CHAPTER – 2

PAIRING MECHANISM, SUPERCONDUCTING AND NORMAL STATE PROPERTIES OF BISMUTH OXIDES

The investigation of an effective dynamic interaction between a pair of carriers is at the centre of a complete microscopic mechanism of superconductivity. In this chapter we first review experimental informations on three-dimensional isotropic Bismuth oxides. We then present a model that incorporates screening of carriers by optical phonons and by plasmons leading to superconductivity in cubic perovskite Ba-Pb/K-BiO. The temperature dependent normal state behaviour of bismuth oxides is studied as a next step. The present analysis points to the importance of both optical phonons and plasmons in the effective electron-electron interaction in revealing the physical properties of doped perovskites.

Paper based on these studies:

1. Superconductivity and Normal state resistivity of Ba_{0.6}K_{0.4}BiO_3: An Optical phonon approach.
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2. Superconductivity inBaPb_{1-x}Bi_xO_3: A coupled charge oscillation with optical-phonon mechanism.
   Dinesh Varshney, Sanjay Shahand R.K.Singh

3. Pairing mechanism and transition temperature of Ba-Pb-BiO superconductors.
   Dinesh Varshney, R.K.Singh and Sanjay Shah
2.1 Introduction

The occurrence of superconductivity in a perovskite oxide $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ with a transition temperature $T_c \approx 13\,\text{K}$ [Sleight et al. 75] and in the multiphased $\text{Ba-K-BiO}$ by Mattheiss et al. [Mattheiss et al. 88] at 22 K are of vital importance. Later on the identification of the superconducting component as $\text{Ba}_x\text{K}_{0.4}\text{BiO}_3$ ($T_c = 30\,\text{K}$) by Cava et al. [Cava et al. 88] provides a real opportunity to understand the nature of the pairing mechanism as well as that of normal state electronic properties.

Let us first briefly discuss the fundamental differences in between bismuth oxides and cuprates. The cuprate superconductors are highly anisotropic in their physical properties due to the two-dimensional character of the conducting copper oxide (CuO$_2$) planes. However, the non-transition metal compound $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ (Ba-Pb-BiO) and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (Ba-K-BiO) are isotropic as the oxygen octahedra form a 3-D network. The parent compound $\text{La}_2\text{CuO}_4$ is an antiferromagnetic insulator, instead BaBiO$_3$ is semiconducting with a low density of states at the Fermi level. The high values of $T_c$ despite essential differences in the copper and bismuth families have raised serious queries regarding the common pairing mechanism.

The mechanism of electron pairing in a copper free phase remains elusive as, the chemical substitution of alkali metal on the Ba sites which do not participate to the conduction band while Ba-Pb-BiO is made superconducting by the substitution of Pb on electronically active Ba sites. Unlike the high-$T_c$ compounds that contain structurally 2-D layered CuO planes, the Ba-K-BiO has a cubic structure in its superconducting phase. This would imply that neither the dimensionality nor the antiferromagnetism must be at the origin of the pairing mechanism in bismuth oxides.

The parent compound BaBiO$_3$ is a diamagnetic and the mechanism of electron pairing in the bismuth-based oxides with magnetic models can easily be ruled out. The chemical substitution and doping in the parent compounds introduces free holes as carriers in the lattice. The bismuth compounds show the tetragonal structure while to that the cuprates are low dimensional materials and exhibit
anisotropy. The cuprates have orthorhombic structure and with the increase in doping, they show transition to tetragonal structure.

The formal charge valence of Bi ions of BaBiO$_3$ is +4 and since neutral Bi atoms have five valence electrons, one valence electron exists at each Bi site. Neutron powder diffraction studies [Hinks et al. 88] suggested that potassium might enter the compound only in an oxygen deficient environment. At lower compositions i.e., $x < 0.3$, the system shows the semiconductor properties. Superconductivity occurs only in a cubic phase ($x \geq 0.37$) and has an undistorted cubic perovskite structure. For $x = 0.35$, a transition from cubic to orthorhombic phase occurs between 200 and 100 K. Within this cubic phase, $T_c$ is highest for composition $x \approx 0.4$ as 30 K.

Mattheiss and Hamann [Mattheiss & Hamann 88b] have performed band structure calculations on cubic phase of Ba-Pb/K-BiO. According to their studies the antibonding Bi (6s)-O (2p) conduction of Ba-K-BiO ($x = 0.3$) is nearly the same as in BaBO$_3$. It is pointed that the doping at the Ba sites extends the metallic range of BaBiO$_3$ closer to half filling then the doping at Bi sites does and hence maximises the electron phonon interaction. They stress that K doping at Ba sites not only increase the coupling of conduction electrons to the bond stretching oxygen phonons but also $T_c$ in the framework of conventional phonon mechanism.

The augmented plane wave method within the tight binding model is used to determine, the McMillan Hopefield parameter, $\eta$, and found that the values are sufficiently large to indicate the coupling of electrons with soft phonon modes and result in $T_c$ in the observed range [Papaconstantopoulos et al. 89]. Shirai et al. [Shirai et al. 90] have studied the electron lattice interaction of both Ba-Pb-BiO and Ba-K-BiO using realistic electronic bands of BaBiO$_3$ reproduced by tight binding model and superconductivity was successfully discussed in the frame work of strong coupling theory of electron-phonon interactions caused by the longitudinal modes of oxygen stretching/breathing vibrations.

The Raman study of lattice vibrations together with infrared spectroscopy results [Sugai et al. 87], confirm the presence of LO and TO breathing vibrations in Ba-Pb/K-BiO perovskites. It is pointed that the charge transfer via the Forhlich type
electron-phonon interaction causes the resonant Raman effect. The electron-lattice interaction of Ba-Pb/K-BiO is studied microscopically by using realistic electronic bands of BaBiO₃ reproduced by the tight binding model [Shirai et al. 90].

