Experimental and Theoretical Constraints of Bipolaronic Superconductivity in High T_c Materials: An Impossibility

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The bipolaronic scenario for high T_c superconductivity is critically examined. The underlying assumption that at low temperatures all the charge carriers exist in the form of itinerant bipolarons is shown to be incompatible on theoretical and experimental grounds. Superfluidity of such bipolarons cannot give the values of T_c nor explain the fermionic nature of the quasiparticles observed in the cuprates. [S0031-9007(98)06566-1]

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Electron-phonon interactions in solids show up in a variety of ways: from relatively small mass renormalization of the carriers in metals due to inherently weak screened interaction to almost localized quasiparticles in ionic solids and oxides—known as small polarons—as a result of enormous mass enhancement in case of strong unscreened interaction. Although the literature [1] on polarons is vast and sometimes confusing, one calls a polaron a small polaron when it results from strong interaction with acoustic or local phonons (with a concomitant lattice distortion, localized within the unit cell). In order to explain some of the properties of amorphous chalcogenide glasses Anderson [2] in 1975 introduced the idea of on-site small bipolarons i.e., two electrons localized on the same lattice site due to intense local lattice distortion, ultimately behaving as so-called negative U centers. This idea was soon extended to intersite [3]—so-called Heitler London bipolarons which were invoked successfully to explain a host of properties in transition oxide bronzes and the insulator-metal transition in $Ti_{4-x}V_xO_7$, intensively studied in Grenoble in the late 1970s [4]. About the same period one of the authors [5] pointed out that in a many electron system the ground state should continuously evolve as a function of the electron-phonon coupling constant from a BCS like superconducting to an ultimately insulating ground state as the Cooper pairs localize in the form of heavy massive bipolarons. Although the discovery of high T_c superconductivity [6] may owe something to these ideas, there was never any question of evoking a Bose-Enstein condensation (BEC) of bipolarons as relevant to its explanation in any of those papers. The idea published in 1981 [7] suggesting that small bipolarons may be considered as itinerant hard core bosons on a lattice which can become superfluid had lately been taken very literally by certain authors [8], suggesting it to be the reason for high T_c superconductivity. We shall show in the following that extending the bipolaron theory for superconductivity to high T_c materials is fallacious, that it is incompatible with experiments, and that bipolaron condensation—*within the original scheme of such a theory of bipolaronic superconductivity [7]*—is impossible to occur in those materials.

The low carrier concentration ($\sim 10^{21}$ cm^{-3}) together with the small coherence length (of the order of a few tens of angstroms) in high T_c compounds is, at a first view, indeed tempting to consider a scenario where tightly bound electron pairs exist in the normal state and which, as the temperature is lowered, condense at a temperature typical for BEC. We examine in the following the feasibility of such a scenario in the context of the present day experimental results and our theoretical understanding. Our approach will concern the following questions.

(i) Is a BEC of electron pairs at least in principle conceivable in a crystalline solid?

(ii) If so, could the possible origin for those electron pairs be of bipolaronic nature?

(iii) Is the picture of bipolaronic superconductivity compatible with our present day experimental knowledge?

Let us assume to begin with that systems exist where tightly bound electron pairs have the properties of hard core Bosons and can move on a lattice in an itinerant Bloch wavelike way. As long as their density is low, such bosons can in principle condense at the BEC temperature which for an isotropic 3D system is given by

$$k_B T_{\mathrm{BEC}}^{3\mathrm{D}} \simeq 3.31 \hbar^2 n_B^{2/3} / m_B \,. \tag{1}$$

n_B denotes the concentration (total number of bosonic carriers per cm^3) and m_B the effective mass of such hypothetical bosons. As an indication, for a typical hole density of 6×10^{21} cm^{-3}—corresponding to a pair density n_B at half this number—and for a temperature T_c of say 100 K, m_B comes out to be 60 times the free electron mass m_e. Taking into account the layered structure (CuO_2 planes) of high T_c materials, a more appropriate way of defining a transition temperature is the BEC temperature for quasi-2D systems, given by

