

# The Mechanisms of Some High Temperature and Novel Superconductors

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**Key Words :** High Velocity Superconductivity; Phonons and Photons; High Temperature; Combined Mechanisms; Local Charged Bosons; Boson-Fermion Model; Microscopic Origin

## 1. Introduction

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Vj g'ewr tcvgu'j cxg'rc { g'g'f "ut vewt g'y kj 'EwQ4 eqpf vevkpi "lj g'w'v'g' c'v'g'f "d { 'ej cti g't'g'ug'x'q'k'rc { gtu \*p'qp/eq'p'f vevkpi +0Vj g'ej cti g't'g'ug'x'q'k'ut'c'k'ug'ht'qo NcQ"rc { gtu"kp"Nc4 "EwQ6. "DkQ"cpf "VrQ"rc { gtu"cp cu'q'ek'v'g'f "y kj "dkuo wj "cpf "vj c'ik'wo ewr tcvgu'cpf EwQ'ej c'kp'u'kp'l "Dc4'Ew5'Q8-x"cpf l "Dc4'Ew6'Q: "gve0 Vj g'r wt g"\*wpf qr g'f "+"ewr tcvgu'ct'g'erc'u'k'k' "O qw kp'wv'v'q'tu'cpf "cp'v'k'ht'g'g'qo ci p'g'v'k' "u' { ugo u'0f qr kpi t'gu'w'u'kp'ht'g'g'ect'k'g'u" \*j q'rg'u'qt "g'ng'ev't'q'pu' "cpf "cnuq

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generates centers or complexes which can harbour lochons (local pairs in the singlet state). The charge transfer in the process is correlated and hence the bosonic character is maintained. If in this charge transfer the spins are localized one gets real space pairing giving a mechanism for antiferromagnetic spin coupling.

On the other hand if on doping the carriers are delocalized by maintaining spin correlations, this will lead to Cooper pairing in momentum space ( $\mathbf{k}\uparrow, -\mathbf{k}\uparrow$ ). The chemical species harbouring lochons in chains, charge reservoirs, non-conducting layers are  $Cu^{1+}$ ,  $O^{2-}$ ,  $O_2^{2-}$ ,  $Bi^{3+}$ ,  $Tl^{1+}$ ,  $Pb^{2+}$ , Hg or complexes such as  $O^- - Cu^{1+} - O^-$ ,  $[O^- - Cu^{2+} - O^{2-}] - O^{2-}$   $[O^{2-} - Cu^{2+} - O^{2-}]$ .

In this article, a self-review of the mechanisms suggested by the author and collaborators is presented. This will comprise a combined pairing mechanism involving phonons and other bosons (Sinha 1998) (lochons-acronym for ‘local charged bosons’ which in turn refer to ‘local pairs (Ganguly, Upadhyaya and Sinha 1996) or localized bipolarons Alexandrow and MoHNF 1995). These entities (lochons) arise from correlated double charge fluctuations (Sinha and Singh 1998) at some ionic species or complexes of the system. Further details along with diagrammatic representation of the lochon induced pairing interaction can be found in reference (Singh and Kukani) and its Fig. 6.3 on page 220. The role of ‘‘local charged bosons’’ called lochons by us, has been used by other workers also for pairing in cuprates (Sinha 1961; Friedberg, Lee and Ren 1991; Bar-Yam 1991; Eagles 1993; Ranninger and Robin 1995 and Enz 1990). Some workers have proposed a boson-fermion model with boson field introduced phenomenological without discussing its microscopic origin (Sinha and Kakani 1994; Friedberg, Lee and Ran 1991). The combined mechanism provides reasonable account of the anomalous normal state and superconducting properties of cuprate systems (Sinha and Kakani 2002; Sinha 1998). A similar concept has been extended to doped fullerenes ( $M_xC_{60}$ , where  $M=K, Rb$  etc). A combined phononic and electronic excitation causing bond polarization accounts for the

high  $T_c$  observed isotope effect which differs from the BCS value (Sinha 1992; 1993).

For iron pnictide systems  $LnO_{(1-x)}F_xFeAs$  (Kamihara *et al.* 2008) some early work demonstrates that electron-phonon interaction is too weak to give the observed high  $T_c$  (26k to 55K, depending on the Ln ion e.g. La, Ce, Sm, Pr, Nd or application of pressure) and superconductivity is unconventional Boeri *et al.* 2008; Hazi *et al.* 2008). However, combined with distortion field modes arising from Jahn-Teller or pseudo Jahn-Teller effects, the desired  $T_c$  is achievable (Sinha 2009).

A more exciting mechanism is the pairing under non-equilibrium conditions involving two-bosons fields (phonons and photons) in systems, which are otherwise, in the semi conducting or insulating state (Kumar and Sinha 1968). In fact, photo-induced transient superconductivity has indeed been observed in films of  $YBa_2Cu_3O_x$ , which are on the borderline of insulator-metal transition (Yu *et al.* 1992). The results are explained by a two boson model (Sinha 1993).

The recent claim of near room temperature superconductivity in  $Pd-[H(D)]_x$  system when x is varied from 0.6 to 1.6 has been explained by the combined model of phonon and lochon mediated pairing (Sinha 2006).

In what follows, the salient features of the combined mechanisms for each system discussed above will be presented.

## 2. The Model for Cuprate Superconductors

The structural and electronic properties of high  $T_c$  cuprates have been dealt within books and review articles (Sinha and Kakani 1994; 2002). Among the various theoretical models suggested for cuprates, we shall discuss the combined mechanism of pairing mediated by phonon and lochons (local charged bosons or local singlet pairs or local bipolarons). The lochon mechanism is also referred to as the boson-fermion model. For the stabilization of real space singlet pair of electrons via transition to an empty orbital, a mechanism was suggested

longtime back (Sinha 1961). It was invoked for the pairing of fermions in conventional superconductors to boost the  $T_c$  (Ganguly *et al.* 1996).

