

## Theory of high temperature superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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**Abstract.** A theory of high temperature superconductivity in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compound has been developed on the basis of the momentum pairing of electrons through the relativistic Darwin interaction. The transport behaviour of electrons is explained in terms of a mechanism of correlated electron transfer arising from the electron–phonon coupling. A model Hamiltonian has been developed to describe the superconducting properties of the system. This gives an energy gap which is higher than the BCS value. Attempts have been made to explain the absence of isotope effect, the linear dependence of specific heat, the presence of larger temperature-independent paramagnetism in the normal phase and the softening of some of the optic phonon modes observed in this system.

**Keywords.** High temperature superconductivity, Y-Ba-Cu-O; electron transport; Darwin interaction.

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### 1. Introduction

Several mechanisms of high temperature superconductivity have been proposed since its discovery by Bednorz and Müller in 1986. Amongst these, the resonating valence bond (Anderson 1987; Baskaran *et al* 1987; Kivelson 1987; Kotliar 1988), the charge transfer excitations (Varma *et al* 1987), the plasmon (Gersten 1988) and the bipolaron (Chakaravarty *et al* 1987) models have been developed and discussed with varying degrees of success. These attempts aim at finding a non-phononic mechanism which could account for the observed magnitude of the critical temperature and explain some of the exotic properties which the high  $T_c$  materials possess.

It is well known that superconductivity in oxidic systems depends critically on both the structure and composition. As there have been a large number of studies on different types of such materials, it is difficult to present a unified theory which can account for all the reported observations. In this paper we, therefore, confine our analysis to one system,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , which has been extensively studied. We present a theory of high-temperature superconductivity in this compound based on the Darwin interaction which we proposed earlier to account for momentum pairing in the superconducting phase (Srivastava 1984, 1985). We had also explained the origin of mobile electrons in these compounds based on a model of correlated electron transfer due to electron–phonon interaction (Srinivasan and Srivastava 1981; Srivastava 1987; Srivastava *et al* 1988).

The present theory depends heavily on the valence exchange process arising from a breathing type of mode of vibration of oxygen ions. The existence of this mode and

the presence of an ion which has large contribution to Darwin interaction to its on-site energy permit us to calculate the transition temperature and to account for some of the observed properties of this compound. In particular, we have explained the reason for the high values of  $2\Delta/k_B T_c$ , the linear dependence of resistivity on temperature in the normal phase, linear specific heat versus temperature dependence in the superconducting phase, large temperature-independent paramagnetic susceptibility in the normal phase and lack of isotope effect observed in this compound.

## 2. High $T_c$ oxides vs BCS superconductors

The normal state properties of high  $T_c$  oxides differ in several ways from the conventional BCS superconductors. Some of these are discussed below.

Experimental results indicate very little isotope effect. Batlogg *et al* (1987) and Bourne *et al* (1987) have found the value of  $\alpha$  in  $T_c \propto M^{-\alpha}$  as  $0 \pm 0.02$  and  $0 \pm 0.027$  when  $^{16}\text{O}$  is replaced by  $^{18}\text{O}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  by diffusion. Bourne *et al* (1987) have shown that  $\alpha = 0 \pm 0.1$  for Ba isotope substitution and  $\alpha = 0 \pm 0.07$  for Cu isotope substitution. Batlogg *et al* (1988) find a systematic decrease in  $\alpha$  with increasing  $T_c$  going from  $\text{Ba}(\text{Pb}, \text{Bi})\text{O}_3$  ( $T_c = 11$  K) ( $\alpha = 0.22 \pm 0.03$ ) to  $(\text{La}, \text{Sr})_2\text{CuO}_4$  ( $T_c = 36$  K,  $\alpha = 0.16 \pm 0.02$ ) and to the 1-2-3 compound quoted above.

The low temperature specific heat,  $C(T)$ , of the high  $T_c$  superconductors of  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\text{R} = \text{Y}, \text{Eu}, \text{Ho}, \text{Tm}$  and  $\text{Yb}$ ) observed by Ferreira *et al* (1988) indicate that for  $\text{R} = \text{Y}$  in the temperature range  $1.5 \text{ K} < T < 50 \text{ K}$ ,  $C(T)$  can be fitted to an equation

$$C(T) = C_e(T) + C_D(T) + C_E(T), \quad (1)$$

where  $C_e(T) = \gamma T$  and the subscripts  $D$  and  $E$  denote the Debye and Einstein terms for the lattice contribution to the specific heat. The observed values are  $\gamma = 8.21 \text{ mJ/mol K}^2$  and  $\theta_D = 383 \text{ K}$ . For  $T < 6 \text{ K}$  there is an upturn in the  $C$  vs  $T$  curve. On substitution with  $\text{R} = \text{Ho}, \text{Tm}$  and  $\text{Yb}$  there is no feature due to magnetic order above  $0.5 \text{ K}$  but there exist Schottky anomalies associated with crystalline electric field splitting of the ground state multiplet of the  $\text{R}^{3+}$  ion. The insensitivity of  $T_c$  to the incompletely filled shells of  $\text{R}$  ions possessing magnetic moments is quite different from the behaviour of conventional superconductors where the presence of paramagnetic ions significantly affects  $T_c$  (Maple 1973).

The presence of the linear term instead of the exponential dependence on  $T$  for the electronic contribution as  $T_c$  tends to zero is a major deviation from the BCS theory.

The energy gap has been investigated using the two well-known techniques viz. far infra-red (FIR) reflectance spectroscopy and tunnelling. In conventional superconductors the two techniques give identical results and measurements on temperature dependence of the energy gap are routinely obtained which agree with the BCS theory. In fact, tunnelling experiments have been used to obtain the density of states of phonons in metals which are in fair agreement with those obtained using neutron technique (Ginzburg and Kirzhnits 1982).

The early measurements of  $2\Delta/k_B T_c$  in lanthanum-strontium-copper oxide by several investigators (Walter *et al* 1987; Sulewski *et al* 1987; Schlesinger *et al* 1987) indicated that the values of the ratio obtained by the i.r. technique were smaller than

the BCS weak coupling result of 3.53 while the tunnelling measurements gave higher values. Similar conclusions were also obtained for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples (Kirtley *et al* 1987a, b; Bonn *et al* 1987). Recent measurements of Choudhari *et al* (1987) on epitaxial films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  have shown that both i.r. and tunnelling measurements give the same value of 4.5.