$$k_B T_{\mathrm{BEC}}^{2\mathrm{D}+\varepsilon} = \frac{2\pi \hbar^2 n_B^{ab}}{m_B^{ab} \ln[2 k_B T_{\mathrm{BEC}}^{2\mathrm{D}+\varepsilon} m_B^c d^2/\hbar^2]} \,. \tag{2}$$

m_B^{ab} and m_B^c denote, respectively, the mass of the bosons in the ab plane and orthogonal to that plane in the c direction, and $n_B^{ab} = n_B d$ is the concentration of bosons in the ab plane. The lattice constant in the c direction is denoted by d. As an example let us consider the case of the most studied high T_c material, i.e., $YBa_2Cu_3O_{6+x}$ for which the lattice parameters are given by $a = b = 3.8$ Å and $d = 11.6$ Å. Let us take the density of bosons $n_B = n_0 10^{21}$ cm^{-3} with n_0 being some number varying between 0.3 and 4, the latter being rather on the high side (the optimum doped $YB_2Cu_3O_{6.97}$ has an n_0 of about 3). The adjoining Table I shows the typical values obtained for m_B^{ab} for a T_c of 100 K and two mass ratios $m_B^c/m_B^{ab} = 100$ and $m_B^c/m_B^{ab*} = 25$. The evaluated m_B^{ab} is now about $35m_e$ for $n_0 = 3$ and hence smaller than its value m_B calculated on the basis of an isotropic 3D scenario. Applying such arguments to a wide class of high T_c compounds one invariably finds m_B^{ab} between a few tens m_e to $100m_e$ [9].

The first problem we run into with this picture arises when we estimate the hypothetical boson mass directly from the experiments of the London penetration depth which for magnetic fields in the direction orthogonal to the CuO_2 layers is given by

$$\lambda^{ab} = (m^{ab}c^2/4\pi n_s e^2)^{1/2}, \tag{3}$$

where e denotes the electron charge, n_s is the superfluid fraction of the charge carriers, and m^{ab} is their mass. For a condensed single particle carrier density corresponding to optimum doped YBCO, i.e., $n_s = 2n_0 \times 10^{21}$ with $n_0 = 3$ and a measured value for λ^{ab} of the order of 1600 Å [10], we find a single particle carrier mass m^{ab} of approximately $5m_e$ which gives a minimum boson mass $m_B^{ab} = 10m_e$. This is less than one-third of the mass determined via the BEC temperature using the quasi-2D BEC formula for the transition temperature given above. For a not perfectly clean superconductor or one with considerable quantum fluctuations [11] the superfluid density is less than the bare hole density and m_B^{ab} estimated from the same penetration depth will become even smaller.

These considerations of the BEC scenario clearly indicate the constraints imposed on the density and the mass of those hypothetical bosonic charge carriers. Can these constraints be respected (i) if these bosonic charge carriers are bipolarons as the advocates [8] of bipolaron theory for high T_c superconductivity pretend, and (ii) in a more general sense and independent on any particular mechanism for electron pairing, can such a BEC scenario be compatible with the present day experimental results on high T_c materials? As we shall see below the answer to both of these questions is *no*.

TABLE I. The effective boson masses m_B^{ab}, m_B^{ab*} (in units of the free electron mass) as evaluated from the formulas for BEC for a quasi-2D [Eq. (2)] system with a mass ratio $m_c/m_B^{ab} = 100$ and $m_c/m_B^{ab*} = 25$, respectively, and m_B obtained for a 3D [Eq. (1)] system.

n_0	0.3	0.5	0.8	1.0	2.0	3.0	4.0
m_B^{ab}	4	6	9	11	20	29	37
m_B^{ab*}	5	8	12	14	25	35	44
m_B	13	18	25	30	46	60	73