The discovery of cuprate superconductors with unusual properties led to the revival of this mechanism by us and several other groups from 1987 on words (Sinha and Singh 1998, Enz 1990). Physically, the interaction mechanism involves the splitting of a lochon (local charged boson) into a pair of fermions of the conduction band and the inverse process in which there is confluence of a fermion pair to result in a localized boson. However, there is an important difference between our approach and that of others; we consider a combined lochon and photon mediated pairing of fermions (holes or electrons) belonging to a wideband.

The Hamiltonian for the combined mechanism in the Nambu spinor representation is given by:

$$H = H_0 + H_{cp} + H_{cl}, \quad (2.1)$$

where

$$H_0 = \sum_{\underline{k}} \varepsilon_{\underline{k}} \Psi_{\underline{k}} + \sigma_z \Psi_{\underline{k}} + \sum_{\underline{q}} \hbar \omega_{\underline{q}} a_{\underline{q}} + a_{\underline{q}} + \sum_l E_l b_l + b_l \quad (2.2)$$

$$H_{cp} = \sum_{\underline{q}, \underline{k}} P_{\underline{q}} \phi_{\underline{q}} \Psi_{\underline{k}} + \sigma_z \Psi_{\underline{k}} \quad (2.3)$$

$$H_{cl} = \sum_{\underline{k}, l} B_l \Psi_{\underline{k}}^+ [\alpha_+ b_l + \alpha_- b_l^+] \Psi_{\underline{k}} \quad (2.4)$$

In the above equations, the Nambu field operators are denoted as:

$$\Psi_{\underline{k}} = \begin{pmatrix} C_{\underline{k}\uparrow} \\ C_{-\underline{k}\downarrow}^+ \end{pmatrix}, \Psi_{\underline{k}}^+ = (C_{-\underline{k}\uparrow}^+ C_{-\underline{k}\downarrow}) \quad (2.5)$$

$C_{\underline{k}\sigma} (C_{\underline{k}\sigma}^+)$  are the fermion (hole) annihilation (creation) operators in the state  $|\underline{k}\sigma\rangle$ ; here  $\underline{k}$  is the wave vector,  $\sigma$  is the spin index and  $\varepsilon_{\underline{k}}$  is the single particle energy. The phonon field operator

$\phi_{\underline{q}} = (a_{\underline{q}} + a_{\underline{q}}^+)$ ,  $a_{\underline{q}}^+ (a_{\underline{q}})$  being the phonon creation (annihilation) operator corresponding to the frequency  $\omega_{\underline{q}}$ ,  $P_{\underline{q}}$  is the coupling constant for the carrier (hole) - phonon interaction. The lochon creation and annihilation operators are expressed as

$$b_l^+ = C_{l\uparrow}^+ C_{l\downarrow}^+, b_l = C_{l\downarrow} C_{l\uparrow} \quad (2.6)$$

And their structure shows that they are composites of fermions in the singlet spin state and localized in the orbital state  $|l\rangle$  at site  $l$ .

$E_l$  denotes the lochon energy and  $B_l$  is the coupling content for the fermion (carrier) lochon interaction. The entities  $\sigma_x, \sigma_y, \sigma_z$  are the usual Pauli matrices with  $\sigma_+ = (\sigma_x + i\sigma_y)/2$ . Both charge and spin are conserved in the interaction processes given above. However, the number of free and localized fermions is not independently conserved. We must have

$$n_{\sigma} (\text{total}) = \sum_{\underline{k}} n_{\underline{k}\sigma} + \sum_l n_{l\sigma} \quad (2.7)$$

For each spin, where,

$$n_{\underline{k}\sigma} = C_{\underline{k}\sigma}^+ C_{\underline{k}\sigma} : n_{l\sigma} = C_{l\sigma}^+ C_{l\sigma}$$

These conditions require that there be a common chemical potential for the itinerant and localized charge carriers (Sinha and Singh 1998; Ranninger and Robin 1995). For lochons, we have the commutation relations

$$[b_l, b_{l'}^+] = [1 - (n_{l\uparrow} + n_{l\downarrow})] \delta_{(ul')} \quad (2.8)$$

$$[b_l, b_{l'}] = [(b_l^+, b_{l'}^+)] = 0 \quad (2.9)$$

with the additional relations  $(b_l^+)^2 = b_l^2 = 0$  a requirement of the exclusion principle

In the temperature Green function formalism the order parameter is expressed as Abrikosov *et al.* (1963).

$$Z\Delta(\omega_n, \underline{k}) = \frac{T}{(2\pi)^d} \sum_{\omega_n} dk' \Gamma(i(\omega_n - \omega_n'), \underline{k} - \underline{k}'), F^+(i\omega_n' \underline{k}') \quad (2.10)$$

where,  $Z$  is the renormalization function, and  $\omega_n = 2n\pi T$  for phonon and lochons and is equal to  $(2n + 1)\pi T$  for fermions;  $d$  is the dimensionality and  $T$  is the temperature in Kelvin, ( $k_B$  and  $\hbar$  are taken as unity).  $F^+$  ( $i\omega_n, \mathbf{k}$ ) is the anomalous Green's function [25]. The vertex function  $\Gamma$  is a sum of the phononic and lochonic parts

$$\Gamma = \Gamma_{ph} + \Gamma_l \quad (2.11)$$

The solution of (2.10) turns out to be (for details see [4, 5]) near  $T = T_c$

$$1 = \lambda_p \ln\left(1.13 \frac{\omega_p}{T_c}\right) + \lambda_l \ln\left(1.13 \frac{\omega_l}{T_c}\right), \quad (2.12)$$

where,  $\lambda_p$  and  $\lambda_l$  are respectively the carrier phonon and carrier lochon coupling constants (dimensionless);  $\omega_p$  and  $\omega_l$  are the Lorentzian cutoffs (in temperature units) for phonon and lochon mechanisms. The critical temperature (taken for  $Z = 1$ , as the phonon mechanism is weak) is given by

$$T_c = 1.13(\omega_p)^{\gamma_p} (\omega_l)^{\gamma_l} \text{Exp}\left(\frac{-1}{(\lambda_p + \lambda_l)}\right); \quad (2.13)$$

$$\gamma_p = \frac{\lambda_p}{\lambda_p + \lambda_l}, \gamma_l = \frac{\lambda_l}{\lambda_p + \lambda_l}, \lambda_l = \bar{\lambda}_l - \bar{\mu}_c, \quad (2.14)$$