The analysis of FIR spectra using the Kramers-Kronig transformation of the reflectance by Bonn *et al* (1987, 1988) shows that there is no evidence of a true gap in the FIR spectra of the 1–2–3 compounds. The absence of the absorption band in i.r. studies is considered to be against the exciton-mediated electron pairing (Bozovic *et al* 1987).

Study of temperature dependence of infra-red and Raman spectra (Cardona *et al* 1988) of  $\text{MBa}_2\text{Cu}_3\text{O}_7$  ( $M = \text{rare earth}$ ) has shown an anomalous behaviour of optical phonons at  $310\text{ cm}^{-1}$  and  $280\text{ cm}^{-1}$ . A weak anomalous softening of these frequencies has been found when cooling below  $T_c$ . Such softening is not observed in BCS superconductors.

The Hall effect measurements on 1–2–3 compound have shown that sample-to-sample variations in oxygen content can affect the carrier concentration without affecting the  $T_c$  of the material. On the other hand, the change in density of states at the Fermi surface affects  $T_c$  in conventional superconductors in accordance with the BCS prediction.

We attempt to account for these differences between the high  $T_c$  and BCS superconductors on the model developed here.

### 3. Electronic structure and interaction with short wavelength phonons

The structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  compound was extensively discussed and it was concluded that it is orthorhombic and its space group symmetry is  $D_{2h}^1$  ( $Pmm$ ) (David *et al* 1987). The cations are located on four different sites O1, O2, O3, O4 and copper on two different sites. Cu1 is surrounded by a square planar oxygen (2O1 + 2O4) configuration and Cu2 is five-fold coordinated by a square pyramidal arrangement of oxygens (2O2 + 2O3 + O4). The Ba ions are ten-fold coordinated by oxygen ions that form a cubo-octahedron with two vertices missing. Yttrium is eight-fold coordinated with an approximate cube of oxygen ions. The planar O2-Cu2-O3 bonds lie between 1.93 Å and 1.96 Å. The apical Cu2-O4 bond length is 2.308 Å. Cu1-O4 bond length is the shortest and is 1.843 Å while Cu1-O1 is 1.942 Å. Cu1 forms one-dimensional chains of CuO in the  $b$ - $c$  plane linked parallel to the  $b$ -axis. The Cu2 forms planar-like groups corner-linked in the  $a$ - $b$  plane. These are weakly coupled to the  $b$ - $c$  plane CuO groups by the long apical Cu2-O4 bond.

Starting from a purely ionic picture of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (with oxidation numbers  $\text{Y}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{O}^{2-}$ ) Cu has a fractional oxidation number of 2.33. Since there is a large variation in the Cu-O bond length (1.843 Å to 2.306 Å) there are suggestions that disproportionation of  $\text{Cu}^{2+}(d^9)$  into  $\text{Cu}^+(d^{10})$  and  $\text{Cu}^{3+}(d^8)$  occurs in the compound which might even be responsible for superconductivity (David *et al* 1987). It has also been suggested that oxygen ions exist in  $\text{O}^{-1}$  states and there are evidences of  $\text{O}_2^{-}$  dimers in the compound (Rao 1987).

Electronic band properties of tetragonal  $\text{La}_{2-x}\text{Y}_x\text{CuO}_4$  have been investigated by several workers (Mattheiss 1987; Yu *et al* 1987). The study reveals that these properties

are dominated by the layered Cu3d-O-2p interactions. A half-filled band with two-dimensional character and a nearly square Fermi surface produces a Peierl's instability for  $x=0$  which leads via a soft-phonon mode to an orthorhombic phase and causes a semiconductor gap to open over the Fermi surface. Addition of divalent metals (Y = Ba, Sr) suppresses the instability and stabilizes the tetragonal phase.

Similar studies of electronic band structure for 1-2-3 compound have not been attempted. Although the structure of 1-2-3 is substantially different from  $\text{La}_2\text{CuO}_4$  both structures may be derived from the perovskite structure and contain corner-linked  $\text{CuO}_4$  square planar arrangements. We attempt a semi-empirical energy band diagram for the 1-2-3 compound based on studies made on the analogous  $\text{La}_{2-y}\text{X}_y\text{CuO}_4$  (Mattheiss 1987) and  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  alloy series (Mattheiss and Hamann 1983). In both systems the Fermi surface electrons have a substantially O2p character. Further, there are strong Cu-O or Pb/Bi-O bonds in both cases.

The essential features of the bands which are near the Fermi surface in  $\text{La}_2\text{CuO}_4$  arise from the strong nearest neighbour ( $pd\sigma$ ) interaction between Cu3d orbitals with  $x^2 - y^2$  symmetry and neighbouring O2p orbitals that are directed along the Cu-O bond axes in the  $xy$  plane. In the 1-2-3 compound the nature of the bands near the Fermi surface will depend on the oxidation states of the copper and oxygen atoms in the square planar configuration around Cu1 and square pyramidal configuration around Cu2. Despite extensive photoelectron studies (Alp *et al* 1987; Fjellvag *et al* 1987; Rao *et al* 1987), there is as yet no unanimity on the charge states present in the system. Despite other possibilities we take the oxidation states in the 1-2-3 compound as  $\text{Y}^{3+}\text{Ba}_2^+\text{Cu}_{3-2\delta}^{2+}\text{Cu}_{\delta/2}^{1+}\text{Cu}_{\delta/2}^{3+}\text{O}_{1-\delta}^{1-}\text{O}_6^{2-}$  which satisfies charge neutrality and is based on the current experimental evidence. This gives the total number of electrons per unit cell in the 3d-2p band as  $68 - 4\delta$  in the region  $0 \leq \delta \leq 1$ . We further assume that around the Cu1 site along the chain the repeating Cu-O complex is  $(\text{Cu}^{2+}\text{O}_{1-\delta}^{1-}\text{O}_2^{2-})$ . For the Cu2 site there are two  $(\text{Cu}_{3\delta/4}^{1+}\text{Cu}_{1-\delta}^{2+}\text{Cu}_{\delta/4}^{3+}\text{O}_2^{2-})$  complexes per unit cell which repeat. The arrangement for Cu1-O is shown in figure 1.

