

# Phonon Drag and Carrier Diffusion Contributions in Thermoelectric Power of $M_3C_{60}$ ( $M = K, Rb$ ) Fullerides

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The thermoelectric power ( $S$ ) of  $M_3C_{60}$  ( $M = K, Rb$ ) alkali intercalated fullerides is theoretically investigated by considering the Mott expression within parabolic band approximation to reveal the electron diffusive thermoelectric power ( $S_c^{\text{diff}}$ ). We follow the Fermi energy as electron parameter and  $S_c^{\text{diff}}$  discerned linear temperature dependence.  $S$  infers a change in slope above transition temperature and becomes almost linear above 70 K for  $M_3C_{60}$  alkali intercalated fullerides. As a next step, the phonon drag thermoelectric power ( $S_{\text{ph}}^{\text{drag}}$ ) is computed within relaxation time approximation when thermoelectric power is limited by scattering of phonons from defects, grain boundaries, phonons and electrons as carriers. It is noticed that the  $S_{\text{ph}}^{\text{drag}}$  of  $K_3C_{60}$  is anomalous and it is an artifact of strong phonon–electron and –phonon scattering mechanism. The thermoelectric power within relaxation time approximation has been taken into account ignoring a possible energy dependence of the scattering rates. Behaviour of  $S(T)$  is determined by competition among the several operating scattering mechanisms for the heat carriers and a balance between carrier diffusion and phonon drag contributions in  $M_3C_{60}$  ( $M = K, Rb$ ) alkali intercalated fullerides.

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## 1. Introduction

Among non-cuprate superconductors, organic materials as alkali metal intercalated fullerides  $M_3C_{60}$  ( $M = K, Rb, Cs$ ) have been focused since the trace of superconductivity was obtained [1]. The unusual normal state transport properties of alkali metal-intercalated-fullerides are vital giving clues to the basic mechanism responsible for superconductivity [2]. The pristine  $C_{60}$ , the most stable fullerene considered as an atom-like building block of fulleride solids is an insulator, and by doping with alkali metal atoms  $M_3C_{60}$  (which opt for a face-centered-cubic structure) superconductivity in intercalated compounds will appear in limited conditions. The parent  $C_{60}$  has potential applications in molecular- as well optoelectronics. By suitable doping of alkali atoms as K, Rb or Cs pristine  $C_{60}$  is engineered as superconducting, metallic, semiconducting, and insulating. Among these materials are the  $M_3C_{60}$  fullerides with M standing for K, Rb or Cs with a superconducting transition temperature  $T_c \approx 40$  K ( $Rb_3C_{60}$ ) at ambient pressure. These transition temperatures are the second highest among non-cuprate superconductors. Alkali metal intercalated  $C_{60}$  continues to generate excitement due to the conducting polymeric phase in  $MC_{60}$  [3].

Aromatic organic materials such as made of large organic molecules exhibit a characteristic separation of energy scales as well separation of the length scales. Usually, the covalent bonds within the molecules are dis-

tinctly stronger than the inter-molecular binding, and fullerides with molecular character are members of a larger family of organic conductors. Due to the strong C–C bonds, the electron–phonon interaction is expected to play a vital role. In  $C_{60}$ , the intermolecular binding forces are weaker as compared to the chemical bonds within the molecule, and it is safe to consider  $C_{60}$  molecule as a rigid body. The pristine  $C_{60}$ , with 60 atoms documents 174 vibrational modes. Henceforth, the phonon spectrum has a wide frequency region in alkali-metal-doped fullerenes. Usually, the vibrational spectrum is classified into two regions. One of them belongs to the rotation of  $C_{60}$  molecule and the intermolecular vibrations. The intermolecular vibrations and soccer ball vibrations (restricted rotations) are low energy vibrations ranging from 10–100  $\text{cm}^{-1}$ . The others are the intramolecular vibrations span a large frequency range  $\approx 250$   $\text{cm}^{-1}$  to 1600  $\text{cm}^{-1}$  [4]. The electronic structure of alkali-metal-doped fullerenes in the normal state is important for understanding the mechanism of superconductivity. The experimental technique as NMR measurements [5], photoemission measurements [6] and infrared reflectivity measurements [7] reports the bandwidth ranging from 0.2 to 1.2 eV.

The structure and large size of organic molecule as  $C_{60}$  favors the hopping of carriers for conduction. For  $C_{60}$  molecule, the separation of the energy scales between inter- and intramolecular bindings as well the similar energy range of vibrational and electronic excitations as the collective excitations offers great challenges to the electrical and thermal transport. Doping of alkali metal in the parent  $C_{60}$  essentially expands the lattice and causes an increase in the lattice constant, the result is enhanced

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density of states at the Fermi level. An intermediate consequence is fairly large electron–phonon interaction depending upon whether inter- or intramolecular phonon is the mediating boson. In this regard, the thermoelectric power  $S(T)$  is a powerful probe to understand not only the electronic structure but also shed light on the electron–phonon interaction. The mass enhancement effects can increase the thermoelectric power of a metal at low temperatures [8]. The mass enhancement is proportional to electron–phonon coupling strength and this correction is normally masked by large phonon-drag effect. Apart from mass renormalization, the electron correlation effects are important in pristine  $C_{60}$  and are less explored in intercalated fullerenes as on-ball Coulomb energy ( $> 1$  eV) is considerably larger than the bandwidth of typical fullerenes.