$\bar{\mu}_c$  is the screened Coulomb repulsion between the free carriers which are subject to strong correlation. Hence  $\bar{\mu}_c$  will have a small value. Owing to the condition (2.7),

$$\bar{\lambda}_l = \bar{\lambda}_l^0 x_c (1 - x_c), \quad (2.15)$$

where,  $x_c$  is the concentration of carriers, the maximum value of  $\bar{\lambda}_l$  will occur at some value of  $x_c$  and may be further modulated if some remnants of Van Hove singularity in the density of states remain.

Further,

$$\bar{\lambda}_l^0 = \lambda_l^0 \exp[-g^2], \quad (2.16)$$

where,  $g$  is a dimensionless coupling constant involved in the formation of lochons caused by interaction with some optical phonon modes. The form (2.16) arises because of polaronic modulation of mixing between wide band and localized state. The reduction factor  $\exp[-g^2]$  is temperature independent for  $T \ll \omega_0$ , with  $\omega_0$  being the frequency of the boson mode involved.

Note that the renormalisation of lochon energy from doping may produce some asymmetry in  $T_c$  versus  $x_c$  curve. Theoretical plot of  $T_c$  against  $x_c$  do show a bell shape curve. (Fig. 1 of ref. [5]).

The superconducting gap at  $T = 0$  for the combined mechanism has the structure

$$\Delta(o) = \Delta_p(o) \ln\left[\frac{\omega_p + (\omega_p^2 + \Delta_p^2(o))^{1/2}}{\Delta_p(o)}\right]^{\lambda_p} + \Delta_l(o) \ln\left[\frac{\omega_l + (\omega_l^2 + \Delta_l^2(o))^{1/2}}{\Delta_l(o)}\right]^{\lambda_l} \quad (2.17)$$

where,  $\Delta_p(o)$  and  $\Delta_l(o)$  denote the gaps for pure phonon and lochon parts. It is clear that the ratio  $2\Delta(o)/T_c$  (as seen from (2.13) and (2.17)) does not have the universal value 3.52 as in the Bardeen, Cooper and Schrieffer (BCS) theory [26]. The ratio may vary from 3 to larger than 10 depending on the value of parameters involved for each system, which is in agreement with the results of different cuprate systems.

The superconducting condensation energy is derived from the above formulation as

$$W_N - W_S = \frac{1}{2} N_c(o) \Delta^2(o), \quad (2.18)$$

where  $\Delta(o)$  is given by (2.17) and  $N_c(o)$  is the density of states per unit cell at the Fermi surface. The estimated value is an order of magnitude larger than the BCS Value.

### 2a. Isotope Effect in Cuprates

The isotope effect in cuprates shows strong difference from the BCS value. Measurement of oxygen isotope effect in these systems revealed that on decreasing  $T_c$  by appropriate doping the isotope exponent tends towards larger values.

For deriving the expression for the oxygen isotope effect, we consider the relations (2.13) to (2.16) and note that:

$$\omega_p = \text{constant } M_o^{-1/2} \quad (2.17a)$$

$$g^2 = \text{constant } M_o^{-1/2} \quad (2.17b)$$

where,  $M_o$  is the oxygen mass in dimensionless unit. The expression for the oxygen isotope exponent ( $\alpha_o$ ) is obtained as (Sinha KP and Rastogi A 1995).

$$\begin{aligned} (\alpha_o) &= -\frac{\delta \ln T_c}{\delta \ln M_o} \\ &= \frac{1}{2} \left[ \frac{\lambda_p}{\lambda_p + \lambda_l} + g^2 \ln \left( \frac{\omega_l}{\omega_p} \right) \frac{\lambda_p \lambda_l}{(\lambda_p + \lambda_l)^2} + g^2 \frac{\lambda_l}{(\lambda_p + \lambda_l)^2} \right] \end{aligned} \quad (2.18a)$$

An examination of the above expression clearly shows that when the lochon part dominates and the  $T_c$  value is near the maximum, the oxygen isotope exponent is small. It tends towards larger values with  $\lambda_p$ , decreasing and for  $\lambda_l = 0$ ,  $\alpha_o = \frac{1}{2}$ . The variation of  $\alpha_o$  with  $x_c$  (and in turn on  $T_c$ ) is determined by the dependence of  $\lambda_p$ , on  $x_c$  shown by (2.15) and the increase of  $g^2$  with decreasing  $x_c$ . The variation of  $\alpha_o$  against  $(T_c/T_c^{\max})$  for the system  $\text{YBa}_{(2-x)}\text{La}_x\text{Cu}_3\text{O}_7$  along with the experimental points of Bornemann *et al.* 1991 is shown in Fig. 1 of reference (Sinha and Rastogi 1995). The agreement with general trend is good. It may be noted that the above behaviour is not universal but depends on the values of parameters involved for each system; however the trend will be similar.

