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Recent advances in the search for mechanism of high Tc superconductivity*

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Abstract: A brief survey of the situation prior to the advent of high *Tc* superconductors in 1986 is made. The principal characteristics of the new superconductors are mentioned. Some mechanisms suggested for explaining the origin of these superconductors are discussed. Directions of research useful for the understanding of the mechanism for high *Tc* are pointed out.

Keywords: High *Tc* superconductivity, theoretical models, search for mechanism

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1. A brief survey of the situation prior to the advent of high *Tc* superconductivity in 1986

We shall first make a brief survey of the history of the development of the superconductivity from 1911 to 1986–i.e. the discovery of the superconductivity in Hg by Kammerling Onnes (1911) to 1986 when new type of superconductivity was discovered in Copper oxide materials by Bednorz and Müller (1986). Kammeling Onnes found Hg to be resistanceless when cooled below 4 K and called this zero-resistance state of matter as superconductivity. Work was then initiated in Leiden and other laboratories where liquid He was available for investigating the characteristics of this new state in Hg and other metallic elements. In Table 1 we give the principal properties exhibited by a superconductor. The first two characteristics e.g., the zero resistance state and existence of perfect diamagnetism $\left[\chi_d = -\frac{1}{4\pi}\right]$ are considered as principal identifying properties of a superconductor. Systematic studies were then done not only on the elemental metals but also in alloys, the binary compounds (e.g. *A*-15 compounds with A_3X structure), the ternary Chevrel phase compounds–both magnetic and non-magnetic and *f*-band heavy Fermion systems (Ray, to be published). The highest *Tc* obtained among all these compounds are in Nb_3Ge with $Tc \simeq 24$ K (Weger and Goldberg 1973).

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The principal mechanism for these superconductors was found to be electron-phonon (*e-p*) interaction. The first microscopic theory based on this interaction was given by Bardeen *et al* (1957) which gave universal relationships between Tc, the critical temperature, C_v, the specific heat and the gap Δ. These relationships were found to be obeyed by many metallic elements with $Tc \leqslant 3$ K in which *e-p* interaction was weak. But in strong-coupled superconductors like

Table 1. Characteristics of a superconductor.

1. Zero-resistance state below $T=Tc$ ($<10^{-28}\ \Omega$ cm for an ideal one)
2. Perfect diamagnetism $\left(X_d = -\frac{1}{4\pi}\right)$ (Meissner effect)
3. Existence of a critical magnetic field above which superconductivity disappears
4. Pinning of magnetic flux inside a hole
5. Quantization of magnetic flux - carriers have charge $2e$
6. Existence of an energy gap separating the ground and excited state of pairs of carriers
7. Penetration depth of magnetic field λ and coherence length of a superconducting pair (Cooper pairs) ξ
   $\xi > \lambda$ type I
   $\xi < \lambda$ type II
8. Isotope effect $Tc \propto M^{-\alpha}$ with $\alpha \simeq 0.5$ for conventional superconductors

transition metals, their alloys and compounds, McMillan extended the BCS theory by renormalising the *e-p* interaction (McMillan 1968) denoted by a parameter λ. He showed that $\lambda = VN(0)$ [where $N(0)$ is the density of states at the Fermi energy and V is the interaction between electrons and phonons] $\ll 1$ for BCS type of superconductors whereas for strong coupling cases it can be as high as 2. In these narrow band systems, apart from the strong *e-p* interaction the screened Coulomb interaction has also to be taken into account (Morel and Anderson 1962). Also, in very narrow *f*-band systems e.g. compounds of Cerium and Uranium, the possibility of having magnetic interaction cannot be ruled out as the origin of superconductivity (Lee *et al* 1986). Finally, superconductivity in some one-dimensional polymers particularly under pressure is still not understood.

Parallel to the experimental and theoretical work on superconductivity, studies have been done of the effects of the Coulomb correlation on magnetic properties of transition metals and their compounds (Moriya 1980). Hubbard hamiltonian (Hubbard 1963) and its approximate solutions for both Hartree-Fock and kinetic exchange limits of U/W, where U is the on-site Coulomb

correlation and W is the width of the band, have been studied in understanding the Mott transition in solids (Mott 1974). We would like to point out that we have recently investigated the metal-insulator transition in NiS on the basis of a strongly correlated d band interacting with a wide p band (Ray and Kajzar 1980). Recently there have been much discussions to understand the role of Coulomb correlation on the electronic structure of transition metal monoxides (Terakura *et al* 1984, and references therein).

Table 2. Different high Tc compounds.