Raman spectroscopic studies [McCarty et al 89] of superconducting Ba-K-BiO reveals a Raman peak at 348 cm⁻¹ (43 meV) that exhibits the distinctive Fano line shape as a result of significant coupling between the optical phonons to the electronic states in superconducting BaₓK₁₋ₓBiO₃ but not in BaₓK₁₋ₓBiO₃. The Raman peak at 348 cm⁻¹ excludes the possibility of scattering from acoustic phonons since the acoustic phonon occurs below ~140 cm⁻¹. Although these studies could not detect the expected longitudinal optical branch of breathing type vibrations of oxygen octahedra. Instead, scattering intensity was found at 340 cm⁻¹ in a longitudinal geometry for phonon wave vectors away from the Γ point.

High resolution tunnelling spectroscopy on Ba-K-BiO (x = 0.375, Tc = 29 K) have been reported by Zasadzinski et al. [Zasadzinski et al. 89]. Tunnelling phonon structures between 40 and 65 meV are the most strongly coupled and these correspond to the optical modes of oxygen atoms. Tunnelling data exhibit strong features, which correspond to peaks in phonon density of states of Ba-K-BiO as those obtained from Raman spectroscopy [McCarty et al. 89]. The tunnelling results strongly suggest the electron-optical phonon is the mechanism for superconductivity in Ba-K-BiO systems with electron-optical phonon strength as 1.0.

At this stage it is clear from Band structure studies [Mattheiss & Hamann 88; Papaconstantpoulous et al. 89; Shirai et al. 90] and spectroscopic data [McCarty et al. 89; Wagener et al. 89; Zasadzinski et al. 89] that high energy optical phonons are significantly participating in the pairing mechanism for superconducting states in Ba₀.₆K₀.₄BiO₃ system.

Photoemission and inverse photoemission studies have been performed by Wagener et al. [Wagener et al. 89] for the occupied and unoccupied electronic states of Ba₁₋ₓKₓBiO₃₋ₓ. The results indicate the metallic characteristic with a low density of states on either side of Fermi energy. The low energy plasmon features are shown in the core level spectrum, which are similar in those of observed in high-Tc cuprates. Reflectivity measurements have been carried out by Tajima et al. [Tajima
et al. 87] over a wide energy range and also over the whole composition range in 
BaPb\(_{1-x}\)Bi\(_x\)O\(_3\) superconductors. The phonon structure is observed by far-infrared optical and Raman scattering measurements and plasma excitations are seen in the visible and near infrared region. They have focussed their attention on the plasmon behaviour determined from the reflectivity spectra on single crystals as well as polycrystalline samples at the Bi concentration \((x \geq 0.27)\), where the system shows semiconductor characteristics.

It is suggested that carriers supplied by the Bi atoms be involved in this collective excitation (plasmons) although an energy gap is formed at the Fermi surface. The existence of plasmons is well confirmed by this group [Tajima et al. 88] from the electron-energy loss spectroscopy (EELS) at the bismuth dopant level \((x = 0.27)\). This suggests the participation of the collective excitation besides optical phonons in the pairing mechanism in BaPb\(_{1-x}\)Bi\(_x\)O\(_3\) superconductors. However, the presence of an oxygen isotope effect [Batlogg et al. 88] \((\alpha = 0.22)\) and the energy gap ratio \((\beta = 2\Delta/k_B T_c = 3.5 \pm 0.5)\), now clearly indicate that the usual electron-phonon interaction plays an important role. All these results are suggestive of the presence of ionic excitations as well as the electronic excitations.

Switching to normal state resistivity behaviour, Affronte et al. [Affronte et al. 93] have reported the resistivity data for a single crystal of Ba\(_{1-x}\)K\(_x\)Bi\(_3\)O\(_5\) \((0.35 < x < 0.4)\) and found that resistivity \((\rho)\) shows metallic temperature dependence. The \(\rho\)-vs-\(T\) behaviour of single crystal as prepared by electrochemical process shows the lowest residual resistivity \((\rho_0 = 0.57 \text{ m}\Omega\text{cm})\). The behaviour is not simply linear as those observed in most of the superconducting oxides and it looks like that of more conventional metals. They have fitted the resistivity data between 35 K and room temperature with an explicit form of Bloch-Gruneisen expression using \(\theta_E = 233 \text{ K}\).

Subsequently, Hellman and Hartford Jr. [Hellman & Hartford93] have measured the normal state resistivity of epitaxial films of Ba-K-BiO, and the temperature dependence of films as grown by the molecular beam epitaxy (MBE) technique shows nearly linear temperature dependence. The lowest resistivity films are quite metallic, with resistivity ratios \([\rho(300)/\rho(30)]\) as high as 1.9, but the temperature dependence of the resistivity becomes more semiconductors like as the
resistivity increases. The high resistivity and its semiconductor like temperature dependence is interpreted using parallel conductivity channels concept. A metallic channel responsible for the conductivity at low temperature and a semiconducting channel that freezes out at low temperatures. They have fitted the resistivity data using $\rho_0 = 0.224 \text{ m}\Omega\text{cm}$ and a scaling factor as fitting parameters. The fit is reasonably good and the estimation of coupling strength $\lambda$ from the temperature dependence would be revised down to about 1.0.

The resistivity of single crystals of cubic $\text{Ba}_0.9\text{K}_{0.1}\text{Bi}_2\text{O}_3$ with $T_c = 30 \text{ K}$ has been reported in the temperature range from 4.2 K-300 K [Golovashkin et al. 94]. The temperature dependence of resistivity of single crystal displays a metal like behaviour. The experimental data is well approximated in the framework of electron-phonon model of resistivity by the Gruneisen type dependence using the phonon spectrum in the form of an acoustic branch and a widely separated narrow optical peak. The analysis reveals that $\rho (T)$ is quadratic versus temperature at low temperature ($T < 180 \text{ K}$) and rises linearly with temperature when $T > 200 \text{ K}$.

Quadratic temperature dependence of $\rho$ is interpreted in terms of dominant electron-electron interaction at low temperatures. Characteristic Debye and Einstein temperatures are estimated as 320 K and 680 K from the generalised phonon density of states as obtained from neutron experiments. Furthermore, the optical phonons of the oxygen-breathing mode yield a relatively larger contribution to the resistivity as well as to the electron-phonon interaction, $\lambda$.