Thus, the physical properties of trivalent organic superconductors offer a great challenge to researchers that is reflected from the electronic structure of the molecules. Inabe et al. has first reported the thermoelectric power of single crystal  $K_3C_{60}$  and  $Rb_3C_{60}$  superconductors [9]. Non-linear temperature dependences of  $S(T)$  with negative sign are documented above  $T_c$  for both K- and Rb-doped fullerenes. The room temperature value of  $S(T)$  is about  $-11 \mu V/K$  indicating metallic nature in the normal state with electron as sole carriers. The absolute value of  $S$  decreases linearly until dropping discontinuously to zero at  $T_c$  and a broad hump around 70 K. The analysis of density of states in  $K_3C_{60}$  reveals that low frequency phonon modes are significant in normal state transport and the non-linear behaviour in low temperature regime ( $T < 70$  K) is ascribed to phonon drag.

Furthermore, the measured thermoelectric power in  $K_4C_{70}$  thin films also shows a negative  $S$  indicating that charge carriers are electron and roughly linear temperature dependence below 100 K. For higher temperatures  $T > 100$  K,  $S(T)$  decreases slowly with a deviation from linearity [10]. Since the conduction band in  $K_4C_{70}$  is half-filled similar to that of  $K_3C_{60}$ , an estimate of bandwidth is about 0.5–0.6 eV, consistent with a value of  $\approx 0.6$  eV in  $K_3C_{60}$ . Henceforth, the normal state of  $K_3C_{60}$  is a metallic state with a bandwidth of  $\approx 0.6$  eV, the electron–phonon interaction and electron–electron interactions are important for charge transport. Later on, Sugihara et al. have discussed the possibility of phonon drag thermopower in doped fullerenes [11]. It is concluded that small but clear deviation from the linear relation at low temperatures is ascribed to the phonon drag effect. The broad dip over 100 K and its small magnitude suggest that the anomaly is not related to the electron–intramolecular phonon interaction but to the electron–intermolecular phonon interaction. A visual comparison of data [12] indicates that the temperature dependence of the thermopower of superconducting fullerenes is very similar to that of systems in which mass enhancement effects have been observable.

The pristine  $C_{60}$  is diamagnetic and doping with alkali atoms discerns the changes in the magnetic origin. The available experimental data on thermoelectric power [9–11] and importance of carrier diffusion term with mass enhancement [12] motivated us to understand the role of scattering of phonon with defects, grain boundaries, phonon and electrons for phonon drag thermoelectric power as well the carrier diffusion contribution. This improves our understanding of the interplay of scattering processes between the heat carriers themselves and between the carriers and the impurities for the explanation of the reported behaviour of the thermoelectric power  $S(T)$ . Also it is important to look for the relative magnitudes of these scattering processes, which lead to the anomalous behaviour, and this is another motivation for the present investigation. The results we report here do indeed shed some very important light on the nature of phonon and electron as carrier channel of thermoelectric power in alkali metal intercalated fullerenes  $M_3C_{60}$ .

In the present study, we begin by outlining the approximations for the method of calculation, give further details of the results, and speculate on the reliability of our approach to the problem of  $S(T)$  in alkali metal intercalated fullerenes. In Sect. 2 we give details about the scattering rates within the relaxation time approximation to estimate the phonon drag thermoelectric power ( $S_{ph}^{drag}$ ) incorporating the scattering of phonons with defects, electrons as carriers, grain boundaries, and phonon–phonon interactions, respectively. While obtaining the numerical results, we place particular emphasis on the acoustic phonons as a source of  $S_{ph}^{drag}$  in the model Hamiltonian. As well the role of carrier diffusion contribution up to room temperature and zero magnetic field for  $S(T)$  is investigated. We find that the  $S(T)$  behaviour can be well accounted for, through the use of the Debye model. In Sect. 3, we give the numerical estimation of various scattering rates for the calculation of diffusion and phonon drag processes and discuss the results obtained. Section 4 dealt with conclusions where we provide physical descriptions of the numerical results calculated herein for alkali intercalated  $M_3C_{60}$ .

