Interpretation of anomalies in thermal conductivity of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ superconductors

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Abstract. We propose a theoretical model to account the anomalies reported for the thermal conductivity ($\kappa$) of the high-$T_c$ superconductor $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$. We begin with the lattice thermal conductivity by incorporating the scattering of phonons with defects, grain boundaries, electrons, and phonons in the model Hamiltonian. The lattice thermal conductivity dominates in this material is an artefact of strong phonon-defects, and impurity scattering mechanism below $T_c$. Later on, the scattering of electrons with electrons is investigated in order to assess their role towards thermal conduction. We find that at much low temperatures ($T < 10$ K), $\kappa$ increases and show the power temperature dependence are attributed to phonon–electron interaction. Further at higher temperatures $\kappa$ become almost linear. The anomalies are well accounted in terms of interaction among the phonons-impurity and the carrier-carrier. In conclusion the behaviour of the thermal conductivity depends on competition among the several operating scattering mechanisms for the heat carriers and a balance between electronic and phononic contributions.

1. Introduction

The source of anomalous physical properties and attractive pairing mechanism in high-$T_c$ superconductors holds to create a wide interest, as no straightforward mechanism is currently known. Phonons are important in an ionic lattice such as $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, phonon density of states of superconducting $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ are determined by inelastic neutron scattering measurements [1], the phonon spectrum of this material is soften and is comprised of two bands around 30 and 60 meV. The Raman spectra [2] show the broad peak centered around 325 cm$^{-1}$ and an extremely broad peak extending from about 375 to 650 cm$^{-1}$.

Peacor et al. [3] has reported the experimental results of thermal conductivity $\kappa(T)$ of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, results shows the anomalous temperature dependence of $\kappa$. The measurement of the thermal conductivity can yield valuable information not only about phonons and carriers, the interaction between them but also about the impurities in the system. To account the observed anomalies, we have employed the Debye model and a BCS-like model by incorporating the scattering of heat and charge carriers with various irregularities in the crystal.

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2. The model

We start with a model Hamiltonian that follows [4]

\[ H = \sum_k \varepsilon_k a_k^+ a_k + \sum_q \omega_q b_q^+ b_q + \sum_{k_1, k_2} \phi(k_1, k_2) a_{k_1}^+ a_{k_2} + D \sum_{k, q} \left( -\frac{\hbar}{2 \rho \omega_q} \right)^{1/2} a_{k+q}^+ a_k (b_q + b_{-q}) \]

(1)

Here, initial two terms is holes as carriers and phonon excitation. The third and fourth terms represent the carrier-impurity interactions and carrier-phonon interactions, respectively. The fifth term denotes the phonon-impurity interactions and the last term stands for the phonon-phonon interaction.

The notations \( a (a^+) \) and \( b (b^+) \) are the creation (annihilation) operators for holes and phonons. Further, \( \varepsilon_q \) is hole free energy, phonon frequency of a wave vector \( q \) is \( \omega_q \), \( D_p \) is the deformation-potential constant. \( R \) is the relative ionic-mass difference \( (M'' - M)/M'' \) where \( M \) and \( M'' \) are mass of Oxygen and Bismuth ions respectively, respectively. \( N \) is number of cells. \( \rho \) is the mass density of ions and \( r_i \) stands for the position of defects. We begin with phonon contribution to thermal conduction.

2.1. Lattice (Phonon) contribution

The thermal conductivity can be calculated from the Kubo formula [4]. It has contributions from both the phonons and the carriers. We first look for the lattice part and in the continuum approximation it follows

\[ \kappa_{ph} = \frac{k_B \hbar^2}{2 \pi^2 \nu_s} \int_0^{\omega_D} d\omega \omega^2 \tau(\omega) (\beta \omega)^2 \frac{e^{\beta \omega}}{(e^{\beta \omega} - 1)^2}, \]

