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ELECTRON-PHONON INTERACTION WITHIN THE FRAMEWORK OF THE FLUCTUATING VALENCE OF COPPER ATOMS - A THEORETICAL MODEL FOR HIGH TEMPERATURE SUPERCONDUCTIVITY

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Electron-phonon interaction is considered within the framework of the fluctuating valence of Cu atoms. Anderson's lattice Hamiltonian is suitably modified to take this into account. Using Green's function technique the possible quasiparticle excitations are determined. The quantity $2\Delta_k(0) / k_B T_c$ is calculated for $T_c = 40$ K. The calculated values are in good agreement with the experimental results.

The recent discovery of superconducting transition at high temperature in ceramic oxides[1,2] necessitates reconsideration of the conventional theoretical framework of superconductivity. The microscopic theory of BCS[3] with phonons plays the role of exchange particle cannot explain superconducting transition at temperatures as high as 40 K or 90 K.[4,5] Experiments show nearly the absence of isotope effect in these ceramic oxides.[6] The $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ group of materials have Cu–O layers which are the conducting planes of the crystal.[7,8] There is strong anisotropy in these materials.[9,10] By substituting Sr atoms with the La atoms of the parent compound La_2CuO_4, we can introduce holes into the oxygen $2p$ bands of the Cu–O planes.[11] In $YBa_2Cu_3O_{7-\delta}$ the introduction of oxygen vacancies affects the number of holes in the oxygen $2p$ bands of the Cu–O planes.[12] It is found that T_c in these materials have a strong dependence on hole concentration.[13]

Various theoretical models have been suggested to explain superconductivity in these ceramic oxides. Some of these theories assume a model system where the role of the $2p$ bands is not appropriately taken into account. Hubbard model Hamiltonian with the hopping term and the on site repulsive term are considered to contain the essential interactions to describe the superconducting transition. The RVB theory approaches the situation along these lines.[14] We are of the view that RVB description is correct in the insulating limit where antiferromagnetic

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correlation of the Cu spins is possible. When the material is doped, it leads to the creation of holes in the oxygen $2p$ bands unfavorably affecting super-exchange interaction between Cu spins. The Copper $3d^9$ electrons hybridizes with the oxygen $2p$ bands when there are holes in the $2p$ bands. The strength of this hybridization depends on the doping concentration. In this framework we are taking into account the interaction of the $2p$ band electrons with the lattice. Double occupancy of the Cu sites is energy-wise made unfavorable by the Hubbard on site repulsive term.[15] These requirements are satisfied by Andersons lattice Hamiltonian[16] with a few additional terms.

We assume that the electron-electron repulsive interaction is only of the on site Hubbard type and the effective electron phonon interaction can be replaced by a Frohlich type electron-electron interaction term.[17]

Under the above conditions, the Hamiltonian for the system takes the form

$$\begin{aligned} H = & \sum_{k,\sigma} \varepsilon_k C^\dagger_{k,\sigma} C_{k,\sigma} + E_0 \sum_{i,\sigma} a^\dagger_{i,\sigma} a_{i,\sigma} + \sum_q \hbar\omega_q b^\dagger_q b_q + U/2 \sum_{i,\sigma,\sigma'}{}' a^\dagger_{i,\sigma} a_{i,\sigma} a^\dagger_{i,\sigma'} a_{i,\sigma'} \\ & + V_1 / \sqrt{N} \sum_{i,k,\sigma} \{ e^{-ikRi} a^\dagger_{i,\sigma} C_{k,\sigma} + e^{ikRi} C^\dagger_{k,\sigma} a_{i,\sigma} \} \\ & + \sum_{q,k,\sigma} V_2(q) \{ C^\dagger_{k+q,\sigma} C_{k,\sigma} b_q + b^\dagger_q C^\dagger_{k,\sigma} C_{k+q,\sigma} \} , \end{aligned} \tag{1}$$

where ε_k is the band energy with wave vector k. $C^\dagger_{k,\sigma}$ and $C_{k,\sigma}$ are the fermion creation and annihilation operators for electrons in oxygen $2p$ bands. E_0 is the orbitally nondegenerate $3d^9$ energy level of Cu atom. $a^\dagger_{i,\sigma}$ and $a_{i,\sigma}$ are the Fermi creation and annihilation operators for electrons at site i in Cu $3d^9$ orbital. $b^\dagger_q$ and b_q are the phonon creation and annihilation operators. $\hbar\omega_q$ is the energy of the phonons in the qth mode. V_1 is the strength of hybridization between localized and band states. $V_2(q)$ is the strength of the electron phonon interaction.