For a square planar  $(\text{CuO}_4)^{6-}$  complex, Kivelson and Nieman (1961) examined the correlation diagram and find that the  $d$ - $p$  bonding involving  $3dx^2 - y^2$  leads to the antibonding  $B_{1g}$  level which is the top occupied level in the complex. This level is singly occupied and as  $E_d > E_p$  Cu is magnetic.

Let us consider the 1-2-3 compound with  $\delta=0$  and assume that the system is tetragonal. The repeating  $(\text{CuO}_3)^{3-}$  complex along the chain involving Cu1 atoms has 14 electrons in the  $d$ - $p$  bonded states. The ordering of the levels depends on the relative magnitude of  $E_d$  and  $E_p$  on-site energies. If  $E_p$  is greater than  $E_d$ , we obtain the electron levels as shown in figure 2. The top level occupied is the bonding  $4p-2p$ ,

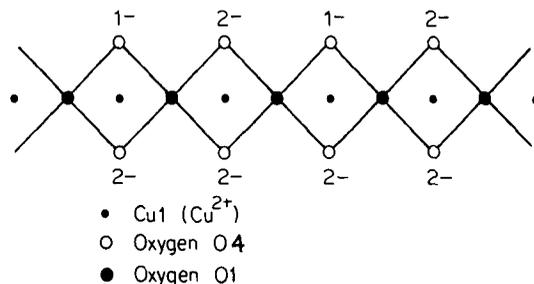


Figure 1. The chain linking of Cu1 atoms in the bc plane.

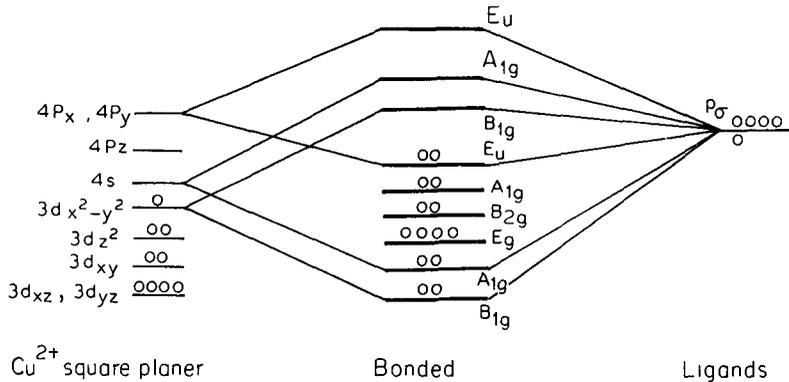


Figure 2. The electron states of  $(\text{CuO}_3)^{3-}$  which is the repeating complex unit along the chain involving CuI in a tetragonal structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

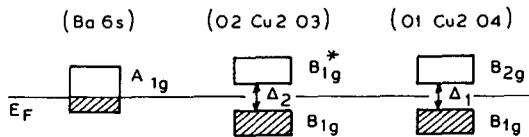


Figure 3. The electron band structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , near the Fermi surface without valence exchange

doubly degenerate Eu orbital which is only partially occupied. If there is orthorhombic transformation Eu will split into two orbital singlets  $B_{1g}$  and  $B_{2g}$  and if  $B_{1g}$  is lower it would be completely filled and  $B_{2g}$  will be completely empty and there will be a separation,  $\Delta_1$ , between them as shown in figure 3.

We next consider the Cu2 complex  $(\text{CuO}_2)^{2-}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . There are two such complexes per unit cell. There are only 13 electrons per unit complex and if  $B_{1g}$  is again the lower level it is only partially filled. But two neighbouring  $B_{1g}$  orbitals could combine to form bonding and antibonding orbitals, the bonding then would form the valence band and it is likely, if the width of the band is small, that it would be separated from the antibonding, i.e., conduction band by an energy gap,  $\Delta_2$ , as shown in figure 3.

Including the Ba6s states we may then have the electron band structure near the Fermi surface as shown in figure 3.

We have shown (Srinivasan and Srivastava 1981) that when mixed valent states of an ion are present on crystallographically equivalent sites the electron subsystem, by coupling with an active optical vibration, can reduce the energy of the system by an amount,  $\epsilon_p$ , the small polaron stabilization energy. This can be studied using the model Hamiltonian (Khomskii, 1982).

$$H = E \sum_i c_i^+ c_i + \sum_q \omega_q a_q^+ a_q + \sum_{i,q} g_{iq} c_i^+ c_i (a_q^+ + a_{-q}), \quad (2)$$

where  $g_{iq} = g_q \exp(iq \cdot \mathbf{R})$ . Here,  $c_i^+$  and  $c_i$  are the creation and annihilation operators for an electron at site  $i$ ,  $a_q^+$ ,  $a_q$  relate to phonons of wave vector  $\mathbf{q}$  and frequency  $\omega_q$ . The last term in (2) is the interaction between the electron and the phonon. Using

the polaron canonical transformation

$$\mathcal{H} \rightarrow \tilde{\mathcal{H}} = \exp(iR)\mathcal{H} \exp(-iR) \quad (3)$$

$$R = i \sum_{i,q} \frac{g_{iq}}{\omega_q} c_i^\dagger c_i (a_q^+ - a_{-q}) \quad (4)$$

yields

$$\tilde{\mathcal{H}} = \sum_i \left( E_d - \sum_q \frac{g_{iq}^2}{\omega_q} \right) c_i^\dagger c_i + \sum_q \omega_q \tilde{a}_q^\dagger \tilde{a}_q - \sum_{i,i'} J_{ii'} c_i^\dagger c_i c_{i'}^\dagger c_{i'}, \quad (5)$$

where

$$J_{ii'} = \sum_q \frac{g_q^2}{\omega_q} \exp\{iq \cdot (\mathbf{R}_i - \mathbf{R}_{i'})\} \quad (6)$$

and

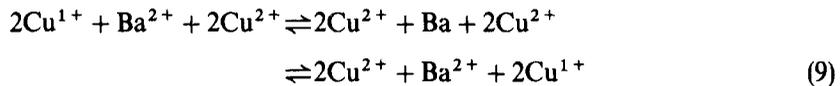
$$\tilde{a}_q = a_q + \sum_i \frac{g_{iq}}{\omega_q} c_i^\dagger c_i. \quad (7)$$

