Possible scenario of the spatially separated Fermi-Bose mixture in the superconductive bismuthates $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$

M. Yu. Kagan$^{a,b}$

$^a$P. L. Kapitza Institute for Physical Problems, Kosygin Str. 2, 117334 Moscow, Russia.
$^b$Max-Planck-Institut fuer Physik Komplexer Systeme, Nöthnitzer Str. 38, D-01187, Dresden, Germany.

A. P. Menushenkov, K. V. Klementev, and A. V. Kuznetsov
Moscow State Engineering Physics Institute, Kashirskoe shosse 31, 115409 Moscow, Russia.
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A new scenario for superconductivity in the bismuthates based on the concept of a spatially separated Fermi-Bose mixture is proposed. In the framework of this scenario we qualitatively explain the insulator-metal transition and the nature of the superconductivity which occur in Ba$_{1-x}$K$_x$BiO$_3$ under doping by K. We also analyze briefly an applicability of this scenario for the high-$T_c$ superconductors. In conclusion some additional experiments required to elucidate more precisely the nature of the superconductivity in the bismuthates are discussed.

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I. INTRODUCTION

The concept of the extremely strong-coupling superconductivity with the preexisted local pairs was firstly introduced by Shafroth$^{[1]}$ in the middle of fifties. His statement was that in the extremely type-II superconductors, where the parameter $\xi_0 k_F \lesssim 1$, the nature of the superconductive transition corresponds to the local pair formation (pairing in the real, and not in the momentum space) at some relatively high temperature $T^*$, and their Bose-Einstein condensation (BEC) at a lower critical temperature $T_c < T^*$. Later on Alexanderov and Ranninger developed this concept$^{[2]}$ in connection with the narrow-band materials with an extremely strong electron-phonon coupling constant ($\lambda \gg 1$), where a standard Eliashberg theory$^{[3]}$ starts to fail. The key issue of their approach was a statement that in narrow bands, where polaron formation is important, it is possible, in principle, to create the conditions where the two polarons could effectively occupy the same potential well, prepared in a self-consistent fashion. Approximately in the same time Leggett and Nozieres$^{[4]}$ developed a general theory which yields a smooth interpolation between a BCS-type of pairing in the momentum space for a small electron-electron attraction and the pairing in the real space for a large electron-electron attraction.

There were two crucial points in the papers$^{[4,5]}$: (i) Their results are valid independently of the precise nature of the short-range effective attraction between electrons; (ii) they investigated self-consistently a standard equation for the superconductive gap and an equation for the number of particles conservation. The most important result of Nozieres and Leggett is that for $T^* > T_c$ (or, in other words, for a binding energy of a local pair $|E_b| > \xi_F$) the chemical potential $\mu$ is always large and negative $\mu = -|E_b|/2 + \xi_F < 0$. Hence in a strongly-coupling limit a superconductive pairing takes place not on the Fermi-surface, as in the BCS-theory, but below the bottom of a conductive band. This is a crucial drawback of all local-pairs theories. We cannot match two basic facts: the existence of the Fermi-surface and the presence of preformed pairs above $T_c$. First one who emphasized this contradiction was J. Ranninger$^{[6,7]}$, who introduced the concept of the two-band Fermi-Bose mixture. In this scenario the presence of a degenerate fermionic band guarantees the existence of a Fermi-surface, while the Bose-Einstein condensation is responsible for the superconductivity in a bosonic band. Soon after the discovery of high-$T_c$ superconductors P. W. Anderson$^{[8]}$ reintroduced the concept of the local pairs. He also introduced two bands of the fermionic and bosonic quasiparticles. In his approach, a superconductive transition was connected with the BEC in the bosonic band of the charge excitations — holons, while the presence of a large Fermi-surface was guaranteed by the fermionic band of the spin excitations — spinons. Unfortunately, even this beautiful approach was not totally successful because at least in a one layer the BEC of holons yields a charge of a superconductive pair equal to $e$ instead of $2e$ measured experimentally. Later on Geshkenbein, Ioffe, and Larkin$^{[9]}$ phenomenologically reintroduced a concept of the Fermi-Bose mixture on the level of the coefficients in the Ginzburg-Landau expansion and showed that several important experiments in the underdoped high-$T_c$ materials can be explained naturally within this form of the Ginzburg-Landau functional.

So, up to now a question whether a two-band Fermi-Bose mixture scenario is applicable to the high-temperature superconductive (HTSC) materials is still open. Probably, the best chances to be described by this scenario has a bismuth family of high-$T_c$ superconductors $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, where the parameter $k_F\xi_0 \sim 2$, and the tunneling experiments of Fischer$^{[10]}$ et al.$^{[11]}$ signal the formation of a pretty large and a stable pseudogap at temperatures well above $T_c$. In our paper we would like
to discuss a possibility of a two-band Fermi-Bose mixture scenario in a quite different class of superconductors with a relatively high $T_c \sim 30\,\text{K}$, namely in the superconductive bismuthates $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BKBO). The key issue of our paper is a possibility of the existence of the two spatially separated bands of fermionic and bosonic quasiparticles in these materials.