## 2. The model

We shall use the well-known Mott formula within parabolic band approximation to estimate the contribution of electrons towards thermoelectric power. The low temperature carrier diffusion thermoelectric power [9] is

$$S_c^{diff}(T) = -\frac{\pi^2 k_B^2 T}{3|e|} \left[ \frac{\partial \ln \sigma(\epsilon)}{\partial \epsilon} \right]_{\epsilon=\epsilon_F} \quad (1)$$

with  $\sigma(\omega)$  [ $= ne^2\tau(\epsilon)/m$ ] is the energy dependence of electrical conductivity in the relaxation time approximation. Here,  $n$  ( $m$ ) is the density (mass) of carriers and  $\tau$  — the relaxation time. We clarify that this expression is true within parabolic band approximation and not the relaxation time approximation alone. For the sake of simplicity, it is sufficient to neglect the energy dependence

in  $\tau(\varepsilon)$  taking  $\tau(\varepsilon) = \tau(\varepsilon_F)$ , for three-dimensional model Eq. (1) becomes

$$S_c^{\text{diff}}(T) = -\frac{\pi^2 k_B^2 T}{6|e|\varepsilon_F}. \quad (2)$$

Keeping in mind that  $\tau = \lambda/v_F$ , the method point to the scattering of carriers by impurities is dominant for constant relaxation times. Such a procedure has found success in explaining previous data on high temperature superconductors on a wide temperature range [13]. For the carrier diffusion thermopower given by Eq. (2), a linear variation with temperature is predicted. However, the magnitude and sign depends on how the conductivity changes with electron energy at the Fermi surface. Quite generally, the conductivity is expected to enhance with increasing energy of the electrons. In the present investigations, it is assumed that the common relaxation time exists for scattering in both the temperature gradient and in an electric field in turn, it requires the elastic scattering ( $T > \omega_D$ ). Besides, there is no restriction on the shape of the Fermi surface in the present case of alkali metal doped fullerides as  $k_B T/\varepsilon_F$  is small and hence the carrier diffusion power as defined in Eq. (2) is valid.

In the next step, in order to assess the role of phonons for thermoelectric power, we develop a model Hamiltonian where the low energy intermolecular vibrations (phonons) in  $K_3C_{60}$  are described in the Debye model and the electrons as charge carriers are treated in an isotropic BCS-like model. It is common practice to interpret the transport data with a Debye model. As in the Debye model, the summation over the phonon modes can be replaced by the introduction of one effective phonon branch with linear dispersion. Since the true phonon spectrum differs from a Debye model, one cannot get a perfect fit of electrical, thermal and thermoelectrical properties with a single Debye temperature for all temperatures. Usually the Debye temperature is constant at higher temperatures. Furthermore instead of considering the entire frequency spectrum, only that narrow frequency interval is considered that contributes most to the heat transport and these phonons possess an energy comparable with the thermal energy  $k_B T$ .

The charge carriers are quasiparticles in a periodic crystal, and hence have a well-defined dispersion relation  $\varepsilon_{\mathbf{k}}$ . The alkali-metal-doped fullerides although, are impure crystals, where the excitations may not be quasiparticles at all, but for which the physical properties are qualitatively the same. The phonon inelastic scattering events are assumed to be independent and scattering of phonon with various scattering sources is additive. The Debye model with acoustic phonon is valid for  $K_3C_{60}$  ( $Rb_3C_{60}$ ) as the temperature domain of interest lies well below the effective Debye temperature  $\theta_D \approx 185$  K [14].

We shall use the isotropic BCS-like model with intermolecular acoustic phonon to derive qualitative results for thermoelectric power. The attractive interaction in BCS theory is in between electrons essential for pairing and is brought about indirectly by the interaction between the electrons and the vibrating crystal lattice i.e.,

the phonons (intermolecular acoustic). A pair of the electrons then becomes correlated. The deformation of the lattice causes another electron, with opposite spin, to move into the region of higher positive charge density. It requires only that the potential be attractive, regardless of its origin. Further, some attraction between electrons can overcome the Coulomb repulsion.

The model Hamiltonian is [15]:

$$\begin{aligned} H = & \sum_p \varepsilon_p a_p^+ a_p + \sum_q \omega_q b_q^+ b_q + \sum_{p_1, p_2} \varphi(p_1, p_2) a_{p_1}^+ a_{p_2} \\ & + D_p \sum_{p, q} q \left[ \frac{\hbar}{2\rho\omega_q} \right]^{1/2} a_{p+q}^+ a_p (b_p + b_{-q}^+) \\ & + \frac{R}{2n} \sum_{q_1, q_2} e^{i(q_1+q_2)R_i} \left[ \frac{\hbar\omega_{q_1}\hbar\omega_{q_2}}{4} \right]^{1/2} \\ & \times (b_{q_1} - b_{-q_1}^+)(b_{q_2} - b_{-q_2}^+) + H_{p-p}. \end{aligned} \quad (3)$$

Herein, the initial two terms are carrier (electron), and phonon excitation, the third and fourth terms represent carrier-impurity and carrier-phonon interactions, respectively. The fifth term is phonon-impurity interaction and last term stands for the phonon-phonon interaction. The symbols appear in Eq. (3) are:  $\varepsilon_p$  the carrier free energy,  $a$  ( $a^+$ ) and  $b$  ( $b^+$ ) are the creation (annihilation) operators for phonon and electron,  $\varphi$  is coupling parameter of electron and impurity potential,  $D_p$  is deformation-potential constant,  $\rho$  is ionic mass density,  $\omega_q$  is acoustic phonon frequency of a wave vector  $\mathbf{q}$ ,  $R$  is relative ionic-mass difference  $[(M'' - M)/M'']$ ,  $M$  ( $M''$ ) symbolizes for  $C_{60}$  (K), number of cells is  $n$  and  $R_i$  stands for the position of defects due to substitutions.

