BI-POLARON CONDENSATION IN HIGH T_c SUPERCONDUCTORS

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ABSTRACT

On the basis of optical measurements-, photoemission-, EXAFS- and neutron scattering-experiments we conclude that itinerant valence electrons coexist with localized bi-polarons. Entering the metallic phase upon chemical doping, a charge transfer between the two electronic subsystems is triggered off. We show that as the temperature is lowered towards T_c this process leads to a delocalization of bi-polarons due to a precursor effect of superfluidity of those bi-polarons. Upon entering the superconducting phase, these bi-polarons ultimately condense into a superfluid state which is expected to largely determine the superconducting properties of high T_c materials.

The discovery of high T_c superconductors[1] has brought up the question yet again how high in principle we can expect critical temperatures T_c to be. In the standart classical BCS-Eliashberg theory of superconductivity, T_c is not a calculable quantity, in the sense of an ab inito calculation. This theory rather relies on the input of an in principle measureable function $\alpha^2F(\omega)$ and the implicit supposition of adiabaticity. The applicability or in-applicability of this theory is being judged a posteriori by whether its predictions of the various thermodynamic, electromagnetic and transport properties are bourne out by the experimental verifications.

- The large gap/T_c ratio ($2\Delta/k_BT_c$) being of the order 5–7 in these materials suggests on the basis of this theory large values of the effective coupling constant λ —being of the order of 3 or bigger. Such large values of λ are indeed expected on the basis of experiments which clearly show that at least part of the charge carriers in those systems have small polaron characteristics.
- The small coherence length ξ, being of the order of $\sim$ 20 Å, is found to be hardly bigger than the average distance between charge carriers having densities of the order $10^{21} - 10^{22}/\mathrm{cm}^3$.

Given the fact that i) polaronic charge carries have a tendency to pair up into bi-polarons and that ii) the density of charge carriers is small in high T_c materials, one is led to conjecture that superconductivity in those systems could appreciably deviate from the BCS-Eliashberg formulation and possibly be closely connected to a superfluid state of bi-polarons.

Experimentally, high T_c materials are known to exhibit local lattice instabilities caused by a strong local interaction between charge carriers and local lattice deformations which are of dynamical rather than static nature. Experiments which show that are EXAFS (see articles by A. Bianconi and J. Röhler), diffusive pulsed neutron scattering techniques (see article by T. Egami) and infrared absorption measurements in insulating samples with photoinduced carriers (see article by Ruani). Chemists[2] very early on pointed out that in those materials the ligand environments of anions exist in "ambiguous" configurations i.e. between two stable ligand configurations having definite anion valence states. Such a situations naturally favours charge fluctuations of such clusters which are accompanied by the appropriate ligand environment deformations. Examples for that are :

- the $Cu^{+}(1) \leftrightarrow Cu^{++}(1)$ fluctuations accompanied by dumbbell $\leftrightarrow$ square configurations of the surrounding oxygens of the chains in $YBa_2Cu_3O_{6+x}$,
- the $Bi^{3+} \leftrightarrow Bi^{5+}$ fluctuations accompanied by the octahedral $\leftrightarrow$ tetrahedral configurations of the oxygens in $Ba(Bi_xPb_{1-x})O_3$ compounds.
- The $C_{60}^{-} \leftrightarrow C_{60}$ fluctuations accompanied by the tangential pentagon deformations, fluctuating between two extreme tendencies of sp^2 configurations, typical for graphite and sp^3 configurations, typical for diamond.

The strongly coupled dynamical fluctuations of the anion valency and of the atomic positions of the ligand environments show up as polaronic features of i) local phonon modes which correspond to the specific deformations of the ligand environments mentioned above and of ii) the electronic spectra of the charge carriers self-trapped on those clusters. These features can be tested by experimental means by which an electron is removed from the system either by photoemission or resonant Raman scattering. Such processes lead to large amplitude vibrations of the ligand environment having been stripped of an electron and, as a consequence, resulting in a shower of phonons which show up as a series of well defined overtones of the basic local modes.