### 2b. The Role of Lochons in the Pairing Symmetry

Let us consider a system having single conducting layer per unit cell in addition to having an adjoining dielectric (semi-conducting) layer e.g.  $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\alpha}$ . Both s- and d- wave pairing is possible for lochon mediated interaction in layered systems such as Cuprates (Enz 1990; Sinha and Vytheeswaran 1996).

According to Muller 1995 experimental measurement of the gap parameter does indicate a superposition of s- and d- waves. One has to be careful in assessing the relative importance of one over the other. There is a danger of overestimating one symmetry relative to the other if the values of the parameters involved are not carefully evaluated.

For a two-dimensional plane having a square lattice configuration of atomic distribution in  $\text{CuO}_2$  planes, the coupling constant for the fermion-lochon interaction will have the general form (Sinha 1998, Enz 1990).

$$B_l(\underline{k}) = \phi_{\underline{k}} B, \quad (2.19)$$

where,

$$\phi_{\underline{k}} = m_s \phi_{sk} + m_d \phi_{dk} \quad (2.20)$$

with

$$\phi_{sk} = [\cos(k_x a) + \cos(k_y a)] \quad (2.21a)$$

$$\phi_{dk} = [\cos(k_x a) - \cos(k_y a)]; \quad (2.21b)$$

$a$  is the lattice constant of the square. For normalized  $\phi_{\underline{k}}$  the mixing coefficients must satisfy

$$|m_s|^2 + |m_d|^2 = 1 \quad (2.22)$$

It should be noted that  $\phi_{sk}$  and  $\phi_{dk}$  belong to different irreducible representations of the square symmetry.

The two-dimensional dispersion relation, limited to the situation of nearest neighbour (NN) hopping of carriers, is given by

$$\epsilon_{\underline{k}} = 2t [\cos(k_x a) + \cos(k_y a)], \quad (2.23)$$

where,  $t$  is the hopping integral. This has a bandwidth of  $8t$ . The density of the states may contain a

singularity near half filling, which is close to the Fermi energy  $e_F$ .

We will not discuss the origin of singularity here. The situation is described by the density of states in this region as (Enz 1990).

$$N(\epsilon_F) = \frac{2}{\pi D} \ln \left| \frac{D}{\epsilon_F} \right|, \quad (2.24)$$

where,  $D$  is the width of the singularity at  $\epsilon_F$ . Expanding the cosine functions in (2.21) in their arguments up to the second order with the constraint  $\delta(\phi_{sk} - |\epsilon_F|2t)$  etc, we get

$$(\phi_{sk}^2) = \left( \frac{|\epsilon_F|^2}{2t} \right)^2 \quad (2.25)$$

$$(\phi_{dk}^2) = \left[ 4 - 4 \left( \frac{|\epsilon_F|}{2t} \right) + \left( \frac{|\epsilon_F|}{2t} \right)^2 \right] \quad (2.26)$$

The  $T_{cs}$  and  $T_{cd}$  for the s-wave and d-wave components turn out to be

$$T_{cs} = 1.13\omega_l \text{Exp} \left[ - \frac{1}{V_l \frac{|\epsilon_F|^2}{4t^2} \left( \left( \frac{2}{\pi D} \right) \ln \left( \frac{D}{|\epsilon_F|} \right) \right)} \right] \quad (2.27)$$

$$T_{cd} = 1.13\omega_l \text{Exp} \left[ - \frac{1}{V_l \left( 4 - 4 \frac{|\epsilon_F|}{2t} \right) + \left( \frac{|\epsilon_F|}{2t} \right)^2 \left( \frac{2}{\pi D} \right) \ln \left( \frac{D}{|\epsilon_F|} \right)} \right] \quad (2.28)$$

The ratio  $\left( \frac{|\epsilon_F|}{2t} \right)$  determines the relative values of  $T_{cs}$  and  $T_{cd}$ . We get the following three possibilities:

$$(i) |\epsilon_F| \ll 2t \text{ then } T_{cd} \gg T_{cs};$$

$$(ii) |\epsilon_F| \gg 2t \text{ then } T_{cs} \gg T_{cd}$$

$$(iii) |\epsilon_F| \sim 2t, T_{cs} \sim T_{cd}$$

Let us consider the third possibility with  $D \leq 4t$ . Note that for a two dimensional system  $|\epsilon_F| \propto n_c$ , where is the areal carrier density on each  $\text{CuO}_2$  layer. The expression for  $T_c$  is finally obtained as (Sinha KP 1998).

$$T_{cs} = 1.13\omega_l \text{Exp} \left[ - \frac{1}{\lambda_l(x_c)} \right], \quad (2.29)$$

where,

$$\lambda_l(x_c) = \lambda_l^o x_c (1 - x_c) \quad (2.30)$$

$x_c$  being the carrier concentration and  $\lambda_l^o = V_l N_r(\epsilon_F)$ ,  $N_r(\epsilon_F)$  is the density of states without the factor  $x_c(1 - x_c)$ . The expression (2.29) includes contribution from both s-wave and d-wave pairing. The form (2.30) was indeed suggested earlier by us for the lochon mechanism (Sinha and Singh 1998). In the above discussion, only the lochon mechanism was considered to highlight the pairing symmetry. The complete picture including the phonon contribution is given in (2.13).

### 2c. The Pseudogap in Cuprate Superconductors

In the last section fermion-lochon model was discussed in the context of pairing symmetry. The lochons (local charged bosons) are located at polarizable dielectric regions in the layered cuprate systems. In the present section, the role of lochon model in the appearance of resonance peak and the pseudogap seen above  $T_c$  is identified with the local pair fluctuation (Sinha 1999). The model can give rise to both intralayer and interlayer pairing because the lochon centers are also located in the intervening polarisable dielectric layers. The gap equation at  $T = 0$  and on the Fermi surface has the form

$$\Delta(K_F) = \phi_{kF} \left( \Delta_o + \sum_l \phi_{kF} \Delta_l / 2 \right)$$

where,  $\Delta_o$  is a positive quantity connected with intralayer contribution, and comes from interlayer contribution (Sinha 1999).