Our paper is organized as follows. In the first part we present the basic experimental facts concerning the local electronic and crystal structure peculiarities, and their connection with the superconductive and the normal transport properties of BKBO. In the second part we try to show how these basic facts could be naturally explained within a scenario of the two spatially separated bands of the fermionic and bosonic quasiparticles. We conclude the paper by a summary of our model and a discussion of the several additional experiments, which would help us to give a definite answer whether our proposal is the only possibility for a superconductive pairing in the bismuthates.

II. SPATIALLY SEPARATED FERMI-BOSE MIXTURE

The $\text{BaBiO}_3$, which is a parent compound for the bismuthates $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ and $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ (BPBO), represents a charge-density-wave (CDW) insulator having the two gaps: an optical gap $E_o = 1.9\,\text{eV}$ and an activation (transport) gap $E_a = 0.24\,\text{eV}$ [11]. A partial replacing of Ba by K in BKBO causes the decrease of the gaps, and as a result the insulator-metal transition as well as the superconductivity are observed at the doping levels $x \gtrsim 0.37$. The superconductivity remains up to the doping level $x = 0.5$ corresponding to the solubility limit of K in BKBO but a maximal critical temperature $T_c \approx 30\,\text{K}$ is achieved for $x \approx 0.4$ [2,3].

A. Local crystal structure peculiarities

A three-dimensional character of a cubic perovskite-like structure of the bismuthates differs from a two-dimensional one in the HTSC cuprates. The building block in the bismuthates is a $\text{BiO}_6$ octahedral complex (analogue of $\text{CuO}_n$ ($n = 4, 5, 6$) in the HTSC-materials). The octahedral complexes are the most tightly bound items of the structure because of a strong covalence of the $\text{Bi}_6s$-$\text{O}2p$ bonds. According to the crystallographic data [17], the crystal structure of a parent $\text{BaBiO}_3$ represents the alternating arrangement of the expanded and contracted $\text{BiO}_6$ octahedra in a barium lattice, spoken as a “breathing” distortion. Such an alternation together with a static rotation of the octahedra around [110] axis produce the monoclinic distortion of a cubic lattice. As shown in Refs. [15,17], to the larger soft octahedron corresponds the complex $\text{BiO}_6$ with the completely filled $\text{Bi}_6s$-$\text{O}2p$ orbitals and to the smaller rigid octahedron corresponds a complex $\text{Bi}_6^2\text{O}_4$. Here $L^2$ denotes the free level in the antibonding $\text{Bi}_6s$-$\text{O}2p_{\sigma^*}$ orbital of the smaller octahedral complex.

The K doping of $\text{BaBiO}_3$ is equivalent to a hole doping and leads to a partial replacement of the larger soft octahedra $\text{BiO}_6$ by the smaller rigid octahedra $\text{Bi}_6^2\text{O}_6$ [17]. This causes a decrease and finally a disappearance of the static breathing and tilting distortions, and the lattice should contract despite a practically equal ionic radii of $\text{K}^+$ and $\text{Ba}^{2+}$. As a result, the average structure according to the neutron diffraction data [18] at the doping level $x = 0.37$ becomes a simple cubic. However, the local EXAFS probes [14,13,17] showed the essential difference of the local crystal structure from the average one. We found out that the oxygen ions belonging to the different $\text{BiO}_6$ and $\text{Bi}_6^2\text{O}_6$ octahedra vibrate in a double-well potential, while those having equivalent environment of the two equal $\text{Bi}_6^2\text{O}_6$ octahedra oscillate in a simple harmonic potential [15,17,17]. This very unusual behavior is in a close connection with a local electronic structure of BKBO.

B. Local electronic structure

The coexistence in $\text{BaBiO}_3$ of the different types of the octahedra with the two Bi-O bond lengths and strengths reflects the different electronic structures of $\text{BiO}_6$ complexes. The valence band of $\text{BaBiO}_3$ is determined by the overlap of $\text{Bi}_6s$ and $\text{O}2p$ orbitals [21,22], and, owing to a strong $\text{Bi}_6s$-$\text{O}2p_{\sigma^*}$ hybridization, the octahedra can be considered as the quasi-molecular complexes [22]. In each complex there are ten electron levels consisting of the four bonding-antibonding $\text{Bi}_6s$-$\text{O}2p_{\sigma^*}$ orbitals and the six nonbonding $\text{O}2p_{\pi}$ orbitals. A monoclinic unit cell includes the two octahedra and contains 38 valence electrons (10 from the two bismuth ions, 4 from the two barium ions, and 24 from the six oxygen ions). All the Bi-O bond lengths should be equal and the local magnetic moments should be present in the case of equal electron filling for nearest octahedra ($\text{Bi}_6^1\text{O}_6$+$\text{Bi}_6^1\text{O}_6$). In contrast both the presence of the two types of octahedral complexes and an absence of any local magnetic moment are experimentally observed [1,23], so the mentioned above scheme of the valence disproportionation $2\text{Bi}_6^1\text{O}_6 \rightarrow \text{Bi}_6^2\text{O}_6$+$\text{BiO}_6$ was proposed [17]. In this scheme the numbers of occupied states in the neighbouring octahedral complexes are different: the octahedron $\text{Bi}_6^2\text{O}_6$ contains 18 electrons and has one free level or a hole pair $L^2$ in the upper antibonding $\text{Bi}_6s$-$\text{O}2p_{\pi}$ orbital, while in the octahedron $\text{BiO}_6$ with 20 electrons this antibonding orbital is filled as shown in Fig. 1. It is quite natural that the $\text{Bi}_6^2\text{O}_6$ octahedra have the stiff (quasi-molecular) Bi-O bonds and a smaller radius, while the $\text{BiO}_6$ octahedra represent the non-stable molecules with a filled antibonding orbital and a larger radius. Because
the sum of the two nearest octahedra radii overcomes the lattice parameter, the octahedral system must tilt around [110] axis, producing together with a breathing a monoclinic distortion in BaBiO$_3$.