Equations (5) and (6) show respectively that there is a constant shift of the polaron energy and the electrons at different Cu-sites interact. The small polaron stabilization energy is

$$\varepsilon_p = \sum_q g_{iq}^2 / \omega_q. \quad (8)$$

In ionic crystals, we have shown that if mixed valent states of the ion are present on crystallographically equivalent sites the electron subsystem by coupling with optic modes of phonons can reduce its energy by a correlated electron transfer from one quantum state to another. Suppose an ion exists in a system in equal number with oxidation states  $+m$  and  $+n$  on a linear lattice. The charges are arranged in sequence  $mnmn \dots$ . For charge neutrality, the positive ions are separated by negative ions having charges  $-(m+n)/2$ . It is easy to see that in the static lattice approximation the two states,  $\psi_1$  and  $\psi_2$ , obtained by interchanging the ions  $+m$  and  $+n$  are degenerate. On coupling with a longitudinal optic mode the degeneracy of the system is removed and as shown by us (Srinivasan and Srivastava 1981) in magnetite the electron subsystem gains an energy  $\varepsilon_p = 0.055$  eV if the system exchanges between the two states on account of the electron-phonon coupling.

An electron-phonon interaction leading to the correlated electron transfer is possible also in the mixed valence 1-2-3 compound. When the value of  $\delta$  is non-zero Cu2 exists in the mixed valent state and the repeating complex O2-Cu2-O3 is in the state  $(\text{Cu}_{3\delta/4}^{1+} \text{Cu}_{1-\delta}^{2+} \text{Cu}_{\delta/4}^{3+} \text{O}_2^{2-})^{-2-\delta/2}$ . The valence exchange  $\text{Cu}^{1+} \rightleftharpoons \text{Cu}^{2+}$  or  $\text{Cu}^{2+} \rightleftharpoons \text{Cu}^{3+}$  can take place energetically more favourably via the  $\text{Ba}^{2+}$  ions using the reaction



There is evidence of the presence of neutral Ba in photoelectron spectroscopy (Fjellvag *et al* 1987).

The presence of a pair of electrons on the Ba site is important for superconductivity. It is on account of large Darwin interaction to this ion that momentum pairing leads to significant condensation energy in the superconducting phase. A relationship between the density of 6s states and  $T_c$  is derived later in §8.

The valence exchange  $O^{1-} \rightleftharpoons O^{2-}$  in the Cu1-O4 complex will lead to a uniform gain in energy,  $\epsilon_p$ , for electrons in the  $B_{1g}$  band. If the width of this band,  $\Gamma$ , is smaller than  $\epsilon_p$  we obtain the band structure as shown in figure 4. We have denoted the occupied correlated bands by  $\bar{B}_{1g}$ . The mobility of the charge carriers in the (O1Cu2O4) will be highest in the normal phase. After the superconducting gap opens in the 6s band below  $T_c$  (see figure 5) the transport is through the process given in (9).

If we have two neighbouring bands as shown in figure 3 and if an active optical vibration renormalizes the electronic spectrum, there is a change in the frequency of the vibration of the active mode (Fridkin 1980)

$$\omega'^2 = \omega^2 + \frac{4g^2\omega}{\hbar\Delta_1} [f_2 - f_1], \tag{10}$$

where  $f_1$  and  $f_2$  are the Fermi functions of the  $B_{1g}$  and  $B_{2g}$  bands respectively and  $\Delta_1$  is the separation between the bands. Here  $g$  is the electron-phonon interaction constant,  $w$  is the frequency of the phonon and  $w'$  is the modified frequency. Since

$$f_2 - f_1 = -\tanh(\Delta_1/4k_B T), \tag{11}$$

we obtain

$$\Delta\bar{\nu} = \bar{\nu}' - \bar{\nu} = -\frac{g^2}{\pi c \hbar \Delta_1} \tanh(\Delta_1/4k_B T). \tag{12}$$

A softening of the optical phonons associated with O2-Cu2-O3 bond stretching and bond bending modes of vibration is observed below  $T_c$  by Cardona *et al* (1987). Such softening is described by them as a universal property of all superconducting cuprates. We have made an attempt to fit the temperature dependence of the  $275 \text{ cm}^{-1}$  line observed by them to (12). Assuming that the unperturbed line has a wavenumber

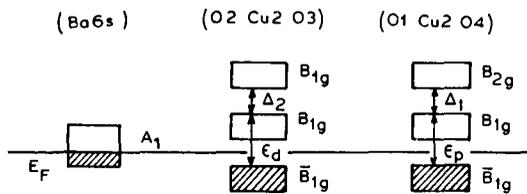


Figure 4. The electron band structure of  $YBa_2Cu_3O_{7-\delta}$  with electron-phonon coupling.

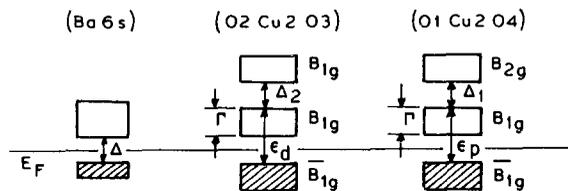
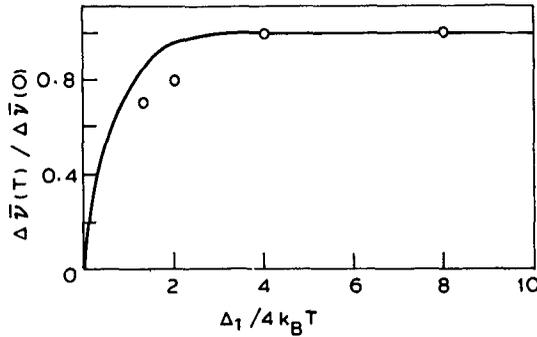


Figure 5. The electron band structure of  $YBa_2Cu_3O_{7-\delta}$  with electron-phonon coupling and with momentum pairing for the electrons in 6s band leading to the superconducting energy gap,  $\Delta$ .



**Figure 6.** The theoretical curve shown by the solid line is based on equation (12) (see text). Experimental points are from Cardona *et al* (1987).

of  $301 \text{ cm}^{-1}$ , and  $g = 0.028 \text{ eV}$ ,  $\Delta_1 = 0.13 \text{ eV}$ , we have plotted  $\Delta\bar{v}(T)/\Delta\bar{v}(0)$  in figure 6 where  $\Delta\bar{v}(0)$  refers to the 0 K value of  $\Delta\bar{v}$ . There is fair agreement of the observed data with theory.