Compound	Tc
$La_{2-x}(Sr, Ba)_x Cu O_4$	$\simeq$ 40 K
$Y Ba_2 Cu_3 O_{7-x}$	90 K
$Si Sr Ca Cu_2 O_r$	105 K
$Tl Ba Ca Cu_2 O_2$	125 K
$Bi_2 Ca Sr_2 Cu_2 O_w$	85 K
$Ba_{0.6} K_{0.4} Bi O_3$	30 K

In the background of all these developments, superconductivity of a new type was discovered in perovskite Copper oxides (Bednnorz and Müller 1986) with Tc as high as 125 K. A list of these compounds and their Tc values are given in Table 2. Only Ba – K – Bi – O is not planar and does not contain Cu. We shall first discuss the special features of these superconductors :

1. Until recently, all the superconductors had holes at the oxygen sites as charge carriers (Fulde 1988). But now new superconductors have been discovered which have excess electrons as charge carriers (Tokura *et al* 1989). So in the first case it was the renormalized p holes at O sites and d electrons at Cu sites are responsible for superconductivity and antiferromagnetism respectively whereas for the latter group of superconductors both superconductivity and magnetism might be due to renormalized d electrons at Cu sites. Both superconductivity and antiferromagnetism occurs close to a half filled d holes band in Cu.

2. There is mixed valent character of the Cu ion. The configuration corresponding to Cu^{1+}, Cu^{2+} and Cu^{3+} have been identified by spectroscopic experiments (Raveau *et al* 1988, Maurer *et al* 1988).

3. The coherence length i.e. the distance up to which the superconducting pairs are bound together is of the order of 10-12 Å. This indicates that the distance between pairs is of very short range in real space (Cava *et al* 1997).

4. Both electron-phonon interaction and Coulomb correlation are important in these superconductors. But which of these two interactions is more important is not yet clear.

5. The phase diagram shows that the pure sample of both La_2CuO_4 and $YBa_2Cu_3O_{6.5}$ are antiferromagnets. This phase disappears for very small doping at oxygen sites. Then before superconducting phase appears there is a spin glass phase (Aharony *et al* 1988).

6. Disorder arising from the random distribution of holes at the oxygen sites is typical characteristics of these materials. The pairing potential would then have random distribution.

7. Theoretical model calculation of a single Hubbard band depends on the ratio of U/W (U, being the Hubbard on site Coulomb correlation and W, is the band width). Experimental determination of these two quantities is still not conclusive (Fulde 1988 and Friedel 1988). So the controversies between the theoretical models cannot be resolved untill the value of these two parameters is unambigously determined.

8. Neutron scattering experiments in the superconducting phase do not give clear indication of magnetic excitations (Alexandrov, private communication).

9. The nature of the ground state is still not clear. Whether it is quantum spin liquid state as RVB model (Anderson 1987a, b) predicts or the Néel state has yet to be settled experimentally. Theoretical calculation on the basis of variational method (Dasgupta *et al* 1989) gives the Néel state as the ground state.

10. Positron annihilation experiments show clearly that the Fermi surface of the holes is two dimensional (Peter 1988) in character in $YBa_2Cu_3O_7$. Since Bi- and Tl-compounds do not contain any Cu–O chain, it is the CuO_4 planes where the superconductivity lies. The interlayer interactions between the planes cannot be neglected.

11. Infrared reflection and Raman scattering experiments done on $YBa_2Cu_3O_7$ single crystals show a shift of some optical phonons of the order of 10 cm^{-1} when T is varied from Tc to 0 (Macfarlane *et al* 1987a, b); Thomsen *et al* 1988). The observed phonon softening has been explained (Fulde 1988) for a value of $\lambda \simeq 1.7$. But to get $Tc \simeq 90$ K solely by *e-p* interaction in the McMillan model λ should be ~ 2.9. So either a new type of *e-p* mechanism is present or, other mechanism of pair interactions may be active in addition to the *e-p* coupling.

12. The electron specific heat in the normal state ($T > Tc$) has been obtained by substracting the phonon contribution from the total heat capacity (Reeves *et al* 1987) and given by :

$$\lambda_N \geqslant 40 \text{ mJ/mol K}^2 \text{ for La–Ba–CuO}$$

which is very high and the heat jump at $T = Tc$ is :

$$\Delta C \geqslant 5 \text{ J/mol K (Nevitt } et\ al \text{ 1987)}$$

similar measurements of the electronic specific heat of $y\ Ba_2Cu_3O_7$ have been done (Loram and Mirza 1988) for $T \leqslant Tc$ giving the coefficient of linear specific heat term as ~ 5.2 mJ/mol K^2 which becomes 16 ± 3 mJ/mol K^2 in the normal state.

13. In the BCS-model of *e-p* interaction *Tc* should vary with the mass of exygen as $m^{-\alpha}$ where $\alpha = 0.5$ if the motion of oxygen around Cu is predominent source of *e-p* coupling in the new supercoductors. The measured values of α for these oxide superconductors have been found to lie between 0.1 to 1 (Hans-Conrad *et al* 1987). The two superconductors $BaPb_{0.75}Bi_{0.25}O_3$ and $La_{1.85}Ca_{0.15}CuO$ have α values greater than the BCS value of 0.5.

