ELECTRON - PHONON INTERACTIONS AND ITS ROLE IN HIGH-T_c SUPERCONDUCTIVITY

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A THESIS SUBMITTED IN PARTIAL FULLFILLMENT FOR
THE REQUIREMENTS OF THE DEGREE OF MASTER OF SCIENCE
IN PHYSICS IN THE ADDIS ABABA UNIVERSITY

JUNE, 1989
ADDIS ABABA,

ACKNOWLEDGEMENTS

My first and foremost heartfelt gratitude should go to my advisor and instructor Dr. V.N. Malnev for his keen encouragement and invaluable guidance throughout the work. I whould also like to acknowledge my debt to Dr. V.N. Malnev who aroused my interest in the field of superconductivity.

I also would like to thank Dr. S.C. Chhajlany for his helpful discussions, specially on the part of double-wells and to SAREC for financial support through Ethiopian Science and Technology Commission.

Last but not least I would like to express my deep indebtedness to W/o Birikty Paulos who typed the manuscript so neatly.

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ABSTRACT

The electron-phonon interaction based on the harmonic approximation for phonons is discussed by considering several physical models. Some consequences of this interaction, such as the possibility of cooper pairing and the BCS theory of superconductivity are described.

Two proposed mechanisms of High-T_c superconductivity both based on the electron-ion interaction of electron pairing are discussed. A 2D BCS model results the observed values of T_c and the absence of the isotope effect in its conventional form. Another model based on the non harmonic double-well potentials in the cu-o chain in YBCO is also studied. A qualitative prediction of the effect of pressure on T_c and the smallness of the critical current is made.

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INTRODUCTION

The main objective of this work is primarily the description of the electron-phonon interaction, that is the interaction between electrons in solids arising through a medium of ions. The most impressive result of such an interaction is that two electrons may attract each other with a potential exceeding the coulomb repulsion. In the case of a harmonic motion of ions in a crystal the situation is well understood and the application of standard methods of the electron-phonon interaction, like the deformation potential gives results which are in good agreement with experiment. The greatest success of the modern theory of the electron-phonon interactions is undoubtedly the BCS microscopic theory of low temperature superconductivity.

In the first chapter of this work we give a brief description of the concept of phonons in solids. The second chapter contains a discussion of electrons in metals using some simple models like the homogeneous electron gas. The idea of Copper instability is also considered in this chapter. The third chapter is devoted to a review of the electron-phonon interaction and some physical consequences of such an interaction, like polarons and the coupling of electrons in the BCS theory.

The discovery of materials with a comparatively high transition temperature by Bednorz and Müller in 1986 and Wu etal in 1987 lead people to a study of the behavour of these materials.

From experimental evidences these newely discovered materials exhibit new features which were not observed in the conventional superconductors. Their superconducting properties are influenced by 2D layer of cu-o atoms or a 1D chain of cu-o atoms. Some of these atoms (o) are observed to be in a non-harmonic crystal potential.

Another obstacle in the theory of this materials is that the properties observed experimentally are as diverse as the kind of materials. Most properties which were common in the low-T_c superconductors, like the isotope effect are not now a universal feature of all these materials. Up to now there is no single theory which could explain successfuly all these diverse features. At present a lot of attempts have been made by theoretists to understand the mechanism of high-T_c superconductivity.

In the last chapter we have studies some properties of high-T_c superconductivity. A short review of the relevant experimental facts of this materials is first given. We then considered two possible mechanisms of high-T_c superconductivity based on the electron-ion interaction as the cause of superconductivity.

Some original qualitative predictions are also made as the outcomes of the models.

CHAPTER I

1.1 PHONONS IN THE HARMONIC APPROXIMATION

An important component of solids is the crystaline lattice. The motion of ions in a solid is relatively slow due to their large mass compared to the mass of an electron. The interaction between ions in a solid is of short range due to screening effects by electrons.

For comparatively low temperatures and small amplitudes of vibrations the lattice can be considered as a system of coupled oscillators. Using the theory of small vibrations it is possible to reduce the motion of this coupled oscillators to the motion of independent oscillators (normal modes) [1]

Let us expand the potential energy of the crystalline lattice in to a Taylor series with respect to the displacements of ions from their equilibrium position which is assumed to be small as:

$$V = V_0 + \frac{1}{2} \sum_{\substack{\bar{l},\bar{j},s \\ \ell,j',s'}} \frac{\partial^2 V}{\partial U^{s}_{\bar{\ell} j} \; U^{s'}_{\bar{\ell}' j'}} \left(U^{s}_{\bar{\ell},j} - U^{s'}_{\bar{\ell}',j'}\right)^2 + \qquad (1.1.1)$$

Where V_0 is the potential energy of the crystal when all atoms are at their lattice sites. $\vec{\ell}$ and $\vec{\ell}'$ are position vectors of lattice sites, j and j' are cartesian components of the lattice displacement vector. s and s' are the kind of atomsin a given primitive cell.

$U_{\bar{\ell},j}^{s'}$ are the displacement of the corresponding ion from equilibrium

The equation of motion of the system will be:

$$M_s \ddot{U}_{\bar{\ell}j}^{s} = - \sum_{\bar{\ell},\bar{j},s'} \frac{\partial^2 V}{\partial U_{\bar{\ell}j}^{s} \, \partial U_{\bar{\ell}'j'}^{s'}} U_{\bar{\ell}'j'}^{s'} \qquad (1.1.2)$$

The translation symmetry of the crystal permits U_s to seek the solution in the form:

$$U_{\bar{\ell}j}^{s} = U_{o}^{s} \; e^{i\bar{k}.\bar{\ell} - i\omega t}$$

ω - is the frequency of the collective motion of all atoms and the allowed set of $\bar{k}$ - values is determined from cyclic boundary condition.

One can get a nontrivial solution by demanding the derterminant to be zero. i.e.

$$\mathrm{Det} \; \{ D_{ss}^{jj'} \; (\bar{k}) \; - \omega^2 M_s \; \delta_{ss'} \; \delta_{jj'} \} = 0 \qquad (1.1.3)$$

Where

$$D_{ss}^{jj'} \; (\bar{k}) = \sum_{(\bar{\ell}-\bar{\ell}')} \frac{\partial^2 V}{\partial U_{\bar{\ell}j}^{s} \; \partial U_{\bar{\ell}'j'}^{s}} \; \exp\{ i\bar{k}.(\bar{\ell}-\bar{\ell}') \}$$

is the Dynamical matrix.

Here summation over s is to run through 3ν values, where ν is the number of atoms in a primitive cell.

This is an equation of power 3ν in ω^2, which has 3ν roots denoted by ω^2_{α} (k), where α has 3ν values.

These frequencies are referred to as the normal mode frequencies of the lattice vibrations.

Due to time reversal symmetry we have:

$$\omega_\alpha(\vec{k}) = \omega_\alpha(-\vec{k})$$

and from the translational invariance of the solid we found that:

$\omega_\alpha(\vec{k}) = \omega_\alpha(\vec{k}+\vec{G})$, where $\vec{G}$ is a reciprocal lattice vector defined by:

$\vec{G} = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3$, n_1, n_2, n_3 are integers and $\vec{b}_i$'s are the reciprocal basis vectors of the crystal. The lattice frequency spectrum $\omega_\alpha(\vec{k})$ has in general two branches dependending on their behaviour for small $\vec{k}, \vec{k} \to 0$. Three of the branches have the property that, the frequency goes to zero as $k \to 0$ as:

$\omega_\alpha(k) = C_\alpha k, \alpha = 1,2,3$, where C_α's are the speed of sound in the solid. Two of the modes are transverse and one is longituidnal. We call these three modes the acoustic branch. The rest $3\nu - 3$ modes have a non zero frequency when $k \to 0$, i.e.

$\omega_\alpha(k) = \omega_{o\alpha}$, for $\alpha = 4, \ldots, 3\nu$ and $\omega_{o\alpha}$ are constants. We refer to these modes as the optical branch. If there is no degeneracy in the frequency spectrum we can expand the optical modes for small $\vec{k}$ as:

$$\omega_\alpha(\vec{k}) = \omega_{o\alpha} + \tfrac{1}{2} a_{ij} k_i k_j \qquad (1.1.4)$$

Here a_{ij} is a constant matrix.

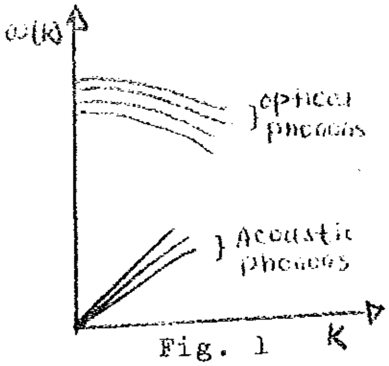

Fig. 1

Optical modes are high frequency vibrations. In ionic crystals these modes particularily the transverse optical mode strongly couples with the electromagnetic wave.

Most properties of a solid depend on the form of the lattice spectrum $\omega_\alpha(\vec{k})$. Usually it is impossible to get analytical solution for $\omega_\alpha(\vec{k})$ in three dimensions. It is only in one and two dimensions taking nearest neighbour interactions that on can get a simple form of $\omega_\alpha(\vec{k})$. For many applications in thermodynamics, transport and electrical properties it is desirable to introduce the density of states or the frequency distribution function defined as:

$G_\lambda(\omega)\ d\omega_\lambda$ - is the fractional number of frequencies in the range between ω and $\omega + d\omega$ in mode λ.

The counting of states is done using either Kronecker delta $\delta_{\omega',\omega j}(\vec{k})$ or by the delta function $\delta(\omega - \omega_j(\vec{k}))$. Thus

$$G_\lambda\ (\omega) = \sum_{\lambda k} \delta_{\omega',\omega\lambda}(k) \simeq \int d^3k\ \delta(\omega - \omega_\lambda(k)) \qquad (1.1.5)$$

Another possible form of the density of states is to reduce the integral into a surface integral by replacing [2].

$$d^3k \to \left(\frac{ds_\omega}{|\nabla_K \omega|} \right) d\omega$$

Where ds_ω is an element of area on a surface of constan frequency and $\nabla_\kappa \omega$ is the gradient of the frequency function with respect to wave vector κ.

Hence,

$$G_\lambda(\omega) = \frac{\Omega}{8\pi^3} \int \frac{ds_{\omega\lambda}}{|\nabla_\kappa \omega_\lambda(\kappa)|} \text{, and integration} \qquad (1.1.6)$$

is over a surface of constant frequency ω. Ω is the volume of the primitive cell.

There are many points in the Brillouin zone where $|\nabla_\kappa \omega|$ is required to vanish by reasons of symmetry. This is also a result of the Van Hove theorem that the lattice spectrum must contain at least one critical point. Hence the density of states will have singularity points.

These singularities are also found in electron density of states because the band energy $\varepsilon(\kappa)$ is a continous function in the reciprocal lattice vector, with the periodicity of the reciprocal lattice. Hence the arguments of Van Hove's theorem applies to it. A special interest is when the singularities lie at the Fermi level. Because most electron properties in metals are affected by those electrons near the Fermi level it will have observable effects. When we come to superconductivity the coupling constant in the BSC theory is directly proportional to the density of electron states at the Fermi level as given in (3.6.14). Hence these singularities will enhance the critical temperature considerably [11].

In general for one dimensional systems we will have singularities of the form:

$$G(\omega) \;\alpha\; \frac{1}{\omega - \omega_o} \qquad \text{at} \qquad \omega = \omega_o \qquad (1.1.7)$$

and in two dimensional lattice systems the density of states will have logarithmic singularities as:

$$G(\omega) \;\alpha\; \ell_n\left(\frac{1}{\omega - \omega_o}\right) \qquad (1.1.8)$$

1.2 Quantization of Lattice Vibrations

The classical Hamiltonian written interms of normal coordinates is given by

$$H = \tfrac{1}{2} \sum_{\lambda,\kappa} \{ P_\lambda(\kappa) P_\lambda(-\bar{\kappa}) + \omega_\lambda{}^2(\kappa)\; Q_\lambda(\kappa) Q_\lambda(-\kappa) \qquad (1.2.1)$$

Where

$Q_\lambda(\bar{\kappa})$ is defined by [2]

$$U^s_{\vec{\ell} j} = (NM_s)^{-\frac{1}{2}} \sum_{\lambda,\bar{\kappa}} \vec{e}^{\,\lambda}_{js}(\bar{\kappa})\; Q_\lambda(\kappa)\; \exp\{ i\bar{\kappa}.\bar{R}_j \}$$

Here $\vec{e}^{\,\lambda}_{js}$ are the eigen unit vectors of the dynamical matrix given in (1.1.3), $U_{\ell j}$ is the j^{th} component of the displacement of an atom of kind s in a unit cell at position $\vec{R}_\ell$.