#### 4. Normal state electrical transport

We obtain the expression for the conductivity of the system when the correlated electron transfer due to electron-phonon interaction occurs and the small polaron stabilization energy,  $\varepsilon_p$ , given by (8) is present. This problem has been examined by us for magnetite. It is shown (Srinivasan and Srivastava, 1981) that in this case the conductivity in the temperature range  $T_v < T < 300 \text{ K}$  is given by

$$\sigma = (f_+ - f_-)ne^2l^2\nu_0/k_B T, \quad (13)$$

where  $n$  is the electron density,  $l$  is the distance between neighbouring cations and  $\nu_0$  is the phonon frequency. Here  $T_v$  is the Verwey transition temperature. The expression

$$f_+ - f_- = [\exp(\varepsilon_p/2k_B T) + \exp(-\varepsilon_p/2k_B T)]^{-2} \quad (14)$$

is obtained from the one-dimensional random walk probability function (Goodenough 1982).

From (13) we obtain (Srivastava 1987)

$$\frac{\rho(T)}{\rho(300)} = \frac{T}{300} \frac{(f_+ - f_-)_{300}}{(f_+ - f_-)_T} \propto T \cosh^2(\varepsilon_p/2k_B T). \quad (15)$$

It has been shown that this model also applies to high  $T_c$  superconductors in the normal phase and (15) satisfactorily explains the data for several high  $T_c$   $\text{YBa}_2\text{Cu}_3\text{O}_{7-\varepsilon}$  samples (Srivastava *et al* 1988). In polycrystalline samples, the values of  $\varepsilon_p$  depend on the presence of superconducting and non-superconducting phases and their volume fractions.

From (15) it follows that for  $\varepsilon_p \ll k_B T$ ,  $\cosh(\varepsilon_p/2k_B T) \sim 1$  so  $\rho(T)/\rho(300)$  varies as  $T$ . This is observed for most of the well-prepared high  $T_c$  oxidic superconductors for which  $\varepsilon_p \approx 0.017 \text{ eV}$ . For a non-superconducting system as  $T_c$  is lowered we reach a

region where  $\epsilon_p > k_B T$ . The ratio then varies as  $T \exp(\epsilon_p/k_B T)$  and rises steeply as the temperature is lowered. Such a steep rise in resistivity is observed for  $\text{La}_2\text{CuO}_4$  for which  $\epsilon_p = 0.0075 \text{ eV}$  (Srivastava 1987). We conclude that for single phase materials (15) gives a satisfactory explanation for the conductivity data.

The measurement of Hall constant in epitaxial films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  by Choudhari *et al* (1987) has shown that the charge carriers are holes and their concentration decreases almost linearly from about 1 hole per formula unit at 300 K to 0.5 hole per formula unit at  $T_c$  which is at 90 K. This can be understood on the basis that the  $\bar{B}_{1g}$  band may have close to it acceptor levels with  $\text{O}^{2-}$  occupying lattice sites where  $\text{O}^{-1}$  should have been present. The concentration of occupied acceptor levels will decrease with decrease in temperature so that the concentration of the carrier density will decrease when temperature is lowered. However a simple application of semiconductor physics does not give satisfactory results, because, though the dominant source of charge carriers is provided by the Cu1-O band, Cu2-O band also plays a significant role in transport phenomena specially towards lower temperatures.

### 5. Hamiltonian for the superconducting phase

It has been proposed by us that the Cooper pairs in the superconducting phase are formed to lower the Darwin interaction energy of *s*-type conduction electrons to the minimum value possible by momentum pairing (Srivastava 1984, 1985).

In the model that we have developed the Hamiltonian for the superconducting phase can be written in the form

$$\mathcal{H} = \sum_i 2\epsilon_d d_i^+ d_i + \sum_i 2\epsilon_{ki} b_{ki}^+ b_{ki} + G \sum_i (b_{ki}^+ d_i + hc) + V \sum_{ii} b_{ki}^+ b_{ki} \quad (16)$$

Here  $d_i^+$ ,  $d_i$  are the pair creation and annihilation operators at site *i* for electrons in the O2-Cu2-O3 band,  $b_{ki}^+$  and  $b_{ki}$  are the pair creation and annihilation operators for the 6s conduction band near site *i*.

The first term describes the energy of the pairs of electrons associated with the O2-Cu2-O3 complexes, the second is the energy of the pair in the Ba6s conduction band, the third is the energy due to hybridization of the 6s conduction band state and the Cu2-O band state and the last term is the gain in energy due to momentum pairing in the conduction band which results in the vanishing of the Darwin interaction.

Following BCS, we attempt a trial wavefunction

$$\psi = \prod_i [\omega_i d_i^+ + u_i + v_i b_{ki}^+] |0\rangle. \quad (17)$$

With the normalization condition  $\langle \psi / \psi \rangle = 1$ , we obtain

$$\prod_i (\omega_i^2 + u_i^2 + v_i^2) = 1$$

or

$$\omega_i^2 + v_i^2 + u_i^2 = 1 \quad (18)$$

for all *i*.

The total number of particles  $N$  is fixed,

$$N = \frac{2 \langle \psi | \sum_i (d_i^+ d_i + b_{k_i}^+ b_{k_i}) | \psi \rangle}{\langle \psi | \psi \rangle} = 2 \sum_i (\omega_i^2 + v_i^2).$$

We use the method of Lagrange multipliers and minimize the energy

$$W = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} - 2\mu \frac{\langle \psi | \sum_i (d_i^+ d_i + b_{k_i}^+ b_{k_i}) | \psi \rangle}{\langle \psi | \psi \rangle} + \mu N \quad (19)$$

$\mu$  here is a Lagrange multiplier.

As  $N$  is fixed, we can neglect the last term. Using condition (18), we obtain, using another Lagrange multiplier,  $\lambda_i$ ,

$$W' = \sum_i 2(\varepsilon_d - \mu)\omega_i^2 + \sum_i 2(\varepsilon_{k_i} - \mu)v_i^2 + \sum_i \lambda_i(u_i^2 + v_i^2 + \omega_i^2) + 2G \sum_i \omega_i v_i + \sum_{\bar{u}} V u_i v_i u_{\bar{u}} v_{\bar{u}}. \quad (20)$$

Here

$$\mathbf{k}_{\bar{u}} = \mathbf{k}_i + \mathbf{g} + \mathbf{s}, \quad (21)$$

where  $\mathbf{g}$  is the reciprocal vector and  $\mathbf{s}$  is the satellite to  $\mathbf{g}$  due to phonon modes of vibration.