The validity of Eq. (3) presupposes that heat transport is a random process because otherwise the flux would not be determined by the gradient of temperature but rather by the temperature difference. Herein, we have considered the ensemble of phonons with inelastic phonon-phonon collision maintaining the local equilibrium implying that the temperature can be defined locally.

While estimating the phonon drag thermoelectric power, we work with the Kubo formula [16] following model Hamiltonian. In alkali metal intercalated fulleride superconductors, the phonon-drag on electrons has important consequence on thermoelectric power. As the carrier concentration is low in  $M_3C_{60}$  ( $\approx 10^{21}$  cm $^{-3}$ ), the phonon contribution dominates and the change in the electron distribution produced by the phonon flow is expected to be small. We thus suppose that phonon drag thermoelectric power has contributions from both the phonons and the carriers. In the continuum approximation the lattice part follows [17]:

$$\begin{aligned} S_{\text{ph}}^{\text{drag}}(T) = & -\frac{k_B}{|e|} \left[ \frac{T}{\theta_D} \right]^3 \int_0^{\omega_D} d\omega (\beta\omega)^4 A(\omega) (\beta\omega)^4 \\ & \times \frac{e^{\beta\omega}}{(e^{\beta\omega} - 1)^2}. \end{aligned} \quad (4)$$

$k_B$  is the Boltzmann constant,  $e$  is the charge of carriers,  $\omega_D$  is the Debye frequency and  $\beta = \hbar/2\pi k_B T$ .

The relaxation time is inhibited in  $A(\omega)$  and is proportional to the imaginary part of the self-energy  $\Sigma$ . The relaxation times ratio can be calculated to the lowest order of the various interactions in the weak interaction case. The phonon drag thermoelectric power relaxation times ratio  $A(\omega)$  follows:

$$A(\omega) = [1/\tau_{\text{ph-d}} + 1/\tau_{\text{ph-gb}} + 1/\tau_{\text{ph-ph}}]^{-1} \times [1/\tau_{\text{ph-d}} + 1/\tau_{\text{ph-gb}} + 1/\tau_{\text{ph-ph}} + 1/\tau_{\text{ph-c}}]. \quad (5)$$

Usually, doping of alkali metal K (Rb) in the host lattice of  $\text{C}_{60}$  brings about changes in the vibrational spectrum. A change in the normal modes of the crystal is expected depending upon the nature of the doped impurity in terms of phonon mean free path by various scattering processes. In a true sense, the influence of temperature gradient, the phonon distribution deviates as a consequence of scattering with defects, grain boundaries and phonon themselves. Henceforth, a current generates due to the deviation of phonon distribution from its equilibrium value.

The relaxation times are expressed as

$$1/\tau(\omega) = 2 |\text{Im}P(\omega/v_s, \omega)|. \quad (6)$$

The inverse addition of relaxation time to obtain the total relaxation time is appreciable approximation as it accounts for the various processes that are non-interacting and also for elastic scattering with a random distribution of the scatterers. The various phonon relaxation times are defined in terms of transport coefficients as

$$\tau_{\text{ph-d}}^{-1}(\omega) = D_{\text{phd}}/k_B^3 \omega^4 \hbar^3, \quad (7)$$

$$\tau_{\text{ph-gb}}^{-1}(\omega) = D_{\text{phgb}} v_s / L, \quad (8)$$

$$\tau_{\text{ph-ph}}^{-1}(\omega) = D_{\text{phph}} (T\omega\hbar/k_B)^3, \quad (9)$$

and

$$\tau_{\text{ph-c}}^{-1}(\omega) = D_{\text{phe}} \omega n_F(\Delta), \quad (10)$$

$v_s$  being the velocity of sound,  $L$  is the crystal dimension,  $n_F$  is the Fermi-Dirac distribution function and  $\Delta$  is the  $s$ -wave energy gap parameter. The notation  $\tau_{\text{ph-d}}$ ,  $\tau_{\text{ph-gb}}$ ,  $\tau_{\text{ph-ph}}$  and  $\tau_{\text{ph-c}}$  are the phonon scattering relaxation time due to substitutional defects, grain boundaries, phonon and phonon-carrier 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.

Equation (7) refers for defects; the scattering of phonons is caused by density of impurities and the difference in mass of K (Rb) and  $\text{C}_{60}$ . The relative change in atomic mass, which in turn is the relative change in force constant, causes thermal conduction and is attributed to fluctuations in mass difference. Thus, point defect scattering is effective ( $\omega^4$  dependence) for short-wavelength phonons. However, the short-wavelength phonons are scattered effectively with point defects and most of the heat is carried by long-wavelength phonons. The grain boundaries are another plausible cause of phonon diffusion contributing to thermoelectric power. The phonons can then be scattered by grain boundaries. The grain

boundary scattering is limited by size dependence. The relaxation time in finite grained materials is influenced by appreciable size dependence as evident from Eq. (8),  $L$  is the crystal dimension. The normal processes or momentum conservation does not contribute to conduction; however, they contribute significantly in an indirect way by distributing momentum among all phonons. The group velocity associated with optical phonons is smaller as compared to that of intermolecular acoustic phonons. Henceforth, all heat is carried out by intermolecular acoustic phonons and the contribution of optic phonon has been neglected.