$P_\lambda(\kappa) \doteq \dot{Q}_\lambda(\kappa)$ is the normal mode momentum.

The transition to quantum mechanics is made by regarding the $Q_\lambda(\kappa)$ and $P_\lambda(\kappa)$ as quantum mechanical operators with the commutation relation:

$$[Q_\lambda(\kappa), P_{\lambda'}(\kappa')] = i\hbar\, \delta_{\kappa\kappa'}\, \delta_{\lambda\lambda'} \tag{1.2.2}$$

and

$$[Q_\lambda(\kappa), Q_{\lambda'}(\kappa')] = [P_\lambda(\kappa), P_{\lambda'}(\kappa')] = 0$$

Where all wave vectors are inside the 1st Brillouin Zone.

We will now introduce creation and annihilation operators

$$a^+_{\kappa\lambda} = \left(\frac{M.\omega_\lambda(\kappa)}{2\hbar}\right)^{\frac{1}{2}} . \left(Q_\lambda(-\kappa) - \frac{i\,P_\lambda(\kappa)}{M\omega_\lambda(\kappa)}\right) \tag{1.2.3}$$

$$a_{\kappa\lambda} = \left(\frac{M\omega_\lambda(\kappa)}{2\hbar}\right)^{\frac{1}{2}} . \left(Q_\lambda(\kappa) + \frac{i\,P_\lambda(-\kappa)}{M\omega_\lambda(\kappa)}\right)$$

With Bose type of commutation relations.

The Hamiltonian of the system expressed interms of these operators will be:

$$\hat{H}_{ph} = \sum_{\kappa,\lambda} \hbar\omega_\lambda(\kappa)\left(a^+_{\kappa\lambda} a_{\kappa\lambda} + \tfrac{1}{2}\right) \tag{1.2.4}$$

With its eigen functions given by:

$$|\, n_1, \ldots, n_s, \ldots > = \frac{(a_1^+)^{n_1} \ldots (a_s^+)^{n_s} \ldots |0>}{n_1! \ldots n_s! \ldots} \tag{1.2.5}$$

Here $|\,0>$ is the vacuum state with no phonons excited.

If we compare the thermal average energy of the system with the average energy of a system of independent oscillators

We get:

$$< a^{+}_{\kappa\lambda} a_{\kappa\lambda} > = n_{\kappa\lambda} = \frac{1}{\exp(\hbar\omega_{\lambda}(\kappa)/T)-1} \qquad (1.2.6)$$

Which signifies the fact that we have a Bose type of particles with no particle number conservation or with zero chemical potential. We call these Bose quasiparticles phonons. The concept of phonons is so fruitful that any process in the crystal could be treated as if we have an ideal gas of phonons for low temperatures.

As the temperature increases we have to take interaction of phonons in to account because the number of phonons also increases with temperature. A phonon may collide with another phonon or with electrons as if we have a particle with definite energy & momentum.

$$E_{\kappa\lambda} = \hbar\omega_{\lambda}(\kappa) \quad \text{and} \quad \vec{P} = \hbar\vec{\kappa} \qquad (1.2.7)$$

All thermodynamic properties of the crystal could easily be derived using the phonon picture, [3]. At low temperatures we can consider the phonon gas as ideal.

The free energy of the crystal is then:

$$F = - T\ell nZ \quad , \text{where } Z = \sum_{\kappa,\lambda} \exp\{- \frac{\hbar\omega_{\lambda}(\vec{\kappa})(n_{\lambda}(\kappa)+\frac{1}{2})}{T}\}$$

is the partition function. Hence

$$F = \sum_{\kappa,\lambda} \{ \frac{\hbar\omega_{\lambda}(\kappa)}{2} + T\ell n\ (1-\exp\{ \frac{-\hbar\omega_{\lambda}(\kappa)}{T}\}) \} \qquad (1.2.8)$$

Using this free energy the thermal average engergy will be:

$$\bar{\bar{E}} = \sum_{\kappa\ \lambda} \hbar\omega_\lambda(\kappa) \quad \left(\tfrac{1}{2} + \{\exp(\hbar\omega_\lambda(\kappa)/T) - 1\}^{-1}\right) \tag{1.2.9 }$$

and the specific heat of the crystal which is related to $\bar{\bar{E}}$ by

$$C_v = \frac{d\bar{\bar{E}}}{dT} \quad \text{will be :}$$

$$C_v = \sum_\lambda \int_0^{\omega_{m\lambda}} \left(\frac{\hbar\omega_\lambda(\kappa)}{T}\right)^2 \frac{\exp(\hbar\omega_\lambda(\kappa)/T)\ G(\omega_\lambda(\kappa))}{[\exp(\hbar\omega_\lambda/T) - 1]^2}\, d\omega_\lambda \tag{1.2.10}$$

Where $G(\omega_\lambda)$ is the density of states of ω in mode λ and $\omega_{m\lambda}$ is the maximum frequency in a given mode λ.

For relatively low temperatures there is a simple model given by Debye. The approximation consists in ignoring dispersion. Because at these temperatures the only phonons excited are acoustic phonons, with the relation [3].

$\omega_j(\kappa) = C_j\, \kappa$, where C_j is the speed of sound waves in the crystal and $j = 1.2.3$ two transverse and one longituidnal. The result for the specific heat in this approximation is given by:

$C_v = \frac{12}{5}\pi 4N\left(\frac{T}{\theta_D}\right)^3$ which is the famous Debye $-T^3$ law.

Where θ_D is the Debye temperature related to the Debye frequency ω_D by $h\omega_D = \theta_D$ and $\omega_D{}^3 = \frac{6\pi^2}{V}\ \overline{C_s}^3$, where $\overline{C_s}^3$ is the cube average speed of sound in the crystal.

1.3 Effects of Anharmonicity

In the harmonic approximation for lattice vibrations it was shown that the normal modes or phonons are independent with no interaction. This is not true as we increase the temperature. Because more and more terms of higher order in the expansion (1.1.1) for the crystal potential becomes significant.

Anharmonic effects gives rise to an important and interesting physical effect in solids which cannot be explained only using the harmonic approximation [4]. The most familiar of these is the thermal expansion of solids. When the temperature rises the amplitude of vibration of atoms increases. This makes anharmonic terms important. The assumption that the lattice sites are equilibrium positions fails and the crystal adjusts itself to a new equilibrium position with the anharmonic terms included, in the process the crystal expands.

Another effect due to anharmonicity of the crystal potential is that we have two or more phonon processes. Two phonons may collide with each other to produce a third phonon. Also a single phonon may decay into two other phonons. All these processes are results of anharmonic terms taken as a perturbation on the phonon system.

The selection rule for two phonon processes is:

$-\vec{q} + \vec{q}_1 + \vec{q}_2 = \vec{G}$ where $\vec{G}$ is a reciprocal lattice vector.

The thermal conductivity of solids is highly affected by these two phonon processes.

CHAPTER II

ELECTRONS IN METALS

Electrons in solids play a major role in determining most thermal, electrical and optical properties of the solid. Electrons interact both with each other and with the ions of the crystalline lattice.

In metals we have almost free electrons while in semiconductors and dielectrics we have bound electrons. In general the Hamiltonian of the electron system can be given in the form:

$$H_{el} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_i U(r_i) \qquad (2.1.1)$$

Where the first term is the kinetic energy of electrons and the second term contains the coulomb interaction between electrons, the last term is the potential energy of interaction of the electrons with some external potential including the crystalline lattice.

In second quantized form H will be:

$$\hat{H}_{el} = \sum \varepsilon_k C^{+}_{k\sigma} C_{k\sigma} + \sum_q U(\bar{q})\, C^{+}_{\bar{k}+\bar{q}\sigma} C_{q\sigma} +$$

$$+ \frac{1}{2V} \sum_{q,\bar{k},\bar{k}^1} \frac{4\pi e^2}{q^2} (C^{+}_{k+q,\sigma} C^{+}_{k'-\bar{q},\sigma'} C_{k'\sigma'} C_{k\sigma}) \qquad (2.1.2)$$

Where σ, is a spin index up or down

V- is the volume of the crystal and ε_k is the kinetic energy of electrons $\qquad \varepsilon_k = \frac{\hbar^2 k^2}{2m}$

Here we have used the plane wave expansion , which is appropriate for electrons in metals.

Here, $U(q\ ) = \int e^{i\,\bar{q}.\bar{r}}\, U(\bar{r})\, d^3 r$, and $q = \bar{K} - \bar{k}'$

The above Hamiltonian of the electron system is impossible to solve. Usually we replace it by some model Hamiltonians for different physical situations we have like, the Homogeneous electron gas, the tight binding electron model, etc... We will discuss here the Homogenous electron gas - an appropriate model for metals.

2.1 Homogeneous Electron Gas

This is a model frequently studied to learn about correlation effects. In this model we replace all the ions of the lattice by a uniform rigid background of charge density n_c. It is usually referred to as the jellium model.

The model - Hamiltonian in this case is:

$$H_{e\ell} = \sum_{\kappa,\sigma} \varepsilon_{\kappa} C^{+}_{\kappa\sigma} C_{\kappa\sigma} + \frac{1}{2V} \sum_{\substack{q\neq o \\ \kappa,\kappa'}} \frac{4\pi e^{2}}{q^{2}} C^{+}_{\kappa+q\sigma} C^{+}_{\kappa'-q\sigma'} \times C_{\kappa'\sigma'} C_{\kappa\sigma} \tag{2.2.1}$$

The term with $q = o$ exactly cancells the sum of the electron-ion interaction and the interaction of the rigid background with itself.

The Hamiltonian describes a system which has charge neutrality and terms with $q \neq o$ describe fluctuations due to electron-electron interactions.

It is also impossible to solve this model - Hamiltonian exactly but there are approximate solution like the Hartree-Fock approximation and other modern manybody techniques.

Of all the results one important finding is that the electr electron interaction will be screened out up to a very short distance. Which strengthen the validity of the free-electron model of metals.

2.2 Collective Properties of the Electron System

As we have seen in sec.(2.1) the electron Hamiltonian including the electron-electron interactions is impossible to solve even in the jellium model. This is a many-body problem with interactions.

Electrons in metals have a very high density $\sim 10^{22}\text{cm}^{-3}$. Hence we have a dense system in which a large number of electrons are interacting with each other. This dense system will show properties in which a large number of the electrons are involved simultaneously in a correlated way. This collective modes of the electron system are an important aspect of the many body theory. It is these collective modes that one excites when the system is coupled to some external perturbing system.

Let us perturb the electron system by an external charge density

$$\rho_q \sim A_q e^{i(\bar{q},\bar{r} - \omega t)}$$

and study the response of the system.

In the absence of any perturbation the crystal as a whole is neutral, i.e. $\langle \rho_q \rangle = 0$ But in the presence of the perturbation we will have density fluctuation induced, and $\langle \rho_q \rangle \neq 0$. Where.

$$\rho_q = \sum_K C_K^{+} C_{K+q}$$

If the displacement vector and the electric field inside the system are $\vec{D}$ and $\vec{E}$ respectively: Then

$$\vec{\nabla}.\vec{D} = 4\pi \text{ (test charge density)}$$

because we have no charge in the system and

$$\vec{\nabla}.\vec{E} = 4\pi \text{ (test charge density + induced charge density)}$$

If $\varepsilon(\omega,q)$ is the longitudinal dielectric constant of the system

With

$$\vec{D}(\omega,\bar{q}) = \varepsilon(\omega,\bar{q})\ E(\omega,\vec{q})$$

Then we get

$$i\vec{q}.\vec{D}_q = -i\ \varepsilon(\omega,\vec{q})\ \vec{q},\vec{E}_q = 4\pi\ A_q\ e^{-i(\bar{\omega}t)}$$

and

$$-i\bar{q}.\ \vec{E}_q = 4\pi e\ (Aq\ e^{-i\omega t} + <\rho q>)$$

Hence the longituidnal dielectric constant will be

$$\frac{1}{\varepsilon(\omega,\bar{q})} = 1 + \frac{<\rho_q>}{A_q\ e^{-i\omega t}} = \frac{A_q\ e^{-i\omega t} + <\rho_q>}{A_q\ e^{-i\omega t}}$$

This has a simple interpretation that

$$\frac{1}{\varepsilon(\omega,\bar{q})} = \frac{\text{total charge density}}{\text{test charge density}}$$

The normal modes of the system or the collective mode of oscillations are given by the equation, i.e.

$$\varepsilon(\omega,\bar{q}) = 0$$

Under this condition the system oscillates without any external perturbing charge density. In general $\varepsilon(\omega,\bar{q})$ may have an imaginary part which determines the life time of a collective mode, i.e

$$\tau_q \sim \frac{1}{\text{Im } \omega(\bar{q})} ,$$

If its imagninary part is very small we can take this mode as a well definal collective vibration of the system.

