmosphere, after the experiment the samples were kept in the sealed calorimeter for six weeks. After this time the experiments were continued. The results are shown in Fig. 4, curve 2. The jump in the specific heat is absent, just as in the first series of experiments, in spite of the steps taken to prevent adsorption. Thus we can conclude that the observed effect is not due to the effect of foreign atoms.

2. DISCUSSION OF RESULTS

Because of the specific heat anomaly which occured in this investigation at $T = T_c$ but which was not observed in Refs. 4 or 14, it is of interest to analyze the quantity ΔC within the framework of existing theories. From curve 1 of Fig. 3 we obtain $\Delta C \approx 48$ mJ/mole · deg and $T_c \approx 6.3$ K. To compare this value with theoretical predictions[9,10] it is necessary to have experimental values for the Sommerfeld constant γ. Unfortunately, it is not possible to determine γ from the data given in Figs. 3 and 4. Indeed, even though the dependence $C/T(T^2)$ in this temperature range is practically linear, its extrapolation does not intersect the ordinate, but rather the abscissa (the T^2 axis), i.e., here the specific heat is not described by the asymptotic law

$$C=\gamma T+\beta T^3. \tag{2}$$

We note that similar behavior of the curve $C(T)$ above T_c for $BaPb_{1-x}Bi_xO_3$, with $x = 0.25$, was observed in Ref. 4.

We shall try to estimate the value of γ under the assumption that it is possible to describe all the experimental data within the framework of the usual BCS theory.[22] Here the following relation must be satisfied

$$\Delta C/\gamma T_c=12/7\zeta(3), \tag{3}$$

where $\zeta(x)$ is the Riemann zeta function ($\zeta(3) \approx 1.202$). Substituting the experimental values of $\Delta C/T_c$ into (3) we obtain $\gamma = 5.6$ mJ/mole · deg^2, where the renormalized density of electron states at the Fermi level is

$$N^*(0)=N(0)(1+\lambda)=3\gamma/2\pi^2k_B^2\approx 9{,}5\cdot 10^{33}\ \text{erg}^{-1}\,\text{cm}^{-3}. \tag{4}$$

Here λ is the electron-phonon coupling constant, and the calculated volume of a gram-molecule of $BaPb_{1-x}Bi_xO_3$, for $x = 0.25$, is

$$V=N_A a_0^3=47{,}4\ \text{cm}^3, \tag{5}$$

where N_A is Avogadro's number, and $a_0 = 4.287$ Å is the lattice constant of the pseudocubic lattice as determined from our x-ray measurements.

The value of γ which we have calculated from the BCS relation is 7.5 times greater than that obtained experimentally for $BaPb_{1-x}Bi_xO_3$ of this composition in Ref. 4. On the other hand, the density of electron states determined from the Seebeck effect[3] is $N(0) \approx 9 \cdot 10^{21}$ eV^{-1}cm^{-3} $= 9.4 \cdot 10^{32}$ erg^{-1}cm^{-3}. This leads to a Sommerfeld constant $\gamma \approx 0.56(1 + \lambda)$ mJ/mole · deg^2, which, for reasonable values of λ agrees with the corresponding value $\gamma = 0.15$ mJ/g · atom · deg^2 from Ref. 4. The discrepancy in the values of the Sommerfeld constants obtained for $BaPb_{1-x}Bi_xO_3$ of the identical composition indicates that the BCS theory cannot explain the nature of the superconductivity in solid solutions of $BaPbO_3$–$BaBiO_3$. However, if we postulate a high degree of dielectrization of the ceramic in the experiments of Refs. 4 and 14, then it is possible to account for the disagreement in the values of γ by assuming a complete absence of dielectrization in our samples in the first series of measurements and assuming that relation (3) is correct. However, this contradicts the low-temperature behavior of the specific heat at $T \approx T_c$, since formula (1), with the value $\varepsilon/k_B \approx 7.94$ K, does not agree with the known approximation for the temperature dependence of the specific heat according to the BCS theory[22]:

$$\frac{C_{es}}{\gamma T_c}=8{,}5e^{-1{,}44T_c/T}. \tag{6}$$

Moreover, without going outside the limits of the BCS theory it is not possible to account for the disappearance of the specific heat anomaly in the subsequent series of experiments. Therefore, in the subsequent development we shall proceed from a theory of superconductivity in which a dielectric gap Σ of a collective nature is formed at a part of the Fermi surface.[9,10,23,24]