14. The charge carriers have effective mass of the order of 10 m_e (m_e being the mass of a free electron) as obtained from optical measurements (Thomas *et al* 1988). From measurements of quantized flux the total charge was found to be $+2e$ i.e 2 holes are involved in the first goup of new superconductors (Colclough *et al* 1987). The fact that thermo-power is independent of applied field upto 30 *T* (Yu *et al* 1988) indicates that the total spin is zero or the pair is a singlet. Tunnelling experiments (Geerk *et al*, 1989) show a gap in the excitation spectra such that $2\Delta/K_B T_C \sim 6$-8 which is larger than the BCS value of 3.5 (Lynton 1962).

15. The orthorhombic structure seems to favour the superconducting phase. The phase diagram of $Y\ Ba_2Cu_3O_{7-x}$ shows that is a structural transition from tetragonal to orthorhombic phase close to $T = Tc$ (Aharony *et al*). Also, the Bi- and Tl-compounds with high *Tc* have orthorhombic structure (Subramarian *et al* 1988). Neutron studies of orthorhombic strain mode for $La_{1.85}Sr_{0.15}CuO_4$ by MckPaul *et al* (1987) show the correlation between the superconducting phase and this elastic strain.

16. The transport properties show unusual behaviour for the oxide superconductors. The resistivity is linearly proportional to *T* above *Tc* whereas the thermal conductivity is temperature independent for $T > Tc$ and shows a sharp rise for $T < Tc$ (Morelli *et al* 1987). The Hall coefficient is positive and varies inversely with the number of holes (Ong *et al* 1987) upto $x = 0.15$ and then it drops.

17. Both elastic constants and ultrasonic attenuation show anomalies near $T = Tc$ (Wolf *et al* 1988, MckPaul *et al* 1987).

18. Systematic studies of the effects of substitution of different ions in these oxides have been done (Narlikar *et al* 1989). These substitutions have profound effects on *Tc* and other superconducting and structural properties and depend largely to which site the substitution is done. The modification of the magnetic susceptibility due to the substitution has also been studies.

19. The magnetic properties of these superconductors particularly, those with rare earth elements have been studied to find the interrelationship between the magnetic behaviour of rare earth inos and their superconducting properties (Green *et al* 1988).

These features of the oxide superconductors, therefore, indicate that the mechansim responsible for high *Tc* and other properties is more complex than the conventional superconductors obeying BCS theory. We shall now discuss some of the theoretical models proposed for these superconductors.

2. Some proposed theoretical models

After the discovery of the oxide superconductors, there was a rush for publishing theoretical models which could justify the obsered values of *Tc* in these materials. Subsequently, more and more detailed experimental results on various special superconducting properties (some of which have been indicated earlier) begin to be available – particularly with single crystals of $Y Ba_2Cu_3O_{7-x}$. This has given good possibility of checking the theoretical models.

The principal models proposed are :

1. Electron-phonon induced :

(i) Since the BCS theory could explain the basic features of the conventional superconductors at least qualitatively the BCS theory was extended to take account of the singularity in the 2*D*-density of states and the hybridization between *d* and *p* electrons (Labbé and Bok 1987). But this model does not take any account of the electron correlation in the narrow *d* band nor does it associate the charge carriers with the *p* holes oxygen sites. Also, the BCS model is basically based on long range *e-p* interaction. This makes it difficult to explain the very short coherence length observed in the new superconductors. The observed very large values of penetration depth of magnetic field λ and critical magnetic field HC_2 and many other properties are difficult to understand on the basis of the BCS theory.

(ii) McMillan's strong coupling theory has been used by Weber (1987) using the calculated band structure of this compound (Matheiss 1987) and a force-constant model developed by him. A very strong coupling of O phonons to the conduction electrons ($\lambda \sim 2$) given $Tc \sim 30-40$ K so that for $Tc \sim 100$ an unusually large value of λ is required.

(iii) Beside the inter-site *e-p* coupling with gives rise to BCS+McMillan theories, there exists on-site *e-p* coupling generated from the vibrations of ions around the charge carrier. This local *e-p* coupling may cause small polarons to be formed in these systems with interaction which can be attractive in nature. Also, the width of the polaronic band is reduced due to the phonons which are coupled with the electrons. Two polarons lying close to each other can ferm bipolarons. Special type of superconductivity might arise from polarons (Alexandrov 1983) and bipolarons (Alexndrov *et al* 1986 and references therein). The oxides may be belonging to the intermediate case where the dominant *e-p* interaction is local (on-site) but the long range (inter-site) interaction might not be negligible. This would require proper treatment of the *e-p* interaction close to Mott-Hubbard transition (i.e. in narrow band systems). .