The Hamiltonian of the electron system without perturbation is

$$H_o = \Sigma \frac{1}{2m} Pi^2 + \sum_q \frac{\pi e^2}{q^2} (\rho_q^+ \rho_q - n) \qquad (2.3.1)$$

and the perturbing Hamiltonian

$$H' = \frac{4\pi e^2}{q^2} \rho_{-q} A_q e^{-i\omega t + st} \quad ,s>o \qquad (2.3.2)$$

Using 1st order time-dependent perturbation theory we get

$$<\rho_q> = \frac{-4\pi e^2}{q^2} A_q e^{-i\omega t + st} \quad x$$

$$x \quad \Sigma |<n|\rho_q|o>|^2 \left(\frac{1}{\omega+\omega_{no} + is} - \frac{1}{-\omega+\omega_{no} - is} \right)$$

Where the states $|n\rangle$ are the true eigen states of the electron system without any perturbation but including the electron-electron interactions, i.e.

$$H_o|n\rangle = E_n|n\rangle \quad \text{and} \quad \omega_{no} = \frac{E_n - E_o}{\hbar}$$

Finally we get for $\varepsilon(\omega,\tilde{q})$ the relation:

$$\frac{1}{\varepsilon(\omega,\bar{q})} = 1 - \frac{4\pi e^2}{q^2} \sum_n |\langle n|\rho_q| \;\rangle|^2 \left\{ \frac{1}{\omega+\omega_{no}+is} + \frac{1}{-\omega+\omega_{no}-is}\right\}$$

Whose imagniary part is

$$\mathrm{Im}\,\left(\frac{1}{\varepsilon(\omega,q)}\right) = \frac{4\pi e^2}{q^2} \sum_n |\langle n|\rho_q|o\rangle|^2 \; |\rho(\omega+\omega_{no})-\rho(\omega-\omega_{no})|$$

In the simplest approximation where the electrons are non-interacting we get for $\varepsilon(\omega,q)$ and for $\omega>>\omega_{nc}$. In the long wave length limit, $\tilde{q}\to o$

$$\varepsilon(\omega,q) = 1 - \frac{\omega_p^2}{\omega^2} + \alpha\, q^2$$

Where

$$\omega_p^2 = \frac{4\pi e^2 n}{m}$$

α is a constant and ω_p is the plasma frequency, at $T=o$ the $\mathrm{Im}(\varepsilon(\omega,q)$ = 0 for this frequency range and the collective excitations are well defined with despersion

$$\omega^2(q) = \omega_p^2 + \alpha q^2 , \quad \alpha > 0$$

The collective excitation with this dispersion are referred to as plasmons. Plasmons are observed in metals as peaks in the energy loss of fast electrons in thin metallic foils.
The other kind of excitations in the system are those with $\omega = \omega_{no}$
In this approximation it means

$$\hbar\omega = \varepsilon_{k+q} - \varepsilon_{k}$$

Where ε_{k+q} and ε_{k} are energies of a free electron with momentum $\vec{k}+\vec{q}$ and $\vec{k}$ respectively, this are single particle excitations corresponding to the creation of electron - hole pairs in a filled Fermi sea. An electron in state $\vec{k}$ inside the Fermi sea is excited to a state $\vec{k}+\vec{q}$, leaving a hole in state $\vec{k}$.

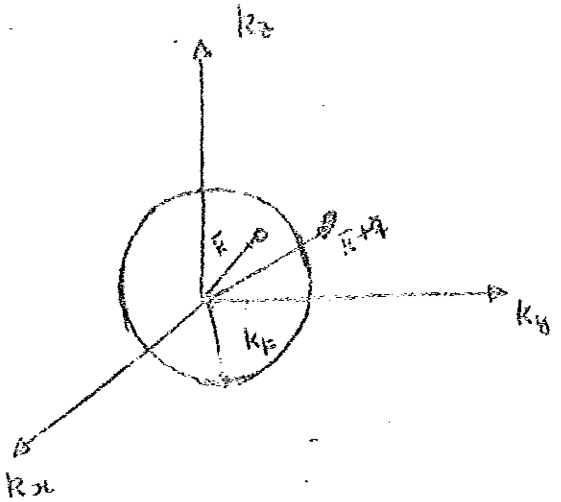

Fig. 3 Single particle excitations consisting of electron-hole production.

2.3 Origin of the Attractive Interaction Between Electrons

It seems at first very strange when one says that electrons in metals may attract each other despite the fact that the coulomb interaction between two free electrons is repulsive.

However it should be noted that the two electrons in a solid are not free electrons interacting only through the pure coulomb potential, rather they are parts of a large electron-ion system, in which the positive ions as well play a part.

Qualitatively one can understand this strange property by saying that, one of the electrons in moving inside the solid pushes other electrons out of its way while it pulls +ve ions around it self producing a phonon cloud accompanying the first electron. The other electron interacts with the polarized medium giving an attractive interaction. Here the attractive interaction between the two electrons is not a direct interaction, it is an indirect interaction mediated by phonons.

The interaction between electrons and phonons is non-linear, each system is bound to be coupled to itself. To see this let us disturb the e^- distribution some how, this will disturb the phonon

disturb phonons → disturb electrons
→ disturb phonons

distribution and this in turn will alter the distribution of the electrons.

To get a crude idea of how it is possible for two electrons to attract each other let us take the two fluid model of the electron and the ion system.

Our model [3] is a macroscopic model in which we approximate the charges as a continuum of charged fluid.

Now if we perturb the system by an external density of charge given by $\sim$

$$e^{i\vec{q}.\vec{r} - iwt}$$

and study the response of the system we get:

With
v_F - the Fermi velocity
$\bar{U}_e$ - displacement of the electron fluid
$\bar{U}_L$ - displacement of the ion fluid

The equation of motion of the two fluids is

$$m\ddot{\vec{u}}_e = \frac{mv_F^2}{3} \nabla^2 \vec{u}_e - e\vec{E} \qquad (2.4.1)$$

$$M\ddot{\vec{u}}_L = Ze\vec{E}$$

Here Ze is the charge of a single ion. M and m are masses of the ion and the electron respectively.

$\vec{E}$ is the self consistent macroscopic electric field given by

$$\mathrm{div}\ \vec{E} = 4\pi e \mid \rho_q + \rho_o\ \mathrm{div}\ (\vec{U}_L - \vec{U}_e) \mid \qquad (2.4.2)$$

If we assume that all quantities have $\approx e^{i(\vec{q}\cdot\vec{r}-\omega t)}$ dependence, we get the equation simplified to

$$-m\omega^2\vec{u}_e = \frac{-m v_F{}^2 q^2}{3}\ \vec{U}_e + 4\pi e^2\rho_o(\vec{U}_L - \vec{U}_e) - i\frac{4\pi Z_e{}^2\rho_q\bar{q}}{q^2}$$

$$-M\omega^2\vec{u}_L = 4\pi Z_e{}^2\rho_o\ (\bar{U}_L - \bar{U}_e) + i\frac{4\pi Z_e{}^2\rho_q}{q^2}\ \bar{q}$$

Where ρ_q is the density fluctuation induced by the perturbation and ρ_o is the equilibrium concentration of electrons in the unperturbed system.

Solving this equations for $\bar{U}_e$ and $\bar{U}_L$, the potential energy of another charge e placed in the system will be.

$$\Phi(\omega,\vec{q}) = \frac{4\pi e^2\rho_q}{q^2}\ \left\{ \frac{\omega^2 - v_F{}^2q^2/3}{\omega^2 - \omega_p{}^2(q)} + \frac{(\omega^2 - v_F{}^2q^2/3)\omega_q{}^2}{(\omega^2-\omega_p{}^2(q))(\omega^2 - \omega_q{}^2)} \right\}$$

Where

$$\omega_p{}^2(q) = \omega_{po}{}^2 + v_F{}^2q^2/3 \qquad (2.4.3)$$

and

$$\omega_q{}^2 = \frac{v_s{}^2 q^2}{1 + v_F{}^2\ q^2/3\ \ \omega_{po}{}^2}$$

v_s - is the speed of sound in the medium.

$$\operatorname{div} \vec{E} = 4\pi e \mid \rho_q + \rho_o \operatorname{div} (\vec{U}_L - \vec{U}_e) \mid \qquad (2.4.2)$$

If we assume that all quantities have $\simeq e^{i(\vec{q}\cdot\vec{r}-\omega t)}$ dependence, we get the equation simplified to

$$-m\omega^2\vec{u}_e = \frac{-m v_F{}^2 q^2}{3}\vec{U}_e + 4\pi e^2\rho_o(\bar{U}_L - \bar{U}_e) - \frac{i 4\pi Z_e{}^2\rho_q\bar{q}}{q^2}$$

$$-M\omega^2\vec{u}_L = 4\pi Z_e{}^2\rho_o\ (\bar{U}_L - \bar{U}_e) + \frac{i 4\pi Z_e{}^2\rho_q}{q^2}\ \bar{q}$$

Where ρ_q is the density fluctuation induced by the perturbation and ρ_o is the equilibrium concentration of electrons in the unperturbed system.

Solving this equations for $\bar{U}_e$ and $\bar{U}_L$, the potential energy of another charge e placed in the system will be.

$$\Phi(\omega,\vec{q}) = \frac{4\pi e^2\rho_q}{q^2}\left\{\frac{\omega^2 - v_F{}^2 q^2/3}{\omega^2 - \omega_p{}^2(q)} + \frac{(\omega^2 - v_F{}^2 q^2/3)\,\omega_q{}^2}{(\omega^2 - \omega_p{}^2(q))(\omega^2 - \omega_q{}^2)}\right\}$$

Where

$$\omega_p{}^2(q) = \omega_{po}{}^2 + v_F{}^2 q^2/3 \qquad (2.4.3)$$

and

$$\omega_q{}^2 = \frac{v_s{}^2 q^2}{1 + v_F{}^2 q^2/3\ \omega_{po}{}^2}$$

v_s - is the speed of sound in the medium.

For the case of a superconductor in which the transitions are only near the fermi surface and $\sim kT_c$ and wave length $\sim k_F$ we have

$$\omega << \frac{v_F q}{3} \quad \text{and} \quad \omega << \omega_p\ (q)$$

which simplifies the expression for $\Phi(\omega,\vec{q})$ to:

$$\Phi(\omega,\vec{q}) = \frac{4\pi e^2 \rho_q}{q^2} \left\{ \frac{v_F{}^2 q^2/3}{\omega_{po}^2 + v_F{}^2 q^2/3} \left\{ 1 + \frac{\omega_q{}^2}{\omega^2 - \omega_q{}^2} \right\} \right\} \tag{2.4.4}$$

Now, if the electron were free the potential would be

$$\Phi_e(\vec{q}) = \frac{4\pi e \rho_q}{q^2} ,$$

The effect of the e^- fluid alone is to give the screened coulomb potential which is contained in the first term. The last term gives an extra contribution due to the presence of the ions.

This last term will be negative (or attractive) for frequencies $\omega < \omega_q$. If this term dominates the screened coulomb potential, which is true for $\omega \simeq \omega_q$, we get a net attraction between electrons.

The attractive interaction between two electrons in a solid has many interesting and important effects. Cooper [7] proved that for attractive interaction between electron in a metal the Fermi sea will be unstable against pairing of $\bar{e}$ wi anti parallel spins and momenta.

And using his idea Bardeen, Cooper & Schrieffer [7] succeded to solve the puzzle of superconductivity by explaining all the observed facts using only the fact that electrons attract each other near the Fermi surface.

The modern way of treating the indirect electron-electron interaction was done by Fröhlich using a canonical transformation from H_{e-ph} and keeping terms of second order in the Hamiltonian; the reult is [3]

$$H_{e-ph} = \sum_{\kappa\kappa'\sigma\sigma' q} \frac{|g_q|^2 \hbar\omega}{(\varepsilon_{\kappa+q} - \varepsilon_\kappa)^2 - (\hbar\omega_q)^2} C^+_{\kappa\sigma} C^+_{\kappa'+q\sigma'} C_{\kappa'\sigma'} C_{\kappa+q\sigma} \tag{2.4.5}$$

Which will be attractive for transitions, in the range

$$|\varepsilon_{\kappa+q} - \varepsilon_\kappa| < \hbar\omega q \ .$$

Where ω_q is a typical phonon frequency. In the BCS theory $\omega_q \approx \omega_D$, the Debye frequency.