We shall use the relations that connect the critical temperature T_c of the transition into the superconducting state, the critical temperature T_{c0} in the absence of dielectricization, the ratio of the densities of states at the non-dielectric and dielectric parts of the Fermi surface: $\nu = N_{nd}(0)/N_d(0)$, and the magnitude of the specific heat jump $\Delta C/T_c$ $(\Sigma \gg T_c)$, (Refs 9, 10, 23, and 24)

$$T_c = T_{c0}(\pi T_{c0}/\tilde{\gamma}\Sigma)^{1/\nu}, \qquad (7)$$

$$\frac{\Delta C}{T_c} = \frac{8\pi^2}{7\zeta(3)} \frac{[\nu + (2\pi\Sigma/T_c)^{1/2}\exp(-\Sigma/T_c)]^2}{[\nu + (2\pi T_c/\Sigma)^2/7\zeta(3)]}, \qquad (8)$$

where $\tilde{\gamma} = 1.781\ldots$ is the Euler constant. As a result we obtain a system of two equations (7) and (8) in three unknowns, T_{c0}, ν and Σ since T_c and $\Delta C/T_c$ are determined from our experiments. Here there is an obvious lower limit to T_{c0}, since in Ref. 13 a maximum critical temperature the order of 13.4 K was attained (measured via the resistivity). Identifying this temperature with T_{c0}, we obtain from (7) and (8) $\Sigma \approx 46$ K and $\nu = 0.89$. The value of Σ agrees well with the activation energy of the conductivity $\varepsilon_3' = 50$ K for the sintered ceramic with $x = 0.4$ (Ref. 5). We have used precisely this value previously[9,10] in explaining the results of the investigation of Ref. 4. Even a small increase in the intrinsic temperature T_{c0}, according to (7) and (8), will lead to a rapid increase in Σ to improbably high values. Thus, for $T_{c0} \approx 20$ K, the dielectric gap is $\Sigma = 93$ K $(\nu \approx 0.84)$.

As can be seen, the phenomenological theory of the superconducting phase transition of materials with a partial dielectrization of the electron spectrum[9,10] reproduces the observed value of $\Delta C(T_c)$. On the other hand, the disappearance of the jump in the specific heat can also be explained naturally within the framework of this model. Actually, a decrease in the number of nondielectrified states at the Fermi surface $(\nu \to 0)$ will lead to a decrease in T_c and a decrease in ΔC all the way to experimentally unobservable values, a result that is in accord with the data of our investigation and those of Refs. 4 and 14.

The restoration of the superconducting properties in the bulk of the ceramic upon repeated annealing is evidently related to the restoration of ν. At the same time, the insensitivity of the Meissner effect (see Fig. 1) to dielectrization effects which bring about a change in the thermal behavior of the specific heat below T_c can be explained by a screening action due to the regions with a higher critical temperature.

It should be noted that the microscopic reasons for the complex nonequilibrium processes that occur in the oxide system $BaPb_{1-x}Bi_xO_3$ are still unknown. In this connection, the suggestion of a phase transition into a charge-ordered state with alternating Bi^{3+}–Bi^{5+} pairs[15] is of interest, as is the suggestion of superconductivity of localized electrons in systems with $(-U)$-centers.[25]

In conclusion, we call attention to the fact that a more detailed quantitative analysis of the dependence $C(T)$ (in particular a determination of the values of $N_{nd}(0)$ and $N_d(0)$) is not possible until the contribution of the optical phonons to the specific heat both above and below T_c is elucidated. The existence of low-frequency phonon peaks in perovskite systems has been demonstrated experimentally, e. g., in the case of superconducting tungsten bronzes.[26]

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