Both photoemission[3] and resonant Raman scattering[4] and out of equilibrium Raman scattering (see article by D. Mihailovic) have in this way clearly established the polaronic nature of localized charge carriers in the insulating phase of high T_c materials. There is increasing experimental evidence that polaronic charge carriers continue to exist when doping insulating materials into the metallic phase. Photoemission spectroscopy on metallic Rb_3C_{60} clearly shows[5] remnants of the first few overtones of the 1500 cm^{-1} pentagonal pitch-mode characteristic of isolated C_{60}^{-} molecules. In the cuprate high T_c materials we do not for the time being have such direct evidence for polaronic charge carries, not unless the flat dispersion observed in the $Y - \Gamma$ direction and extending over practically half a reciprocal lattice vector[6] (see article by A. Arko) turns out to be of polaronic origin. Moreover, measurements of the optical conductivity, when interpreted in terms of a regular Drude contribution plus some broad mid infrared band (see article by Timusk), provide indirect evidence of polaronic charge carriers in the metallic phase. In particular c axes polarized far infrared reflectance measurements show evidence for strong coupling of certain c-axes longitudinal phonons to a,b plane electronic excitations. One also observes a doping

and temperature induced transfer of oscillator strength from the planar oxygen to apical oxygen modes. Moreover the electronic background shows condensation upon entering the superconducting state. The existence of the mid infrared band seems to be common to metallic oxides[7] including V_2O_3, $La_{0.5}Sr_{0.5}CoO_3$, $Ca_{0.5}Sr_{0.5}RuO_3$ and $Ba_{1-x}K_xPbO_3$, $Sr_{0.9}La_{0.1}TiO_3$, $SrTiO_{3-x}$, $Bi_2Sr_3Co_2O_9$, etc. all of which a very polar compounds.

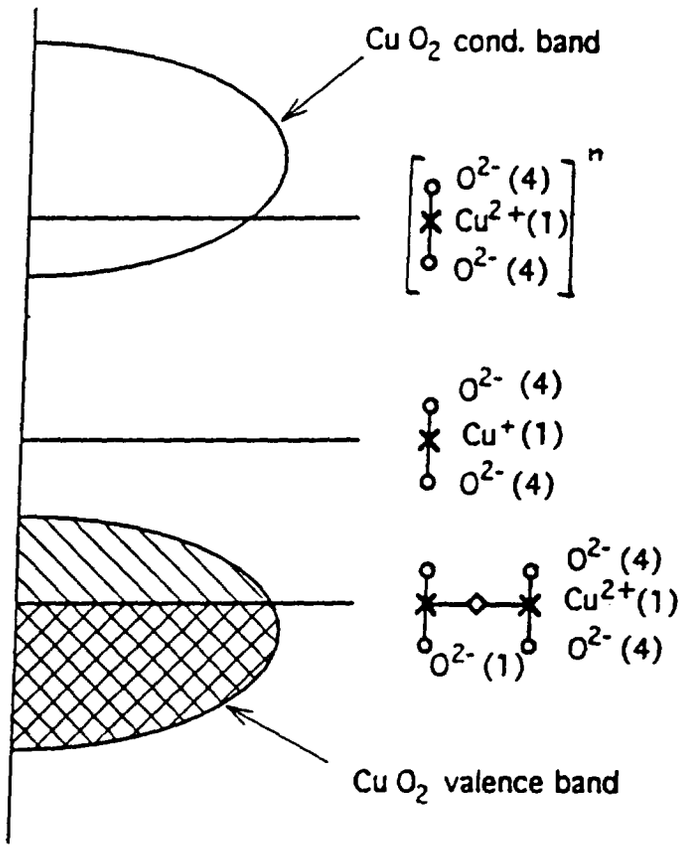


Fig. 1 : The band and level scheme of $YBa_2Cu_3O_{6+x}$, $x = 0$ corresponding to the filled lower band of the charge transfer insulator (simple hatched) and $x \geq 0.4$ corresponding to this band being filled up to the level of the dopant centers (double hatched).

On the basis of these experimental facts and in particular
- the existence of localized polaronic or bi-polaronic charge carriers in the insulating phase,
- the onset of charge transfer between those localized polaronic or bi-polaronic states with an electronic continuum of itinerant electrons when the system is doped into the metallic regime,
- the disappearance of the electronic continuum into the condensation upon entering the superconductivity state,

we propose the following scenario for high T_c superconductor : Bipolarons exist as localized states inside a filled valence band. Upon doping, electrons from the top of this band are transfered into the bipolaronic states. When the chemical potential is thus lowered below the electronic level of the bipolaronic state, a charge transfer between the two subsystems triggers off a metallic state and ultimately a condensation of bi-polarons leading to superconductivity.