2.4 Cooper Instability

Cooper presented his classic paper in 1956, and it is his idea which stimulated Bardeen, Cooper and Schrieffer to find their wave function for the superconductive state months after the publication of this paper.

He considered, what would happen if, to a system of electrons filling the Fermi sea, we add two more electrons with a small attractive interaction between each other. But there is no interaction between these electrons and those inside the sea.

It was supposed that the electrons with in the Fermi sea are held rigidly in their states so that these states are forbidden by the exclusion principle to the extra electrons. Then, Cooper proved that the Fermi sea will be unstable with respect to the formation of the bound pair of electrons. The electrons will form a bound state with energy less than the Fermi energy. To show this let us consider the two extra electrons to be in antisymmetric spin state. The unperturbed eigen function of this pair is, for unit volume, [5]

$$\Psi(\vec{k}_1, \vec{k}_2, \vec{x}_1, \vec{x}_2) = \exp i\{\vec{k}_1 \cdot \vec{x}_1 + \vec{k}_2 \cdot \vec{x}_2\}$$

Using the center of mass coordinates

$$\vec{R} = \tfrac{1}{2}(\vec{x}_1 + \vec{x}_2) \quad , \quad \vec{K} = \tfrac{1}{2}(\vec{k}_1 + \vec{k}_2)$$

$$\vec{r} = (\vec{x}_1 - \vec{x}_2) \quad , \quad \vec{k} = (\vec{k}_1 - \vec{k}_2)$$

We get the wave function in the form:

$$\Psi\,(\vec{K},\ \vec{\kappa},\ \vec{R},\ \vec{r}\,) = e^{\,i(\vec{K}.\vec{R}. + \vec{\kappa}.\vec{r})}$$

The Kinetic energy of the pair in this state will be:

$$K.E. = \frac{1}{m}\ \left(\frac{k^2}{4} + \kappa^2\right)$$

If we subject these electrons to an attractive interaction $\hat{H}''$, the total Hamiltonian of the pair will be

$$H = H'' + \frac{p^2}{m} \qquad (2.5.1)$$

Where we have choosen the momentum k = 0

$$\text{i.e.}\quad \vec{K}_1 = -\vec{k}_2$$

Let the eigen function of the pair be given by:

$$\Psi(\vec{r}) = \sum_{\kappa} g_{\kappa}\ e^{\,i\vec{\kappa}\,.\,\vec{r}} = \sum_{\kappa} g_{\kappa}\ e^{\,i\vec{\kappa}.\vec{x}_1 - i\vec{\kappa}.\vec{x}_2} \qquad (2.5.2)$$

These function statisfy Schrodinger's equation:

$$H\Psi(\vec{r}) = \lambda\Psi(\vec{r})\ ,\ \text{Then}$$

$$(H-\lambda)\ \Psi(\vec{r}) = 0\ ,$$

If we take matrix elements between eigen states of the unperturbed system,

$$\int d\tau\ e^{-i\vec{\kappa}.\ (\vec{x}_1 - \vec{x}_2)}\ (\hat{H}-\lambda)\ \sum_{\kappa'} g_{\kappa'}\ e^{\,i\vec{\kappa}'.\ (\vec{x}_1 - \vec{x}_2)} = 0$$

After taking the integration we get.

$$(\varepsilon_{\kappa} - \lambda)\ g_{\kappa} + \sum_{\kappa'} g_{\kappa'}\ \langle\kappa,\ -\kappa|\ \hat{H}''|\kappa',\ -\kappa'\rangle = 0 \qquad (2.5.3)$$

To change summation into integration let $N(\varepsilon)$ be the density of two electron states $k,-k$ per unit energy range, with energy ε, then

$$(\varepsilon-\lambda)g(\varepsilon) + \int d\varepsilon' N(\varepsilon)\ g(\varepsilon)\langle\varepsilon|H''|\varepsilon'\rangle = 0$$

We will show latter that, according to Cooper's assumption,

$$\begin{aligned}\langle\varepsilon|H''|\varepsilon\rangle &= -V\ , \text{ for } (\varepsilon-\varepsilon') \leq \pm\hbar\omega_D \\ &= 0 \quad \text{for } (\varepsilon-\varepsilon') > \pm\hbar\omega_D \qquad (2.5.4)\end{aligned}$$

Where V is a positive constant and ω_D is the Debye frequency

The possible states for the two electrons are above the Fermi level, between ε_F and $\varepsilon_F + h\omega_D$. Using these assumptions we get the equation for λ, given by:

$$(\varepsilon-\lambda)\ g\ (\varepsilon) = V \int_{2\varepsilon_F}^{2\varepsilon_m} d\varepsilon'\ N(\varepsilon')\ g(\varepsilon') = C \qquad (2.5.5)$$

Where C is a constant and $\varepsilon_m = \varepsilon_F + \hbar\omega_D$

and we get,

$$g(\varepsilon) = \frac{C}{\varepsilon - \lambda} \qquad (*)$$

Using eq (*) for $g\ (\varepsilon)$, the equation determing λ is:

$$1 - V \int_{2\varepsilon_F}^{2\varepsilon_m} d\varepsilon'\ \frac{N(\varepsilon')}{\varepsilon'-\lambda} = 0$$

In the above range of energy $\varepsilon_F >> h\omega_D$, and we can take

$N(\varepsilon') \approx N(o)$, at the Fermi level, Hence

$$\frac{1}{N(o)V} = \int_{2\varepsilon_F}^{2\varepsilon_m} \frac{d\varepsilon'}{\varepsilon'-\lambda} = \ln\left(\frac{2\varepsilon_m - \lambda}{2\varepsilon_F - \lambda}\right) \qquad (2.5.6)$$

λ- is the eigen value of the pair, if its ground state has energy λ_o , and anticipating the result we write,

$\lambda_o = 2\varepsilon_F - \Delta$, and we find

$$\Delta = \frac{2\omega_D}{e^{\frac{1}{N(o)V}} - 1} \qquad (2.5.7)$$

Here Δ is the energy of the pair below the fermi level. It is the binding energy of the pair of electrons, which is true only when V is positive, or the potential is attractive. This is an important discovery from the point of view of oridinary perturbation theory. If there is an infinitesimal attractive interaction between electrons it will lead to an instability of the Fermi sea due to lowering of energy of the ground state of the system by formation of bound pairs below the Fermi sea.

Note that there will be no instability if the interaction between electrons were repulsive.

This instability modifies the Fermi sea in an important way and we must study the Fermi surface carefully taking account of the exclusion principle.

It can be seen that the equation for Δ cannot be found using ordinary perturbation theory summed to any finite order because it is not an analytic function of the coupling constant V. This fact delayed the theory of superconductivity for many years after its discovery, because all attempts were based on perturbation theory.

The theory of Cooper is not a theory of superconductivity. The BCS theory is a many - body theory treating all electrons of the metal on equal footing, and its solution is much more difficult. But Cooper's idea gave some impetus into the theory. It gives how to choose pairing of electrons in the BCS coupling.

CHAPTER III

3.1 Electron-Phonon Interactions

In the previous two chapters we have discussed the two sub-systems of a solid, i.e. the electron and the lattice vibrations independently. Now we let these two sub-systems interact with each other. The interaction between electrons and the lattice vibrations (Phonons) is an important and complex part of interactions in solid.

The basic assumption in the electron - phonon interactions is the adiabatic approximation. This means that we can consider the motion of electrons and ions separately to the zeroth approximation. And because ions are heavy compared to electrons they move slowly, in which the electron can follow the motion of the ion adiabatically.

Electron - phonon interaction has important effects on the properties of solids. It causes electrons to scatter from one state $|k>$ to another state $|k'>$ with the creation or destruction of phonons leading to electrical resistance. It causes superconductivity by modifying the electron-electron interaction into an attractive potential due exchange of virtual phonons. It also influences transport properties of every metal. In ionic solids and semi conductors it dominates the transport properties of the solid. A slowly moving electron in ionic crystals carries with it a polarizing field and it will have a heavier mass than the electrons in a perfect crystal, we call this dressed electron a polaron.

The Hamiltonian of the crystal including the electron-phonon interaction can be written as:

$$H = H_{ph} + H_{ee} + H_{e-ph} \qquad (3.1.1)$$

Where H_{ph}, the phonon Hamiltonian in the harmonic approximation.

[illegible]

And H_{ee} is the electron Hamiltonian including the pure coulomb interaction between electrons and their interaction with the external field including the perfect crystal as in eq (2.1.1).

H_{e-ph} - is the Hamiltonian containing the interaction of the electrons with the lattice vibrations.

To get an explicit form of H_{e-ph}. Let the interaction potential between an electron at $\bar{r}_i$ and an ion at $\bar{R}_j$ be [6]

$$V_{e-i}\ (\vec{r}_i - \vec{R}_j)$$

The total potential energy of interaction of an electron at $\bar{r}_i$ with the lattice will be

$$V(\vec{r}_i) = \sum_j V_{e-i}\ (\vec{r}_i - \vec{R}_j) \qquad (3.1.2)$$

For the case of small temperature and small amplitude of vibration. The position of the ions could be written as:

$$\vec{R}_j = \vec{R}_j^{(o)} + \vec{U}_j\ ,\ \text{where}\quad \vec{R}_j^{(o)}$$

is the position of the $j^{\underline{th}}$ ion in the perfect crystal and $\bar{u}_j$ is its displacement from equilibruim we assume that $\vec{u}_j$ is small compared to the lattice constant.

Hence

$$V_{e-i}\ (\vec{r}_i - \vec{R}_j) = V_{e-i}(\vec{r}_i - \vec{R}_j^{(o)} - \vec{U}_j)$$

Expanding V_{e-i} in to a Taylor series with respect to $\vec{U}_j$ and keeping terms up to 1st order in U we get

$$V_{e-i} = (\vec{r}_i - \vec{R}_j^{(o)} - \vec{U}_j) = V_{e-i}(\vec{r}_i - \vec{R}_j^{(o)})$$

$$+ \vec{U}_j \cdot \nabla V_{e-i}\ (\vec{r}_i - \vec{R}_j)\big|_{\vec{R}_j^{(o)}} \qquad (3.1.3)$$

Here $V_{e-i}\ (\vec{r}_i - \vec{R}_j^{(o)})$ is the potential produced by the crystal lattice and can be included in the electron Hamiltonian. For the independent particle approximation this potential gives the Bloch states of the electron.

The term containing the electron - phonon interaction is the second term, i.e.

$$V_{e-ph}(\vec{r}) = \sum_j \vec{U}_j \cdot \nabla V_{e-i}(\vec{r} - \vec{R}_j) \qquad (3.1.4)$$

$V_{e-i}\ (\vec{r} - \vec{R}_j)$ is assumed to have a fourier expansion due to its translational symmetry

$$V_{e-i}(\vec{r} - \vec{R}_j) = \frac{1}{N} \sum_q e^{iq.(\vec{r} - \vec{R}_j)} V_{e-i}(\vec{q})$$

and expressing $\vec{U}_j\ (\vec{r})$ in phonon operators we get:

$$\vec{U}_j = \frac{1}{\sqrt{N}} \sum \vec{U}_q\ e^{i\vec{q}.\vec{R}_j^{(o)}}$$

and

$$\frac{1}{N} \sum_j \vec{U}_j\ e^{-i\vec{q}.\vec{R}_j^{(o)}} = \frac{1}{\sqrt{N}} \sum_G \vec{U}_{\vec{q}} + \vec{G} ,$$

Where

$\vec{G}$ is a reciprocal lattice vector. Finally

$$\frac{1}{\sqrt{N}} \Sigma \vec{U}_{\vec{q}+\vec{G}} = \sum_{G\lambda} \left(\frac{\hbar}{2MN\omega_{q+G\lambda}}\right)^{\frac{1}{2}} \vec{\Sigma}_{\vec{q}+\vec{G},\lambda}(a_{\vec{q}+\vec{G}} + a^{+}_{-\vec{q}-\vec{G}})$$

Where

$\vec{e}_{\vec{q}+\vec{G},\vec{\lambda}}$ is the polarization vector for the phonon mode $\vec{q}+\vec{G},\lambda$ and M - is mass of the ions and N the total number of primitive cells in the crystal.

a_q , $a_q{+}$ are phonon anihilation and creation operators.

Using all these notations we finally arrive at the following expression for $V(\vec{r})$

$$V(\vec{r}) = \sum_{\vec{q}\vec{G}} e^{i\vec{r}.(\vec{q}+\vec{G})} V_{e-i}(\vec{q}+\vec{G})(\vec{q}+\vec{G}) . \vec{\varepsilon}_{\vec{q}+\vec{G}} \quad x$$

$$x \quad \left(\frac{\hbar}{2\rho\omega V}\right)^{\frac{1}{2}} \quad (a_q + a^{+}_{-q}) \qquad (3.1.5)$$

$\rho V = mN$, ρ is the density of the crystal.