The transport coefficients appearing in Eqs. (7)–(10) are defined as:

$$D_{\text{phd}} = \frac{3n_i R^2}{4\theta_D^3} \quad (11)$$

with  $n_i$  is the density of impurities or point defects,  $R$  is the relative ionic-mass difference  $\theta_D$  the Debye temperature. The above essentially accounts for the density of real point defects in  $\text{K(Rb)}_3\text{C}_{60}$ , such as impurities, vacancies and interstitials, which should be fairly large in a weakly bound crystal such as orientationally ordered  $\text{C}_{60}$  and increases in orientationally disordered  $\text{K(Rb)}_3\text{C}_{60}$ . Let the potential exerted on electron as free carriers in the doped  $\text{C}_{60}$  is due to ionized cage of orientationally ordered  $\text{C}_{60}$ . The strength of the electron-phonon scattering in terms of deformation potential  $D_p$ , carrier mass  $m$ , ionic mass  $M$  and the Fermi energy ( $\varepsilon_F$ ) is

$$D_{\text{phe}} = \frac{9\pi}{4} \left( \frac{m}{3M} \right)^{1/2} \frac{D_p^2}{\varepsilon_F^2}. \quad (12)$$

Herein, the Thomas-Fermi approximation defines electron-acoustic phonon coupling strength  $D_p = -\varepsilon_F/2$ . The scattering of phonon by paired electrons coupled with intermolecular acoustic phonon induces screening due to carriers. The strength of electron-phonon coupling decreases when the phonon wavelength is of the order of or greater than electron mean free path. Besides, this scattering mechanism is important at low temperatures. The temperature dependence of the  $s$ -wave order parameter for  $\text{K(Rb)}_3\text{C}_{60}$  follows:

$$\Delta = \chi k_B T_c \tanh \left( 2\sqrt{\frac{T_c - T}{T_c}} \right) \quad (13)$$

with  $\chi = 2\Delta(0)/k_B T_c$ ,  $\Delta(0)$  is the zero-temperature gap parameter.

The estimation and numerical computation of the carrier diffusion and phonon drag contributions to the thermoelectric power of  $\text{K(Rb)}_3\text{C}_{60}$  by incorporating the effects of different scattering mechanisms are presented in the following section.

### 3. Results and discussion

Any discussion of the non-cuprate superconductors, organic materials as alkali metal intercalated fullerenes  $\text{M}_3\text{C}_{60}$  necessitates the knowledge of the structural aspects, and this is particularly true for the calculations

reviewed here. Also applying the available information on the developed theory inevitably entails certain complications and one has to find suitable data that varies from technique to technique. Special attention is paid in this approach to address the issue molecular vibrations which are at the origin of the substantial properties of the alkali intercalated trivalent fullerenes  $\text{K(Rb)}_3\text{C}_{60}$ . We first elaborate the main findings and motivate them by simple physical arguments.

We begin our estimation with the carrier diffusion thermoelectric power ( $S_c^{\text{diff}}$ ), which is earlier expressed by Eqs. (1) and (2). While considering the electronic structure, if all the electrons are free in  $\text{K(Rb)}_3\text{C}_{60}$ , the estimation of the Fermi energy  $\varepsilon_F$  in the free electron approximation leads to a value of about 0.36 (0.23) eV, which is used for the computation of  $S_c^{\text{diff}}$ . The carrier-impurity contribution to the thermoelectric power  $S_c^{\text{diff}}$  is documented in Fig. 1 for  $\text{K(Rb)}_3\text{C}_{60}$  as functions of temperature. It is evident from the plot that  $S_c^{\text{diff}}(T)$  increases linearly for increasing temperature in  $\text{K(Rb)}_3\text{C}_{60}$ . Estimated  $S_c^{\text{diff}}$  has been subtracted from the experimental data [9] and the difference ( $S_{\text{difference}} = S_{\text{experimental}} - S_c^{\text{diff}}$ ) has been obtained for  $\text{K(Rb)}_3\text{C}_{60}$ . The difference  $S_{\text{difference}}$  is characterized as phonon drag thermoelectric power and fitted within the relaxation time approximation in next step.

The model calculations assumes electrons as carrier for thermoelectric power and negative behaviour of thermoelectric power up to room temperature with a value of 12.4 (18.9)  $\mu\text{V/K}$  is in good agreement with the room temperature values in the range 10–20  $\mu\text{V/K}$  [9].