Thus, in BaBiO$_3$ one has an alternating system of the two types of the octahedral complexes filled with the local pairs: the hole pairs in BiL$_2$O$_6$ complexes and the electron pairs in BiO$_6$ complexes. The local pair formation in BaBiO$_3$ was advocated previously, see for example [11,23,29]. The binding mechanism for the pairs is probably of an electronic nature [22,24] in accordance with Varma’s picture of the pairing due to the skipping of the valence “4+” by the Bi ion [25]. However one cannot fully exclude the lattice mediated pairing [11,24–27] in accordance with de Jongh’s statement [28] that the preference to retain the closed-shell structures overcomes the Coulomb repulsion involved with an intrasite bipolaron formation.

The local electronic structure of BaBiO$_3$ combined with the real-space local crystal structure is presented in Fig. 2(a). In such a system there are no free fermions, and the conductivity occurs only due to the transfer of the carrier pairs [11,15]. The dissociation of the pairs and the hopping of a single electron from one octahedron to another, in similarity with Varma’s [22] suggestion, cost an energy:

$$E_b = 2E(\text{BiL}^2\text{O}_6) - [E(\text{BiO}_6) + E(\text{BiL}^2\text{O}_6)],$$

and is observed experimentally as an optical conductivity peak at the photon energy $h\nu = 1.9$ eV [11].

Thus we have an example of the normal bosonic liquid of the pairs bound with an energy $E_b$ (as in Ref. [23]). Experimentally, BaBiO$_3$ shows a semiconductor-like behavior with an energy gap $E_a = 0.24$ eV, which can be explained only as a two-particle transport with the activation energy $2E_a$ due to the delocalization of the pairs. From our point of view, the transport gap is defined by the combined effect of the Coulomb interaction and the deformation potential between the neighboring octahedral complexes.

In principle, the electronic structure of BaBiO$_3$ presented in Fig. 3(a) is similar to that proposed by Namatame et al. [31]. They supposed that the thermally excited charge carriers in BaBiO$_3$ are the polaron with a substantial band narrowing due to a strong electron-phonon coupling. In our case the carriers are the local pairs (the bipolarons), the empty and the occupied bosonic bands are very narrow, and that is why in Fig. 3(a) they are shown as energy levels. So, the transport gap $2E_a$ is the gap between the empty and the occupied bosonic states, and the conductivity in BaBiO$_3$ arises from the thermo-activated bosonic quasiparticles. This fact is in agreement with the suggestion of Karpfer et al. about a bosonic character of the ground state in BaBiO$_3$. [28]

Another key question in the bismuthates is a nature of the optical gap $E_g = 1.9$ eV. In accordance with the band structure calculations [21], this gap arises from the peak-to-peak splitting of the Bi6s band due to CDW formation. Namatame et al. [31] attribute this gap to the Frank-Condon transition under which the lattice should be frozen. That contradicts to the observation in the Raman spectra [22,27,28] of the abnormally large amplitude of the breathing-type vibrations of the oxygen octahedra. The required mode arises only at a resonant excitation by the laser radiation with an energy $h\nu = E_g$. The resonance was destroyed and the abrupt decrease of the mode amplitude was observed when the lasers with an other frequency were used [22]. Obviously, the photons cannot excite a carrier pair as a whole and should destroy it. Such a behavior directly proves that the lattice is involved in this optical transition. In our scheme an excitation over the optical gap corresponds to the pair destruction BiL$_2$O$_6$+BiO$_6$ $\rightarrow$ 2BiL$^2$O$_6$, which produces a local deformation of the lattice due to the changing of the two different octahedra on equivalent ones. This dynamic deformation is manifested in the Raman spectra as an abnormally high amplitude of the breathing mode. Thus the nature of the optical gap is just the pair binding energy $E_g = E_b$. It is important to emphasize that there are no free fermions in the system. Only the excited fermions can be produced by the unpairing, and they do not give any input into the charge transport because of a high value of $E_b = 1.9$ eV. Thus the bosonic and the fermionic subsystems are separated both spatially and energetically, and therefore the Fermi-Bose mixture is absent in the parent compound.