In the above form we have restricted the summation on $\vec{q}$ to be only in the first Brillouin Zone. The total interaction potential of the electron system and the ion system in second quantized form is:

$$H_{e-ph} = \int \hat{\Psi}^{+}(\vec{r}) \; V(\vec{r})\hat{\Psi}(\vec{r})d^3r$$

and, using the plane waves as our complete set,

$$H_{e-ph} = - \frac{1}{\sqrt{V}} \sum_{\vec{q},\vec{G}} M_{\vec{q}+\vec{G}} \; \rho(\vec{q}+\vec{G}) \; (a_q + a^{+}_{-q}) \qquad (3.1.6a)$$

Where

$$M_{\vec{q}+\vec{G}} = V_{e-i}(\vec{q}+\vec{G}) \cdot (\vec{q}+\vec{G}) \cdot \hat{\varepsilon}_q \left(\frac{\hbar}{2\rho V\omega_{q_\lambda}}\right)^{\frac{1}{2}}$$

and the fourier transform of the electron density operator is given by

$$\rho(\vec{q}+\vec{G}) = \sum_k C^{+}_{\vec{k}+\vec{q}+\vec{G}} \; C_{\vec{k}+\vec{G}}$$

The Hamiltonian describing the electron - phonon interaction will then be:

$$H_{e-ph} = -\sum_{\vec{q},\vec{G}} \rho(\vec{q}+\vec{G}) \; V_{e-i}(\vec{q}+\vec{G}) \; (\vec{q}+\vec{G}) \cdot \hat{e}_q \left(\frac{\hbar}{2\ Vm\omega_q}\right)^{\frac{1}{2}}$$

$$x \; (a_q + a^{+}_{-q}) \qquad (3.1.6b)$$

Usually the form of the interaction between an electron and an atom is not known a priori. The ion itself is a complex system with many electrons and Nucleons, and its interaction with an external electron will not be simple.

Hence what we will do is we take different physical situations and replace them by an appropriate models in which we can get the form of V_{e-i} interms of macroscopic properties of the system. This parmeters will be easily measurable experimentally.

Some of these models which we will discuss are

- The deformation potential, the piezoelectric coupling and the polar coupling.

.2 Deformation Potential

In covalent crystals the electron-phonon interaction is often relatively weak, and in semiconductors because the concentration of charge carriers is low we can neglect screening effects of the carriers on each other. For this systems we can apply the deformation potential method developed by Bardeen and Schockley for the coupling of electrons with acoustical phonons.

The basic idea here is that we can treat the system as an elastic continuum and apply the theory of deformation of an elastic media. We will neglect all long range coulomb effects. From the out set it should be clear that this method doesn't work for optical phonons due to their long range polarization field carried by them. It is also valid for processes of long wave length i.e. $\vec{q} \to o$ or $\lambda >> a$ where a is the lattice constant.

From the general form of the Hamiltonian H_{e-ph} (3.1.6b) we take only terms with $\vec{q} \to o$ and $\vec{G} = o$

We also assume that

$$\lim_{q \to o} V_{e-i}(q) = D$$

where D is a constant known as the deformation constant; it is related to the elastic properties of the system.

Hence in this model the Hamiltonian will be:

$$H_{e-ph} = iD \sum_{\vec{\kappa},\vec{q}} \left(\frac{\hbar}{2\rho\omega_q V}\right)^{\frac{1}{2}} |\vec{q}| \, (a_q - a_{-q}^{+}) \, C_{\kappa+q}^{+} C_{\kappa} \qquad (3.2.1)$$

Where

ρ-is the density of the solid and ω_q - is the longituidnal acoustic phonon frequency.

We can also obtain this Hamiltonian from some simple physical arguments. [5]

Consider a cubic crystal which is unstrained and have a non degenerate spherical energy surface, by:

$$\varepsilon_o(k) = \frac{\hbar^2 k^2}{2m^*}$$

In which m* is the effective band mass of the electrons. If we now apply a small static deformation on the solid, the perturbed energy surface will be

$$\varepsilon(\vec{k},\vec{x}) = \varepsilon_o(k) + D\,\Delta(x) \qquad (3.2.2)$$

Where $\Delta(x)$ is the dilation of the crystal,the dilation can be expressed interms of the phonon displacement field as:

$$\Delta(x) = \frac{\partial R_\mu}{\partial X_\mu} \qquad (3.2.3)$$

Where now, $D\Delta(x)$ acts as a potential energy for the electrons. In second quantaized form

$$H_{e-ph} = D \int d^3x \, \hat{\Psi}^{+}(x) \Delta(x) \hat{\Psi}(x)$$

$$= D \sum_{\kappa\,\kappa'} C_{\kappa'}^{+} C_{\kappa} \langle \kappa' | \Delta(x) | \kappa \rangle$$

Using the plane wave expansion for $\hat{\Psi}$.

Expanding $\Delta(x)$ interms of phonon operators and taking $\vec{G} = 0$, we get:

$$H_{e-ph} = iD \sum_{\bar{\kappa},\bar{q}} \left(\frac{\hbar}{2\rho\omega q V}\right)^{\frac{1}{2}} q \, (a_q - a_{-q}^{+}) \, C_{\kappa+q}^{+} \, C_{\kappa}$$

Which is identical with the above form (3.2.1)

Using this hamiltonian as a perturbation on the electron-phonon system we can get important results for the properties of electrons in these crystals.

For example an electron will have with it a cloud of virtual phonons even at T=0 whose numer is;

$\langle N \rangle \simeq 0.02$ for typical parameters of a covalent crystal

Since $\langle N \rangle \ll 1$, it means that perturbation theory works in these systems. But for some metals we get $\langle N \rangle \simeq 1$ which means that we have a strong coupling and we can not apply perturbation theory.

In the presence of the electron-phonon interaction the wave vector $\vec{k}$ is not a constant of motion for electrons alone. Hence an electron will change its wave vector in time from $|k\rangle \rightarrow |k'\rangle$

The probability per unit time that an electron in state $|k\rangle$ will absorb a phonon $\bar{q}$ is :

$$\omega(\bar{k}+\bar{q}; n_q - 1 | k, n_q) = 2\pi |\langle K+q_j n_q - 1 | H_{e-ph} | k_j \; n_q \rangle|^2$$

$$\times \; \delta(\varepsilon_\kappa + \omega_q - \varepsilon_{\kappa+q}) \qquad (3.2.4)$$

Where n_q is the initial population of the phonon $\vec{q}$. at $T = 0$ we get the result that,

$$W = \frac{ZD\ m^* k^2}{3\pi\rho C_s} \qquad \text{which is proportional to } \varepsilon_K$$

Where

W is the probability per unit time for emission of a phonon $\vec{q}$ by an electron in state $|k>$

ρ - is the density of the substance

3.3 Localized Electrons

A simple but important physical model which can be solved easily in the electron -phonon interaction is that if all electrons are fixed in position forming a crystal.
We can have localized electrons in impurity levels and electrons in a strongly bounded core states.
Two electrons could interact as follows: One of the electrons disturb the ions and this disturbance acts on the other electron, leading to indirect interaction between the two electrons.
The Hamiltonian of this system is [6]

$$H = H_{ph} + H'_{e-ph} \tag{3.3.1}$$

Where we neglect the electron kinetic energy and electron-electron interactions. (No recoil)

$$H = \sum_q \hbar\omega_{q\lambda} \left(a^+_{q\lambda} a_{q\lambda} + \tfrac{1}{2}\right) + \sum_i \left(a_q + a^+_{-q}\right) \frac{e^{i\vec{q}.\vec{r}i}}{V^{\frac{1}{2}}}$$

$$\times \sum_G M_{\vec{q}+\vec{G}} \ \rho_o \ (\vec{q}+\vec{G}) \ e^{i\vec{G}.\vec{r}_i} \tag{3.3.2}$$

Which is obtained from H_{e-ph}, taking the density operator

$$\rho_0(q+G) = \int d^3r \, e^{i\vec{r}.(\vec{q} + \vec{G})} \, |\phi(r)|^2$$

Where

$\phi(r)$ is the localized eigen state of the electron.

This can be written in the form:

$$H = \sum_q \hbar\omega_q(a_q^+ a_q + \tfrac{1}{2}) \quad \frac{1}{V^{\frac{1}{2}}}(a_q + a_{-q}^+) \sum_i e^{i\vec{q}.\vec{r}i} F_q(ri) \tag{3.3.3}$$

With

$$F_q(r) = \sum_G \rho_0 \, (q+G) \, e^{i\vec{G}.\vec{r}} \, M_{\vec{q} + \vec{G}}$$

F being periodic with the lattice translation can be taken the same for all electrons.

The Hamiltonian in (3.3.2) is simple to solve exactly:

Let us define new operators by:

$$\Delta_q = a_q + \frac{1}{V^{\frac{1}{2}}} \frac{F_q}{\omega q} \sum_i e^{i\bar{q}.\bar{r}i}$$

$$\Delta_q^+ = a_q^+ + \frac{1}{V^{\frac{1}{2}}} \frac{F_q^*}{\omega q} \sum_i e^{-i\bar{q}.\bar{r}i} \tag{3.3.4}$$

the Hamiltonian then reduces to

$$H = \sum_q \hbar\omega_q \, (\Delta_q^+ \Delta_q + \tfrac{1}{2}) - \frac{1}{V} \sum \frac{|F_q|^2}{\omega q} \tag{3.3.5}$$

The first term is the modified phonon energy which has the same frequincy as the original phonon.

The second term gives the contribution to the potential energy due to the presence of localized electrons. We call this term the relaxation energy. V_R

$$V_R(r) = -\frac{1}{V} \sum \frac{F_q}{q} \sum_{i,j} e^{i\vec{q}.(\vec{r}_i - \vec{r}_j)} = \tfrac{1}{2}\sum_{i,j} V_R(\vec{r}_i - \vec{r}_j)$$

(3.3.6)

One important point here is, even though we haven't assumed a direct electron-electron interaction originally we get an interaction potential $V_e(\vec{r}_i - \vec{r}_j)$ between two electron at position $\vec{r}_i$ and $\vec{r}_j$ which is an indirect interaction through phonons.

$$V_R(r) = -2 \sum \int \frac{d^3q}{(2\pi)^3} \frac{|F_q|^2}{\omega_{q\lambda}} e^{i\vec{q}.\vec{r}} \qquad (3.3.7)$$

$V_R(o)$, when $\vec{r}_i = \vec{r}_j$ is referred to as the electron self energ

The form of the potential V_R depends on the type of phonons involved. It may be short ranged or could even be $\sim \frac{1}{r}$, and attractive.

3.4 Piezoelectric Interaction

Substances like Zno and Cds generate an electric field when we apply a stress, and will be under stress when exposed to external electric fields. Acoustic phonons which are a periodic variation of density modulation will produce a periodic variation of stress giving a periodic electric field with which the electrons will interact strongly.