Looking to the earlier experimental and theoretical studies, a creative approach is required to associate the standard phonon model with an exotic model that can explain the observed $T_c$ and associated physical parameters. During the recent past the plasmon mechanism [Kresin87] has emerged as a central theme in the formation of additional pairing and could lead to the high-$T_c$ values in copper oxides. Earlier, Varshney and Singh have made an attempt to study the joint phonon and plasmon mechanism in some cuprates based on a layered electron gas (LEG) model [Varshney & Singh95b]. Deduced results from the LEG approach on superconducting state parameters on some cuprates [Varshney et al. 96c] are consistent with the experimental observations.
The purpose of the present investigation is to study the role of charge oscillations as well as of the phonon breathing mode in the cubic perovskite Ba-Pb-K-BiO and to see what set of parameters can explain the experimental measurements in the normal metallic state. In the present studies, we have confined ourselves to the metallic state; the semiconducting state of this system will be studied separately. Such studies on Ba-Pb/K-BiO system have wide potential as the $T_c$ is high and resembles that of CuO based superconductors. We may also refer to an earlier work of Tachiki and Takahashi [Tachiki & Takahashi 88, 89] who explained the superconductivity in copper oxides, when the pairing interaction is mediated by the charge transfer oscillations associated with LO phonons and suggested a similar mechanism in Ba-Pb-BiO superconductors.

Keeping in mind the dominant role of high frequency oxygen breathing vibrations and the presence of low energy plasmons, we first formulate a 3-D effective interaction potential for the cubic, magnetic free ion Ba-Pb/K-BiO by considering the breathing modes of oxygen in BiO octahedra and charge oscillations developed by the charge transfer from stable Bi atoms. The polarizability of the charge carriers is included through a model longitudinal dielectric function, which fulfills the $f$-sum rule. The coupling parameters such as the interaction strength, $\lambda$, and the Coulomb repulsive parameter, $\mu^*$, are then deduced for a renormalized optical phonon frequency to predict the transition temperature. Ziman’s formula is used to analyse the temperature-dependent part of the electron-optical phonon resistivity. The zero temperature-limited resistivity is deduced from the scattering rate using an experimental value of the critical magnetic field and the theoretically developed coupling parameters. Section 2.4 is devoted to results and discussions.

The main findings of the present analysis include: (a) the participation of optical phonons in the pairing as well for predicting the physical properties and (b) the significant contribution of 3D electron-electron scattering on resistivity from low to moderate temperatures.
2.2. Effective Interaction potential

The parent BaBiO$_3$ system is regarded as diamagnetic charge ordered insulator and the valence configuration is Ba$^{2+}$ and 3O$^{2-}$. The charge of Bi ions of BaBiO$_3$ is +4 and since the neutral Bi atoms have five valence electrons (two 6s and three 6p), an average of one valence electron is left at each Bi atom, making BaBiO$_3$ a system with half filled band. Chemical substitution of monovalent alkali metal K (six 3p and one 4s) at the donar site Ba (six 5p and two 6s) introduces free holes as carriers in the conduction band and the doped systems Ba$_{1-x}$K$_x$BiO$_3$ becomes metallic. The free holes as carriers of effective mass m* actively participate in the pairing mechanism. Also the contraction and expansion of oxygen octahedra around the Bi atoms leads to breathing modes.

As a first step, we write the electron-electron matrix element between the states $|K>$ and $|K'>$ in terms of dielectric function $\varepsilon(q, \omega_{kk'})$ as

$$V_{kk'} = \frac{4\pi e^2}{q^2 \varepsilon(q, \omega_{kk'})},$$

where $q = K-K'$, $\omega_{kk'} = [E(K) - E(K')]/\hbar$ and $E(K), E(K')$ denote the corresponding energies of the states.

The dielectric function of a metal oxide, will be the sum of contributions of electronic and ionic polarizabilities. The model dielectric function is

$$\varepsilon(q, \omega) = \varepsilon_\infty + \frac{\omega_p^2}{(\omega_0^2 - \omega^2)} + \frac{\varepsilon_\infty (\omega_{LO}^2 - \omega_{TO}^2)}{(\omega_{TO} - \omega^2)},$$

where $\omega_0^2 = q^2e^2/2$ with $v_F$ as the Fermi velocity. The notations $\omega_{LO}$ and $\omega_{TO}$ are the usual frequencies of the longitudinal and transverse optical phonons. In a true sense, the Bi atom has two stable ionic states in the form of Bi$^{+3}$ and Bi$^{+5}$ and the bond stretching oxygen displacements leads to a charge density wave distortion in which the oxygen octahedra surrounding adjacent Bi sites are alternatively expanded or contracted. It is useful to consider a single optical phonon whose vibrational frequencies are independent of wave vector ($q$). The first term in the previous equation is the polarisability of core electrons and in the frequency region of interest it is independent of frequency and is constant denoted as $\varepsilon_\infty$. 
The model dielectric function for the polarized waves becomes

\[
\varepsilon(q, \omega) = \left[1 + \frac{D_1}{\omega^2 - \omega_1^2} + \frac{D_2}{\omega^2 - \omega_2^2}\right]
\]

(3)

where \(D_1 = \sigma_\text{p}^2\) is the screened plasma frequency, \(D_2 = \omega_{LO}^2 - \omega_{TO}^2\) and \(\omega_{\text{TO}}^2\) are respectively. The main input parameter which determines the superconducting and the normal states transport parameters is inhibited in the dynamic interaction potential \(V(q, \omega)\) or equivalently \(\varepsilon^{-1}(q, \omega)\) of the system under consideration. The inverse dielectric function is associated with different longitudinal modes, corresponding to the exchange of ionic as well as electronic excitations. The separation of individual contributions from different longitudinal modes can be made possible by inverting Eq.(3) of the following from

\[
\varepsilon(q, \omega) = \left[1 + \sum_{i=1}^{2} \frac{f_i}{\omega^2 - \Omega_i^2}\right]
\]

(4)

with \(\Omega_i\) are the frequencies of two longitudinal modes and the resonant frequencies are expressed as

\[
(\Omega^2 - A_1^2) (\Omega^2 - A_2^2) + D_1 (A_2^2 - \Omega^2) + D_2 (A_1^2 - \Omega^2) = 0
\]