### C. Formation of the Fermi-Bose mixture

The substitution of the each two K$^+$ for the two Ba$^{2+}$ modifies the BiO$_6$ complex to the BiL$_2$O$_6$ one. As a result, the number of the small stiff BiL$_2$O$_6$ octahedra increases as $n_0(1 + x)/2$, while the number of large soft BiO$_6$ octahedra decreases as $n_0(1 - x)/2$, where $n_0 = 1/a^3$ is the number of the unit cells and $a$ is a lattice parameter. The spatial overlap of the BiL$_2$O$_6$ complexes appears at the finite doping levels, which, taking into
FIG. 2. The scheme of the insulator-metal phase transition for the K-doping of Ba$_{1-x}$K$_x$BiO$_3$ in the framework of the relationship between the local crystal and the local electronic structures. The local crystal structure of the octahedral complexes (at the top) and the local electronic structure (at the bottom) are shown on the pictures (a)-(d). The occupied states of the Bi$_6$s$_2$O$_2$p valence band are marked by gray. $2E_a$ is the activation gap. Black and white circles with arrows denote, correspondingly, the electrons and the holes with the opposite spin orientations. (a) A monoclinic phase of an insulator BaBiO$_3$. (b) An orthorhombic phase of a semiconducting BKBO at $0 < x < 0.37$. The splitting of free level $L_2$ at a spatial overlap of the Bi$L_2$O$_6$ octahedra is sketched. (c) An undistorted cubic phase of a superconducting metal at $x > 0.37$. The formation of a Fermi-liquid state is shown arising due to the overlap of an unoccupied fermionic band $F$ with an occupied Bi$_6$s$_2$O$_2$p valence band when the percolation threshold is reached. (d) An undistorted cubic phase of a nonsuperconducting metal at $x = 1$. A Fermi liquid state with Fermi level $E_F$ is shown.

account their small radii and the rigid bonds, contracts the lattice.

The structural changes are accompanied by the essential changes in the local electronic structure and in the physical properties of BKBO. A spatial overlap of the $L^2$ levels leads to their splitting into an empty fermionic-like band $F$ inside the Bi$L^2$O$_6$ -- Bi$L^2$O$_6$ Fermi-cluster [see Fig. 2(b)]. In the doping range $x < 0.37$ the band is narrow enough due to a polaronic effect and is still separated from an occupied Bi$_6$s$_2$O$_2$p subband. The number of the empty electronic states in the $F$ band increases with $x$ as $n_F = n_0(1 + x)$, while the number of the local electron pairs decreases as $n_B = n_0(1 - x)/2$.

A free motion of the pairs is still prevented by the intersite Coulomb repulsion [25], which becomes strongly screened inside the clusters. When the Fermi-clusters are formed, the conductivity occurs due to the motion of the pairs through the clusters of the different lengths. The BKBO compounds demonstrate a semiconducting-like conductivity changing from a simple activation type to the variable-range-hopping Mott’s law [3]. Moreover the activation energy lowers with the doping down to $E_a \approx 0$ at $x \approx 0.37$. One can understand the decrease of the activation energy as a suppression of the Coulomb blockade due to the formation of the Fermi-clusters and due to the decrease of an energy shift between the empty and the occupied bosonic levels as the lattice distortion is diminished.

At the doping level $x \approx 0.37$ (see Fig. 2(c) and Fig. 3(c)) the following cardinal changes take place:

(i) Both the breathing and the rotational static lattice distortions transform to the dynamic ones. At the cluster borders, where all oxygen ions belongs to BiO$_6$ and Bi$L^2$O$_6$ octahedra, the local breathing dynamic distortion is observed as a vibration in a double-well potential of $(1 - x)$ part of the oxygen ions [16,17] but cannot be detected by the integral methods of the structural analysis such as an X-ray and a neutron diffraction.

(ii) The infinite percolating Fermi cluster (formed from the spatially overlapped Bi$L^2$O$_6$ octahedra) appears, which leads to the overlap of an empty fermionic band with a filled one, and as a result $F$ becomes a conduction band. Overcoming of the percolation threshold provides the insulator-metal phase transition and the formation of the Fermi-liquid state for $x > 0.37$. The valence electrons of the Bi$L^2$O$_6$ complexes previously localized become itinerant which is in agreement with the experiments [34].

(iii) The pair localization energy disappears $E_a \approx 0$ so the local electron pairs (from the BiO$_6$ complexes) can freely move in the real space providing a bosonic contribution into the conductivity. Thus, in the metallic...
phase the two types of carriers are present: the itinerant electrons from the \( \text{Bi}_2\text{O}_6 \) complexes (fermions) and the delocalized electron pairs from the \( \text{BiO}_6 \) complexes (bosons). Despite the normal state conductivity is mainly due to a fermionic subsystem, the contribution from a bosonic subsystem was also observed by Hellman and Hartford as the two-particle normal state tunneling.

As a result at doping levels \( x > 0.37 \) we have a new type of a spatially separated mixture of the bosonic \( B \) and the fermionic \( F \) subsystems, which describes metallic properties of BKBO. It should be stressed that the fermions and the bosons belong to the complexes with the different electronic structure, therefore the Fermi and the Bose subsystems are spatially separated at any doping level. These subsystems are connected by the relations \( 2n_B + \tilde{n}_F = 2n_0 \) and \( 2n_B/\tilde{n}_F = (1 - x)/(1 + x) \). The high enough value of the binding energy, which in the superconductive compositions becomes apparent as a pseudogap \( E_b = E_g \approx 0.5 \text{ eV} \), is the guarantee against the pair destruction. The unpairing is possible only under the optical excitation to the band \( F' \) (see Fig. 3), which does not play any role in the charge transport.

At \( x = 1 \) all the \( \text{BiO}_6 \) octahedra are transformed to the \( \text{Bi}_2\text{O}_6 \) ones. The Bose system disappears \( (n_B = 0) \) together with an excited fermionic band \( F'' \). As a result, KBO\(_3\) should behave as a simple Fermi-liquid metal without superconductive properties (see Fig. 3(d)).