Let us tackle the first question and, assuming that the charge carriers are small bipolarons (to be distinguished from large bipolarons [12]), let us estimate their mass. We shall examine this question on the basis of the familiar Holstein molecular crystal model [1] which is considered to adequately describe the local electron lattice interaction. The Hamiltonian for this model is given by

$$H = (zt - \mu)\sum_{i\sigma} n_{i\sigma} - t\sum_{i\neq j,\sigma}(c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U\sum_i n_{i\uparrow}n_{i\downarrow} - g\sum_{i,\sigma} n_{i\sigma}(a_i + a_i^\dagger) + \sum_i \hbar\omega_0(a_i^\dagger a_i + 1/2), \tag{4}$$

where $c_{j\sigma}^\dagger$ denotes the creation operators for tight binding electrons with hopping integral t and a chemical potential μ. The electron-phonon interaction with strength g is taken to be local, in view of the interaction with primarily local modes which favors small polaron formation. U denotes some effective Coulomb repulsion. The sites i, j are generally understood as effective sites comprising certain cations together with their respective ligand evironments and hence U corresponds to intersite rather than on-site Coulomb repulsion. Transforming the above Hamiltonian into a picture of small polarons described by the polaron creation operators $\tilde{c}_i^\dagger = c_i^\dagger e^{-(g/\hbar\omega_0)(a_i - a_i^\dagger)}$ one obtains, following the standard procedure [13], an effective Hamiltonian given by that of Eq. (1) upon replacing $zt \to zt - \varepsilon_p$, $U \to U - 2\varepsilon_p$, and $t \to t^* = te^{-\alpha^2}$ denoting the polaron hopping integral. In order for small polarons to form, two conditions must be satisfied. The first one is that the gain in energy by self-trapping of the charge carriers (given by the polaron level shift $\varepsilon_p = g^2/\hbar\omega_0$) must be bigger than the gain in energy of the charge carrier becoming itinerant (given by half the bare bandwidth $D = zt$, z denoting the coordination number). This requires the dimensionless coupling constant: $\lambda \equiv \varepsilon_p/D \equiv g^2/D\hbar\omega_0 \geq 1$. The second condition is that the deformation $\alpha = \langle \frac{1}{2}(a_i + a_i^\dagger)\rangle$ induced by the charge carriers remains fairly local: $\alpha = g/\hbar\omega_0 = \sqrt{\varepsilon_p/\hbar\omega_0} \geq 1$. These conditions apply when the Coulomb interaction is strong enough to prevent the formation of bipolarons. If this is not the case, then the conditions for bipolaron formation apply which, following similar arguments as above, lead to $2\lambda - U/2 \geq 1$ and $2\alpha \geq 1$.

Let us now check to what extent bipolarons can satisfy the experimental and theoretical constraints necessary to act as itinerant bosons in order to ultimately describe high T_c superconductivity as a BEC of bipolarons. High T_c compounds are known to be narrow band systems with strong Hubbard type correlations, having a bandwidth corresponding to a bare effective hopping integral of the order of $t \simeq 0.1$ eV [14]. This value has to be compared with the frequency of the local phonon modes which have typical frequencies of the order of $\hbar\omega_0 \simeq 0.05$ eV. Hence the adiabaticity parameter $\gamma = \omega_0/D \simeq 0.1$ is small in typical high T_c materials, and we are closer to the adiabatic than to the antiadiabatic limit. Since the most favorable condition for bipolaron formation occurs for $U = 0$, this implies $2\varepsilon_p/D \geq 1$ or $2\alpha^2\gamma \geq 1$. For a $\gamma = 0.1$ we thus find $\alpha \simeq 2.23$. We therefore expect in the regime of adiabaticity parameters γ which apply to high T_c materials large values of α in order for bipolaron formation to occur.