(5)

The effective interaction potential \(V(q, \omega)\) is the sum of electronic and ionic contributions i.e., \(V(q, \omega) = \varepsilon_c(q) \varepsilon^{-1}(q, \omega)\) from the individual longitudinal modes. The oscillator strength is defined as

\[
f_i = \sum_{i=1}^{2} \left[\Omega_i^2 - A_i^2\right] / \sum_{i \neq j} \left[\Omega_i^2 - \Omega_j^2\right]
\]

(6)

The following f- sum rules are valid:

\[
\sum_{i=1}^{2} \Omega_i^2(q) = D_1 + D_2 + A_1^2 + A_2^2
\]

(7)

\[
\sum_{i=1}^{2} f_i(q) = D_1 + D_2
\]

(8)

\[
\sum_{i=1}^{2} f_i(0) / \Omega_i^2(0) = 1
\]

(9)
where, \( \frac{f(0)}{\Omega^2(0)} \) is the limiting value of \( \frac{f(q)}{\Omega^2(q)} \) in the long wavelength limit. This implies that \( \epsilon \rightarrow (q \rightarrow 0,0) > 0 \) when \( \omega = 0 \).

Zero's of the model dielectric function will lead two modes of the polarized waves and the frequencies of the coupled mode in the long wave length limit are expressed as

\[
30.2^2 = [\omega_p^2 + A_1^2 + \omega_{LO}^2] \pm [(\omega_p^2 + A_1^2 + \omega_{LO}^2)^2 - 4(A_1^2 \omega_{LO}^2 + \omega_{TO}^2 \omega_p^2)]^{1/2} \quad (10)
\]

A simple algebra yields

\[
\Omega^2_+ \equiv \omega_p^2 + A_1^2
\]

which infers the 3D plasmon characteristics. The lower mode is expressed as

\[
\Omega^2 = \frac{(\omega_{LO}^2 + \omega_{TO}^2) \omega_p^2}{2 \omega_p^2 + \omega_{LO}^2} \approx \omega_{LO}^2 \quad (12)
\]

that is a longitudinal optical phonon mode, in the adiabatic approximation i.e., \( \omega_p \gg \omega_{LO} \) and \( \omega_{TO} \).

The modelled longitudinal dielectric function in terms of lower \( (\hbar \Omega_-) \) and upper \( (\hbar \Omega_+) \) mode is

\[
\frac{\epsilon(q, \omega)}{\epsilon_{\infty}} = \frac{(\omega^2 - \Omega^2_+) (\omega^2 - \Omega^2_-)}{\omega^2 (\omega^2 - A_1^2)} \quad (13)
\]

and the interaction potential takes the following form

\[
V(q, \omega) = \frac{4 \pi e^2}{q^2 \epsilon_{\infty}} \left[ 1 + \frac{\Omega^2_+ (\Omega^2_- - A_1^2)}{\omega^2 (\omega^2 - \Omega^2_-)(\omega^2 - \Omega^2_+)} + \frac{\Omega^2_- (\Omega^2_- - A_1^2)}{\omega^2 (\omega^2 - \Omega^2_-)(\omega^2 - \Omega^2_-)} \right] \quad (14)
\]

which essentially describes the coupling strength for scattering a Fermion from \( |k\rangle \) to \( |k'\rangle \) state in the long wavelength limit. To justify the above approach for Ba-Pb/K-BiO\(_3\) superconductors, the parameters describing the superconducting states are investigated in the next subsection.

### 2.3 Superconducting states parameters

Any theory of pairing mechanism to yield superconducting transition temperature \( T_c \) requires the information about the coupling constants as electron-phonon coupling strength and the Coulomb repulsive parameters. In the traditional
approach to the theory of superconductivity, the phonon mediated interaction strength is usually treated first and the direct Coulomb interaction is subsequently introduced in terms of Morel Anderson pseudopotential, $\mu^*$. In a true sense, from the viewpoint of considering the energy scales, it might appear more reasonable to first take into account the large electron-electron interaction and later the electron-phonon interaction strength is incorporated.

The effect of screening of electrons is determined by the renormalized Coulomb repulsive parameter [Bogolyubov et al. 59. Morel & Anderson62] as

$$\mu^* = \frac{\mu}{[1 + \mu \ln (\varepsilon_F / \hbar \Omega_\ell) \varepsilon]}$$

with $\hbar \Omega_\ell$ as the longitudinal optical phonon energy and $\mu$ is the repulsive parameter obtained from the Thomas Fermi wave vector ($k_F$) as

$$\mu = a^2 \ln \left[ \frac{1 + a^2}{a^2} \right]$$

Here, $a^2 = k_s^2/4k_F^2$ with the screening length $k_s^2 = 4\pi\varepsilon^2 N(\varepsilon_F)$. The density of states at Fermi energy $N(\varepsilon_F)$ in three dimensions is

$$N(\varepsilon_F) = \frac{1}{2\pi^2} \left[ \frac{2m^*}{\hbar^2} \right]^{3/2} \varepsilon_F^{1/2}$$

Inelastic neutron scattering measurements and the superconducting tunnelling spectroscopy yields the electron phonon spectral weight $\alpha^2 F(\omega)$ from a strong coupling inversion procedure and hence the electron-phonon coupling strength with great accuracy. Alternately, the coupling strength can also be evaluated from the McMillan expression which is related to the mean square electron ion matrix element, $\langle I^2 \rangle$, the density of states at the Fermi level, $N(\varepsilon_F)$, the ionic mass, $M$, and the renormalized phonon frequency, $\langle \omega^2 \rangle^{1/2}$. The use of McMillan expression in the present system Ba-Pb/K-BiO seems to be appropriate because of large density of states as well the large mass difference of Bi and O.