It is worth to notice that a metallic KBO\(_3\) compound exists only hypothetically because of the exceeding of the potassium solubility limit in BKBO, which in this case equals to \( x \approx 0.5 \). However BaPbO\(_3\) as an electronic analogue of KBO\(_3\) demonstrates the metallic but not the superconductive properties. Recent attempts to synthesize KBO\(_3\) at a high pressure found out that only \( K_{1-y}\text{Bi}_y\text{BiO}_3 \) with a partial replacement of \( K^+ \) ions by \( \text{Bi}^{3+} \) ones is formed. Such a replacement should lead to the appearance of the \( \text{BiO}_6 \) octahedra with the local electron pairs, and hence the compound \( K_{1-y}\text{Bi}_y\text{BiO}_3 \) should be superconductive in accordance with the discussion above. Indeed, a superconductivity with \( T_c = 10.2 \text{ K} \) was experimentally observed in this compound. From this point of view, it follows that BaPbO\(_3\) should be superconductive at a partial substitution of the \( \text{Ba}^{2+} \) ions for the \( \text{La}^{3+} \) ones (or for the other trivalent ions) because such a substitution produces the local electronic pairs as in the case of \( K_{1-y}\text{Bi}_y\text{BiO}_3 \).

### III. Discussion

The most important point which differs our model from the ones considered by Rice and Sneddon, Varma...
23, and De Jongh 26 is the claim that the local hole pair belongs to the whole BiL₂O₆ complex and not only to the Bi₁⁺ site. Analogously the local electron pair belongs to the whole BiO₃ complex and not only to the Bi³⁺ site. From this point of view we do not believe in the Bi6⁺ [25], and De Jongh [26] is the claim that the local hole in the upper antibonding orbital of the whole octahedral complex. To some extent our idea has a certain similarity with Zhang-Rice construction for HTSC-materials [38]. The essential difference is that Zhang-Rice singlet is a boson (a holon in Anderson terminology) with zero spin and charge difference is that Zhang-Rice singlet is a boson (a holon in Anderson terminology) with zero spin and charge

Of course, a total spin of the biholon is again zero, so their Bose-Einstein condensation corresponds to a standard s-wave superconductivity. The existence of the biholons before was only proved rigorously in the quasi one-dimensional ladder materials at a strong coupling along the rungs (Dagotto and Rice [21]). Our scheme immediately gives us an understanding of a spatial separation of the fermionic and the bosonic bands in the bismuthates.

Namely, our model identifies an optical gap with the binding energy of a preformed pair Eₕ = Eₙ. In the same time a transport gap 2Eₐ corresponds to the pair localization energy. As a result we have the picture for the one-particle density of states presented in Fig. 1. In this picture for x = 0 there is a filled bosonic band separated by the large gap Eₙ = Eₖ from an empty fermionic band (an excited band F') and by a smaller transport gap 2Eₐ from an empty bosonic band B, which plays the role of the conduction band for the bosonic quasiparticles involved in the activation transport. In accordance with Ref. [24] in the representation of the one-particle density of states the filled bosonic band has the hole-like dispersion while the empty bosonic band has the electron-like dispersion. The above bands are on top of the completely filled wide (~16 eV) Bi₆S₂O₂p hybridized band, which includes 18 valence electrons per unit cell. Since the occupied and the empty bands belong to the different octahedra, they are always spatially separated.

Formally, the transport gap is similar to the impurity band in doped semiconductors. However, the combined transport and the Hall-effect measurements showed that the number of carriers participated in an activation conductivity is extraordinary large and is estimated as a number of unit cells [1]. This rejects any impurity mechanisms and suggests that the conduction process in the doping range 0 < x < 0.37 can not be understood by the conventional transport mechanisms of the ordinary semiconductors. The attempts have been made to identify the excitation with the energy gap Eₐ using some optical methods: the reflectivity, the photoconductivity, and the photoacoustic spectroscopy measurements. However, no photoresponse could be detected by either method in the energy region near Eₐ [10]. So the meaning of this gap is just a localization energy of the local pairs. Hence for x = 0 we have the normal bosonic semiconductor with an activation character of the conductivity σ(T) = σ₀ exp(−2Eₐ/kT).

As we pointed above, the localization energy is influenced by at least two effects: the Coulomb intersite repulsion due to CDW state and the energy shift between the empty and the occupied bosonic bands due to a static lattice distortion. With the doping both effects diminish, which leads to the decrease of the pair localization energy. The reason is that the appearing Fermi clusters screen the Coulomb intersite repulsion and the decrease of the static lattice distortion lowers the energy shift between the bosonic bands. At 0 < x < 0.37 the lengths of the Fermi-cluster islands along [100] directions are variable due to the random distribution of the dopant atoms, so the temperature dependence of the conductivity becomes more complicated, but remains a semiconducting-like. It corresponds to the experimentally observed variable-range-hopping conductivity according to the Mott’s law σ = σ₀ exp(T₀/T)−1/4 [33, 34]. The value of T₀ ≈ (3–6) × 10⁵ K obtained by Hellman et al. [35] implies a strong carrier localization as in our model. On the language of the fermionic and the bosonic bands, at 0 < x < 0.37 the Fermi and the Bose subsystems are both energetically and spatially separated.