We introduce the energy gap parameter

$$\Delta_i = - \sum_{\bar{u}} V u_i v_{\bar{u}}. \quad (22)$$

Further, we minimize  $W'$  with respect to  $u_i$ ,  $v_i$  and  $\omega_i$  and obtain

$$\begin{aligned} 2(\varepsilon_d - \mu)\omega_i + \lambda_i \omega_i + G v_i &= 0, \\ 2(\varepsilon_{k_i} - \mu)v_i + \lambda_i v_i + G \omega_i + \Delta u_i &= 0, \\ \lambda u_i - \Delta v_i &= 0. \end{aligned} \quad (23)$$

Taking

$$\lambda_i = E_{k_i} - (\varepsilon_d - \mu) - (\varepsilon_{k_i} - \mu) \quad (24)$$

we obtain

$$\begin{aligned} [E_{k_i} + (\varepsilon_d - \mu) - (\varepsilon_{k_i} - \mu)]\omega_i + G v_i &= 0, \\ [E_{k_i} - (\varepsilon_d - \mu) + (\varepsilon_{k_i} - \mu)]v_i + G \omega_i + \Delta u_i &= 0, \\ [E_{k_i} - (\varepsilon_d - \mu) - (\varepsilon_{k_i} - \mu)]u_i - \Delta v_i &= 0. \end{aligned} \quad (25)$$

From (18) and (25) we obtain

$$\begin{aligned} u_i^2 &= (\Delta/E_1)^2 D, \quad v_i^2 = D, \quad \omega_i^2 = (G/E_2)^2 D \\ D &= \left( \frac{\Delta^2}{E_1^2} + \frac{G^2}{E_2^2} + 1 \right)^{-1}, \end{aligned} \quad (26)$$

where

$$E_1 = E_{ki} - (\varepsilon_d + \varepsilon_{ki}), \quad (27)$$

$$E_2 = E_{ki} + (\varepsilon_d - \varepsilon_{ki}),$$

$$E_{ki} = \pm [(\varepsilon_{ki} - \varepsilon_d)^2 + G^2 + \Delta^2]^{1/2}. \quad (28)$$

The energy gap equation gives

$$\Delta = \sum_{\vec{i}} V u_i v_i = N(0)V \int_{-\hbar\omega_c}^{\hbar\omega_c} \frac{\Delta}{E_1} \left( \frac{\Delta^2}{E_1^2} + \frac{G^2}{E_2^2} + 1 \right)^{-1} d\varepsilon, \quad (29)$$

where  $\omega_c$  is a cut-off frequency and  $N(0)$  is the density of states at  $E_F$ . This may be determined from the requirement that  $-E_1$  which is a measure of the condensation energy should be less than zero. For lower values of  $\varepsilon_k$ , we take the limit  $\varepsilon_{ki} = \varepsilon_d$ . In that case

$$E_1 = (G^2 + \Delta^2)^{1/2} - 2\varepsilon_d \geq 0. \quad (30)$$

For large  $\varepsilon_{ki}$  ( $\varepsilon_{ki} \gg \varepsilon_d$ )

$$E_1 = [(\varepsilon_{ki}^2 + G^2 + \Delta^2)]^{1/2} - \varepsilon_{ki} \simeq \frac{1}{2} \frac{G^2 + \Delta^2}{\varepsilon_{ki}}. \quad (31)$$

This tends to zero if  $\varepsilon_{ki} = \hbar\omega_c \gg (G^2 + \Delta^2)^{1/2}$ . In (29)

$$\begin{aligned} I &= \int \frac{\Delta}{E_1} \left( \frac{\Delta^2}{E_1^2} + \frac{G^2}{E_2^2} + 1 \right)^{-1} d\varepsilon \\ &= - \int \frac{E_1^2 + G^2 + \Delta^2}{2(E_1 + \varepsilon_d)^2} \frac{1}{E_1} \left( \frac{\Delta^2}{E_1^2} + \frac{G^2}{(E_1 + 2\varepsilon_d)^2} + 1 \right)^{-1} dE_1. \end{aligned}$$

For  $\varepsilon_d$  small compared to  $E_1$

$$I = \int \frac{dE_1}{2E_1} = -\frac{1}{2} \ln E_1.$$

On substituting the limits and using the approximation  $\hbar\omega_c \gg G, \Delta$  we obtain

$$(G^2 + \Delta^2)^{1/2} = 2\hbar\omega_c \exp(-1/N(0)V). \quad (32)$$

Proceeding as in BCS

$$\Delta_i = \sum_{\vec{k}, \vec{k}'} V_{k, k'} \frac{\Delta_{\vec{k}'}}{2E_{k'}} [1 - 2f(E_{\vec{k}'})] \quad (33)$$

leads to the relation

$$k_B T_c = 1.13 \hbar\omega_c \exp(-1/N(0)V). \quad (34)$$

This gives the critical temperature in terms of the cut-off frequency  $\omega_c$ ,  $N(0)$  and  $V$ .

## 6. Isotope effect

The cut-off frequency in (34) would be determined by the relevant  $g$  and  $s$  vectors in (21) which is decided by the structure and the phonon spectrum specially of the longitudinal optic mode. The physical requirement is the Bragg-like recoilless scattering of the electrons which satisfies Bragg condition even in the presence of lattice distortions due to phonons. The cut-off ensures that the condensation energy  $-E_1$  is negative. This, therefore, is, independent of the Debye frequency. This is shown below.

To put a pair of electrons in the coherent phase the pair  $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$  should be scattered to all possible  $(\mathbf{k} + \mathbf{g} + \mathbf{s}\uparrow, -\mathbf{k} - \mathbf{g} - \mathbf{s}\downarrow)$  modes by the lattice. The total number of electron states so coupled are

$$N = \left(\frac{L}{2\pi}\right)^3 \oint d\left(k_F^2 - \frac{g^2}{4}\right)^{1/2} \int dS_{\perp}. \quad (35)$$

where  $g$  is a reciprocal lattice vector less than  $2k_F$  and  $dS_{\perp}$  represents the area in momentum space generated by the lattice displacements and  $L^3$  is the volume of the crystal. We take  $(\mathbf{g} + \mathbf{s}) \cdot (\mathbf{X}_0 + \delta\mathbf{X}) = 2\pi n$  with  $\mathbf{g} \cdot \mathbf{X}_0 = 2\pi n$ . Here,  $\mathbf{X}_0$  is the nearest neighbour distance and  $\delta\mathbf{X}$  is the displacement.