In such cases we have :

$$\mathcal{H} = \mathcal{H}_H + \mathcal{H}_{ph} + \mathcal{H}_{e-p} \tag{1}$$

where $\mathcal{H}_H$ is the Hubbard hamiltonian for a single and is given by :

$$\mathcal{H}_H = \sum_{ij\sigma} t_{ij} C^+_{i\sigma} C_{i\sigma} + U \sum_i \hat{N}_{i\uparrow} \hat{N}_{i\downarrow} + \sum_{ij>\sigma,\sigma'} U_{ij} \hat{N}_{i\sigma} \hat{N}_{j\sigma} \tag{2}$$

$$\mathcal{H}_{ph} = \sum \hbar\omega_q \left[b^+_q b_q + \frac{1}{2} \right]$$

$$\mathcal{H}_{e-p} = \mathcal{H}^I_{e-p} + \mathcal{H}^{II}_{e-p} \tag{3}$$

where

$$\mathcal{H}^I_{e-p} = \sum_{iq\sigma} V_{iq} (b_q + b^+_{-q}) \hat{N}_{i\sigma} \tag{4}$$

and

$$\mathcal{H}^{II}_{e-p} = \sum_{<ij>,q,\sigma} V_{ijq} C^+_{i\sigma} C_{j\sigma} (b_q + b^+_{-q}) \tag{5}$$

The constants V_{iq} and V_{ijq} in the on-site and inter-site *e-p* interactions can be expressed as :

$$V_{iq} = \sum_i \langle i \mid \frac{\partial V_i}{\partial (\boldsymbol{R}_i - \boldsymbol{R}_i)} (\partial R_i - \partial R_i) \mid i \rangle$$

and

$$V_{ijq} \simeq q_0 \sum_i t_{ij} \frac{\boldsymbol{Rn} \cdot \boldsymbol{c}_q}{|\boldsymbol{Rn}|} \sqrt{\frac{\hbar}{2M_i N\omega_q}} (e^{i\boldsymbol{q}\cdot\boldsymbol{R}i} - e^{i\boldsymbol{q}\cdot\boldsymbol{R}j}) \tag{6}$$

with

$$Rn = Ri - Rj.$$

q_0 is a constant with value of the order of unity ; e_q is an unit vector along the direction of phonon momentum q ; t_{ij} is the hopping matrix element of electrons between i and j atoms. It is seen that inter-site e-p interaction is proportional to the width of the band and consequently in wide band systems is relatively more important than the on-site term. In the BCS type superconductivity and charge density wave propagation and ordering this e-p interaction only have been considered. So in the limit $\mathcal{H}^{I}_{e-p} \simeq 0$, i.e. in systems where the long range $e-p$ coupling is more important the effective electronic hamiltonian can be obtained through a canonical transformation which eliminatels $\mathcal{H}^{II}_{e-p}$ (Kittel 1963) and this is given by :

$$\mathcal{H} = \mathcal{H}_0 + \sum_{\substack{K,q,\sigma \\ K',q',\sigma}} \frac{V_{kq}|^2 C^{+}_{K+q\sigma} C_{K\sigma} C^{+}_{K'-q'\sigma'} C_{K'\sigma'} \hbar\omega_q}{\{\epsilon_K - \epsilon_{K-q}|^2 - (\hbar} \tag{7}$$

where $\mathcal{H}_0$ is the hmiltonian for non-interacting electron-phonon systems and V_{kq} is the Fourier transform of $\mathcal{H}_{ijq}$. The second term in eq. (7) shows that for weak e-p coupling the net effect of such e-p interaction is the scattering between two electrons with emission or absorption of a single phonon. It is also evident from this term, if the phonon energy is larger than electronic excitation energy, the interaction between a pair of electrons is attractive and when this attractive interaction dominates over the Coulomb repulsive interaction between the pair of electrons, a bound pair of electrons can be formed. Such a pair of electrons called Cooper pairs (Cooper 1956) can have maximum attractive interaction when both momentum and spin are opposite. Also, the individual momentum lie close to to Fermi wave vector K_F. The hamiltonian for such a system of pairs is given by :

$$\mathcal{H} = \sum \epsilon_K C^{+}_{K\sigma} C_{K\sigma} + \sum V_{KK'} b^{+}_{K} b_{K'} \tag{8}$$

where

$$b^{+}_{K'} = C^{+}_{K'} \uparrow C_{-K'} \downarrow$$

and

$$b_K = C_{-K} \uparrow C_K \downarrow$$

where for generalities we consider a pair being formed with wave vectors K and K'. The commutation relations of $b^{+}_{K'}$ and b_K are neither of Fermionic type

nor boson-like. The above hamiltonian has been solved using various techniques and all these give the ground state as the condensation of all these pairs state and the excited state to be separated from the ground state by the gap energy Δ_K which at finite temperature is given by :

$$\Delta_K = -\sum_{K'} V_{KK'} \frac{\Delta_K}{2E_{K'}} \tanh \beta E_K/2 \tag{10}$$

where E_K is the quasi particle energy (i.e. the Cooper pairs here) which is given as :

$$E_K^2 = \epsilon_K^2 + |\Delta_K|^2 \tag{11}$$

Two other basic approximations in the BCS theory are :

(i) $V_{KK} =$, V a constant

(ii) $V \neq 0$ for $E_F - \hbar\omega_D < V < F_F + \hbar\omega_D$ only where ω_D is the Debye frequency.