Mathematically we put the piezoelectric property as [6]

$$E_\kappa = \sum_{ij} M_{ij\kappa} S_{ij} \qquad (3.4.1)$$

Where E_κ is the κ^{th} component of the piezoelectric field S_{ij} is the stress tensor in the solid and M_{ijk} a matrix representing the proportionality constant.

$$S_{ij} = \frac{1}{2}\left(\frac{\partial Q_j}{\partial x_i} + \frac{\partial Q_i}{\partial x_j}\right) \qquad (3.4.2)$$

Where Q - is the phonon displacement.

the electric fielf being longitudnal can be expressed inter of a scalas potential,

$$E_\kappa = \frac{\partial}{\partial x_\kappa} \Phi(\vec{r})$$

Using this we get

$$\Phi(\vec{r}) \; \alpha \; Q(\vec{r}) \qquad (3.4.3)$$

The expression for $\Phi(\vec{r})$ is:

$$\Phi(\vec{r}) = i \sum_{q\lambda} \left(\frac{\hbar}{2\rho\nu\omega_{q\nu}}\right)^{\frac{1}{2}} M_\lambda(\hat{q}) \, e^{i\vec{q}\cdot\vec{r}} \left(a^{+}_{-q\lambda} + a_{q\lambda}\right) \qquad (3.4.4)$$

With

$$M_\lambda(-\hat{q}) = -M_\lambda(\hat{q})$$

and

$$H_{eph} = i \sum_{q\lambda} \left(\frac{\hbar}{2\rho\nu\omega_{q\lambda}}\right)^{\frac{1}{2}} M_\lambda(\hat{q}) \rho(\hat{q}) \left(a^{+}_{q\lambda} + a_{q\lambda}\right) \qquad (3.4.5)$$

$M_\lambda(\hat{q})$ depend not on the magnitude of $\vec{q}$ but on its direction. (3.4.5)

If we use this Hamiltonian to evaluate the effective potential between two fixed electrons using 2nd order perturbation theory,

We get

$$V_R(r) = -2 \int \frac{d^3q}{(\pi)^3} \sum_{\lambda} M_{\lambda}^2 \frac{1}{2\rho\omega^2_{q\lambda}} e^{i\vec{q}.\vec{r}}$$

And in the case of low temperature using the Debye model

$$\omega_{q\lambda} = C_{\lambda} q ,$$

$$V_R (r) = -\frac{1}{r} \frac{1}{4\pi\rho} \sum_{\lambda} \frac{M_{\lambda}^2}{C_{\lambda}^2} = -\frac{e^2}{r} \gamma \qquad (3.4.6)$$

Where $\gamma = \frac{1}{e^2 4\pi\rho} \sum_{\lambda} \frac{M_{\lambda}^2}{C_{\lambda}^2}$

This potential is the potential energy contribution from the piezoelectric interaction due to phonons. The total potential energy is

$$V_{tot} (\vec{r}) = \frac{e^2}{r \, \varepsilon_{tot}} \qquad (3.4.7)$$

ε_{tot} is the total static dielectric constant

If $\varepsilon_{tot} = \varepsilon_o + \varepsilon_{piezo}$

We get, with

$$\frac{e^2}{r \, \varepsilon_{tot}} = \frac{e^2}{r \, \varepsilon_o} - \frac{e^2 r}{r}$$

$$\varepsilon_{piezo} = \frac{\varepsilon_o^2 \gamma}{1-\varepsilon_{o\gamma}} \qquad (3.4.8)$$

The potential energy due to the piezoelectric interaction is attractive, which is due to screening of the ions.

Polar Coupling:

Optical phonon produce displacements of ions in opposite direction, in ionic crystals this opposing displacements of oppositely charged ions may give a very large electric field specially for Lo phonons. Its magnitude is large and could interact with electrons, producing a long range coulomb interaction.

The electric displacement vector in Lo mode statisfies

$\bar{\nabla}.\bar{D} = 0$

because we have no free charges. The field is also longitudnal resulting that $D = 0$ or $\vec{E} + 4\pi\vec{P} = 0$

$\vec{E} = -4\pi\vec{P}$, for each fourier component

$\vec{E}_q = -4\pi\vec{P}_q$

An obvious assumption is that the polarization is proportional to the phonon displacement

$$\text{i.e.} \quad P_q = U_e Q_q \qquad (3.5.1)$$

U is a constant to be determined

Hence,

$$E_q = -4\pi e \;\; UQ_q = -4\pi U_e \left(\frac{1}{\rho v \omega_{Lo}}\right)^{\frac{1}{2}} q \; (a_q + a^{+}_{-q}) \qquad (3.5.2)$$

We take ω_{Lo} to be constant

$\vec{E} = \nabla\phi$ because $\vec{E}$ is longitudinal

With

$$\phi = \sum_q \phi_q \, e^{i\vec{q}.\vec{r}} ,$$

$$\vec{E} = i \sum_q \vec{q} \, \phi_q \, e^{i\vec{q}.\vec{r}}$$

and

$$\phi\,(\vec{r}) = \sum_q \frac{4\pi e U}{q} \left(\frac{\hbar}{2\rho\nu\omega_{Lo}}\right)^{\frac{1}{2}} \left(a_q + a^{+}_{-q}\right) \, e^{i\vec{q}.\vec{r}} \tag{3.5.3}$$

This is the potential produced by the Lo phonons

The potential energy between two fixed electrons will be

$$V_R\,(r) = \frac{-2}{\hbar\omega_{Lo}} \, (4\pi U e) \, \frac{\hbar}{2\rho\omega_{Lo}} \int \frac{d^3q}{(2\pi)^3} \, \frac{e^{i\vec{q}.\vec{r}}}{q^2}$$

$$\rightarrow \quad V_R\,(r) = -\,\beta\,\frac{e^2}{r} \tag{3.5.4}$$

Where

$$\beta = \frac{4\,\hat{U}}{\rho\omega_{Lo}^{2}}$$

This is the potential contribution from optical phonons, i.e. it is the difference between screening with electron transitions only and that with electrons plus optical phonons.

Hence,

$$\frac{e^2}{r\varepsilon_0} = \frac{e^2}{r}\left(\frac{1}{\varepsilon_\infty} - \beta\right)$$

$$U^2 = \frac{\rho\omega_{Lo}^2}{4\pi}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right) \qquad (3.5.5)$$

Using these,

$$H_{eph} = \sum_q \frac{M}{qV^{\frac{1}{2}}}\ \rho(\tilde{q})\ (a_q + a^+_{-q}) \qquad (3.5.6)$$

Where $M^2 = 2\pi e^2\hbar\omega_{Lo}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)$

The importance of this formulation is that both ε_∞ & ε_0 could be determined from experiment with out great difficulty. ε_0 is the static dielectric constant and ε_∞ is the square root of the refractive index.

Again the polaron contribution to the e-e potential is attractive (or negative).

3.6 Coupling in the BCS Theory

One of the greatest successes of many body theory is the theory of Bardeen, Cooper and Shrieffer(BCS)to explain superconductivity [7].

The spring board for the BCS theory is the isotope effect. The experimental fact is that the critical temperature of a substance dependence on the mass of the isotope as:

$$T_c \propto M^\alpha \qquad (3.6.1)$$

Usually $\alpha \approx -\frac{1}{2}$ for most metals

Where M is the ionic mass

This suggested to Fröhlich that some how the crystal lattice or phonons should be involved in the superconducting state formation.

All attempts to solve the electron - phonon Hamiltonian fails to give a reasonable result. As we have seen in sec. (2.4) the gap parameter is a non-analytic function of the coupling constant. It needs a new mathematical method other than the ordinary perturbation theory. This was the introduction of the canonical transformation, which converts the electron-phonon interaction to the direct electron - electron interaction.

Although the transformation was achieved by assuming a weak coupling, it was not equivalent to second order perturbation theory. The Hamiltonian still allows the repeated scattering of many electrons by each other.

In the BCS theory the coupling is between an electron in a metal and the longitudinal acoustical phonons. The electron - phonon interaction Hamiltonian appropriate to this model is, as given in (3.2.1)

$$H_{e-ph} = i \sum_{\bar{K},\bar{q}} D_q \; C^+_{K+q} \; C_K (a_q - a^+_{-q}) \qquad (3.6.2)$$

To first order in D, H_{e-ph} leads to electron scattering and to electrical resistance but in second order it leads to self energy and also to indirect interaction between electrons.

The total Hamiltonian of electrons phonons and their interaction neglecting the screened coulomb interaction between electrons will be:

$$H = \sum \hbar\omega_q a_q^+ a_q + \sum_K \varepsilon_K C^+_K C_K + iD \sum_{\bar{K},\bar{q}} C^+_{K+q} C_K (a_q - a^+_{-q}) \qquad (3.6.3)$$

If we now make a canonical transformation on H such that we have no terms of order D, we get

$$H_{red} = \sum \hbar\omega_q a_q^+ a_q + \sum_K C^+_K C_K + \frac{1}{4} D^2 \sum_{\bar{q},\bar{K}\,\bar{K}'} \frac{\omega_q}{(\varepsilon_K - \varepsilon_{K-q})^2 - \omega_q^2} C^+_{K'+q} C_{K'} \, X$$

$$X \; C^+_{K-q} \; C_K \qquad (3.6.4)$$

In a graphical representation the interaction part gives scattering of to electron by exchange of virtual phonons.

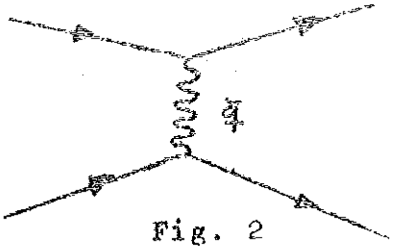

Fig. 2

Electron-electron interaction Via phonons.

The electron-electron interaction part in the Hamiltonian will be attractive for electron transitions such that $|\varepsilon_K - \varepsilon_{K-q}| < \hbar\omega_q$, where $\hbar\omega_q$ is a typical phonon energy. for $|\varepsilon_K - \varepsilon_{K-q}| \approx \hbar\omega_q$ it will dominate the screened coulomb potential. In the BCS theory this potential is approximated by the model potential that it is

$- V$, a constant and $V > 0$

For $|\varepsilon_F - \varepsilon_{K-q}| < \hbar\omega D$

and $|\varepsilon_F - \varepsilon_K| < \hbar\omega_D$

and is 0, for the rest of electron transitions . This means, all electron transitions near the Fermi surface and are in the range $\hbar\omega_D$ about ε_F are attractive.

The corresponding Hamiltonian will be

$$H = \sum_K \varepsilon_K C_K^+ C_K - V \sum_{\vec{K}\,\vec{K}',\vec{q}} C_{K+q}^+ C_{K'} C_{K'-q}^+ C_K \qquad (3.6.5)$$

Where we have neglected the phonon energy.

Even though we have choosen the electron interactions to be attractive, it can be seen that all the matrix elments will not be negative and even cancel out to give a zero contribution.

We can avoid this by choosing the interaction of electron pairs to be restricted to those having equal and opposite momenta and spin. This choice is that dictated by the results of Cooper's problem.

Hence the BCS model Hamiltonian will be

$$H_{red} = \sum_{K} \varepsilon_{K} (C_{K}{}^{+} C_{K} + C_{-K}{}^{+} C_{-K}) - V \sum_{KK} C^{+}_{K'} C_{-K'} C^{+}_{-K} C_{K} \qquad (3.6.6)$$

Where the spins are included by the convention that an electron of momentum $\bar{K}$, has spin up and that with $-\bar{K}$ with spin down.

This Hamiltonian is usually known as the pair Hamiltonian. It generates a state of lower energy by producing a pair Coherent states.

The work of BCS was to solve this Hamiltonian in an approximate way. Now it is well established that it contains all the observed properties of low temperature superconductors. We will see some of its results very briefly.

The BCS wave function is in the space of pair states, i.e. either we have a pair or we have no pair. The ground state wave function has the form:

$$|\Psi_{G}\rangle = \prod_{K} (U_{K} + V_{K} C_{K}{}^{+} C_{-K}{}^{+}) |0\rangle \qquad (3.6.7)$$

Where U_K and V_K are parameters with the property that,

$$U_K = U_{-K} \quad \text{and} \quad V_{-K} = -V_K$$

and

$$U_K^2 + V_K^2 = 1$$

$|0\rangle$ - is the vacuum state with no electrons.
The solution in the BCS theory is then to minimize the energy of the system with respect to this wave function which will yield an equation for U_K and V_K.

As it could be seen in (3.6.7) the wave function of the ground state does not conserve number of particles while $\hat{H}$ commutes with the number operator and conserve particle number. This means we are working in the grand canonical sense and the average number of particles will coincide with the number of electrons present with a negligible error $\left(\frac{1}{N}\right)$

N - is the total number of electrons present in the system.
For large N it makes no error to approximate

$$\langle N \rangle \quad \text{by} \quad N.$$

The solution of the model Hamiltonian (3.6.6) could be determined using Green's function method [23].

To get an approximate solution similar to the Hartree-Fock approximation, let us define thermal averages of two operators by:

$$\Delta = \sum_{K} < C_{-K} C_K > \quad \text{and,} \quad \Delta^* = V \sum_{K} < C_K^+ C_{-K}^+ >$$

(3.6.8)

With these the Hamiltonian reduces into

$$H = \sum_{K} \varepsilon(K) \; (C_K^+ C_K + C_{-K}^+ C_{-K}) - \frac{1}{V} \sum_{K} \{ \Delta^* C_{-K} C + \Delta C_K^+ C_{-K}^+$$

$$+ \Delta^2 / V \qquad (3.6.9)$$

This Hamiltonian is quadratic in the particle operators and may be solved exactly by using Bogoliubov transformations. define new operators; [8,9]

$$\alpha_K = U_K C_K - v_K C_{-K}^+$$

$$\alpha_K^+ = U_K C_K - v_K C_{-K}$$

Using these transformations our Hamiltonian reduces to the following form.