(2)

with \( k_B \) is the Boltzman constant, \( \nu_s \) is the sound velocity, \( \omega_D \) is the Debye frequency and \( \beta = \hbar/k_B T \). The relaxation time is proportional to the imaginary part of the phonon self-energy. In the weak interaction case, it has been calculated to the lowest order of the various interactions. The relaxation times are expressed as

\[ 1/ \tau(\omega) = 2 \left[ \text{Im} P(\omega / \nu_s, \omega) \right] \]

\[ = 1/ \tau_{ph-d} + 1/ \tau_{ph-e} + 1/ \tau_{ph-gb} + 1/ \tau_{ph-ph}, \]

(3)

with the various relaxation times are defined as

\[ \tau^{-1}_{ph-d}(\omega) = (A / k_B^3) \omega^4 \hbar^3, \]

(4)

\[ \tau^{-1}_{ph-e}(\omega) = B \omega n_F(\Delta), \]

(5)

\[ \tau^{-1}_{ph-gb}(\omega) = \nu_s / L, \]

(6)

\[ \tau^{-1}_{ph-ph}(\omega) = C(T \omega \hbar / k_B)^3 \]

(7)

where \( L \) is the sample size, \( n_F \) is the Fermi-Dirac distribution function and \( \Delta \) is the gap function. The notation \( \tau_{ph-d}, \tau_{ph-e}, \tau_{ph-gb}, \) and \( \tau_{ph-ph} \) are the phonon scattering relaxation time due to defects, carriers, grain boundaries, and phonon-phonon interactions respectively. We note that to this order Mathiessen’s rule holds namely, that the inverse of the total relaxation time is the sum of the various contributions for the different scattering channels.

Further we define \( A = \left[ \frac{3n_i R^2}{4 \theta_D^2} \right] \) and \( B = \frac{9 \pi}{4} \left[ \frac{m}{3M} \right]^{1/2} \frac{D_p^2}{E_F^2} \), are parameters, which characterize the strengths of the phonon-defect and phonon-carrier scattering process. Here, \( n_i \) is the density of impurities or defects, \( E_F \) is the Fermi energy of holes as carriers, and \( m \) is its mass. We shall proceed
to include the effect of electrons as carrier contribution towards thermal contribution in the next subsection.

2.2. Carrier (Electrons) contribution

The carrier component of the thermal conductivity following kinetic theory [5] is

$$\kappa_c = \frac{\pi^2}{3} n_e(T) \frac{k_B^2 T}{m^*} \tau_e(T)$$  \hspace{1cm} (8)

with $n_e(T)$ is the concentration of normal charge carriers of effective mass $m^*$ and $\tau_e(T)$ is the temperature-dependent carrier relaxation time.

Let us consider a two-fluid model in which condensation of charge carriers occurs below $T_c$, and supposing that charge carriers are fully condensed into Cooper pair at zero temperature. The temperature dependence of normal charge carriers follows

$$\Delta - = \Delta(T) \exp \left( \frac{-\Delta(T)}{k_B T} \right)$$  \hspace{1cm} (9)

where $n_0$ is density of the electrons as carriers at $T_c$, i.e. of the order of $10^{21}$ electrons cm$^{-3}$ and $\Delta(T)$ a temperature-dependent energy gap. We write the temperature dependence of the s-wave energy gap as

$$\Delta(T) = \chi k_B T_c \tanh \left[ \alpha \sqrt{\frac{T_c - T}{T}} \right]$$  \hspace{1cm} (10)

with $\chi = \Delta(0)/k_B T_c$ where $\Delta(0)$ is the zero temperature gap parameter and $\alpha \approx 2$.

The semi-empirical model [6] gives the carrier relaxation time

$$\tau_e = \beta \left[ \frac{T_c}{T} \right]^2 + \gamma \left[ \frac{T_c - T}{T} \right]^{\zeta}$$  \hspace{1cm} (11)

Here, the first term represents the carrier-carrier relaxation time in a Fermi-liquid and the second term takes into account the increase in the relaxation time of normal carriers due to fluctuations. $\zeta$ is the critical exponent in the fluctuation term. The symbols $\beta$ and $\gamma$ are the relaxation rates associated with the normal carriers and due to fluctuations [7].