Near the insulator-metal transition the characteristic temperature T₀ depends on the stoichiometry, and an agreement with the Mott’s law breaks down [33]. A pair localization energy approaches zero because the movement of BiO₆ octahedron, surrounded by the equivalent BiL₂O₆ octahedra in undistorted lattice, does not change the total energy. In the doping range x > 0.37 we have a two-band Fermi-Bose mixture similar to that proposed earlier by Ranninger et al. [36]. In the same time this mixture of a bosonic metal state with a Fermi-liquid state is rather unusual. The normal conductivity in this mixture is mainly due to the fermionic subsystem which overcomes at x ≈ 0.37 the percolation threshold. Nevertheless, the bosonic two-particle contribution into the normal state conductivity is also present. At the doping level x > 0.37 the occupied and the empty pair levels are in the resonance, therefore the energy separation disappears and the Bose and the Fermi subsystems remain separated only spatially.

Note that there is an interplay between the Bose and the Fermi subsystems since the motion of the carrier pairs leads to the transformation of the Bose octahedral clusters to the Fermi ones and vice versa in the process of the dynamic exchange BiO₆ ↔ BiL₂O₆. Because this process is closely related with the superconductivity, we analyze it below in more details.
Superconductivity in Ba$_{1-x}$K$_x$BiO$_3$

Taking into account an existence of the double-well potential in Ba$_{1-x}$K$_x$BiO$_3$ one can consider superconductivity in this compound in the framework of the anharmonic models for HTSC [42,43]. As it was shown in these models, if the oxygen ions move in a double-well potential, an order-of-magnitude enhancement of a constant of an electron-lattice coupling follows automatically from a consistent treatment of this motion. The pairing mechanism is connected in these models with the enhancement of the coupling constant due to the oxygen ion vibrations in a double-well potential. However, in agreement with Refs. [23,29], we believe that in the bismuthates the pairing mechanism is more probably of the electronic than of the phonon-mediated origin (see Sec. II b). In the same time in our system the local pairs tunnel between the neighboring octahedra due to the vibration of the oxygen ions in the double-well potential. Therefore we suppose that the lattice is involved in the superconductivity more probably by providing the motion of a local pair rather than via a pairing mechanism itself.

The process of a dynamic exchange is illustrated in Fig. 4. An oxygen belonging to the two neighboring octahedra BiO$_6$ and BiL$_2$O$_6$ vibrates in a double-well potential, and hence the tunneling of the electron pair between the neighboring octahedra occurs when the ion tunnels through the potential barrier between the wells. Because of this interconnection between the processes of the pair and the oxygen tunneling, one can estimate the matrix element of the pair tunneling as $t_B \sim \omega_0 e^{-D}$ where $\omega_0$ is the tunneling frequency, $D = (1/h) \int_{x_0}^x |p| dx \simeq (d/h)\sqrt{2MU}$ is a quasiclassical transparency of the barrier in the double-well potential, $U$ and $d$ are the barrier height and width, and $M$ is the oxygen ion mass. Note that rather small tunneling frequency $\omega_0 = 200$ K (see Fig. 5) already incorporates the effects connected with a polaronic narrowing of the one-particle bands $t_p \sim t_0 e^{-(\alpha^2/d)}$ and the hopping of a bosonic pair via virtual dissociation processes. The last ones are described by a second order perturbation theory (see Ref. [3]) and yield an estimate $t_B \sim t^2_p/|E_0|$ for a width of a bosonic band in a spatially homogeneous Bose-system.

The tunneling of the pairs helps to establish a macroscopic long range order (a phase coherence) in the bosonic system. On the language of the spatially separated Fermi-Bose mixture, a local pair is transferred from one Bose cluster to a nearest one over the Fermi-cluster, which, depending on the doping level, consists of several octahedra. The pairs overtake the Fermi-cluster step by step. A single step, corresponding to the pair transfer into a neighboring octahedron, is described by the pair tunneling in the double-well potential. Thus the tunneling frequency $\omega_0$ is the same for each step. If one assumes that the steps are independent events, a probability of the overcoming of the Fermi-cluster can be obtained as a product of the probabilities of an each step. In this case the matrix element of the pair tunneling through the Fermi-cluster can be estimated as $t_B \sim \omega_0 e^{-(N)/D}$ where an average number of steps (which is proportional to a Fermi-cluster linear size) can be obtained from the ratio of the concentrations of BiL$_2$O$_6$ and BiO$_6$ octahedra. Hence a number of steps can be estimated as $\langle N \rangle \simeq \left(\frac{1+x}{1-x}\right)^{1/3}$.

Of course, it is naturally to assume that the critical temperature of superconductivity is of the order of the temperature of the Bose–Einstein condensation $T_c \sim t_B \sqrt{n_B}$ in the bosonic system with a large effective mass $m_B \sim 1/t_B a^2$. We remind that $a^3 n_B = (1-x)/2$ in our case. For $x = 0.4$ and the parameters of the double-well potential obtained in the Ref. [7] (see also Fig. 4) we estimated $T_c \sim 50$ K. This value is larger than the measured $T_c \sim 30$ [13] in the bismuthates.