The phonon drag thermoelectric power is a powerful probe to study the nature of carriers and scattering process between them in the phonon system with either absence or presence of a magnetic field. For the actual calculation of the phonon drag thermoelectric power in normal state of  $\text{K(Rb)}_3\text{C}_{60}$  superconductors, more realistic values of some physical parameters derived from the experimental data follow.

Usually, the Debye frequency is characterized as a cut-off frequency at the Brillouin zone boundary, and it can be expressed in terms of the effective value of ionic mass and the elastic force constant for crystal lattices with two different kinds of atoms such as K (Rb) and  $\text{C}_{60}$ , which we deal with. The acoustic phonon frequencies are estimated in an ionic model using a value of effective ion charge  $Ze = 7e$ .

The Coulomb interactions among the adjacent ions in an ionic crystal such as  $\text{K(Rb)}_3\text{C}_{60}$  are expressed in terms of inverse-power overlap repulsion as [18]:

$$\Phi(r) = -(Ze)^2 \left( \frac{1}{r} - \frac{f}{r^s} \right), \quad (14)$$

$f$  is the repulsion force parameter between the ion cores. The elastic force constant  $\kappa$  is conveniently derived from  $\Phi(r)$  at the equilibrium interionic distance  $r_0$  following:

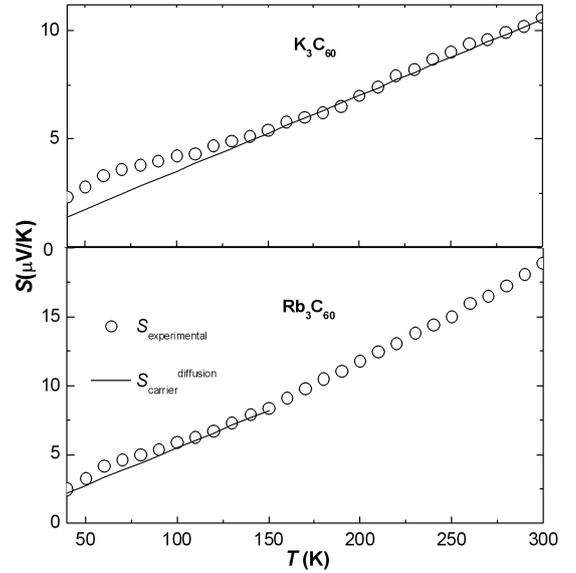


Fig. 1. Variation of carrier diffusion thermoelectric power with temperature and compared with experimental data [Inabe et al. 1992 [9]] for  $\text{K(Rb)}_3\text{C}_{60}$ .

$$\kappa = \left( \frac{\partial^2 \Phi}{\partial r^2} \right)_{r_0} = (Ze)^2 \left( \frac{s-1}{r_0^3} \right). \quad (15)$$

Here,  $s$  is the index number of the overlap repulsive potential. For  $\text{K(Rb)}_3\text{C}_{60}$ , the acoustic mass  $M = [M(\text{K}) + M(\text{C}_{60})]$  as 837.3 (979.29) amu. The elastic force constant  $\kappa^* = 2\kappa$  for each directional oscillation mode to get the acoustic phonon frequency as

$$\omega_D = \sqrt{\frac{\kappa^*}{2M}} = Ze \sqrt{\frac{(s-1)}{2M} \frac{1}{r_0^3}}. \quad (16)$$

The acoustic mode frequencies are estimated in an ionic model using a value of effective ion charge  $Ze = 7e$ . The Debye temperature for  $\text{K(Rb)}_3\text{C}_{60}$  is obtained by taking  $s = 7$  and the bond distance for  $\text{K}\{\text{Rb}\}_3\text{C}_{60}$ :  $r_0 = 10.0 \text{ \AA}$  ( $a/\sqrt{2}$ ) [ $a = 14.28 \text{ \AA}$ ] [ $r_0 = 10.21 \text{ \AA}$  ( $a/\sqrt{2}$ ) [ $a = 14.45 \text{ \AA}$ ]] [14, 19], yielding  $\kappa = 6.77\{6.36\} \times 10^4 \text{ gm s}^{-2}$ . For most ionic crystals the index number of the repulsive potential has been reported to be  $s = 6-8$  [18]. Such procedure yields the Debye temperature of about 106 (95) K. The enhanced mass of Rb as compared to reduce the elastic constant and hence the Debye temperature.

The computed values of the Debye temperature are consistent with normal state resistivity [20], low temperature heat capacity [14] and thermoelectric power data [9, 11]. We do not claim the process to be rigorous, but a consistent agreement following spring model with repulsive force between K cations and  $\text{C}_{60}$  is obtained to evaluate acoustic phonon energy. We note that the present model has only one free parameter, i.e., the index number of the repulsive potential. Value of  $\theta_D$  differs from technique to technique and its value also varies from sample to sample with an average value and standard deviation of  $\theta_D = \theta_D \pm 15 \text{ K}$ .