There is a strong local pair correlation in the normal state, which amplifies as one goes to the superconducting state which is supported by experimental results.

The peak at  $M(\pi, 0)$  point in the Brillouin Zone visible at 40 meV in the normal state sharpens in the superconducting state. These modes are identified with lochon (local pair fluctuation) states and this effect is enhanced below  $T_c$  due to fermion-lochon interaction when more Cooper pairs are formed.

By solving the gap equation for various values of  $\Delta_l$  and the fermion-lochon coupling constant  $\lambda_l$ , the peak is obtained by using the density of states (2.24) in the singularity region, and width  $D \sim 72$  meV. The density of states shows a peak around 40 meV, which sharpens further in the superconducting state. The lochon (local charge boson) configuration can be generalized to comprise both charge and lattice degrees of freedom existing together in a coherent state (Ranninger and Romano 1998). The temperature dependence of the pseudogap is connected with incoherent part of the quasiparticle spectrum. The pseudogap appears because of the resonant exchanges between otherwise free unpaired fermions and lochons. As this is driven by the insulator-metal cross over the pseudogap can open above the superconducting phase transition at  $T_c$ .

There are several theoretical models suggested by different research groups to explain the results (Sinha 1998). Of these the fermion-lochon model appears capable of explaining all these features and other properties of cuprate superconductors (Sinha 1998).

### 3. Mechanism of Superconductivity in Molecular Solids. The Case of Doped Fullerenes

The discovery of superconductivity in alkali doped fullerenes ( $T_c = 18$ K, 28K and 48K respectively) for  $K_xC_{60}$ ,  $Rb_nC_{60}$  and  $RbT_{c2}C_{60}$  provided another systems of moderately high temperature superconductors [33-35]. Like the cuprates, the pure undoped systems (carbon balls ( $C_{60}$ ) clusters) are insulators. However, the pseudospherical molecules ( $C_{60}$ ) are packed in a three-dimensional face centered

cubic structure. The dopants enter the vacant tetrahedral and octahedral sites and the electrons donated by them populate the energy bands arising from the lowest unoccupied antibonding orbitals of  $C_{60}$  namely  $t_{1u}^*$ ,  $t_{1g}^*$  etc. The charge transfer from alkali to the  $C_{60}$  molecule produces the unusual ionic metals which become superconducting below  $T_c$ . These systems also present an interesting case concerning the possible pairing mechanism.

The observed isotope effect is different from the BCS value of 0.5 arising from pure electron phonon interaction. Also the ratio  $\frac{2\Delta(o)}{k_{BT_c}} \sim 5$ , is significantly different from 3.52 (BCS value). The estimated width of the conduction band  $\sim 0.5$  eV and the coherence length in the superconducting state is short ( $\sim$  molecular size  $C_{60}$ ) like the cuprates.

Based on the overall symmetry calculation shows that there are 90  $\sigma$ -type bonds, 30  $\pi$ -type bonds and the latter belongs exclusively to hexagons. The  $\pi$ -type bonds will be more susceptible to polarization than  $\sigma$ -type bonds in interaction with conduction electrons.

In what follows, we present the highlights of a combined phononic and electronic mechanism suggested by us (Sinha 1992, 1993). The latter involves  $\pi$ -bond polarization through charge transfer. The consolidated form of the model is described by (Sinha 1992, 1993).

$$H = \sum E_{\underline{k}} C_{\underline{k}\sigma}^+ C_{\underline{k}\sigma} - \sum (V_{pj} + V_{bp} - V_{sc}) C_{\underline{k}\uparrow}^+ C_{-\underline{k}\downarrow}^+ C_{-\underline{k}'\downarrow} C_{\underline{k}'\downarrow} \quad (3.1)$$

where,  $E_{\underline{k}}$  is the single particle energy of electrons in the conduction band,  $V_{pj}$  is the usual phonon mediated pairing interaction,  $V_{sc}$  is the screened Coulomb repulsion and

$$V_{bp} = \left\langle \frac{|P_j|^2}{\hbar\Omega_{pn}} \right\rangle, \quad (3.2)$$

$$\hbar\Omega_{pn} = E(C^+ - C^-, Q_j^*), -E(C = C, Q_j), \quad (3.3)$$

is the energy difference between the ionic configuration (first term of (3.3)) and the covalent bond (second term);  $Q_j^*, Q_j$  collectively denote the lattice configuration for the two states.  $P_j$  arises from the ‘‘monopole-dipole’’ type interaction of the conduction electron with the dipole ( $C^+ - C^-$ ). This type of polarization induced has been found to be of importance in organic molecules (Geller M, Jaworski A and Pohonilla A 1978). The value of  $P_j$  was estimated to be around 0.5eV (Sinha 1992). The expression for  $T_c$  has the form

$$T_c = 1.14\omega_{ph}^{n_1}\omega_{bp}^{n_2}Exp\left[-(\lambda_{ph} + \lambda_{bp}^*)^{-1}\right] \quad (3.4)$$

$$n_1 = \lambda_{ph}(\lambda_{ph} + \lambda_{bp}^*)^{-1}, n_2 = \lambda_{bp}(\lambda_{ph} + \lambda_{bp}^*)^{-1},$$

$$\lambda_{ph} = N(o)V_{pn}, \lambda_{bp} = N(o)V_{bp}, \lambda_{bp}^* = \lambda_{bp} - u^*$$

$N(o)$  is the density of states at the Fermi energy,  $u^*$  is the usual parameter for screened Coulomb repulsion  $\omega_{ph}$  and  $\omega_{bp}$  are the cut-off frequency (in temperature unit) for the phononic and bond polarization mechanism.