We model such a scenario by a Hamiltonian of the form

$$H = (zt-\mu)\sum_{i\sigma} c^+_{i\sigma}c_{i\sigma} - t\sum_{<i\neq j>\sigma} c^+_{i\sigma}c_{j\sigma} + (\Delta_B - 2\mu)\sum_i b^+_i b_i + v\sum_i (b^+_i c_{i\downarrow}c_{i\uparrow} + h.c.) \quad (1)$$

where the localized bi-polarons are characterized by Boson-annihilation (creation) operators b^+_i and where the charge exchange between those bi-polaronic states and pairs of conduction electrons, characterized by Fermi-annihilation (creation) operators c^+_i, takes place on some effective clusters denoted by a site indices i and j. As a concrete example of such effective sites in the cuprate superconductor $YBa_2Cu_3O_{6+x}$

we take for the location of the electron pairs two adjacent Cu(2)-2O(2)-2O(3) units in the CuO_2 basal planes, separated by effective sites of localized bi-polarons, given by two adjacent O(4)-Cu(1)-O(4) dumbbels on either side of an O(1) (see Fig. 1. In the other cuprate high T_c materials such a clear cut choice of the effective clusters cannot be made for the time being. It now however appears that all the phonon anomalies related to polaronic effects involve apex oxygens and that such apex oxygens are a general feature of all cuprates, the so-called infinite layer compounds and the electron doped materials included (see article by E. Kaldis).

On the basis of resonant Raman scattering and infrared absorption in insulating samples with photoinduced carriers[8] we come to the conclusion that the localized electronic states which corresponds to the bi-polarons overlap with the valence band of the electrons of the a,b planes of the cuprates. This band is separated from the upper Hubbard band of the 3d electrons of the planes by a charge transfer gap of the order of 2 eV.

Photoemission studies measuring directly the number of $Cu^{2+}(1)$ ions show[9] that the number of such bi-polaronic states is directly proportional to the number of dopant atoms. Depending on the specific material these states are either occupied by charge carriers coming from outside the CuO_2 layers or from the CuO_2 layers themselves. In $YBa_2Cu_3O_{6+x}$ there is a critical concentration $x \cong 0.45$ below which these states are filled by a charge transfer inside the centers for bi-polaron formation in form of $2[O^{2-}(4)\text{-}Cu^{+}(1)\text{-}O^{2-}(4)]\text{-}O(1) \Rightarrow 2[O^{2-}(4)\text{-}Cu^{2+}(1)\text{-}O^{2-}(4)]\text{-}O^{2-}(1)$ where the O(1) atom can be considered as the center for bi-polaron formation. For $x \geq 0.045$ the bi-polaronic states are filled by a charge transfer from the CuO_2 valence band electrons, thereby emptying out the valence band. Upon increased doping, this valence band is eventually emptied out (see Fig. 1) to the extent that the chemical potential coincides with the electronic level for the bi-polaronic states. Upon further doping the bipolaronic states can be considered as an infinitesimally small band of bi-polaronic states. In proposing the Hamiltonian Eq. (1) we have precisely this situation in mind which moreover corresponds to the metallic phase of high T_c compounds.

We completely neglect correlation effects between the valence electrons not because they are not present in these materials but simply because deep inside the metallic phase they will influence the picture developed here only in a secondary way. On the other hand correlation effects are expected to be important for the metal-insulator transition.

The purpose of this lecture is to show how for such a system of localized bi-polarons which are in contact with a reservoir of itinerant electrons these bi-polarons can condense below a certain critical temperature and give rise to a superconducting state which is essentially controlled by the superfluidity of charged hardcore Bosons on a lattice.