The dimensionless electron-phonon coupling strength is [McMillan68]

$$\lambda = \frac{N(\varepsilon_F) \langle I^2 \rangle}{M \langle \omega^2 \rangle^{1/2}}$$
The mean square electron-ion matrix element is

\[
\langle |l|^2 \rangle = \frac{\left[ \frac{\Omega_{\text{cell}}}{2\pi^3} \right]^2}{\left[ \frac{\Omega_{\text{cell}}}{2\pi^3} \right]^2} \int d^3k \int d^3k' \left( k-k' \right)^2 \left| V(k-k') \right|^2 \delta(E_k-E_{\text{F}}) \delta(E_{k'}-E_{\text{F}})
\]

\[
\frac{2k_F}{\left[ N(E_{\text{F}}) \right]^2} \int_0^{2k_F} (qdq / 2k_F) q^2 |V(q)|^2
\]

\[
\frac{\int_0^{2k_F} q^2 dq |V(q)|^2}{\int_0^{2k_F} q dq}
\]

where \( V(q) \) is the screened Coulomb potential and the static dielectric function. \( \varepsilon(q) \) is obtained from Eq. (2) as

\[
\varepsilon(q) \approx \frac{4 m^* e^2 k_F}{(\pi \hbar^2 q^2)}
\]

Thus, the screened Coulomb potential is

\[
V(q) = \frac{4 \pi Z e^2 / (q^2 \Omega_{\text{cell}} \varepsilon_x)}{4 m^* e^2 k_F / (\pi \hbar^2 q^2)}
\]

\[
= \frac{\hbar^2 \pi^2 Z}{m^* k_F \Omega_{\text{cell}} \varepsilon_x}
\]

with \( \Omega_{\text{cell}} \) is the volume of the cell and \( Z e \) is the effective ionic charge.

The mean square electron-ion matrix element using Eq. (18) and (20) becomes

\[
\langle |l|^2 \rangle = \frac{1}{2K_F^2} \left[ \frac{\hbar^2 \pi^2 Z}{\varepsilon_x m^* K_F \Omega_{\text{cell}}} \right]^2 \int_0^{2k_F} q^2 dq
\]

and the electron-phonon coupling strength is

\[
\lambda = \frac{2N(E_{\text{F}})}{M} \left[ \frac{\hbar^2 \pi^2 Z}{m^* \Omega_{\text{cell}} \varepsilon_x} \right]^2 \frac{1}{<\Omega^2>}
\]
Using the screened Coulomb repulsive parameter, $\mu^*$ and the electron-phonon coupling strength, $\lambda$, for the renormalized phonon frequency, we estimate $T_c$ for doped BaBiO$_3$ in the weak coupling theory ($\lambda \leq 1$) as [McMillan68]

$$T_c = 0.7 \Omega_0 \exp \left[ -\frac{1+\lambda}{\lambda-\mu^*} \right]$$

In the regime $\lambda \geq 1$, the strong coupling theory applies [Kresin87], yielding

$$T_c = 0.25 \Omega_0^{1/2} \left[ \exp(2/\lambda_{\text{eff}}) - 1 \right]^{1/2}$$

with

$$\lambda_{\text{eff}} = (\lambda - \mu^*) \left[ 1 + 2\mu^* + 2\mu^*t(\lambda) \right]^{-1}$$

and the numerical function, $t(\lambda)$ having the form

$$t(\lambda) = 1.5 \exp(-0.38\lambda)$$

The isotope effect exponent is

$$\alpha = -\frac{\text{d} \ln T_c}{\text{d} \ln M} = \frac{1}{2} \left[ 1 - \frac{\mu^*}{\lambda-\mu^*} \right]$$

The energy gap parameter ($\beta$) is expressed as

$$\beta = \frac{2\Delta}{k_B T_c} = 3.52 \left[ 1 + 5.3 \left( \frac{T_c}{\Omega_0} \right)^2 \ln \left( \frac{\Omega_0}{T_c} \right) \right]$$

Using the developed expressions, the superconducting transition temperature $T_c$, $\alpha$ and $\beta$ in BaPb$_{1-x}$Bi$_x$O$_3$ ($x = 0.25$) and Ba$_{1-x}$K$_x$BiO$_3$ ($x = 0.4$) are estimated in the preceding section. The approach is further applied to investigate the normal state transport properties in particular electrical resistivity in the following subsection.

### 2.4. Normal state resistivity

The Bloch Boltzmann theory based on Migdal approximation, which is valid if the electron-phonon scattering process dominates i.e., on the existence of small parameter $[N(\varepsilon_F)\hbar\Omega_0]$ is understood to describe better the normal state transport properties. The contribution to the normal state resistivity $\rho(T)$ due to electron-phonon scattering is calculated using Ziman's resistivity formula [Krishnan & Bhatia45;Ziman60]
\[ \rho_{e-ph}(T) = \left[ \frac{(4\pi)^2}{\omega_p^2} \right] \int_{0}^{\omega_{\text{max}}} \frac{(\hbar \omega/k_B T) \alpha_{\text{tr}}^2 F(\omega) d\omega}{[\exp(\hbar \omega/k_B T) - 1] [1 - \exp(-\hbar \omega/k_B T)]} \quad (26) \]

where \( \omega_{\text{max}} \) is the cut off frequency of the phonon spectrum and \( \omega_p \) is the bare plasma frequency. At temperatures \( k_B T > \hbar \omega_{\text{ph}} \), the resistivity expression can be reduced to

\[ \rho_{e-ph}(T) = \frac{8 \pi^2 k_B T \lambda_{\text{tr}}}{\hbar \omega_p^2} \quad (27) \]

The bare plasma frequency is related to the density of states at the Fermi level through

\[ \omega_p^2 = \frac{4\pi e^2}{3} 2N(\varepsilon_F)\langle v_F^2 \rangle \quad (28) \]

The transport electron-phonon coupling constant \( \lambda_{\text{tr}} \) which relates to the resistivity requires the spectral weight \( \alpha_{\text{tr}}^2 F(\omega) \) while to that superconducting transition temperature depends on \( \alpha^2 F(\omega) \). The expressions for \( \alpha_{\text{tr}}^2 F(\omega) \) and \( \alpha^2 F(\omega) \) seems to be quite similar except for the fact that the transport expression weighs the differences in the Fermi velocities between different points on the Fermi surface. Use of \( \alpha_{\text{tr}}^2 F(\omega) \) is generally believed to result in no significant qualitative error [Allen & Schulz93].