Within the framework of the bipolaron theory for high T_c superconductors [8] α can also be estimated from the pseudogap in the normal state of these materials [seen by angle-resolved photoemission spectroscopy (ARPES)] if it is assumed that the pseudogap indicates the binding energy of bipolarons. Along such an argumentation one obtains $2\varepsilon_p - U/2 - D \simeq 0.01$ to 0.03 eV. Again assuming $U = 0$ we get $\alpha \simeq 2.23$ which leads to a bipolaron hopping integral $t^{**} = t(t/2\varepsilon_p)e^{-2\alpha^2} \simeq 10^{-5}t$ or an effective mass for bipolarons equal to $2.3 \times 10^5 m_e$. This would give a BEC transition temperature of about 1.3×10^{-2} K which is too small to explain high T_c superconductivity. Hiramoto and Toyozawa [15] have considered in detail the complete phase diagram of large polarons, bipolarons, and small polarons in the parameter space of λ and γ, using the Feynman path integral method. Their results for an adiabaticity ratio $\gamma = 0.1$ gives a bipolaronic mass $m_B^{ab} \simeq (16/3)\varepsilon_p/\gamma\hbar\omega_0$ approximately equal to $210 m_e$ which is smaller than the numbers we just estimated for the complete antiadiabtic case ($\gamma = \infty$) but still quite large and cannot lead to values for T_{BEC} much bigger than 10 K.

Even if we consider a bipolaron hopping integral $(1/4)te^{-\alpha^2}$ which avoids breaking up the bipolarons as they move along—as proposed by the advocates [16] of bipolaron scenario for high T_c superconductivity—we would still find bipolaron masses of the order of roughly $580 m_e$. This can account for BEC transition temperatures of about 5 K but not more. In conclusion, we will be very hard pressed to come up with a bipolaron mass of the order of $10 m_e$ even in the quasiadiabatic limit, as we just saw, or a polaron mass of $5 m_e$—a magic number that the authors of the bipolaronic superconductivity cherish—when we have an electron-phonon coupling constant α of the order of 2.

This analysis rules out that bipolarons and their condensation are the explanation for high T_c superconductivity.

Let us now come to the next question: Is a BEC of tightly bound electron pairs, of whatever origin this binding might be, compatible with the present day experimental findings?

First of all we should remember that a BEC of tightly bound electron pairs assumes that the interparticle distance between such bosonic quasiparticles should be greater than the coherence volume. Is this condition satisfied in high T_c superconductors? A precise estimation of both the number of carriers in the plane as well as of the coherence length ξ_{ab} are not easy to obtain. The empirical relationship of Tokura *et al.* [17] seems to hold well for the number of holes in the plane of $YBa_2Cu_3O_y$ with a hole concentration per copper given by $n_h = (y - 6.5)/2$. This would indicate for $YBa_2Cu_3O_7$ a hole concentration on the plane of $n_h = 1.56 \times 10^{14}$ cm^{-2} (this is a lower estimate as the chain contributions here are neglected [18]). Taking a ξ_{ab} as low as 20 Å we obtain a boson density in the plane $n_{ab} = \frac{1}{2}n_h\xi_{ab}^2 \simeq 3$ bosons in the coherence cell on the *ab* plane. Using the estimate of ξ_{ab} of Alexandrov and Mott [19] will bring down the number of bosons, and the issue cannot be settled to everybody's satisfaction. However, an independent check exists. As BCS theory [20] pointed out long ago, $k_F\xi$ gives the number of carriers in a coherence volume or area. The universal relationship for all superconductors obtained by Pistolesi and Strinati [21] shows that for all high T_c and novel superconductors this number is 2π, that is, on average there are 6–10 carriers in that coherence cell on the plane [$n_{2d} = \frac{1}{8}(k_F\xi)^2$], and thus corroborates precisely our estimate of the number of bosons in a typical coherence cell. The pure bosonic limit of $k_F\xi$ of the order of $1/\pi$ is never reached in any of these materials. Under these circumstances we are at the limit where the internal degrees of those bosons can be considered as being frozen out. The electrons making up those bosons will overlap, and as a consequence the picture of bosonic quasiparticles will break down. As a matter of fact, for the kind of concentrations in the plane that we have, the Fermi exclusion principle will drive the two-particle bound state energy rapidly to zero, as is well known [22].