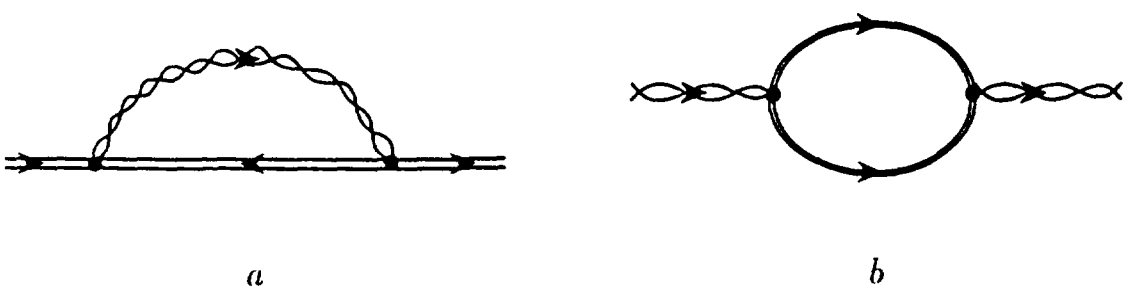
We solve for that purpose the fully self-consistent RPA equations for the one particle Fermion and Boson Green's functions given by :

$$\begin{aligned} G_F(\vec{k},\omega_n) &= \left[i\omega_n - \epsilon_k - \sum_F(\vec{k},\omega_n)\right]^{-1} \\ G_B(\vec{q},\omega_m) &= \left[i\omega_m - E_o - \sum_B(\vec{q},\omega_m)\right]^{-1} \end{aligned} \tag{2}$$

with

$$\begin{aligned} \Sigma_F(\vec{k},\omega_n) &= -\frac{v^2}{N}\sum_{\vec{q}\omega_m} G_F(-\vec{k}+\vec{q},+\omega_m-\omega_n)G_B(\vec{q},\omega_m) \\ \Sigma_B(\vec{q},\omega_m) &= \frac{v^2}{N}\sum_{\vec{k}\omega_n} G_F(-\vec{k}+\vec{q},-\omega_n+\omega_m)G_F(\vec{k},\omega_n) \end{aligned} \tag{3}$$

representing the self-energy diagrams depicted in Fig. 2 . $\vec{k}$ and $\vec{q}$ denote the momenta, ω_n and ω_m the Matsubara frequencies for Fermions and Bosons respectively and N is the number of sites.



a *b*

Fig. 2 : The self-energy diagram for *a*) Fermions and *b*) Bosons.

The unperturbed Fermion dispersion including the chemical potential is given by $\epsilon_{\vec{k}} = \xi_{\vec{k}} - \mu$, $\xi_{\vec{k}} = t(z - \sum_\delta e^{i\vec{k}\vec{\delta}})$, with δ denoting the vectors linking nearest neighbour lattice site. Equivalently the unperturbed Boson energies are given by $E_o = \Delta_B - 2\mu$, the factor two in front of the chemical potential taking account that each Boson is constituted of two Fermions.

The Boson-Fermion model, Equ. 1 can be solved by perturbative methods if either the Bosonic level lies well below the bottom of the Fermionic band i.e. $\Delta_B < 0$ or lies well above the chemical potential i.e. $\Delta_B > 2\mu$. In the first case, the ground state of the system is described by a superfluid state of Bosons. In the second case, the ground state has all the features of a BCS superconductor where the Bosons are only virtually excited.

As characteristic parameters of this model we choose $\Delta_B = 0.4$ and $v = 0.1$ in units of the Fermionic bandwidth $D = 2zt$ and the total number of particles per site (Fermions, Bosons) $n = n_F + 2n_B = 1$. n is chosen in such a way that we have a finite concentration of Bosons for $v = 0$, which for our choice of Δ_B implies $n \geq n_c = 0.2952$. Only for $n > n_c$ Bose condensation can occur if $v \to 0$. For $n < n_c$ a BCS-like superconducting state in the Fermionic subsystem occurs via Fermion pairs being virtually excited into the unoccupied Bosonic states[10]. In the region $n \sim n_c$ the superconducting transition temperature shows[11] a rapid rise as first shown by an interpolation between the two limits $n < n_c$ and $n > n_c$ and more recently by a self-consistent RPA calculation of this model in the superconducting phase.[12]

The self-consistent determinations of the Fermion, respectively Boson Green's functions and their self-energies were performed for a one-dimensional system which,

as far as the normal state properties are concerned, should be rather similar to those expected for two and three dimensions. For the one-dimensional case, T_c —the transition temperature for the onset of superconductivity— will evidently be zero. Our main interest then is to study how the spectral properties of the Fermions and Bosons evolve as one approaches the zero temperature limit and for that purpose we focus on the evaluation of the excitation spectra for the Fermions and Bosons. For Bosons, the excitation spectrum is obtained by solving the equation

$$\omega - (\Delta - 2\mu) - \sum_B^R(q,\omega) = 0 \tag{4}$$

where $\omega = \omega_q^B - \frac{i}{2}\gamma_q^B$ and $\sum_B^R(q,\omega)$ denotes the retarded Boson self-energy.