3. Results and Discussion

In the calculation of temperature dependent thermal conduction of Ba$_{1-x}$K$_x$BiO$_3$, we use the parameters which characterize the strengths of the phonon-defect, phonon-electron, and phonon-phonon scattering process as $A = 4.9 \times 10^{-7} K^{-3}$, $B = 0.22$ and $C = 0.3 K^{-6} \text{ sec}^{-1}$, respectively. The length of the sample is about 3 mm and $v_s = 4.76 \times 10^5 \text{ cm sec}^{-1}$. We first qualitatively discuss the properties of thermal conductivity due to phonons. Figure 2 shows our results for phonon thermal conductivity of Ba$_{1-x}$K$_x$BiO$_3$. As the temperature is lowered through $T_c$, the quasi particle excitation condensed into the ground state and they cannot scatter phonons. The phononic thermal conductivity, thus, increases exponentially as the temperature decreases in the absence of the other scattering mechanism. Although the phonon thermal conductivity experiences an exponential increase below the transition temperature, the presence of the defect, and the electron scatterings set a limit on its growth, as a consequence the phononic thermal conductivity diminishes as the temperature increases. At much higher temperature phonon-phonon scattering becomes more effective and decreased mean free path of phonon is responsible for decrease in thermal conductivity at higher temperature. The maximum position depends on the relative magnitudes of the phonon-electron, phonon-defect and phonon-phonon scattering processes.

We now turn to the calculation of the carrier thermal conductivity from equation (8). While estimating the electronic contribution, we use $D(0) = 4.26 \text{ meV}$ and $T_c = 28 K$, $m^* = 2.4 m_e$ and $n_0 = 1 \times 10^{21} \text{ cm}^{-3}$, respectively for Ba$_{1-x}$K$_x$BiO$_3$ superconductors. Figure 1(a) shows that as the temperature is lowered the energy gap is broadened while to that in the vicinity of $T_c$ the energy gap becomes...
narrower as a consequence of Fermi-Dirac distribution function, that we had employed. Figure 1(b) shows the normalized temperature dependence of normal charge carriers. It is evident from the curve that the holes as carriers are completely condensed at low temperatures and rapidly raises in the neighborhood of $T_c$. The parameter $\zeta$ is a measure of the defect structure and is taken to be 4. Further the ratio $\gamma/\beta$ is about 10 that leads the relaxation rates $\beta$ and $\gamma$ of the order of $10^{-13}$ sec [7]. It is worth to comment that the fluctuation contribution to the relaxation time is negligible in comparison to the electron-impurity scattering mechanism in the vicinity of $T_c$. Also, in the present model $\tau_e$ increases indefinitely as $T \to 0 \, K$, because electrons do not carry entropy as temperature is lowered (see figure 1(c)). In figure 1(d), we present the curve for the temperature dependence of carrier thermal conductivity. It is noticed from the plot that $\kappa_e$ increases with the increase in temperature and a rapid growth is reflected in the vicinity of $T_c$ and is consistent with the condensed superconducting pairs at low temperatures.

It is interesting to note that the carrier contribution to the thermal conductivity is less then 1% of the phonon thermal conductivity below $T_c$. Phonons are, then, the sole carriers of heat in this temperature domain. Further the two contributions (electronic and phononic) are added together and the total temperature dependence of the thermal conductivity is shown in figure 3 along with experimental data.

![Figure 1](image-url)

**Figure 1.** Variation of (a) superconducting energy band gap, (b) carrier density, (c) electron relaxation time and (d) electronic thermal conductivity as a function of normalized temperature.
The present analysis on thermal conductivity shows good agreement with those obtained from the experiments [3]. The anomalies observed in temperature dependence of thermal conductivity depend on the relative magnitude of different operative scattering mechanisms and the balance between electronic and phononic contributions.

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