In alkali metal intercalated fullerenes  $\text{K}(\text{Rb})_3\text{C}_{60}$ , if all the electrons are free, the electron density  $n = (4 \times 3/a^3)$  is estimated as  $4.12$  ( $3.98$ )  $\times 10^{21} \text{ cm}^{-3}$  from the lattice parameter  $a$  of  $14.28$  ( $14.45$ )  $\text{\AA}$  [14, 19] and the band structure value of mass as  $3$  ( $3.6$ )  $m_e$  is used [14, 19]. The electron parameters such as the Fermi velocity and Fermi wave vector are obtained as  $1.91$  ( $1.55$ )  $\times 10^7 \text{ cm s}^{-1}$  and  $0.496$  ( $0.486$ )  $\text{\AA}^{-1}$ , respectively. The length of the sample is about  $3 \text{ mm}$  and  $v_s = 2.0$  ( $2.2$ )  $\times 10^5 \text{ cm s}^{-1}$ . The above corresponds to the weak intermolecular interaction. In the weak coupling limit  $\chi$  is about  $3.6$  to  $4.0$  [2]. Herein, we presume that the high- $T_c$  aromatic organic  $\text{K}(\text{Rb})_3\text{C}_{60}$  superconductors contain the defects, the phonons, and the BCS-like quasiparticles, interacting with one another as evident from model Hamiltonian.

While estimating the temperature dependent thermoelectric power of  $\text{K}(\text{Rb})_3\text{C}_{60}$ , we make use of the transport parameters which characterize the strengths of the phonon-defects, the phonon-grain boundary, the phonon-phonon and the phonon-carrier scattering process as  $D_{\text{ph-d}} = 2.6$  ( $3.1$ )  $\times 10^{-9} \text{ K}^{-3}$ ,  $D_{\text{ph-gb}} = 2.14$  ( $2.5$ )  $\times 10^{-2}$ ,  $D_{\text{ph-ph}} = 0.8$  ( $2.3$ )  $\times 10^{-2} \text{ K}^{-6} \text{ s}^{-1}$  and  $D_{\text{ph-e}} = 3.4$  ( $5.3$ ), respectively. These are material dependent fitting parameters for phonon drag thermoelectric power in the present model. It is instructive to mention that the electron-phonon interaction is limited to the coupling of intermolecular acoustic phonons. The phonon drag term is not related to the intramolecular phonons because of unusual high energy and is responsible for superconductivity in alkali-intercalated fullerenes.

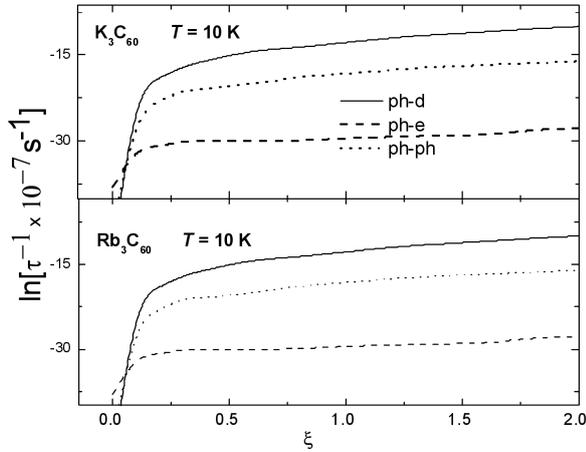


Fig. 2. Variation of various phonon relaxation times as a function of  $\xi$  ( $= \hbar\omega/k_B T$ ) for  $T = 10 \text{ K}$  for  $\text{K}(\text{Rb})_3\text{C}_{60}$ .

Now we discuss the relative magnitudes of the various scattering mechanisms for alkali metal intercalated trivalent fullerenes  $\text{K}(\text{Rb})_3\text{C}_{60}$ . A plot of various scattering phonon relaxation time as a function of  $\xi$  ( $= \hbar\omega/k_B T$ ) in terms of frequency at  $T = 10$ , and  $35 \text{ K}$  from Eqs. (7)–(10) are shown in Figs. 2 and 3, respectively. It can be seen that for low value of  $\xi$ , the phonon-electron scattering is higher while for high value of  $\xi$ , it is the

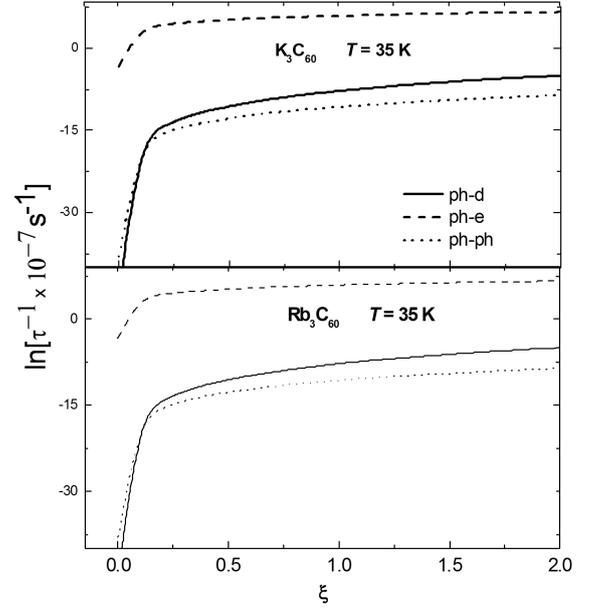


Fig. 3. Variation of various phonon relaxation times as a function of  $\xi$  ( $= \hbar\omega/k_B T$ ) for  $T = 35 \text{ K}$  for  $\text{K}(\text{Rb})_3\text{C}_{60}$ .