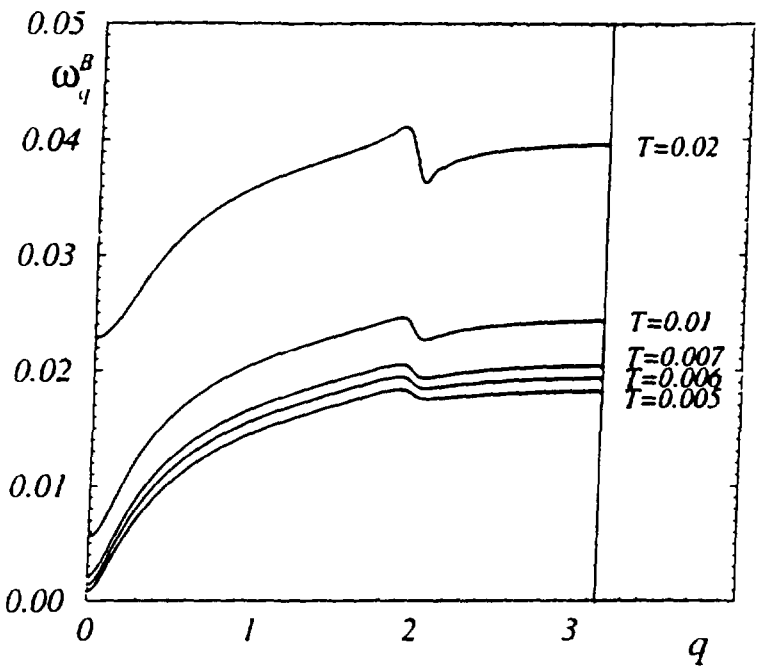


Fig. 3 : Real part of the Boson energies as a function of q (in units of the inverse lattice constant) and for various temperatures (in units of the Fermion bandwidth).

The real part of the Boson excitations having frequency ω_q^B are shown in Fig. 3 as a function of the Boson momenta qa in the entire Brillouin zone $[-\pi, \pi]$ (where a denotes the lattice constant) for different temperatures. We notice that as the temperature is decreased from $T = 0.01$ down to $T = 0.005$ the Boson excitation spectrum develops a q^2 behaviour for $q \to 0$ with effective Boson masses of the order of ten electron masses and becoming increasingly lighter as T decreases and saturates at some fixed value of the order of the free electron mass as T tends to T_c ($= 0$ in our case).

Apart from this strong renormalization of the Boson frequencies in the long wave length limit, the remainder of the Boson excitation spectrum shows little modification of the unperturbed localized Boson spectrum.This is an indication that the long wave length renormalization is due to a precursor effect of superfluidity and is indeed compatible with the behaviour of $< b_{\vec{q}}^+ b_{\vec{q}} >$ which tends to $n_{\vec{q}}^B(T)$—the Bose distribution function—showing a strong build up of the Boson occupation for q going to zero. The overall shift of the Boson spectrum shown in Fig. 3 is due to the renormalization of the chemical potential for the Bosons defined by $\mu_B = -\Delta_B + 2\mu - \sum_B(0,0)$ which goes to zero as $T \to T_c \equiv 0$ as it should. The kink in the Boson spectrum occuring at $q \sim 2k_F$ (k_F denoting the Fermi vector for the unperturbed Boson-Fermion mixture, $v \equiv 0$) is due to a nesting effect in the 1D system considered here.