The expression for the isotope effect turns out to be

$$-\frac{\partial \ln T_c}{\partial \ln M} = \alpha = 0.5 \left[ 1 + \left( \frac{\lambda_{bp}^*}{\lambda_{ph}} \right) \right]^{-1} \quad (3.5)$$

For  $Rb_3C_{60}$  our estimate gave the value  $\alpha = 0.31$  which compares well with the  $0.37 \pm 0.05$  value reported by Ramirez *et al.* (1992).

The ratio  $2\Delta(o)/k_B T_c$ , where  $\Delta(o)$  is the gap at  $T = 0$ , is found to deviate the universal BCS value of 3.52 [10]. It will tend to higher values as indeed observed. However, a strong coupling phononic mechanism has also been found, to account for the higher value.

#### 4. Mechanism of Superconductivity in Ferropnictides (Kamihava *et al.* 2008; Boeni *et al.* 2008; Mazi *et al.*, 2008)

Like the cuprates the structure of iron-based pnictides ( $LnOFeAs$ ,  $Ln = La, Ce, Pr, Nd, Sm$ ) consists of layers. The  $LnO$  layers alternate with layers of  $FeAs$ ; the structure belongs to the tetragonal space group  $P4/nmm$ . It is believed that  $LaO$  bond is ionic and  $FeAs$  bond is largely covalent and the chemical formula can be expressed as  $(La^{3+}O^{2-})^+ (Fe^{2+}As^{3-})^-$ .

Early theoretical calculations gave the magnetic moment of iron  $2.00 u_B$  but experiment at low  $T$  gives the value  $0.35 u_B$ . Some workers claim that the observed magnetic moment may be explained by negative effective Coulomb repulsion and others opine that the magnetic frustration in the system may give rise to reduced moment.

Neutron scattering results show that the parent compound  $LaOFeAs$  undergoes an abrupt structural distortion below 155 K from tetragonal to monoclinic. At  $\sim 137K$  it develops long range antiferromagnetic order with small iron moment. Doping with fluorine suppresses both the magnetic order and large structural distortion and superconductivity results. The crystal field splitting among the 3d orbitals is moderately small.

The suppression of magnetic order on doping with fluorine rules out the mechanism based on spin density wave and spin fluctuation exchange. The mechanism of electron-phonon interaction has been found to be too weak to give the observed high  $T_c$  (Boeri *et al.* 2008). Another, important experimental result is the enhancement of  $T_c$  on applying pressure or replacing  $La$  by a smaller lanthanide ion such as  $Nd, Sm$  etc. which will lead to shrinking of the lattice. As a result of appreciable covalency one expects covalent tetrahedral bonding between hybridized  $Fe$  orbitals and  $As$  (4p) orbitals.

The degeneracy or near degeneracy of  $3d_{xz}$  and  $3d_{yz}$  may be the source of lattice distortion via Jahn-Teller or pseudo Jahn-Teller effects (Sinha 2009). This situation can be described by a two-level configuration distortion at each distorted tetrahedron

at which the Fe ion exists. This can be treated by a pseudo spin-half ( $S = 1/2$ ) formalism. Accordingly, we consider the interaction of conduction electrons (in a narrow band derived from  $d_{xy}$  orbitals of Fe), with phonons and a distortion field (arising from the two level system). The expression for the critical temperature for the combined mechanism turns out to be.

$$T_{cs} = 1.13(\omega_{ph})^{r_p} (\omega_d)^{r_d} \text{Exp} \left[ -\frac{1}{\lambda_{ph} + \lambda_d} \right], \quad (4.1)$$

where,

$$r_p = \left( \frac{\lambda_{ph}}{\lambda_{ph} + \lambda_d} \right), r_d = \left( \frac{\lambda_d}{\lambda_{ph} + \lambda_d} \right); \quad (4.2)$$

$\omega_{ph}$  and  $\omega_d$  are the corresponding frequency in temperature unit and  $\lambda_{ph}$  and  $\lambda_d$  are the dimensionless coupling constants.

Numerical values of  $T_c$  are estimated by using the following values of the relevant parameters.

$$\lambda_{ph} = 0.2, \omega_{ph} = 315.7\text{K}, \lambda_d = 0.8$$

The value  $\lambda_{ph}$  is the same as given in (Boeri *et al.* 2008) and  $\omega_{ph}$  is the Debye temperature of the system. The value of  $\omega_d$  will depend on the separation of the two levels in question. As the unit cell contracts on applying pressure or by replacing La by Sm, Ce, Pr, Nd ions, which have smaller ionic radii,  $\omega_d$  will increase. The computed  $T_c$  for increasing values of  $\omega_d$  are:

**Table 1:  $T_c$  versus  $\omega_d$**

$\omega_d$	$T_c$
40	25
50	29
75	42
100	52

The above estimates show that as in cuprates a combined mechanism mediated by phonons and electron-induced distortion field mode can account for the high  $T_c$  of the ferropnictides.

## 5. Prediction and Discovery of Transient Photo Induced Superconductivity

Over four decades ago, the prediction of possibility of photo-induced superconductivity in a multi band semiconductor was made and followed up in a series of papers (Kumar and Sinha 1968; Shanker and Sinha 1973; Krishna and Sinha 1978; Sinha 1980; Sinha 1994). The central idea of the formulation involved two-boson (photon and phonon) exchange in the mechanism of interband pairing of electrons. The model is, adequately described by two conduction bands (non-overlapping in general) such that radiative electric dipole transitions are allowed between the electronic states of the two bands. The electron-phonon interaction is purely intraband and electron-photon is interband. The details of the mathematical formulation involving a series of canonical transformations followed by normal and anomalous Green's functions evaluation can be found in the original paper (Kumar and Sinha 1968). The important result that emerged from the model is that the coupling constant depends on the photon density impressed on the system. It was possible to attain high enough  $T_c$  by increasing the photon density.