Here U_K and v_K are chosen so as to diagonalize the model Hamiltonian,

$$H_{red} = E_{gs} + \sum_{K} E_K (\alpha_K^+ \alpha_K + \alpha_{-K}^+ \alpha_{-K}) \qquad (3.6.10)$$

Where E_{gs} is the ground state energy

and

$E_K = (\varepsilon_K + \Delta_K^2)^{\frac{1}{2}}$ is the energy of elementary excitation created by α_K^+'s. These quasi particle operators obey the Fermi anticommutation relations.

$$\{\alpha_{\kappa}, \alpha^{+}_{\kappa'}\} = \delta_{\kappa\kappa'} \qquad \{\alpha_{\kappa} \; \alpha_{\kappa}\} = \{\alpha^{+}_{\kappa}, \alpha^{+}_{\kappa'}\} = 0$$

The probability of the excitation in thermal equilibrium then will be the usual Fermi function

$$f\ (E_{\kappa}) = \frac{1}{\exp(\beta E_{\kappa}) + 1}, \quad \beta = \frac{1}{KT}$$

The ground state energy of the superconductor is when we have no excitation, T = 0. Its value truns out to be:

$$E_{gs} = \sum_{\kappa} (\varepsilon_{\kappa} - \frac{\varepsilon_{\kappa}^{2}}{E_{\kappa}}) - \frac{\Delta^{2}}{V} \qquad (3.6.11)$$

and the condensation energy, which is the energy difference between the normal and the superconducting ground states is

$$E_{gs} - E_{gn} = -\tfrac{1}{2}N(0)\Delta^{2} \qquad (3.6.12)$$

This shows the important fact that the superconducting state has a lower ground state energy than the normal metal.
The condensation energy is extremely small showing that the superconducting transition is a very delicate effect.

The energy of excitation $E(\kappa)$ given by

$E(\kappa) = \sqrt{\varepsilon^{2}(\kappa) + \Delta^{2}}$, contains the unique feature of the superconducting state, that the excitation spectrum has a gap.

When = $\kappa = \kappa_{F}$ (at the Fermi level), $\varepsilon(\kappa_{F}) = 0$

and

$E_{min}\ (\kappa) = \Delta$; the energy gap.

For the simple BCS model Δ is a function only of temperature, $\Delta(T)$ but if we take the more realistic models like the strong coupling theory of Macmillan we will get Δ to be a complex function of frequency and temperature. The imaginary part of Δ is connected with the finite life time of the elementary excitation, where they have an infinite value in the BCS theory.

Another result of BCS theory is that the gap at $T = 0, \Delta_0$ and the critical temperature are related as,

$$\frac{2\Delta_0}{Tc} = 3.52 \qquad (3.6.13)$$

Which is independent of the material we have.

Also the critical temperature at which we have a phase transition is given by the relation.

$$T_c = 1.14\ \omega_D \ \exp\{-\frac{1}{N(o)V}\} \qquad (3.6.14)$$

Where we have assumed a weak coupling limit, i.e.

$N(o)V << 1$.

ω_D - is the Debye frequency.

$N(o)$ - is the density of electron states at the Fermi level and V is the strength of the attractive pair potential.

For most metals the coupling constant $N(o)V = \lambda$ is $\simeq$ 0.3 and the corresponding critical temperature $T_c \simeq$ 1.5 upto 4k only.

Later it was found that, some superconductors mostly alloys have a critical temperature $T_c \simeq 20\kappa$ which is beyond the BSC limit.

CHAPTER IV

4.1 High Temperature Superconductivity.

After the BCS theory in 1957 and its strong coupling extension by Scalapino et al [12] 1966, it was thought that the superconducting phenomenon is completely known and explained. This was so until the discovery of materials with high critical temperatures by J.G. Bednorz and K.A. Müller [13] in 1986. This new class of materials are a multiphased Oxides of lanthanum barium, and copper (La- Ba - Cu- o) with transition temperatures ∿ 40k. After Bednorz and Müller, Wu et al [14] in 1987 reported superconductivity about 90k in barium, yittrium and copper ternary oxides (y-Ba-Cu-o). Recently the record on the value of T_c has reached about 125k [15] and some people expect that room temperature superconductivity will come out soon.

This discovery was a challenge to physicists both theoretically and experimentally because these transition-temperatures are well beyond the BCS limit ∿ 4k and its strong coupling theory ∿ 20k.

Since the discovery of these very high-T_c superconducting materials a great amount of work was devoted world wide to this new class of materials. In contrast with the tremendous achievement, in material preparation and improvements in the values of T_c, however, physicists know very little about the mechanism of superconductivity in these materials.

When we come to the mechanism of high - T_c superconductivity; every suggested mechanism seems to be a possible one, and every theoretist active in the field has proposed his own's but no one of these theories successfully explained high - T_c superconductivity in all its aspects.
It is possible to catagorize all these proposed mechanisms in to two. The first of these is based on the conventional theory where the phonon assisted electron-pairing is responsible for the superconductivity [16]. The other class claims that electron-pairing is due to direct electron-electron interactions [17] and other non-phononic mechanisms like plasmons, excitions, etc.

Basically we have two families of cermaic oxides. The first is substituted lanthanum copper oxide (La-Ba/sr-cu-o) system in which a layered-pervoskite phase is responsible for the on set of superconductivity at 35-40k. The second family are the oxygen deficient y-Ba-cu-o compounds. Structuraly it consists of the triple pervoskite unit cell and a layer of Cu-o atoms is responsible for its superconductivity at ∿ 90k.

The most interesting features of these new class of materials are:

(1) The superconducting phase transition is strongly correlated with the crystal structural changes. For example $Y Ba_2Cu_3O_{7-\delta}$ [18] is metallic and hence superconducting in the orthorhombic phase, while in the tetragonal phase it is a semiconductor and non superconducting.

(2) Their superconducting properties are strongly dependent on selected class of atoms in the material. In y - Ba-Cu-o the existence of Cu-o chain is found to be responsible for its superconductivity [19]. These leads us to conclude that superconducting properties of these materials exists in a lower dimension usually two dimensional layers of Cu-o in La-Ba-Cu-o and one dimensional chain of Cu-o atoms in y-Ba-Cu-o.

Some experimental results of High - T_c Superconductivity:

Electrical resistance: As one of the basic properties of a conventional superconductor, the electrical resistance of the newly discovered materials also drops to zero in the superconducting state at ∿ 90k for y-Ba-Cu-o and ∿ 40k in La-Ba-Cu-o ceramics.

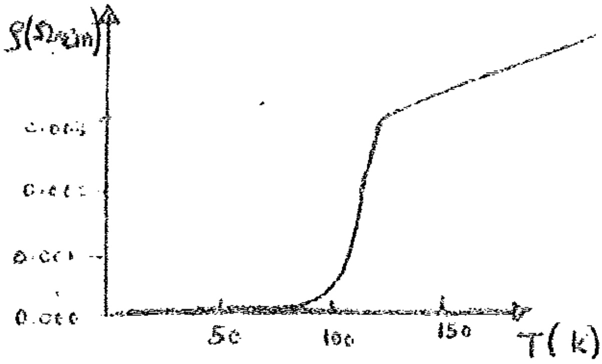

Fig. 3

Experiments reveal [20] that the high $-T_c$ materials show Meissner effect eventhough it is not a complete expulsion of magnetic field.

Flux Quantization: As in the conventional BCS theory the magnetic flux enclosed in a cavity of these high -T_c materials is observed to be quantaized in units of $(0.97 \pm 0.04) \frac{hc}{2e}$. This is a strong experimental evidence that the charge carriers in these materials are electron or hole pairs with a charge of 2e.

Energy gap: Barone. et al [21] found experimentally that y-Ba-Cu-o has an energy gap in the density of states at $\Delta = 19.5mv$ with the result that $\frac{2\Delta_0}{kT_c} = 4.8$ which is larger the BCS value of 3.52. This is a good evidence to suspect strong coupling in these materials. But on the other hand the value found for La-Ba-Cu-o was [22] $\frac{2\Delta_0}{RT_c} \simeq 2.0$ which is below the BCS value.

Isotope effect: One experimental observation in these high-T_c materials which lead people to search for a non-phononic mechanism was the absence of the isotope effect in y-Ba-Cu-o as observed by Baltogg [23]. While an isotope effect was observed in the La compounds by K.A. Müller [24]. But the absence of the isotope effect is not a proof of the non-phononic mechanism, because the isotope effect itself was a result of the BCS theory where we have harmonic phonons and in the weak coupling regiem.

As Zacher [19] remarked the absence of the isotope effect occurs because the very strong electron-phonon interaction causes a softening of the phonon. Softening of the phonon mode can be associated with an insensitivity of T_c to isotope substitutions and to the corresponding frequency shift.

It was suggested [19] that Cu^{2+} in y $Ba_2 Cu_3O_{7-6}$ is in an environment where we have anharmonic crystal potential due to an octahedra of oxygen atoms surrounding Cu^{2+}. Since the BCS theory and its strong-coupling externsion are based on the harmonic approximation for phonons, it is not appropriate to apply this theory to systems with highly anharmonic phonons. As M.T. Beal [24] emphasized any microscopic description of the new high-T_c superconductors should take into account a number of important points concerning strong coupling, low dimensionality, anharmonicity etc.

Guided by all these observations we suspect that lower dimensionality and anharonicity in these systems could result the observed high-T_c values. In the next section we consider the possible outcomes in the case where we have a two dimensional system in the BCS theory.

4.2 Superconductivity in Two Dimensional Copper Oxides.

As it was pointed out in sec.(4.1) the newely discovered high-T_c materials have a lattice structure exhibiting a strong bidimensional character. And as given in eq (1,1.8) the density of electron states in a two dimensional crystal necessarily have one or more logarithmic singularities. A detailed analysis [11] shows that as one of the sub bands in these materials is half filled or nearly half filled the Fermi energy ε_F almost coincides with the energy ε_s of a logarithmic singularity. In this case the electron density of states $n_e(E)$ per spin and N unit cells depends on the one electron energy ε according to an approximate formula as found by J. Labbé and J. Bok |11| as:

$$n(\varepsilon) \simeq \frac{N}{2\pi^2 D} \cdot \ln \frac{D}{|\varepsilon - \varepsilon_s|} \qquad (4.2.1)$$

Where

$$D = \frac{\gamma^2}{\{(\varepsilon_d - \varepsilon_p)^2 + 16\gamma^2\}^{\frac{1}{2}}}$$ and γ is the transfer

integral between nearest neighbouring Cu and o sites and ε_d and ε_p are the d and p atomic energy levels in Cu and o atoms respectively.

It was verified experimentaly |25| that in the superconducting state the energy of the oxygen 2p.orbital and the Cu 3d.orbital coincide in energy. In this case the critical temperature using the BCS weak coupling theory and with the density of states in eq. (4.2.1) Labbé and Bok found that:

$$T_c = 1.13\ D \exp\left(- \frac{1}{\lambda^{\frac{1}{2}}} \right) \qquad (4.2.2)$$

Where

$\lambda = \frac{v}{4\pi^2 D}$ is the effective coupling constant in this model and v is the effective electron - electron coupling constant.

The factor $\sqrt{\lambda}$ in the expression for T_c in this model should be compared with the BCS 3D treatment as given in eq.(3.6.14) with a constant density of states at the Fermi level which gives a factor λ. For small $\lambda \ll 1$ this factor will increase the value of T_c by an order of magnitude than its BCS value. Specifically as found from the experimental results of Matheiss, Oguchi and Yu for y-Ba-Cu-o, we have

$\gamma = 1.4ev$, $D \approx 0.3ev$ and hence $\sqrt{\lambda} \approx 0.27$ yields a value of $T_c = 95k$. For La-Ba-Cu-o $\sqrt{\lambda} \approx 0.21$ and the corresponding temperature is $T_c \approx 32k$.

Another interesting out come of this model is that we have no the usual isotope effect as in the 3D BCS theory. Because the prefactor D in eq. (4.2.2) is not a function of the atomic mass.

4.3 The possibility of increasing coupling constant for non harmonic motion of ions.

Recently J.R. Hadry and J.W Flocken [16] proposed as a possible origin of high - T_c superconductivity the existence of double well potentials in the Cu-o chain for the motion of oxygen atoms. Their assertion is based on the the experimental result by Cohen et al [26] for the Lattice dynamical calculation of pure LCO and YBCO which shows that each system is highly unstable mechanically in the crystal structure, tetragonal for LCO and orthorohombic for YBCO. These instabilities indicate that both systems are at the maxima of a double well potential. The evaluation of the coupling consant in these highly anharmonic potentials using the conventional theory is erroneous, because in all cases it assumed that the lattice response is purely harmonic.