The carrier mass in the normal state m^* can be extracted from a variety of experiments. When ARPES experiments are fitted with a tight binding picture the nearest neighbor hopping integral [14] turns out to be about 0.15 eV which yields a mass for the electronic charge carriers of about $m^* = \hbar^2/2ta^2 \simeq 1.2 m_e$ or a boson mass of $2.4 m_e$. These are mass values well documented in the literature [23] and also compare well with similar values of the order of one or two m_e, obtained from the optical experiments compatible with a plasma frequency of the order of 2–3 eV in the normal state [24]. These values for the masses are clearly incompatible with the ones derived above on the basis of the hypothetical BEC scenario which assumes well defined bosonic quasiparticles even in the normal state.

The existence of a Fermi surface in the high T_c materials has now been established experimentally beyond doubt [25]. Bipolarons being bosons do not have a Fermi surface. Theories of BEC invoking bipolarons take the point of view that the pseudogap observed in ARPES in certain parts of the Brillouin zone indicates the energy needed to break up the bipolarons into individual polarons or electrons. This interpretation is in complete contradiction with experiments. One should remember that the ARPES experiments give a dispersion of the quasiparticles which strongly depends on the **k** vectors of the quasiparticles and furthermore, when integrating the spectral weight over frequency, yield essentially the Fermi distribution function showing a clear steplike feature at the Fermi wave vector. If, on the contrary, the quasiparticles were tightly bound electron pairs which get broken up into individual electrons by the scattering process in photoemission experiments, one should expect essentially **k** independent spectral functions showing a **k** independent gap equal to the binding energy of the pair—resulting from the inherently localized nature of such electrons making up the bosonic electron pairs that have been split off the electron continuum. The Myake-Randeria relationship [26] allows us to estimate the vacuum binding energy of the two-particle s-wave bound state ε_b from the known experimental value of the superconducting gap in two dimensions. It is given by

$$\Delta = \sqrt{2\varepsilon_F \varepsilon_b}\,, \tag{5}$$

where ε_F is the Fermi energy. We can also write $\varepsilon_b \simeq \hbar^2/2m_B^{ab}\xi_{ab}^2$ with $\Delta \simeq 30$ meV and $\varepsilon_F \simeq 0.5$ eV, and we obtain an $\varepsilon_b \simeq 10^{-3}$ eV. This gives for an $\xi_{ab} \simeq 20$ Å, $m_B^{ab} \simeq 10 m_e$, but then this shallow bound state will rapidly disappear around 10 K.

One can, of course, imagine alternative scenarios with bipolarons and single carriers coexisting in a two-band model where the bosonic quasiparticles reside as resonant states inside the Fermi sea and thus lead to Cooper pairing and a concomitant condensation of the bipolarons [27]. But this has nothing to do with bipolaronic superconductivity.

We have in this communication taken considerable care to show once and for all the unsatisfiable experimental constraints and theoretical inconsistencies of the bipolaronic superconductivity scenario in the high-T_c materials. Although a BEC of tightly bound electron pairs is in principle conceivable, the experimental constraints of high T_c materials are such that this scenario is not realized. As concerns the question whether bipolarons could possibly play the role for such bosonic quasiparticles and their condensation, we find that such a possibility is ruled out. The tragedy of beautiful theories, Aldous Huxley once remarked, is that they are often destroyed by ugly facts. One perhaps can add that the comedy of not so beautiful theories is that they cannot even be destroyed; like figures in a cartoon they continue to enjoy the most charming existence until the celluloid runs out.

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