Experimental work by several research group on some cuprate systems ( $\text{YBa}_2\text{Cu}_3\text{O}_{6.3}$ ) which are otherwise in a semi-conducting or insulating state demonstrate photo-induced transient superconductivity (Yu *et al.* 1992). An increase of the critical temperature with radiation dosage has also been found (Kreines and Kudinov 1992) (for other references see (Sinha 1996; 2007)).

### 5.1 Formalism for the Model System

The strongest evidence of photo-induced superconductivity has been found in films of ( $\text{YBa}_2\text{Cu}_3\text{O}_x$ ) which is on the border line of insulator-metal transition and is deficient in oxygen. As a result, two completely degenerate states at  $\Gamma$  and M

points arising from the Cu  $d_{yz}$  and  $d_{xz}$  and  $\pi$ -bonding orbitals of oxygen atoms appear. However, the Fermi level shifts due to ionicity of the missing oxygen atoms. There is significant change in the Fermi surface and the hole count in the  $\text{CuO}_2$  bands leading to the insulating state. There are states above the Fermi energy at these points. The estimated optical gap is around 2.0eV. The same situation occurs in other cuprates.

The Hamiltonian for the model will consist of fermion fields (holes or electrons) a real photon field and other virtual boson fields (phonon, charged or neutral bosons). The Hamiltonian is expressed as

$$H = H_o + H_{fr} + H_{fb}, \quad (5.1)$$

where,

$$H_o = \sum E_{\underline{k}n} C_{\underline{k}n,\sigma}^+ C_{\underline{k}n,\sigma} + H_r + H_b + H_c \quad (5.2)$$

The first term of (5.2) denotes the sum of single particle fermion energies  $E_{\underline{k}n}$   $C_{\underline{k}n,\sigma}^+$   $C_{\underline{k}n,\sigma}$  being the fermion (creation, annihilation) operators in the Bloch state  $|\underline{k}n,\sigma\rangle$ ,  $\underline{k}$  is the wave vector,  $n$  the band index,  $\sigma$  the spin;  $H_r$  and  $H_b$  are the operators representing energies of the radiation and the boson fields respectively and  $H_c$  is the screened Coulomb interaction between fermions (electrons or holes). The structure of these terms is well known (Kumar and Sinha 1968; Abrikosov *et al.* 1963) hence explicit form is not written. The interaction terms are expressed as

$$H_{fr} = \sum D [C_{\underline{k}m,\sigma}^+ C_{\underline{k}n1,\sigma} \text{Exp}(-\Omega t) + C_{\underline{k}n1,\sigma}^+ C_{\underline{k}m,\sigma} \text{Exp}(-\Omega t)], \quad (5.3)$$

where,  $\Omega$  is the radiation frequency

$$D = (2\pi V)^{-1/2} (\Omega/c) A_o d_{mn} \quad (5.4)$$

$$A_o = [(2\pi \hbar c^2 / \Omega) n_r]^{1/2} \quad (5.5)$$

$$d_{mn} = 2\pi \langle \phi_m | e_{\underline{r}} \cdot \underline{\varepsilon} | \phi_n \rangle; \quad (5.6)$$

$d_{mn}$  is the dipole matrix element connecting the

Wannier states  $|\phi_m\rangle$  and  $|\phi_n\rangle$ ,  $\underline{\varepsilon}$  is the polarization vector of the radiation field and  $V$  is the volume,  $c$  and  $\hbar$  are universal constants  $A_o^2$  gives the field intensity and depends on the number of quanta  $n_r$  of the radiation field.

$$H_{fb} = \sum B_q (C_{\underline{k}-q,m,\sigma}^+ C_{\underline{k}n} b_q^+ + hc), \quad (5.7)$$

$b_q^+$  and  $b_q$  are the boson operators of the mode  $q$  and  $B_q$  is the coupling constant.

The Hamiltonian (5.1) can be brought to a time-independent form by using a suitable unitary transformation (Sinha 1980). This leads to the renormalization of parameters involved  $\tilde{E}_{\underline{k},n}$ ,  $B_q$ ,  $\hbar\tilde{\omega}_q$ .

The time independent  $\tilde{H}_{fr}$  will involve mixing of states of bands  $m$  and  $n$ . The mixing terms can again be eliminated by a transformation and the band states diagonalized (Sinha 1980). The normalized band with new fermions interacting via modified processes has the form

$$\tilde{H} = \sum E_{\underline{k}\sigma} a_{\underline{k}\sigma}^+ a_{\underline{k}\sigma} - \sum \frac{\tilde{B}_q D}{\tilde{E}_o} (a_{\underline{k}-q,\sigma}^+ a_{\underline{k},\sigma} b_q^+ + hc), \quad (5.8)$$

where,

$$\tilde{E}_o = [(\hbar\Omega - E_{mn})^2 + D^2]^{1/2} \quad (5.9)$$

$\tilde{E}_o$  is the energy difference involved in the interband transition and  $\tilde{E}_{\underline{k}\sigma}$  is the single particle energy of the new fermion state  $|\underline{k}\sigma\rangle$ .

The modified fermion-boson interaction carries the factor  $D/\tilde{E}_o$  and depend on  $A_o$  and in turn on  $\sqrt{n_r}$ . The system is in a non-equilibrium situation and it is appropriate to define an effective temperature  $\tilde{T}$ . The fermion and bosons have their usual distribution but at temperature  $\tilde{T}$ .