However these exists a noteworthy difference in between \( \lambda \) and \( \lambda_{\text{tr}} \) for the case a) strongly nested Fermi surface where \( \lambda_{\text{tr}} \) is smaller than \( \lambda \) due to back scattering of electrons between the opposite sides of Fermi surface and b) the electron-phonon matrix have a strong dependence on the wave vector \( q \). The situation in Ba-Pb/K-BO is clear, as the Fermi surface is not complex due to its isotropic nature. The high-energy optical phonons should exhibit very little dispersion and suggesting that electron-phonon coupling for these modes is isotropic in \( k \)-space. Thus it is speculated that their does not exists a substantial difference in between \( \lambda \) and \( \lambda_{\text{tr}} \).

The temperature dependent part of the normal state resistivity can now be expressed using Eqs. (22 and 27) as
Besides electron-phonon scattering, other scattering mechanisms as electrons scatter off impurities, defects and disordered regions give rise to a temperature independent contribution are also possible. Knowledge of zero temperature scattering rate and bare plasma frequency will allow us to have an independent estimation of zero temperature-limited resistivity. The zero temperature scattering rate is related through the upper critical magnetic field $H_{c2}(0)$. Using the method described by Carbotte [Carbotte90], we write

$$\frac{1 + \lambda}{\lambda - \mu^*} = 2\pi \frac{T}{T_c} \sum_{i=0}^{N_e} \frac{1}{\chi_i^{-1} - (2\tau^*)^{-1}}$$

(30)

where

$$N_e = \frac{1}{2} \left[ \frac{\omega}{\pi T} + 1 \right]$$

(31)

and

$$\chi_i = \frac{2}{\sqrt{\alpha^*}} \int_0^{\infty} \exp(-q^2) \tan^{-1}(\beta) dq$$

(32)

with

$$\beta = \frac{q\sqrt{\alpha^*}}{[ (2i + 1) \pi T/T_c ] + [ \tau^*/2 ]}$$

(33)

The symbols $\lambda$ and $\mu^*$ are the electron phonon coupling strength and renormalized Coulomb repulsive parameter as expressed by Eqs. (22) and (15) respectively.

The upper critical magnetic field $H_{c2}$ is related to $\alpha^*$ through

$$\alpha^* = \frac{e H_{c2}^* v_F^*}{2}$$

(34)

The renormalized quantities are related with the coupling strength as $H_{c2}^* = H_{c2}[(1+\lambda)T_c]^{-1}$, $v_F^* = v_F[(1+\lambda)^{1/2}T_c]^{-1}$ and $\tau^* = [1+\lambda]T_c$. The zero temperature-limited resistivity is now expressed as

$$\rho(0) = \frac{4\pi \tau^*}{\omega_p^2}$$

(35)

The determination of scattering rate essentially needs the Coulomb repulsive parameter, electron phonon coupling strength, Fermi velocity, plasma frequency and upper critical magnetic field. We use the magnetisation measurement data to
estimate $H_{c2}$ and the remaining parameters are earlier discussed. This allows one to estimate the zero temperature limited resistivity and hence the two component resistivity is modelled as $\rho(T) = \rho(0) + \rho_{e-ph}(T)$.

Using the developed expression for superconducting and normal state parameters in high-$T_c$ Ba-Pb/K-BiO superconductors we have computed the model parameters and the result along with discussions are presented in the following section.

2.5. Results and Discussion

In order to compute the physical parameters describing the superconducting and normal state of high-$T_c$ cubic Ba-Pb/K-BiO superconductors, we have used experimental data as follows. Keeping in mind that the experimentally reported physical parameters provides constraints on any proposed approach the effective mass of the charge carriers (electrons) is evaluated from the electronic specific heat coefficient ($\gamma$) through the expression

$$m^* = \frac{3\hbar^2 \gamma d}{\pi K_B^2} = \frac{N(E_F)}{N(E_F^0)}$$

with $N(E_F)$ is the band density of states calculated from the electronic specific heat coefficient ($\gamma$) data as 1.5 mJmol$^{-1}$K$^{-2}$ [Cava et al. 87]. We use the value of $N(E_F^0) = 1.38 \times 10^{39}$ states mJ$^{-1}$ mol$^{-1}$, as reported by Itoh et al. [Itoh et al. 84] to obtain $m^* = 1.5 m_e$ for Ba-Pb-BiO. Switching to Ba-K-BiO we use $\gamma$ as 1.5 mJmol$^{-1}$K$^{-2}$ from the specific heat measurements [Grabener et al. 89] and the lattice parameter $d = 4.3$ Å to get $m^* = m_e$. The background dielectric constant $\varepsilon_x$ is taken as 4.0 [Tajima et al. 87]. The charge carrier density and Fermi velocity are deduced as 3.2 (3.16) $\times$ 10$^{21}$ cm$^{-3}$ and 3.5 (5.23) $\times$ 10$^7$ cmsec$^{-1}$ for Ba-Pb-BiO (Ba-K-BiO) respectively. Now we wish to estimate the breathing phonon frequency of Ba-Pb/K-BiO superconductors, considering the system as ionic solid.

The Coulomb interaction among the adjacent ions in an ionic crystal is expressed in terms of deformation potential [Born & Huang66; Venkatraman & Sahni70; Singh82] as

$$\phi(r) = - (Ze)^2 \left[ \frac{1}{r} - \frac{a}{r^2} \right]$$

(37)
where $a$ is the repulsion force parameter between the ion cores. The effective ion charge is $Ze$ and is $-2e$. The elastic force constant ($K^*$) can be derived from the ionic potential, $\phi(r)$, at the equilibrium inter ionic distance ($r_0$) as

$$K^* = \left[ \frac{\partial^2 \phi}{\partial r^2} \right]_{r_0} = (Ze)^2 \left[ \frac{n - 1}{r_0^3} \right]$$  \hspace{1cm} (38)

where $n$ is the index number of the repulsive potential. We have used $n = 6$ for the Ba-Pb-BiO (Ba-K-BiO) system under consideration as in most of the ionic solids, the index number have been reported to be $6 \sim 10$ [Tosi & Fumi64]. The equilibrium inter ionic distance $r_0$ is taken as $2.21 \,(2.14)$ A for Ba-Pb-BiO (Ba-K-BiO), respectively.