For the case of rectangular density of states, eq. (10) gives at $T = Tc$

$$\frac{1}{VN(0)} = \int_{-}^{\hbar\omega_D} \frac{\tanh \beta\epsilon/2}{\epsilon} \tag{12}$$

where $N(0)$ is the value of DOS at $E = E_F$. Solution of the integral on the right hand side gives the expression for Tc as

$$K_B T_C = 1.14\, \hbar\omega_D \exp(-1/VN(0)) \tag{13}$$

The expression for the gap parameter Δ and ΔC jump in the specific that $T = Tc$ are obtained as :

$$\frac{2\Delta}{K_B Tc} = 3.5 \tag{14}$$

$$\frac{\Delta C}{\gamma Tc} = 2.43$$

Here γ is the coefficient of the linear term in T for Specific-heat in the normal state.

The relations (13) and (14) – the universal BCS relationships – are obeyed fairly well by the metallic elements where the conduction bands consitst of s and p electrons so that the widths are large and on-site Hubbard interactions U are small. Also since $\omega_D \propto \frac{1}{\sqrt{M}}$, M being the mass of atoms constituting the metallic element, $Tc \propto \frac{1}{\sqrt{M}}$ which gives the isotope dependence of Tc for the metallic elements. This isotope dependence has been experimentally verified for metallic elements with s-p electrons (Lynton 1962). Deviations from the ideal BCS relations became gradually apparent for transition metal with d electrons, their

intermetallic compounds and alloys. The *d* bands are narrower than those formed by *s-p* electrons and consequently, the effect of Coulomb interaction on *e-p* interaction cannot be entirely neglected. The density of states DOS of such metals have spike-like character and have larger values close to the Fermi energy E_F. Also the *e-p* coupling parameter V is large and can no longer be taken as constant. So $\lambda = VN(0)$ in the weak coupling BCS theory is small i.e. $\lambda \ll 1$. So for the case when $\lambda > 1$ i.e. the strong-coupling cases, it was necessary to renormalise λ such that

$$\lambda = 2\int \alpha^2(\omega)F(\omega)d\omega = \frac{N(\epsilon_I)\langle I^2\rangle}{M\langle \omega^2\rangle} \tag{15}$$

where $F(\omega)$ is the phonon DOS and $\alpha(\omega)$ is a measure of *e-p* matrix element. McMillan (1968) derived the following expression of Tc for the strong-coupling case :

$$Tc = \frac{\Theta_D}{1.45}\exp\left[-\frac{1+\lambda}{\lambda-\mu^*}\right] \tag{16}$$

where μ^* is the screened Coulomb interaction as is ~ 0.1. Maximum value of Tc can be obtained from $\frac{\partial Tc}{\partial \lambda}=0$ which gives $Tc \simeq 30$ K for $\lambda \simeq 2$. It is, therefore, seen that for such extreme values of λ, we may be able to reach Tc for La-compounds. But it has been shown by Weber (1987) that for such large values of λ, the system becomes unstable. So *e-p* interaction of inter-site type alone cannot explain high Tc in the oxide materials. Also, properties such as coherence length of the order of atomic distances, very large penetration depth of magnetic field and very high values of critical field ($HC_2 \simeq 100\ T$), etc. are difficult to explain on the basis of BCS theory.

The other extreme approach for *e-p* interaction is to consider H^I_{ep} alone i.e. $\mathcal{H}^{II}_{e-p}=0$. To treat this case, we make a canonical transformation such that the linear *e-p* term $\mathcal{H}^I_{e-p}$ is zero. Such a transformation (Holstein 1959) gives the following effective hamiltonian :

$$\mathcal{H}_{\text{pol}} = \sum_{ij\sigma} t_{ij}\exp-\left[-\sum_{q}\frac{(V_{iq}-V_{iy})}{\hbar\omega_q}(b^\dagger_{-q}-b_q)\right]C^\dagger_{i\sigma}C_{j\sigma}$$

$$+\sum\left[\epsilon_0-\sum_q\frac{|V_{iq}|^2}{\hbar\omega_q}\right]N_{i\sigma}$$

$$+\frac{1}{2}\sum_{i\sigma}\left[U-\sum_q\frac{2V_{iq}V_{i-q}}{\hbar\omega_q}\right]N_{i\sigma}N_{i-}$$

$$+\frac{1}{2}\sum_{<i,j>,\sigma}\left[U_{ij}-\sum\frac{2V_{iq}V_{i-q}}{\hbar\omega_q}\right]N_{i\sigma}N_{j\sigma}$$

$$+\sum_{iq\sigma}V_{iq}(b_q+b^{+}_{-q})N_{i\sigma}$$

$$+\sum_{<ij>q}\frac{(V_{iq}-V_{jq})}{\hbar\omega_q}V_{ijq}(b_q+b^{+}_{-q}).(b_q+b^{+}_{-q})C^{+}_{i\sigma}C_{j\sigma}$$

$$-\sum_{\substack{ijq\\ \sigma\sigma'}}\frac{2V_{iq}V_{ij-q}}{\hbar\omega_q}N_{i\sigma}C^{+}_{i\sigma}C_{j\sigma}$$