The BCS type reduced Hamiltonian in the non-equilibrium state can be expressed as

$$\begin{aligned} \tilde{H}_r = & \sum E_{k\sigma} a_{k\sigma}^+ a_{k\sigma} \\ & - \sum U_{\underline{k}, \underline{k}'} a_{\underline{k}\sigma}^+ a_{\underline{k}'\sigma}^+ a_{-\underline{k}\sigma} a_{-\underline{k}'\sigma} \end{aligned} \quad (5.10)$$

where,

$$U_{\underline{k}\underline{k}'} = U_{rb}(\underline{k}, \underline{k}') - U_c(\underline{k}, \underline{k}') \quad (5.11)$$

$$U_{rb}(\underline{k}, \underline{k}') = \frac{\tilde{B}_{\underline{k}-\underline{k}'}^2 D^2}{\tilde{E}_o^2} \frac{2(\hbar\omega_{\underline{k}-\underline{k}'})}{\left[ (\hbar\omega_{\underline{k}-\underline{k}'})^2 - (\tilde{E}_{\underline{k}} - E_{\underline{k}'})^2 \right]} \quad (5.12)$$

The above denotes the radiation admixed boson mediated attractive [for  $(E_{\underline{k}} - E_{\underline{k}'}) < \hbar\omega_{\underline{k}-\underline{k}'}$ ] pairing interaction which dominates the screened Coulomb interaction  $U_c$  beyond a certain photon density.

A Green's function formalism yields the superconducting gap function as

$$\Delta = W_c \operatorname{cosech} \left( \frac{8\pi^2}{UVN(E_F)} \right), \quad (5.13)$$

where,  $W_c$  is BCS type cut off,  $N(E_F)$  the density of state at Fermi level and  $V$  is the volume. The critical temperature

$$\tilde{T}_c = 1.13(W_c/k_B) \operatorname{Exp}[-1/\lambda_{rb}] \quad (5.14)$$

$$\lambda_{rb} = \lambda_b R(n_r/V)/(1 + R(n_r/V)) \quad (5.15)$$

$$R = 4d_{mn}^2 (\hbar\Omega)/(\Omega - E_{mn})^2 \quad (5.16)$$

$$\lambda_b = (\tilde{B}^2/\hbar\omega)N(E_f)$$

The coupling constant  $\lambda_{rb}$  depends explicitly on density of radiation field quanta ( $n_r/V$ ). In the region  $R(n_r/V) < \lambda^b$  will increase almost linearly with photo excitation density and it will reach a saturation value when  $R(n_r/V) \gg 1$ .

We give a rough estimate of  $T_c$  and its dependence on the photon density for the system  $\text{YBa}_2\text{Cu}_3\text{O}_{6.3}$  in which photo-induced superconductivity has been observed (Yu *et al.* 1992). For the nitrogen laser used in the experiment, we have

$$\hbar\Omega = 3.7\text{eV} = 6 \times 10^{12} \text{ ergs (pulse with 600ps)}$$

$d_{nm} = 10^{-17} \text{ (ergcm}^3)^{1/2}$  (Corresponds to oscillator strength 0.17)

$$(\hbar\Omega - E_{mn}) = 6 \times 10^{-13} \text{ ergs.}$$

$$\lambda_b = 0.5$$

$$(n_r/V) = (2 \text{ to } 7.5) \times 10^{21} \text{ photons/cm}^2$$

$$(W_c/k_B) = 725 \text{ K}$$

**Table 2: Computed values of  $T_c$**

$(n_r/V)(\text{cm}^3)$	$T_c(\text{K})$
$2 \times 10^{21}$	95
$3 \times 10^{21}$	100
$4 \times 10^{21}$	102.5
$5 \times 10^{21}$	104
$7.5 \times 10^{21}$	106.6

From the above experimental work, we expect the hole concentration to be in the range of  $10^{21}$  to  $5 \times 10^{21} \text{ cm}^{-3}$ .

This is in the metallic regime. The corresponding hole concentration in the two dimensional layers (with thickness  $\sim 25 \times 10^{-7}$ ) is estimated =  $1.25 \times 10^{15} \text{ cm}^{-2}$ . This places the  $\text{Cu}_2\text{O}$  layers in the metallic regime.

### **A Few Remarks will be in Order**

The delay in the hole-electron recombination (due to electron trapping) facilitates the build up of the carriers (holes here) towards metallacety. As a result photo-excitation remains virtually frozen during this period. The mechanism discussed involves a dual nature of the radiation field. It creates carriers (hole here), which in unison with traps renders the material

metallic. The second (important) role is the participation in the pairing mechanism due to which  $\lambda_{rb}$  depends on the photon density ( $n_p/V$ ). As we see from eq. (5.16)  $\lambda_{rb}$  will increase with increasing ( $n_p/V$ ) and then tend to saturate beyond a certain limit. The observed photo-induced transient local superconductivity supports the above prediction.

The pairing processes discussed in this section involves two bosons fields namely photons and boson modes of the system. For this mechanism to work we must have photo response time  $\ll$  recombination time.

Experimentally, the phenomenon of photo induced superconductivity continues to be a very active field particularly based on cuprate systems.

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- Thousands of papers have been published. This phenomenon appears capable of giving room temperature and tunable  $T_c$  superconductors. It is desirable that the experimental should work in unison with theoretical models specially the model discussed here.
- Recent work of Fausti *et al.* (2011) demonstrates light induced transient superconductivity in a stripe-ordered cuprates. It is found that light pulses can transform non superconductivity  $\text{La}_{1.675}\text{Eu}_{0.2}\text{Sr}_{0.125}\text{CuO}_4$  into transient three-dimensional superconductor. The important point is that the pairing is intraband and leads to coherent interlayer transport as manifested by Josephson plasma resonance. This is consistent with our papers (Shankar and Sinha 1973; Krishna and Sinha 1978; Sinha 1980).
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