The energy levels ε_k and E_0 are measured from the chemical potential and hence their values depend on the doping strength.

The Hamiltonian is brought from the site representation to the wave vector representation by defining the following relations

$$\begin{aligned} a^\dagger_{i,\sigma} &= 1/\sqrt{N} \sum_k a^\dagger_{k,\sigma} e^{-ikRi} \\ a_{i,\sigma} &= 1/\sqrt{N} \sum_{k'} a_{k',\sigma} e^{ik'Ri} . \end{aligned} \tag{2}$$

After substituting and replacing the electron-phonon interaction terms with the Frohlich type electron-electron interaction term, the Hamiltonian becomes

$$\begin{aligned} H = & \sum_{k,\sigma} \varepsilon_k C^{\dagger}_{k,\sigma} C_{k,\sigma} + E_0 \sum_{k,\sigma} a^{\dagger}_{k,\sigma} a_{k,\sigma} \\ & + U/2N \sum_{\substack{k_0, k_1, k_2, \\ \sigma, \sigma', \sigma = \sigma'}} a^{\dagger}_{k_2 + k_0,\sigma} a^{\dagger}_{k_1 - k_0,\sigma'} a_{k_1,\sigma'} a_{k_2,\sigma} \\ & + V_1 \sum_{k,\sigma} [a^{\dagger}_{k,\sigma} C_{k,\sigma} + C^{\dagger}_{k,\sigma} a_{k,\sigma}] \\ & + \sum_{\substack{k,k', \\ q,\sigma,\sigma'}} V_2 (k,k',q) C^{\dagger}_{k+q,\sigma} C^{\dagger}_{k',\sigma'} C_{k'+q,\sigma'} C_{k,\sigma} \,. \end{aligned} \tag{3}$$

Now consider the retarded Green's functions[18]

$$G_1 \equiv \langle\langle C^{\dagger}_{k,\sigma}(t); C_{k',\sigma'}(t')\rangle\rangle = \theta(t - t') \langle [C^{\dagger}_{k,\sigma}(t), C_{k',\sigma'}(t')] \rangle \tag{4}$$

$$G_2 \equiv \langle\langle a^{\dagger}_{k,\sigma}(t); C_{k',\sigma'}(t')\rangle\rangle = \theta(t - t') \langle [a^{\dagger}_{k,\sigma}(t), C_{k,\sigma'}(t')] \rangle \,. \tag{5}$$

The equation of motion for G_1 and G_2 will be

$$i\frac{d}{dt} G_1 = i\delta(t-t') \langle [C^{\dagger}_{k,\sigma}(t), C_{k,\sigma'}(t')] \rangle + \langle\langle [C^{\dagger}_{k,\sigma}(t), H]; C_{k,\sigma'}(t')\rangle\rangle \tag{6}$$

$$i\frac{d}{dt} G_2 = i\delta(t-t') \langle [a^{\dagger}_{k,\sigma}(t), C_{k,\sigma'}(t')] \rangle + \langle\langle [a^{\dagger}_{k,\sigma}(t), H]; C_{k,\sigma'}(t')\rangle\rangle \,. \tag{7}$$