We have

$$|s| = \mathbf{g} \frac{\langle \delta\mathbf{X}^2 \rangle^{1/2}}{|\mathbf{X}_0|}$$

and

$$\int dS_{\perp} = \pi s^2 = \pi \gamma g^2,$$

where (Pines 1964)

$$\gamma = \frac{\langle \delta\mathbf{X}^2 \rangle}{|\mathbf{X}_0|^2} = \frac{\hbar}{2NM} \frac{1}{X_0^2} \frac{1}{v_s^3} \frac{1}{(2\pi)^3} \sum_{\lambda} \int \frac{F_{\lambda}(\omega_q)}{\omega_q} d\omega_q. \quad (36)$$

Here  $M$  is the mass of the ion,  $N$  is the number of atoms per unit volume,  $v_s$  is the velocity of sound,  $F_{\lambda}(\omega_q)$  is the phonon spectrum and  $\omega_q$  is the frequency of mode. For dispersionless optic mode and a frequency spectrum  $F_{\lambda}(\omega_q)$  which peaks only near  $\omega_D$  from (35) and (36) we find that the cut-off frequency will be independent of  $M$ . The isotope effect thus would not be observed.

## 7. Energy gap

As discussed earlier amongst the two accepted techniques of the determination of the energy gap, the far infra-red reflectance(FIR) does not provide an unambiguous answer to the real gap. Careful tunnelling experiments in high  $T_c$  superconductors give values of  $2\Delta/k_B T_c$  which are higher than 3.53 and are close to 4.5. On the basis of the model that we have developed, as shown in figure 5, a Cooper pair has to be provided energy not only to break the coupling due to momentum pairing arising from the Darwin interaction but also to overcome the small polaron stabilization energy due to

electron-phonon coupling. Consequently, in tunnelling experiments we have an effective gap energy,  $\Delta_t$ , given by

$$\frac{2\Delta_t}{k_B T_c} = \frac{2(G^2 + \Delta^2)^{1/2} + 2(\varepsilon_d - \Gamma)}{k_B T_c} = 3.53 + \frac{2(\varepsilon_d - \Gamma)}{k_B T_c}. \quad (37)$$

If  $2\Delta_t/k_B T_c = 4.5$  and  $T = 90$  K (Choudhari *et al* 1987),  $\varepsilon_d - \Gamma = 0.0036$  eV.

### 8. Critical temperature

In our model from (21) and (22)

$$\Delta_0 = \sum_s V u_{k_i + g + s} v_{k_i + g + s}$$

with  $V$  given by (Srivastava 1985)

$$V = \frac{1}{N'} \frac{\pi}{2} \left( \frac{e\hbar}{mc} \right)^2 \{ Z_{\text{eff}} \langle \delta^3(\mathbf{x}_1) \rangle - \langle \delta^3(\mathbf{x}_1 - \mathbf{x}_2) \rangle \}, \quad (38)$$

$$N' = \left( \frac{L}{2\pi} \right)^3 \oint d \left( k_F^2 - \frac{g^2}{4} \right)^{1/2} \oint dS_{\perp} uv. \quad (39)$$

Here  $N'$  is defined from (35) and other symbols are given in the above reference. As shown by us,

$$T_c = \frac{\pi\eta}{3.53k_B} \left( \frac{e\hbar}{mc} \right)^2 Z_{\text{eff}} \langle \delta^3(\mathbf{x}_1) \rangle \quad (40)$$

Here,  $Z_{\text{eff}}$  is the effective nuclear charge seen by the  $s$ -electrons at the top of the Fermi surface and  $n_{\text{eff}}$  is the effective principal quantum number of the  $s$ -like state in which the electron is placed and

$$\eta = \frac{\int_{-\hbar\omega_c}^{\hbar\omega_i} N_s(0) u \cdot v d\varepsilon}{\left( \frac{L}{2\pi} \right)^3 \oint d \left( k_F^2 - \frac{g^2}{4} \right)^{1/2} \int dS_{\perp} uv}. \quad (41)$$

Here  $N_s(0)$  is the  $s$ -electron density of state at the Fermi surface. The values of  $\eta$  lie between 0 and 1.

The free atom value of the delta function in (38) for a hydrogen-like wavefunction is

$$\langle \delta^3(\mathbf{x}) \rangle = \frac{Z_{\text{eff}}^3}{\pi a_H^3 n_{\text{eff}}^3}. \quad (42)$$

From (17), the electron in the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> system is in the 6s band only for the  $(1 - \omega_i^2) = b^2$  fraction of time, so from (38) and (40), we have

$$T_c = 4.82\eta \frac{b^2 Z_{\text{eff}}^4}{n_{\text{eff}}^3}. \quad (43)$$

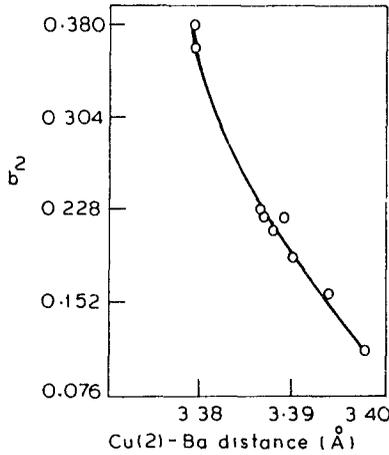


Figure 7. Variation of  $b$  with the distance between Cu(2)-Ba atoms in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

For  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  taking  $b^2 = 0.38$ ,  $\eta = 1$ ,  $Z_{\text{eff}} = (Z_i Z_0^{+2})^{1/3} = 7.96$  and  $n_{\text{eff}} = 4.2$  appropriate for  $\text{Ba}^{2+}$  we obtain  $T_c = 100$  K (Srivastava 1987).

Equation (43) indicates that it is possible to enhance  $T_c$  beyond 125 K, the present limit, by choosing the crystal structure and the ion with high Darwin interaction appropriately.

On this model  $b^2$  in (43) should depend on the distance between Cu2 and Ba ions.