Evaluating the imaginary part of the poles of the Boson Green's function, $-\gamma^B_{\vec{q}}/2$ for small $\vec{q}$ vectors clearly shows how upon decreasing the temperature the initially overdamped Boson excitations become freely propagating modes. This is inherent in $\gamma^B_{\vec{q}}(T)/(\omega^B_{\vec{q}}(T) - \omega^B_{q=0}(T))$ which as a function of T varies as T^3 for small q vectors. We thus end up with a picture in which the Boson dispersion approaches a free particle-like behaviour upon approaching T_c from above.

The onset of coherent free particle-like motion of the Bosons in the long wave length limit as the temperature decreases is combined with a depletion of Fermionic states near the Bosonic energy level i.e. near $\Delta_B/2$. This results in a strong incoherent contribution to the Fermionic spectral functions for k vectors near k_F and the opening up of a pseudo gap which deepens with decreasing temperature and eventually opens into a true gap when a global superconducting state occurs in the Fermionic subsystem. That tendency in the evolution of this pseudo gap is illustrated in Fig. 4 for a set of characteristic temperatures. A detailed analysis of all that has been given recently by us.[13]

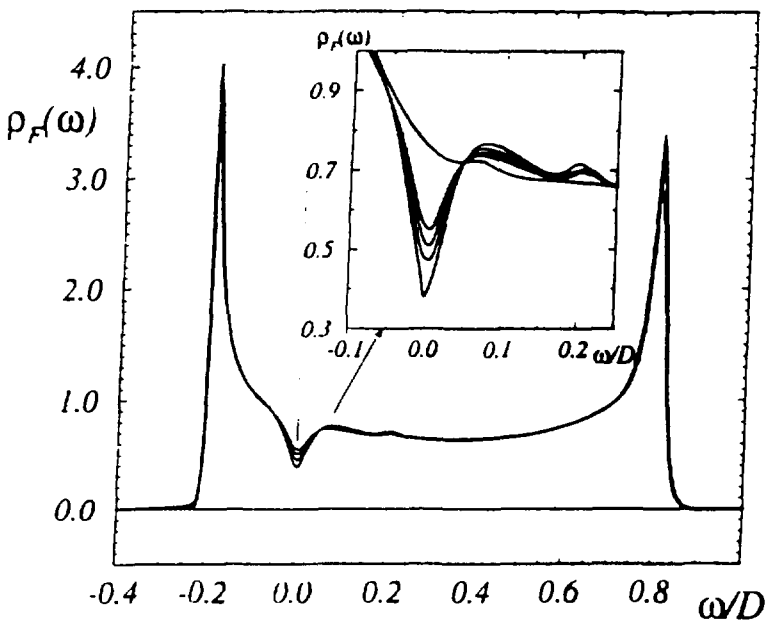


Fig. 4 : The Fermionic density of states for various temperatures T/D (= 0.005, 0.006, 0.007, 0.008 and 0.02) showing a deepening of the pseudogap with decreasing T.

In order to test this physical picture on real systems such as the cuprate high T_c oxides one has to look for experiments which test the hybridization of the bi-polaronic charge carriers with itinerant electronic charge carriers. In these quasi 2D systems with apex oxygens outside the CuO_2 planes such experiments should look for responses in the c-axes —orthogonal to the planes. Indeed c-axes optical conductivity shows charge exchange between the electronic subsystem of the planes and clusters outside these planes and moreover clearly manifests the existence of a pseudogap which deepens as T decreases. The fact that the pseudogap measured in this way in the cuprates is much smaller —by a factor 3 or so— than the superconducting gap obtained from photoemission is in no contradiction since the first is measured in the c direction while the latter is measured in the a,b plane. Angle resolved photoemission experiments if carried out along the c-axes may well show the same pseudogap as observed in the optical conductivity along the c direction. Moreover such experiments might show traces of polaronic charge carriers in form of phonon side peaks just as was observed in metallic Rb_3C_{60}.

In fact in the isotropic 3d system $Ba_{1-x}K_xPbO_3$ the gap measured in the optical conductivity roughly agrees with independent measurements of it.

Finally the most robust feature of this Boson-Fermion scenario for high T_c superconductors is its prediction that the chemical potential hardly changes as a function of doping in the metallic phase. This is indeed observed in photoemission experiments.

It remains to be seen if this model also satisfactorily predicts the temperature dependence of the optical conductivity, the NMR data and the susceptibility showing the famous spin gap. Preliminary results show that there is an overall rather good agreement.

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