When the commutators $[C^{\dagger}_{k,\sigma}(t),H]$ and $[a^{\dagger}_{k,\sigma}(t),H]$ are evaluated and substituted in Eqs. (6) and (7), we find that they contain terms with higher order Green's functions in addition to the terms with the lower order Green's functions G_1 and G_2. These higher order Green's functions are decoupled by writing them as the product of correlation function and a lower order Green's function G_1 or G_2. Thus Eqs. (6) and (7) become

$$i\frac{\partial}{\partial t} G_1 = i\delta(t-t')\, \delta_{\sigma,\sigma'}\, \delta_{k,k'} + P_2 G_1 - V_1 G_2 \tag{8}$$

$$i\frac{\partial}{\partial t} G_2 = P_1 G_2 - V_1 G_1 \,, \tag{9}$$

where

$$P_1 = - [E_0 + U/N + U/N \sum_{k_1} \langle a^{\dagger}_{k_1,\sigma'} a_{k_1,\sigma'}\rangle] \tag{10}$$

$$P_2 = - [\varepsilon_k + 2 \sum_{k',\sigma'} V_2(k' - k) \langle C^{\dagger}_{k',\sigma'} C_{k',\sigma'}\rangle] \,. \tag{11}$$

In obtaining the two equations of motion standard decoupling and approximation methods are adopted at the higher stage. The Fourier transform of the two equations of motion are found. Solving them, $G_1(E)$ and $G_2(E)$ are found.

$$G_1(E) = \frac{i/2\pi\,\delta_{k,k'}\,\delta_{\sigma,\sigma'}}{\{(E - P_2) - V_1^2/(E - P_1)\}} \tag{12}$$

and

$$G_2(E) = \frac{-i/2\pi\,\delta_{k,k'}\,\delta_{\sigma,\sigma'}\,V_1/(E - P_1)}{\{(E - P_2) - V_1^2/(E - P_1)\}} \,. \tag{13}$$

Diagonalizing the set of coupled Fourier transform of the equations of motion, we get

$$G_{\mp} = U_k G_2(k, k', E) \mp V_k G_1(k, k', E) \tag{14}$$

with energies

$$E_{\mp} = [P_2 + P_1 \mp \sqrt{(P_1 - P_2)^2 + 4V_1^2}] \,, \tag{15}$$

where U_k and V_k are given by

$$U_k = 1/\sqrt{2}\left[1 - \frac{(P_2 - P_1)}{\sqrt{(P_2 - P_1)^2 + 4V_1^2}}\right]^{1/2} \tag{16}$$

$$V_k = 1/\sqrt{2}\left[1 - \frac{(P_2 - P_1)}{\sqrt{(P_2 - P_1)^2 + 4V_1^2}}\right]^{1/2} \,. \tag{17}$$

The system can be described as an assembly of noninteracting quasiparticles belonging to two different species, characterized by excitation energies $E_{\pm}$ and the corresponding creation operators are

$$a^{\dagger}_{\pm,\sigma}(k) = U_k a^{\dagger}_{k,\sigma} \pm V_k C^{\dagger}_{k,\sigma} \,. \tag{18}$$

Thus we are making a canonical transformation from the original set to a new set.

The various terms of the Hamiltonian are expressed in terms of the quasiparticle operators. By doing this, we intend to diagonalize the Hamiltonian. Expressing the original operators in terms of the new operators, we have substituted for various operators the combination of new operators. As expected, the Hamiltonian is not in the diagonal form. It contains off-diagonal terms of the form $a^{\dagger}_{+,\sigma}(k)a_{-,\sigma}(k)$ and $a^{\dagger}_{-,\sigma}(k)a_{+,\sigma}(k)$. It also contains terms which involve four operators which do not satisfy the conservation of quasiparticle species. Such terms are neglected. Those fourth order terms which conserve quasiparticle species are combined and their coefficient is equal to zero. Simplifying we get

$$V_2(k,k') = -U/2N\,[V_k^2 V_{k'}^2/U_k^2 U_{k'}^2]\ . \tag{19}$$

At 0 K very few quasiparticles are excited and hence the number operators for quasiparticles $m_{+,\sigma}(k)$, $m_{-,\sigma}(k)$ etc. have vanishingly small expectation values. Therefore off-diagonal terms and fourth order terms containing number operators are neglected.