Note that the estimate above is quite rough. An accurate analysis of the superconductivity in the bismuthates...
should also take into account a significant boson-phonon interaction, arising due to the interconnection between the vibrations of the oxygen ions and the transfer of the pairs. When the pair is transferred from one octahedron to another, the lattice has a sufficient time to relax, forming each time a new configuration before the next tunneling event occurs. As a result the pair’s “deformed” environment (the BiO$_x$ octahedra) may follow the tunneling processes without the retardation. If the local pair motion is slow compared to the frequencies of the optical phonons associated with the deformations of the octahedra, the so-called anti-adiabatic limit is fulfilled in our system [20].

Note that in our case the stretching phonons are associated with the tunneling of the pairs. The following conclusions can be made from the analysis of the phonon modes studied in Ba$_{1-x}$K$_x$BiO$_3$ by an inelastic neutron scattering [14]. (i) The frequencies of the optical modes of the Bi-O vibrations $\omega_{ph} > 630$ K are high enough to provide the anti-adiabatic limit, since the tunneling frequencies are lower, $\omega_0 \leq 300$ K for $x \leq 0.5$ [5]. Note that from a theoretical point of view a polaronic narrow-bandwidth should be coordinated with its neighbors to guarantee a resonant tunneling in the system. Hence a long-range correlation of the vibrations should occur at low temperatures when only the low-energy states are occupied. (iv) The bandwidth of the longitudinal stretching mode with [100] wave-vector direction is lower than the energy of modes with other wave-vector directions or of transversal modes. (iii) The breathing-type vibrations with the wave vector $\mathbf{q}_0=(\pi/2a,0,0)$ are energetically favorable since an energy of the longitudinal stretching phonons is the lowest at the Brillouin band edge. That is why a “breathing” of each octahedron should be coordinated with its neighbors to guarantee a resonant tunneling in the system. Hence a long-range correlation of the vibrations should occur at low temperatures when only the low-energy states are occupied. (iv) The bandwidth of the longitudinal stretching mode is of the order of 100 K, and thus a temperature $T \sim T_c$ is high enough to excite the non-breathing-type longitudinal stretching phonons with the wave vectors shorter than $\mathbf{q}_0$. The thermal excitation of the phonons with such short wave-vectors leads to the destruction of the long-range correlation between the breathing-type vibrations, and hence play a destructive role for the pair tunneling. It should be stressed in addition, that the oscillations of the oxygen ion in the double-well potential corresponds to the breathing-type longitudinal vibrations with [100] directions (see Fig. 4b).

Thus the pair motion is more correctly described as follows. When the local pair is transferred to a neighboring octahedron (for example, from the left to the right in Fig. 4) due to the transition of the oxygen ion from one well to another one in the double-well potential, the charge density corresponding to a pair is quickly redistributed inside the octahedron. As a result a double-well potential, designed for the vibration of the other oxygen ions belonging to the same octahedron, is formed. The longitudinal stretching phonons with $\omega_{ph} > \omega_0$ are involved in this fast process. After the relaxation of the deformed surrounding, the pair becomes prepared for the next hopping, and the described process repeats again and again, providing a resonant tunneling of the pairs on the large distances along [100] directions.

Note that since the BiO$_x$ and BiL$_2$O$_6$ complexes have different strengths of the Bi-O bonds, the pair transfer in turn is able to change both the phase and the wave vectors of the stretching phonons. As the vibration in the double-well potential is of a breathing-type, the wave vectors remain unchanged when the octahedra (which the pair is passing by) vibrates in the breathing mode. However a value of $\mathbf{q}$ can be changed in the case of the vibrations with the short wave-vector. Due to the dispersion of the longitudinal stretching mode such a change can cost some energy. Thus to provide the pair motion in this case, an energy should be transmitted to the phonons and the dissipation of the pair kinetic energy should occur. Of course, this leads to the decrease of the BEC critical temperature for the pair. Hence the more exact estimate for $T_c$ requires the solution of a problem of a self-consistent preparation of the barrier due to the interaction of a pair with a phonon subsystem in a process of underbarrier tunneling. This brings us all the nice physics of the tunneling with the dissipation [45–47]. Remind, that in the problem of the tunneling with the dissipation the shape and the height of a potential barrier in a two-level system are determined self-consistently taking into account an interaction of a tunneling particle with a thermal reservoir. Note that the more exact evaluation of $T_c$ will give us an experimentally observed decrease of the critical temperature as a function of the concentration in the metallic region $x > 0.4$. This decrease should take place mainly due to the following facts: (i) a decrease of a bosonic density $n_B$, (ii) an increase of the width of the barrier $\langle N \rangle$, and maybe the most important, (iii) the decrease of lattice softening which leads to the increase of the dissipation of the pair kinetic energy due to the stretching phonons with $\mathbf{q} \neq \mathbf{q}_0$. Note also, that at temperatures $T > T_c$ a bosonic subsystem behaves for the concentrations $x > 0.37$ as a normal bosonic metal with a heavy mass $m_B \sim 1/\hbar a^2$.

Summarizing the discussion above we point out that the two processes are important for the superconductivity in Ba$_{1-x}$K$_x$BiO$_3$. The vibrations of the oxygen ions in the double-well potential provides the mechanism for a transfer of the local pairs from the one Bose-cluster to the other. At the same time the pair motion is strongly affected by the stretching longitudinal vibrations of the oxygen ions in the octahedra which the pair is passing by. We suppose that the last process should be taken into account to estimate correctly the critical temperature.