$$+\sum\hbar\omega_q(b^{+}_q b_q+1/2) \tag{17}$$

It is to be noted that the last but two terms arise from the canonical transformation on the inter-site *e-p* interaction, i.e. since $[\mathcal{H}^{B}_{e-p}, \mathcal{H}^{II}_{e-p}]\neq 0$, this interaction is modified in presence of strong $\mathcal{H}^{I}_{e-p}$ interaction. The above hamiltonian is an exactly transformed one and gives rise to small polarons i.e. a new quasiparticle of Fermion type in which an electron and local deformation are coupled together and consequently when the electron moves, it arries the deformation with it. The effective mass of this quasiparticle is therefore, more than the free electron and is given by :

$$\frac{m_e}{m_p}=\exp\left[-\sum_{q}\frac{(V_{iq}\ \ V_{jq})}{\hbar\omega_q}(b^{+}_q-b_{-q})\right] \tag{18}$$

where m_p is the effective mass of a polaron.

Keeping only single-phonon excitations the right hand side can be written as :

$$\exp\left[\sum_{q}\frac{V_q^2}{(\hbar\omega_q)^2}\sin^2\frac{\boldsymbol{q}\cdot\boldsymbol{R}_{ij}}{2}\coth\beta\frac{\hbar\omega_q}{2}\right] \tag{19}$$

The second term in eq. (17) gives the shift of the electronic energy due to polaron formation. The third term is the decrease in U due to polaronic effect. In cases where electron U is small, the effective U can be negative—a case considered by Anderson (1975). The 4th term shows that in the case the electronic inter-site Coulomb interaction U_{ij} is small, the effective U_{ij} can become attractive. This attractive interaction is the oigin of polaronic superconductivity. When it is large compound to the polaronic band width, it can give rise to bound polarons

or bipolarons. In the limi $\mathcal{H}_{e-p}^{II} \simeq 0$ the other terms in eq. (17) can be neglected. For the case of new superconductors we shall have to keep all these terms. But for simplifying the problem we shall not consider these any further.

Making mean-field approximation we can write the hamiltonian (17) in the following form :

$$\mathcal{H}_p = \sum_{K\sigma} \xi_K N_{K\sigma} + \sum_K (\Delta_K C_{K\uparrow}^+ C_{-K\downarrow}^+ + h.c)$$
$$- \sum_i \frac{\Delta_0(i)\Delta_0^+(i)}{U_{eff}} - \sum_{ij} \frac{\Delta_i(i)\Delta_i^+(j)}{V_{eff}} \tag{20}$$

where

$$\xi_K = \epsilon_K \exp(-g^2) - \mu$$
$$\Delta_K = \Delta_0 + Z\gamma_K \Delta_i$$
$$\Delta_0(i) = U_{eff} \langle C_{i\downarrow} C_{i\uparrow} \rangle$$
$$\Delta_i = V_{eff}^{ij} \langle C_{j\downarrow} C_{i\uparrow} \rangle$$

$$U_{eff} = U - \sum \frac{2V_{iq}V_{i-q}}{\hbar\omega_q}$$

$$V_{eff}^{ij} = \sum_q \frac{2V_{iq}V_{j-q}}{\hbar\omega_q} - U_{ij}$$

γ_k is the structure factor. $\exp(-g^2)$ is the band narrowing factor due to local $e-p$ interaction whose expression depend on the dimension of the system. It is to be noted that real space decoupling has been doene here in contrast to the BCS case where decoupling is made in the reciprocal space. Solution of eq. (20) by Green function method gives the following gap eq. :

$$\Delta(\xi) = ZV_{eff}^{ij} \int_{-W-\mu}^{W-\mu} \left\{ \frac{(\xi+\mu)(\xi'+\mu)}{\omega^2} - x \right\}$$
$$x \frac{\Delta(\xi')}{2E'} \tanh\left[\frac{\beta E'}{2}\right] N(\xi') d\xi' \tag{21}$$

where

$$x = \frac{U_{eff}}{ZV^{ij}}$$

Z is the number of nearest neighbours around a charge carrier ; $N(\xi)$ is the DOS at energy ξ and W is the width of the polaronic band. General solution of

the gap equation has to be done numerically. Only in the limit of large band width we get

$$K_B T_C = 1.14 W \left[1 - \frac{\mu^2}{\omega^2}\right]^{\frac{1}{2}} \exp\left[-\frac{1}{D} - x\right]$$

where

$$D = Z V_{eff}^{ij} N(0) \left[\frac{\mu^2}{\omega^2}\right]^{\frac{1}{2}} \tag{22}$$

for the case of constant DOS. So in this strong coupling case $Tc \propto W$, whereas in the case of weak coupling BCS case $Tc \propto \oplus_D$, the Debye temperature. This is due to the fact in the case of real space decoupling, all electrons up to Fermi energy take part in the condensation whereas in the case of reciprocal space decoupling, electrons near the Fermi energy are mostly involved. It is also evident that the SC phase appears only when $\frac{\mu}{W} > \frac{U_{eff}}{ZV_{eff}^{ij}}$. So for small values if μ, i.e. close to the half-filled band the SC phase is not stable. So for such a situation, it is necessary to consider both the AF and SC order parameters. It is apparent that for very strong *e-p* interaction W is small and can become much less than U_{eff}. It the this situation, it is necessary to consider first high correlation limit of Hubbard model and then consider the *e-p* interactions. Analysis for such cases are now being carried out.