Equating the coefficient of off-diagonal terms to zero, after simplification, we have

$$E_0 V_k^2/U_k^2 - \varepsilon_k = -\sum_{k'} V_2(k,k')\ . \tag{20}$$

By using Eq. (19) for $V_2(k,k')$, Eq. (20) leads to

$$\frac{E_0 V_k^2}{U_k^2} - \varepsilon_k = U/2N\,[V_k^2/U_k^2] \sum_{k'} V_{k'}^2/U_{k'}^2 \tag{21}$$

putting $\quad U_k = (1/2 + x_k)^{1/2}$ and $V_k = (1/2 - x_k)^{1/2}$.

By substituting U_k and V_k and then putting

$$U/2N \sum_{k'} \left[\frac{(1/2 - x_{k'})}{(1/2 + x_{k'})}\right] = \Delta_k(0) \tag{22}$$

we obtain

$$x_{k'} = \frac{1/2(E_0 - \Delta_{k'}) - \varepsilon_{k'}/2}{(E_0 + \varepsilon_{k'} - \Delta_{k'})}\ . \tag{23}$$

Substituting for $x_{k'}$ in the equation for Δ_k, the energy gap at 0 K leads to

$$\Delta_k(0) = U/2N \sum_{k'} \frac{\varepsilon_{k'}}{\{E_0 - \Delta_{k'}(0)\}}\ . \tag{24}$$

Assuming Δ_k as slowly varying with k and introducing $D(\varepsilon_k)$ as the density of localized states per Cu atom, we get

$$\Delta_k(0) = \frac{U}{2\{E_0 - \Delta_k(0)\}} \int_0^{\varepsilon_{k_0}} D(\varepsilon_{k'})\varepsilon_{k'}\, d\varepsilon_{k'}\ , \tag{25}$$

where ε_{k_0} is the upper bound of the hybridized $2p$ bands, and $D(\varepsilon_k)$ is the density of localized states per Cu atom. For each value of ε_k there are two values of

ω and hence we have to sum the two density of states corresponding to E_+ and E_-. Linear relations are assumed to hold between the doping strength x and the parameters E_0, ε_{k_0} and V_1.

Since the Fermi level decreases linearly with doping, the relationship between E_0 and the doping strength x will be $E_0 = R_1 x + 0.5$. In the undoped case $x = 0$, the localized Cu state and the narrow $2p$ band of oxygen atoms are of nearly equal energy. This justifies the introduction of the small energy difference 0.5 between the upper bound of the $2p$ band and the Cu $3d^9$ level. ε_{k_0} is the top most level of the $2p$ band as measured from the Fermi level and hence the relation $\varepsilon_{k_0} = R_2 x$ holds. The hybridization parameter V_1 should change with the overlapping integral which in turn has a linear dependence on the concentration of the dopants in the out of the plane sites. Therefore we choose $V_1 = V_{10} + R_3 x$, where V_{10} stands for the residual mixing parameter.

We have assigned the following numerical values. R_1, R_2, and R_3 are given the values 2.0, 2.0, and 0.2, respectively. $V_{10} = 0.05$, $V_2 = -0.056$ eV, $U = 6.0$ eV and the density of band states per Cu atom = 1.0.

The set of equations for the Green's functions are solved and the correlation functions in P_1 and P_2 are found by iterative computation. For $x = 0.19$, the computed values are

$$2\sum_k V_2 \langle C^\dagger_{k,\sigma} C_{k,\sigma}\rangle = -0.8866886 \times 10^{-5} \quad \text{and}$$

$$1/N \sum_{k'} \langle a^\dagger_{k',\sigma'} a_{k',\sigma'}\rangle = 0.7841363 \times 10^{-4} \, .$$

The density of localized states is calculated using Green's function technique with the help of a digital computer. Substituting for the density of states, the integration is performed and hence $\Delta_k(0)$ is calculated. Corresponding to $x = 0.19$, $\Delta_k(0)$ has the value 6.4326×10^{-3} eV and $2\Delta(0)/k_B T_c = 3.739$ for a $T_c = 40$ K.

Detailed calculation of the variation of energy gap with doping strength and temperature will be published elsewhere. The mixing parameter is determined by the overlap integral of the band states with the localized states of Cu atom. This integral is determined by the ordering of the out of the plane dopants, which have a quasi periodic character.

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