The force parameter ($\beta^*$) is

$$\beta^* = \frac{8}{3} \frac{(Ze)^2}{\Omega_{cell}}$$  \hspace{1cm} (39)

with $\Omega_{cell}$ is the volume of the cell and is $316.3 \,(316.52)$Å$^3$. With this description the longitudinal and transverse optical phonon frequencies in terms of elastic force constant and force parameter are expressed as

$$\omega_{LO}^2 = \frac{1}{\mu(M)} [K^* + \beta^*]$$  \hspace{1cm} (40)

and

$$\omega_{TO}^2 = \frac{1}{\mu(M)} [K^* - \beta^*]$$  \hspace{1cm} (41)

Here, the reduced mass, $\mu(M)$ is determined as

$$\mu(M) = \frac{M(Bi)M(O)}{M(Bi) + M(O)}$$  \hspace{1cm} (42)

and is $14.84$ amu. The basic premise of the interaction is inhibited in the BiO network where the charge carriers as developed with the chemical doping are dynamic and will lead to an attractive interaction. When the interaction is mediated by phonons, then the breathing phonon modes related to contraction and expansion of oxygen octahedra around bismuth atoms will contribute for the most and in particular the longitudinal modes will contribute effectively to the deformation potential. The force parameters are deduced as $K^* = 30.844 \,(23.293) \times 10^4$ gm sec$^{-2}$ and $\beta^* = 1.763 \,(2.439) \times 10^4$ gm sec$^{-2}$. The estimated $\omega_{LO}$ is about $75.7(67.2)$ meV,

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which is consistent with the high resolution tunnelling spectroscopy data for Ba-Pb-BiO (Ba-K-BiO), respectively.

With these realistic parameters based on experimental information we have calculated the upper and lower mode i.e., \( \hbar \Omega_+ \) and \( \hbar \Omega_- \) respectively. The scattering of charge carriers at Fermi surface is considered for all values of scattering angle \( \theta \). The wave vector \( (q = 2k_F \sin \theta) \) can therefore take maximum values up to \( 2k_F \). The bare plasma frequency from Eq.(28) is estimated as 1.47 eV. The plasmon energy using Eq. (11) is deduced as 1.70 (2.65) eV at \( 2k_F \). The lower mode is 73.47(52.42) meV, which is smaller than the bare longitudinal phonon frequency. The coupling strength between the electrons from the lower mode using density of states at Fermi level and McMillan Hopfield parameter is obtained as 0.73(0.98) for Ba-Pb-BiO (Ba-K-BiO), respectively.

Let us first discuss the \( T_c \) of Ba-Pb-BiO. We estimate density of states at Fermi level from Eq. (16) as 0.59 states/eVspin atom. The screened Coulomb repulsive parameter \( \mu^* \) is deduced as 0.31 for the renormalized optical phonon frequency which clearly infers the poor screening. With these parameters, we deduce \( T_c \) of optimised doped Ba-Pb-BiO as 9.7 K, which is consistent with the reported \( T_c \approx 13 \) K [Sleight et al.75]. This allows one to propose that the coupling of charge oscillations with longitudinal optical phonons plays a key role in the pairing mechanism of Ba-Pb-BiO leading to superconducting state [Varshney et al. 97b,98c].

Switching to Ba-K-BiO system the Coulomb repulsive parameter \( \mu^* \), the numerical function \( t(\lambda) \) and effective coupling strength \( \lambda_{\text{eff}} \) are obtained as 0.26, 1.14 and 0.48 respectively, to get a \( T_c \) of 32 K within the framework of strong coupling theory. The calculated value of \( T_c \) is in reasonably good agreement with the reported experimental data of 30 K. Precisely the above set of coupling parameters \( (\lambda=0.98 \text{ and } \mu^*=0.26) \) for the renormalized optical phonon frequency (52.42 meV) will provide a good choice for the estimation of superconducting transition temperature in high-\( T_c \) Ba-K-BiO superconductors [Varshney et al. 98d].

The proposed model calculation also predicts the existence of an oxygen isotope effect \( (\alpha) \). An oxygen isotope effect has been observed [Batlogg et al.88] as
$\alpha = 0.22$ in a Ba-Pb-BiO system although with a smaller value than in the BCS limit. Since the mass of oxygen directly influences the optical phonon frequencies and hence the $T_c$, one may expect a reasonable oxygen isotope effect. Eq. (25) estimates $\alpha$ as 0.23, which is consistent with the experimental value. Although the pure BCS value of $\alpha$ is 0.5, the theoretically calculated values suggest the crucial role of oxygen breathing vibrations and their coupling to the electronic states at the Fermi level. The smaller value of calculated $\alpha$ in Ba-Pb-BiO is attributed to the proper choice of superconducting state parameters based on the experimental data's of the system in the proposed approach.

Besides transition temperature and oxygen isotope effect, the energy gap parameter ($\beta$) has also been estimated for Ba-Pb-BiO. The BCS gap ratio $2\Delta/k_B T_c$ is evaluated as 3.53, which is in agreement with the reported value of 3.5 ± 0.5 for bismuth compounds [Batlogg et al.88, Gupta92]. Recently, Navarro [Navarro96] has presented the results of thermodynamical analysis on BaPb$_{0.7}$Bi$_{0.3}$O$_3$ and found that the value of energy gap ratio ($\beta=2\Delta/k_B T_c$) is 3.57, close to the BCS limit. With the present analysis on the superconducting state parameters, one cannot escape in stating that Ba-Pb-BiO is a weak coupling superconductor, while to that Ba-K-BiO is strongly coupled superconductor. Reduced isotope effect coefficient and slightly enhanced energy gap in Ba-Pb-BiO supports the active participation of screened phonons in the pairing mechanism that we have treated [Varshney et al.98c].