It is worth to notice, that a similar dispersion of the longitudinal stretching phonons, which leads to the dominant role of the breathing-type phonons at low temperatures, has been observed also for the high $T_c$ cuprates La$_{1.85}$Sr$_{0.15}$CuO$_4$ and YBa$_2$Cu$_3$O$_7$ [13]. Taking into account the recent experimental evidence by Müller et al.
of the coexistence of the small bosonic and fermionic charge carriers in La$_{2-x}$Sr$_x$CuO$_4$, we suppose also to apply our Fermi-Bose mixture scenario to HTSC cuprates. Our paper on this problem is in preparation [50]. Note again that the nature of the pairing itself in the cuprates is definitely of the electronic origin. However, due to the fact that underdoped HTSC-materials are close to the phase-separation on AFM and PM-clusters [21, 22], the lattice here can play an assistant role again providing a pair tunneling between the superconductive PM metallic clusters via an insulating AFM-barrier. It can also serve as a limitation on the estimate of the effective critical temperature for the Bose-condensation of the pairs in our system.

IV. CONCLUSION

In conclusion we briefly summarize the main results.

1. The parent compound BaBiO$_3$ represents a system with the initially preformed local electron and hole pairs. Every pair is spatially and energetically localized inside an octahedron volume. The localization energy of a pair determines the transport activation gap $E_a$. The binding energy of a pair becomes apparent as the optical gap $E_0 = E_b$.

2. The new type of the Fermi-Bose mixture is possibly realized in the superconductive compositions of Ba$_{1-x}$K$_x$BiO$_3$ for $x > 0.37$. The bosonic bands are responsible for the two-particle normal state conductivity. The overlap of the empty fermionic band $F$ with an occupied valence band Bi$_6$O$_{2p}$ provides the insulator-metal phase transition and produces the Fermi-liquid state. This state shunts to a great extent the normal state conductivity arising from the two-particle Bose transport.

3. The fermionic band $F'$ connected with the pair destruction does not play any role in the transport. The excitation energy is high enough to guarantee against the destruction of bosons (a pair binding energy $E_b \approx 0.5$ eV for the superconductive compositions).

4. Pair localization energy is absent for $x > 0.37$ ($E_a = 0$), so the bosonic and the fermionic subsystems are separated only spatially. The interplay between them is due to the dynamic exchange BiL$_2$O$_6 \leftrightarrow$BiO$_6$, which causes a free motion of the local pairs in the real space.

5. The pairing mechanism in the bismuthates is more probably of the electronic than of the phonon-mediated origin. The existence of the local pairs and their tunneling between the neighboring octahedra are the reasons for the appearance of the double-well potential, which describes the vibration of the oxygen ions. The lattice is involved in the superconductivity more probably by providing the motion of the local pairs.

Finally, we would like to emphasize that the scenario of the Fermi-Bose mixture allows us to describe qualitatively an insulator-metal phase transition and a superconductive state in BKBO in the framework of the one common approach. To some extent this scenario explains the contradictions observed experimentally by the UPS and XPS [16, 17, 33], the EXAFS and XANES [17, 18, 38], and the Raman [22, 27, 32] spectroscopies, as well as by an inelastic neutron scattering [14], the transport and the optical measurements [1, 33, 38]. Nevertheless, the additional experiments are required to make a definite conclusion about the nature of the superconductivity in these systems.

First of all we propose two direct experiments to test our model. (i) To synthesize a new compound Ba$_{1-x}$La$_x$PbO$_3$, which should be superconductive in accordance with our point of view. (ii) To provide the Raman scattering experiment of the superconducting Ba$_{0.6}$K$_{0.4}$BiO$_3$ compound using a resonance optical excitation in the range of the optical pseudogap $E_g \approx 0.5$ eV. In this case the appearance of the additional Raman modes due to local dynamic distortions should be observed at the pair destruction in accordance with our model.

Besides, it is important to carry out the more precise measurements of the specific heat in the bismuthates for $T \sim T_c$. We know that the specific heat behaves as $C_B \sim (T/T_c)^{3/2}$ for the temperatures $T < T_c$, and $C_B = const$ for $T \gg T_c$ in a three-dimensional Bose-gas. As a result, there is a $\lambda$-point behavior of the specific heat for $T \sim T_c$. However, in the Fermi-Bose mixture there is an additional contribution from a degenerate Fermi-gas $C_F \sim T$. This contribution could in principle destroy a $\lambda$-point behavior of the specific heat in the Fermi-Bose mixture. Note that the currently available experimental results in the bismuthates signal a smooth behavior of the specific heat near $T_c$ [34], because in all the experiments the contributions from the degenerate Fermi and Bose-gases are masked by a larger lattice contribution.

Another important measurement, which can be proposed to elucidate the nature of the superconductivity, is a measurement of the thermopower in the normal state of the bismuthates. According to the ideas of Larkin et al. [3], the Seebeck coefficient $S_0 = n_B(T)/n_0 \ln(n_B(T)/n_0) + \alpha T/\varepsilon_F$ in the Fermi-Bose mixture is much larger by absolute value than the usual value $S_0 = \alpha T/\varepsilon_F$ in the normal state of an ordinary fermionic metal. Moreover, the sign of the thermopower can become negative, which is also rather unusual. Note that up to now there is a lot of controversy in the measurements of Seebeck coefficient in the bismuthates (see Ref. [57] and references therein).

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