Hui and Allen have found a general expression for the coupling constant for non harmonic crystal potentials, whose results are.

$$\lambda(T) = N(o)\sum_{\kappa\kappa'}^{Fs} \sum_{n>n'} \frac{|<n|V_{\kappa\kappa'}|n'>|^2}{E_{n'}-E_n} (f_n - f_n{}')$$

(4.3.1)

Where N(o) is the density of electron states at the Fermi level and $V_{\kappa\kappa}{}'$ is the electron-phonon matrix element, $|\kappa>$ and $|\kappa>$ are electronic states at the Fermi surface, $|n>$ and $|n'>$ are the eigen states of the oscillator with energies E_n and $E_n{}'$ respectively, f_n and $f_n{}'$ being the thermal weighting factors given by

$$f_n = e^{-En/T} / \sum_{n'} e^{-E_{n'}/T}$$

The form of λ as given above is temperature independent only if the eigen states of the oscillator are chosen to be the harmonic eigen states, otherwise λ will be a function of temperature

As shown by Hadry and Flocken for $(-x^2 + Ax^4)$ double well using numerical values for the energies En, λ(100k) is near the extreme strong coupling regiem ($\lambda > 5$) and the critical temperature in this region is given by [27]

$$T_c = 0.18 \quad (\lambda < \omega^2 >)^{\frac{1}{2}} \qquad (4.3.2)$$

Where

$$<\omega^2> = \frac{N(0)}{h^2\lambda} \sum_{\kappa\kappa' n'>n} |<n|V_{\kappa\kappa'}\, n'>|^2 \; (E_{n'}-E_n) \; (f_n - f_{n'})$$

Using all these it was found that for $\lambda>5$ superconductivity will occur when $T<T_c$. The most interesting result of their theory is that if we have energy levels for the double-well which are slightly lower than, the double well maxima with two closely spaced levels, then the critical temperature $T_c \sim$ look is a possibility as found from numerical results.

In this work the operator method to be discussed in the next section is applied to get analytical solution for the eigen values of the double-well $(-x^2 + \beta^2 x^6)$. The result of the method is that for small β we will have at least two closely spaced levels below the maxima of the double well

These closely spaced level will highly increase the coupling constant and hence the critical temperature according to the results of Hadry and Flocken.

The result we have got for the double-well that there are closely spaced levels in the negative part of the spectrum is a general property of all double-wells in the small β regiem, $\beta<<1$. Which is again the necessary condition for the enhancement of λ in the theory of Hadry and Flocken. But we are not sure at this time about the exponential smallness of the splitting of the levels. What we can say is certainly there are pair of closely spaced levels below the double well maxima in this small β regime and the Hardy-Flocken numerical result for the coupling constant can be taken as a general property of systems in double-wells for $\beta << 1$, not only for the O-motion.

4.4 The Operator Method (OM)

The study of anharmonic oscillators is gaining attention in all branches of physics because of their modeling in non linear systems. A lot of effort has been expended on these oscillators but most of these works are based on numerical methods. To investigate the behaviour of these systems it is necessary to know the dependence of the energy levels and eigen functions in an analytic form interms of the parameters of the potential.

The operator method [12] is an approximation method in which it is possible to get an analytic form both for the eigen values and eigen functions interms of the parameters of the potential. The basic ideas of the method will be illustrated use the following representative potentials:

x^6 Anharmonic Oscillator

This is a potential of the form:

$$V(x) = \frac{x^2}{2} + \beta^2 x^6 \qquad (4.4.1)$$

Whose Hamiltonian in dimensionless units is given by:

$$H = \frac{\hat{p}^2}{2} + \frac{x^2}{2} + \beta^2 x^6 \qquad (4.4.2)$$

First let us introduce the operator defined by:

$$\hat{x} = \frac{1}{\sqrt{2\omega}} (a+a^{+}) \qquad p = i\sqrt{\frac{\omega}{2}} (a^{+} - a) \text{ and}$$

$[a,a^{+}] = 1$, ω is a parameter to be determined later. substituting this in to eq(4.42) for $\hat{H}$ and taking the part which commutes with the particle number operator $a^{+}a$, $(\hat{H}_{o})$, we get for $\hat{H}_{o}$.

$$\hat{H}_{o} = (\frac{\omega}{4} + \frac{1}{4\omega}) (1 + 2a^{+}a) + \frac{\beta^{2}}{8\omega^{3}} (15+20a^{+3}a^{3}+ + 90 a^{+2}a^{2}+90 a^{+}a) \qquad (4.4.3)$$

With the eigen function for H_{o} denoted by $|n>$ and

$$a|o> = 0, \ a^{+}a|n> = n|n>$$

We get for the unperturbed eigen values the result:

$$E_{n}^{(0)}(\omega) = (\frac{\omega}{4} + \frac{1}{4\omega}) (1 +2n) + \frac{5\beta^{2}}{8\omega^{3}}(4n^{3} + 6n^{2} + 8n + 3). \qquad (4.4.4a)$$

Now the parameter ω is determined by minimizing the energy. i.e.

$$\frac{\partial E_{n}^{(0)}(\omega)}{\partial \omega} = 0$$

Which give the value of ω as;

$$\omega_n^2 = \frac{1+\sqrt{1+30\beta^2(n^2+n+\frac{1}{2})}}{2}$$

And the zero order energies are then

$$E_n^{(o)} = \frac{2}{3}\left(2\omega_n + \frac{1}{\omega_n}\right)(n+\tfrac{1}{2}) \qquad (4.4.4b)$$

This is evaluated for the ground state energy and the results compared with numerical result [26] the accuracy of which ranges from 1% - 2%.

We have also determined the 2nd order correction to the ground and 1st excited states by taking the part of $\hat{H}$ excluding $\hat{H}_o$ as a perturbation:

The results are

$$E_o^{(2)} = \frac{-45\beta^4}{\omega_o^2}\left(\frac{15}{8(285\beta^2+4\omega_o^2)} + \frac{1}{2(12\omega_o^2+1645\beta^2)}\right) \qquad (4.4.5)$$

and

$$E_1^{(2)} = \frac{45\beta^4}{\omega_1^3}\left(\frac{33075}{16(4\omega_1^3+315\beta^2)} + \frac{6615\,\beta^4}{8(4\omega_1^2+525\beta^2)}\right.$$

When combined with the unperturbed result will give a better accuracy, at least for the ground state.

x^6 Double-well potential

The Hamiltonian in dimensionless units is

$$\hat{H} = \frac{\hat{p}^2}{2} - \frac{\hat{x}^2}{2} + \beta^2 \hat{x}^6 \tag{4.4.6}$$

Introducting operators defined by:

$$x = \frac{1}{\sqrt{2\omega}} (a+a^+) \;;\quad p = i\sqrt{\frac{\omega}{2}}(a^+ - a)$$

To take into account that the wave function should be localized in the viccinity of the two minima of the well we will define new operators by:

$a = u+b$ and $a^+ = u+b^+$, u and ω are variational parameters. The above transformation breakes the parity of the Hamiltonian in eq (4.4.6). Hence it is necessary to introduce the projection operator,

$$\hat{P}_s = \tfrac{1}{2} (1+se^{i\pi a^+ a}) \quad , s = \pm 1$$

which projects an arbitrary function on a state with definite parity.

Consider the equation

$$\hat{L}_s |\phi_s\rangle \equiv (\hat{H}\hat{P}_s - E_s\hat{P}_s)\,|\phi_s\rangle = 0 \tag{4.4.7}$$

If we select from $\hat{L}_s$ the part which commutes with the operator b^+b, then the energy in the zeroth approximation will be:

$$E_{ns} = \langle n|\hat{H}_o|n\rangle + s \frac{\langle n|V|m\rangle \langle m|\hat{P}_s|n\rangle}{\langle n|P_s|n\rangle}$$

This result would be exact if we know the true eigen vectors of H.

Here $\hat{H}_o$ is the part of $\hat{H}$ which commute with b^+b and the remaining part of H will be taken as the perturbation V.

Using the operator relation,

$$e^{i\pi a^+ a} = e^{-2u^2} e^{-2ub^+} e^{-i\pi b^+ b} e^{-2ub}$$

One can get the zeroth order energy for the ground state the result:

$$E_{os}^{(o)}(\omega,u) = \frac{1}{4}(\omega - \frac{1}{\omega}) - \frac{u^2}{\omega} + \frac{\beta^2}{\omega^3}(15+180u^2+240u^4+64u^6)$$

$$+ \frac{se^{-2u^2}}{1+se^{-2u^2}} (-\omega u^2 + \frac{u^2}{\omega} + \frac{\beta^2}{\omega 3}(-8u^6-30u^4-22.5u^2) \quad)$$

The parameters u and ω will be determined from the equations

$$\frac{\partial E_{os}^{(o)}}{\partial \omega} = \frac{\partial E_{os}^{(o)}}{\partial u} = 0$$

It is possible to get analytic solution for these equations in the small β regime. The energy splitting in this regime for the ground state with opposite parity is found to be:

$$E_{o-}^{(o)} - E_{o+}^{(o)} = \frac{40}{\sqrt{6\beta}} e^{-\sqrt{\frac{4}{3\beta^2}}}$$

But for our further investigation we need the splitting to be finite and in the intermidate regime, $\beta \lesssim \frac{1}{5}$.

As one can expect for $\beta << 1$, the splitting is exponentially small. This feature of deep arbitrary double-wells was investigated at first by Landau [10].

4.5 Doublet transitions in double-wells and electron-electron interactions.

As it was shown by Hadry and Flocken [16] the existence of a doublet below the well maxima can significantly increase the coupling constant and hence the attractive interaction between electrons.

Here a one dimensional chain of cu-O atoms in YBCO in double well potential $(-x^2+\beta^2x^2)$ is considered. An intermediate value of β , $\beta \lesssim \frac{1}{5}$ is to be taken since we need only a single doublet to appear in side the well. In the temperature range $T \approx \Delta E$, where ΔE is the amount of splitting for the ground state and $T << E_2 - E_o$, where E_2 is the immediate higher energy level to the doublet, the coupling constant for electron-electron interactions taking transitions only between the doublet as given in eq (4.3.1) will be:

$$\lambda(T) = N(o) \sum_{K,K'} |<1|M_{K\ K'}|o>|^2 \ \frac{1}{\Delta E} \tan h \frac{\Delta E}{2T} \tag{4.5.1}$$

As in the Bcs theory it will be assumed that strong interaction occurs between electrons of opposite momenta and spin. Hence the interaction potential will be [1]

$$V = \frac{|M_{KK'}|^2}{\hbar\omega_D}$$

This indicates that the critical current in these high-T_c materials should be smaller than in the conventional superconductors.

Because the form of $M_{KK'}$ is not known for double-wells at present, it is not possible to say something about the isotope effect and the above conclusions have only a qualitative nature.

CONCLUSION

The modern formulation of the electron-phonon interaction in solids is a well developed and an important branch of solid state physics. Above all it causes superconductivity by modifying the electron-electron interaction to be attractive through the medium of ions. The BCS theory of superconductivity ranks as one of the greatest achievements of many body theory. All its predictions agree remarkabley with experiment. From its discovery in 1911 to the successful theory of BCS in 1957, the phenomenon of superconductivity was a puzzle for physicists for about 45 years.

After the BCS theory everything about superconductivity was believed to be known. The attention of physicists has been on the technological application of these materials, like the Josephson contact, industrial powerful magents and so on.

When in 1986 materials with a very high transition tempert-ure $T_c \sim 40k$ was observed the theory of superconductivity again flourished. From then on physicists are thoroughly studying these new class of materials both theoretically and experimentaly. In this work we made an attempt to analyze the indirect electron-electron interaction through the medium of ions and some of its physical consequences.

In the first three chapters we have discussed some of the results of the interaction between electrons and phonons using the harmonic approximation for phonons. The cooper instability and some results of the BCS theory of superconductivity are among the exciting outcomes. The values of T_c predicted by the BCS model $T_c \sim 4k$ could not explain the very high critical temperatures observed in the newely discovered materials with $T_c \sim 90k$.

In the fourth chapter we have first given a review of some experimental facts about these new materials. Despite the fact that there is no single theory capable of explaining all features of these materials we have studied two of the proposed mechanisms. Both of these mechanisms are based on the electron-ion interaction as the cause of electron pairing.

The first possible mechanism we have discussed is the 2D BCS model. It is based on the strong bidimensional behaviour exhibited by these materials, particularily LCO. The model results in the observed values of T_c and the absence of the isotope effect in its conventional form can be explained from the model.

The non-harmonic potentials observed in the cu-o chain in YBCO due to the structural instabilities near the superconducting transition leads us to study the effects of the non-harmonic double-well potentials on the electron-phonon coupling constant λ. An anomalous enhancement of the coupling constant is found out from the model and this fact deserves a further investigation.

As our original work we are also able to give some qualitative predictions based on this model. The effect of pressure on the values of T_c is related to the parameters

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