Turning to the normal state resistivity of Ba-K-BiO. we first deduce the zero temperature limited resistivity $\rho(0)$. It naturally demands the estimation of elastic scattering rate which essentially depends on coupling parameters ($\lambda$, $\mu^*$), Fermi velocity and upper critical magnetic field $H_{c2}(0)$. The coupling parameters ($\lambda = 0.98$, $\mu^* = 0.26$) as well as the Fermi velocity ($v_F = 5.23 \times 10^7$ cmsec$^{-1}$) are earlier estimated. We use the experimental value of $H_{c2}(0) = 22.7$ Tesla from the linear extrapolation of upper critical field phase diagram [Kwok89]. With the above deduced model parameters, the zero temperature elastic scattering rates is thus obtained as $2.285 \times 10^{14}$ sec$^{-1}$. It is believed that the smaller the carrier mass, the larger the plasma frequency and hence the enhanced zero temperature elastic scattering rate.
We further estimate the zero temperature mean free path $L = v \tau = 23.2 \text{Å}$ which is one half then the zero temperature coherence length of $53 \pm 1 \text{Å}$ [Sato et al. 91]. The Mott-Ioff-Regel criterion for metallic conductivity is valid, as the mean free path is several times larger than Bi-O bond length (~2Å). A significantly enhanced mean free path is an indicative of metallic conduction as the product $kL (=10.52)$ seems to be much larger than unity. Zero temperature limited resistivity $\rho(0) = 0.5 \text{ mΩcm}$ as deduced from elastic scattering rate and plasma frequency is consistent with the single crystal result of $0.575 \text{ mΩcm}$.

Our numerical results on the temperature dependence of resistivity of Ba$_{0.6}$K$_{0.4}$BiO$_3$ with electron-optical phonon contribution together with residual resistivity are plotted in Fig. 2.1 along with the single crystal data. It is inferred from the plot that the estimated $\rho$ is lower than the reported data from $T_c$ to near room temperature. The deduced values of temperature dependent $\rho$ from the Ziman's formula appears low as $\rho_0$ and $\omega_p$ values are the constraints for the present analysis [Varshney et al. 98d].

![Fig. 2.1. Variations of normal state resistivity ($\rho$) with temperature in Ba$_{0.6}$K$_{0.4}$BiO$_3$ superconductors. The experimental data (closed circles) are taken from Affronte et al. 93. Estimated values are presented by straight line.](image)

Nevertheless, the role of high frequency optical phonons is more explored and found prominent in not only for the interpretation of superconducting state parameters but also normal state transport parameters. Thus the estimated model
parameters \([\lambda, \mu^*, \nu, \omega_p, \tau(0) \text{ and } \rho(0)]\) represents a good set of parameters for the estimation of normal state resistivity in high-\(T_c\) Ba-K-BiO superconductors.

The difference in between the measured \(\rho\) and calculated \(\rho (= \rho_0 + \rho_{\text{el-ph}})\) in the temperature range 30 K to 280 K is plotted in Fig. 2.2. A quadratic temperature dependence of \(\rho\) is depicted at low as well moderate temperature. It is depicted from the plot that \(T^2\) characteristic of \(\rho\) is till 200 K and it deviates in the high temperature limit. The quadratic temperature contribution is indeed from conventional 3-D electron-electron scattering, then its magnitude essentially depends on the charge carrier density \(n\) as \(n^{5/3}\) and plasma frequency \(\omega_p\) as \(\omega_p^{-10/3}\). It is noteworthy to comment that in conventional metals, the electron-electron contribution to the resistivity can at best be seen only at very low temperatures due to its small magnitude when comparison is made with phonon contribution.

It is worth while to refer to an earlier work of Golovashkin et al. [Golovashkin et al. 94] who analysed the temperature dependence of resistivity (\(\rho\)) and found that \(\rho(T)\) is quadratic versus temperature till \(T < 180\) K and rises linearly with temperature when \(T > 200\) K. The existence of \(\rho(T) \propto T^2\) a rather wide temperature range \(30 \leq T \leq 300\) was previously interpreted in terms of electron-electron scattering for \(\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4\) superconductors [Tsuei et al 89]. While interpreting the resistivity data, Golovashkin et al. have used the values of Debye
and Einstein temperatures as determined from the phonon density of states using the neutron scattering data.

On the other hand in the present model calculations, we have used the coupling strength for optical phonons as deduced from density of states at Fermi level and McMillan Hopfield parameter. The electron-ion matrix element in the McMillan Hopfield parameter is derived from the Coulomb potential with static dielectric function in the long wavelength limit. While determining the longitudinal optical phonon frequency, we made an approximation that vibrational frequencies are independent of wave vector \( q \), and used nearest neighbor ionic potential.

Golovashkin et al. has predicted a crossover from \( T^2 \) to \( T \) characteristic of normal state resistivity. It is argued that the change of law \( \rho(T) \propto T^2 \) at low temperature to \( \rho(T) \propto T \) at high temperatures as observed in electron doped cuprates [Tsuei & Koren89] which is related to a 3-D to 2-D crossover is not true for Ba-K-BiO system with cubic structure and its electron system is not likely to change the dimensionality. From the present analysis of normal state resistivity in Ba-K-BiO systems we support the argument made by Golovashkin et al. The 3-D to 2-D crossover concept is although applicable to anisotropic cuprates because of their low dimensionality, but it does not hold for three-dimensional isotropic cubic Ba-K-BiO superconductors. Furthermore, the analysis of normal state resistivity reveals the significant participation of optical phonons of oxygen-breathing modes in electronic transport mechanism, which is consistent with earlier explanation.

In conclusion the developed 3-D effective interaction potential for cubic Ba-Pb/K-BiO superconductors successfully explains the superconducting state properties as well the normal state resistivity behaviour by electron pairing mediated with high-energy optical phonons of the oxygen breathing mode. Looking at the remarkable success of the present effective potential, we have devoted our efforts to understand some of the physical properties of the superconducting state in the layered La-Sr-CuO cuprate superconductors. The details of the 2-D effective dynamic potential are presented and discussed in the next chapter.