It is apparent from eq. (17) that the bipolaron hopping arises from the combined effect of short range and long range *e-p* interactions. Also, interactions between bipolarons would arise from higher order term in V_{iq} and V_{ijq} which were neglected in eq. (17).

In the above treatments we have considered a single band Hubbard model. But in the oxide materials, it is the *p* holes at oxygen sites with weak correlation are the charge carriers whereas the *d* electrons or (holes) at the Cu sites are responsible for the magnetic effects. The two band feature has to be properly introduced in the polaronic and bipolaronic treatments.

(2) *Magnetic models with high on-site Coulomb interaction :*

We shall now consider strong correlation limit of Hubbard hamiltonian. In this limit two theories have been proposed : (i) the kinetic exchange theory of Cyrot (1987) and (ii) the valence resonating valence and (RVB) model of Anderson and coworkers (Anderson 1987a, b).

In the first case, the charge carriers are the Cooper pairs originating from spins at neighbouring spins whereas in the RVB model, it is the holes (called

holons) at oxygen vacancy sites which are principally responsible for superconductivity.

(*A*) *Kinetic exchange model :*

The single band Hubbard model is given by

$$\mathcal{H}=\mathcal{H}_h+U\sum_i \hat{N}_i\uparrow \hat{N}_i\downarrow \tag{23}$$

where $\mathcal{H}_h$ is the hopping term. This can be broken up as follows :

$$\mathcal{H}_h=\mathcal{H}_h^{\text{lower}}+\mathcal{H}_h^{\text{upper}}+\mathcal{H}_h^{\text{inter}} \tag{24}$$

where

$$\mathcal{H}_h^{\text{lower}}=\sum_{ij\sigma} t_{ij}C_{i\sigma}^{+}(1-\hat{N}_{i\,-\sigma})C_{j\sigma}(1-\hat{N}_{j-\sigma})$$

$$\mathcal{H}_h^{\text{upper}}=\sum_{ij\sigma} t_{ij}C_{i\sigma}^{+}\hat{N}_{i-\sigma}C_{j\sigma}\hat{N}_{j-\sigma}$$

$$\mathcal{H}_h^{\text{inter}}=\sum_{ij\sigma} t_{ij}C_{i\sigma}^{+}(1-\hat{N}_{i-\sigma})C_{i\sigma}\hat{N}_{j-\sigma}$$

$$+\sum_{ij\sigma} t_{ij}C_{i\sigma}^{+}\hat{N}_{i-\sigma}C_{j-\sigma}(1-\hat{N}_{j-\sigma}) \tag{25}$$

By a proper canonical transformation we can eliminate $\mathcal{H}_h^{\text{inter}}$ and get the effective lower Hubbard subband as :

$$\mathcal{H}_{\text{Hub}}^{\text{lower}}=\sum_{ij\sigma} t_{ij}b_{i\sigma}^{+}b_{j\sigma}+J\sum\left[S_i.S_j-\frac{1}{4}n_in_j\right]$$

with

$$b_{i-\sigma}=C_{i\sigma}(1-\hat{N}_{i-\sigma}) \text{ and } J=\frac{2t^2}{U} \tag{26}$$

If we neglect the fluctuation in the number of holes from site to site and take the average number of holes at each site as $\delta=1-\hat{N}_{i-\sigma}$ eq. (26) can be written as :

$$\mathcal{H}_{\text{Hub}}^{\text{lower}}=t\delta\sum' C_{i\sigma}^{+}C_{j\sigma}+J\sum\left[S_i.S_j-\frac{1}{4}n_in_j\right] \tag{27}$$

The hamiltonian for the Cooper pairs derived from eq. (27) is then of the same form as derived earlier for the polaronic case (eq. (20)) with substitutions

$\delta=\exp(-g^2)$ and $\Delta_K=\frac{3}{\varphi}J\gamma_K$ and $x=0$. The solutions of the two hamiltonians are the same except for this change of parameters. The excitations in the polaronic case are vibronic type whereas for the other case are of magnon like. It is easy to see that one can have $Tc \simeq 100$ K for reasonable values of parameters in both the cases. Since the interactions are local, both give short coherence length.