In figure 7 we have plotted the variation of  $b^2$  with Cu2-Ba ion distance in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $0 < \delta < 0.7$ ) from the data of Cava *et al* (1987). The strong dependence of  $b^2$  on the bond distance is expected from the theory of bonding. The double plateau structure observed in  $T_c$  vs  $\delta$  curve of Cava *et al* (1987) can be accounted for in terms of the constancy of the Cu2-Ba bond distance in the range of  $\delta$  values within the plateaus

## 9. Specific heat

We show in this section that the linear term in equation (1) arises from the contribution to the heat capacity by the small polarons whose correlated motion, arising from the electron-phonon interaction, accounts for the transport properties. The small polaron can be considered to be a harmonic oscillator located on a linear chain. In the Debye approximation of a one-dimensional lattice, we obtain the energy,

$$E = \int_0^{\omega_m} d\omega \frac{L}{\pi v_s} \frac{\hbar\omega}{(\exp \beta\hbar\omega - 1)}, \quad (44)$$

where  $L$  is the length,  $v_s$  is the velocity of sound and  $\omega_m$  is the maximum oscillator frequency, Equation (44) leads to

$$C_v = \gamma' T, \quad (45)$$

where

$$\gamma' = \frac{1}{3} \frac{\pi^2 N k_B}{\theta}, \quad (46)$$

$$\theta = \hbar\pi v_s / k_B a. \quad (47)$$

Here  $k_B$  is the Boltzmann constant,  $a$  is the interatomic distance and  $N$  is the number of small polarons per mole. Since the small polaron stabilization energy obtained in (6) arises from the electron-phonon interaction only a fraction  $(\epsilon_p/k_B T_F)$  of the charged particles in the band would contribute to the heat capacity. Here  $T_F$  is the Fermi temperature. We then have

$$\gamma' = \frac{1}{3} \frac{\pi k_B}{\theta} \left( \frac{\epsilon_p}{k_B T_F} \right) N_a, \quad (48)$$

where  $N_a$  is the Avagadro's number.

Taking  $v_s = 10^5$  cm/s and  $a = 3.88 \text{ \AA}$  we obtain  $\theta = 56$  K. Further, taking  $\epsilon_p = 0.017$  eV and  $\epsilon_F = 1.14$  eV,  $\gamma' = 9.76$  mJ/mol K<sup>2</sup> which is in fair agreement with the experimental value of 8 mJ/mol K<sup>2</sup> (Ferreira *et al* 1988).

### 10. Magnetic susceptibility

The magnetic susceptibility,  $\chi$ , of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  ( $0.022 < \delta < 0.7$ ) as reported by Cava *et al* (1987) is strongly affected by the microscopic state of the oxygen subsystem  $\chi$  in the normal state is independent of temperature upto  $\delta = 0.5$ . A slight sign of a moment appears only at  $\delta = 0.7$ . The complete absence of ESR and NMR Cu<sup>2+</sup> signals in superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  samples in the normal state (Bowden *et al* 1987) further supports the view that local moments are absent in this compound.

In our model the susceptibility will be contributed by electrons in the two occupied  $\bar{B}_{1g}$  bands. The simple Pauli paramagnetism gives the value

$$\chi_{\text{para}}^{\text{Pauli}} = \left( \frac{g}{2} \mu_B^2 \right) N(0), \quad (49)$$

where  $g$  is the Landé  $g$ -factor,  $N(0)$  is the density of state at the Fermi surface and  $\mu_B$  is the Bohr magneton. Using (49) with 1 electron per formula unit we obtain with  $q = 2$

$$\chi_{\text{para}}^{\text{Pauli}} = 1.85 \times 10^{-6} \text{ emu/mol.}$$

This is about three orders of magnitude smaller than the observed value of  $10^{-3}$  emu/mol. The reason is that as our system has a small density of charge carriers we need to incorporate the exchange and correlation corrections to Pauli susceptibility (Zeiger and Pratt 1973). Expressing the susceptibility in emu per unit volume the Pauli paramagnetic susceptibility after corrections can be rewritten,

$$\chi_{\text{para}} = \frac{\chi_{\text{para}}^{\text{Pauli}}}{1 - \lambda \chi_{\text{para}}^{\text{Pauli}}}, \quad (50)$$

where  $\lambda = \lambda_{\text{ex}} + \lambda_{\text{corr}}$

$$\lambda_{\text{ex}} = \frac{1}{2\mu_B^2} \frac{e^2 (6\pi^2)^{4/3}}{18\pi^3} \left( \frac{n}{2} \right)^{-2/3}, \quad (51)$$

$$\lambda_{\text{corr}} = \frac{1}{2\mu_B^2} \frac{1}{n} \left\{ \frac{20}{9} r_s g'(r_s) + \frac{2}{9} r_s^2 g''(r_s) \right\}.$$

Here  $n$  is the electron density,  $\lambda_{\text{ex}}$  and  $\lambda_{\text{corr}}$  relate to corrections due to exchange and correlations respectively and  $r_s$  is the dimensionless parameter given by

$$\frac{4\pi}{3}(r_s a_B)^3 = \frac{1}{n}. \quad (52)$$

Here,  $a_B$  is the Bohr radius. The correlation energy per particle is given by the Wigner's expression

$$g(r_s) = \frac{0.88}{r_s + 7.8} \text{ Rydbergs}. \quad (53)$$

On evaluation, we obtain,  $\lambda_{\text{ex}} = 2.83 \times 10^6 \text{ (emu/cc)}^{-1}$  and  $\lambda_{\text{corr}} = 1.28 \times 10^6 \text{ (emu/cc)}^{-1}$ . In volume units  $\chi_{\text{para}}^{\text{Pauli}} = 0.393 \times 10^{-6} \text{ emu/cc}$ . We thus find that  $\lambda \chi_{\text{para}}^{\text{Pauli}}$  exceeds 1 indicating that there is a very large enhancement due to exchange and correlation to the simple Pauli temperature-independent susceptibility in accordance with the observations of Cava *et al* (1987).

## 11. Conclusion

We have outlined a theory of the high  $T_c$  superconductivity in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compound based on Darwin interaction which leads to momentum pairing in the superconducting phase. We have also accounted for the transport properties of this compound in the normal phase on the basis of a model of correlated electron transfer induced by the electron-phonon interaction. The theory satisfactorily accounts for the absence of isotope effect and the large magnitude of the critical temperature.

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