(B) RVB model :

RVB model also is based on the single band Hubbard hamiltonian (23). But instead of describing it in terms of b and spin s operators, it can be written in terms of two fermions and two boson operators which Hubbard (1965) did in the atomic limit (i.e. $W=0$). In presence of strong correlation, the charge and spin degrees of freedom are separated. Two fermion like chargeless neutral spin operators are called spinons by Anderson (1987a, b). Creation and destruction of holes (charge e) are denoted by boson operators e_i^+ and e_i. The doubly occupied sites are described by boson like operators d_i and d_i^+. For 1 dimensional case, the ground state can be exactly shown to be a quantum spin liquid state. Anderson started from the assumption that this is also true for $2D$. The RVB state can then be written as a linear combination of all possible valence bonds with singlet pairings. This RVB state has the following characteristics :

(i) There is no long range order so that the ground state can be written as :

$$\langle \psi_{RVB} \rangle = P_D(b^+)^{N/2} \mid 0 \rangle \tag{28}$$

where P_D suppresses all configurations with double occupancy and

$$b^+ = \sum_{<i\,j>} a(R_i - R_j) C_{i\uparrow}^+ C_{j\downarrow}^+ \tag{29}$$

which describes Heitler-London bonds formed by sites i and j with distance R_i and R_j. Since electrons or spins are fluctuating between all these possible bonds, eq. (28) describes spin liquid state. The spin or spinon excitations are, therefore, gapless. The spinons move freely in the ground state and has a pseudo Fermi surface and the specific heat C_V due to the freely moving spinons can, therefore, be written as $C_V=\gamma T$.

(ii) When the system is doped, holes are created at oxygen vacancy sites and these suppress AF ordering. For small but finite doping AF phase is completely suppressed and the holon-holon interaction gives rise to superconducting phase in which the holons condense with characteristics of boson condensation. As the concentration of holons increases, the band-width of the holons becomes comparable to the exchange energy J, the pairs are broken

leading to disappearance of SC phase. For small doping, the holon concentration is small and the phase fluctuations dominate. Tc is given by the Bose condensation temperature i.e. $Tc \propto \delta^{2/3}$.

(iii) The original RVB model was worked out for the $2D$ planes of CuO_4. The inter layer interactions in Bi- and Tl-compounds can not be neglected and so the model was extended to this case (see Fukuyama 1988).

3. Directions of further studies

The key to the understanding of the mechanisms responsible for high Tc oxides are briefly described below :

(i) The present experimental situation indicates that superconducting charge carriers are holes at oxygen sites in hole excess oxide materials. So any calculation which neglects entirely the aspects of two interacting bands, is bound to be unrealistic. The question is whether we can discuss both superconductivity and magnetic properties in terms of an effective band. The three principal models e.g. polaronic, kinetic exchange and RVB are all based on a single band. For the p band, U is small (< 2 eV) (Chang *et al* 1988). Consequently it is difficult to understand the models which are based on the assumption $U/W \gg 1$. Polaronic model stands on a better footing from this consideration. But in the case of strong local e-p interaction, phonon quenching of the band width would be large consequently W_p may become less than U_p so that it would be necessary to consider polaron formation in the strong correlation limit of the Hubbard model. Also, it might be necessary to consider mechanisms which oppose the polaron quenching effect. The single band picture is expected to be more valid for the recently discovered electron excess systems.

(ii) Most of the spectroscopic studies (Takahashi 1989, Chang *et al* 1988, Steiner *et al* 1988, show $U_d \sim 5$ eV or more. So a proper treatment of two-band system with U_d in the strong correlation limit and U_p in the HF limit would be useful for both excess hole and excess electron systems.

(iii) The $3D$-character of these systems can not be neglected. Indeed for Bi- and Tl-systems one can increase the number of interacting CuO_4 planes and this shows higher values of Tc. But of course, it is not possible to increase these layers indefinitely since this is limited by the stability conditions of the crystal structure. Also, it is to be noted that $Ba_{0.6}K_{0.4}BiO_3$ compound which is cubic and 3-dimensional is a superconductor with $Tc = 30$ K.

(iv) It is obvious from physical considerations and also accumulation of experimental results that both e-p interaction and correlation effects are important in these systems. The absence of isotope effect in $YBa_2Cu_3O_{7-\delta}$ systems alone

cannot negate the absence of *e-p* interaction as one of the principal cause of superconductivity in these systems. The presence of strong isotope effects in other systems as well as the recent explanations of the absence of this effect in Y-system show Anderson's arguments against the presence of *e-p* interaction may not be correct. Consequently, it is necessary to incorporate *e-p* interaction within the strongly correlated lower Hubbard subband on the one hand and to incorporate properly U in the polaron-bipolaron theories on the other hand.

(v) Since the pairing mechanism is of *S*-wave type the spin fluctuations do not play important role. But charge fluctuation effects arising from mixed valence character of these compounds might be an additional mechanism to the phonon induced one.

(vi) Since doping of the oxygen vacancies is a random process. The potential at a hole site would be distributed around a mean value. It is recently shown (Chakrabarti and Ray 1989) such disorder effects would influence Tc considerably. Substitution of other ions in these compounds has considerable effects in these compounds (Narlikar *et al* 1989). Validity of different models can be tested from proper analysis of these experimental results.

(vii) Another interesting domain of research is to study the self-energy and lifetime of phonons in these systems from elastic properties, sound wave anomalies, Raman shifts close to $T = Tc$.

We, therefore, see that the first phase of research is already over and we have entered the second phase where new experimental results from good crystals are being available on all the crucial aspects of the new superconductors. Theoretical models need to be further developed for proper understanding of the mechanisms responsible for the interesting properties and for possible applications.

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