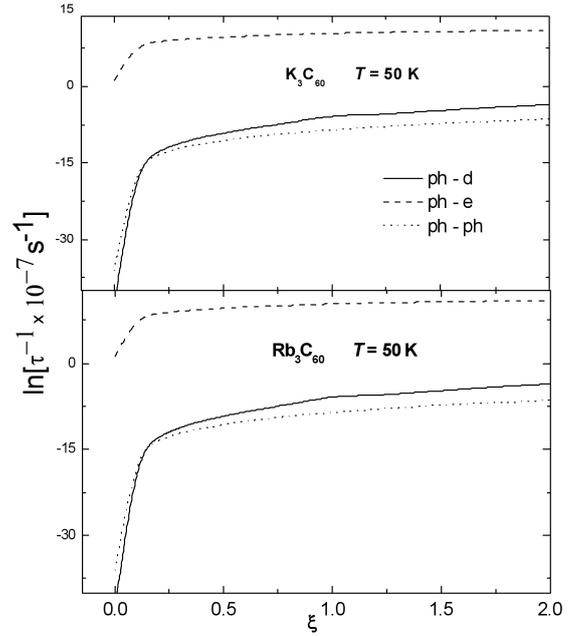


Fig. 4. Variation of various phonon relaxation times as a function of  $\xi$  ( $= \hbar\omega/k_B T$ ) for  $T = 50 \text{ K}$  for  $\text{K}(\text{Rb})_3\text{C}_{60}$ .

phonon-defect scattering that grows faster. However, at both small and large value of  $\xi$ , phonon-phonon scattering process is weaker. As we go above  $T_c$  i.e., with increase in temperature (see Figs. 4, 5 and 6 in the normal state at  $T = 50, 150$  and  $250 \text{ K}$ ) phonon-electron scattering improves and phonon-phonon scattering becomes weaker. In the superconducting state  $T < T_c$ , carriers are condensed in the Cooper pair and with the increase in

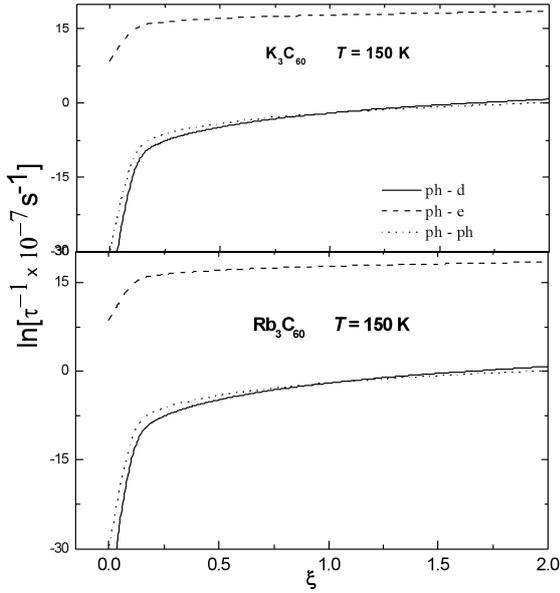


Fig. 5. Variation of various phonon relaxation times as a function of  $\xi$  ( $= \hbar\omega/k_B T$ ) for  $T = 150$  K for  $K(Rb)_3C_{60}$ .

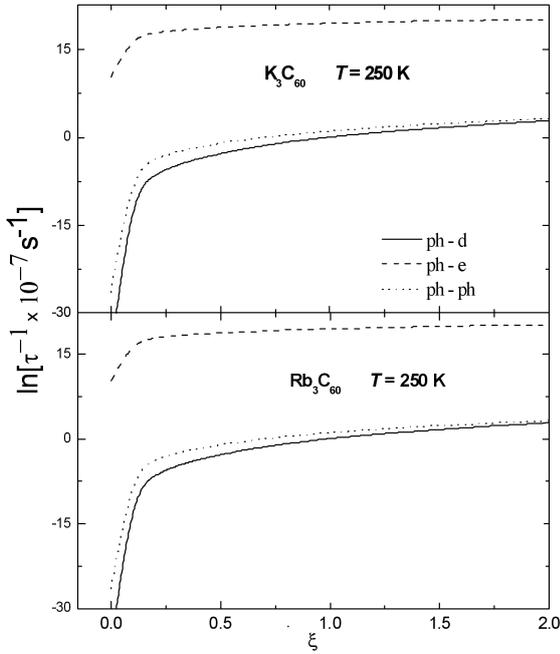


Fig. 6. Variation of various phonon relaxation times as a function of  $\xi$  ( $= \hbar\omega/k_B T$ ) for  $T = 250$  K for  $K(Rb)_3C_{60}$ .

temperature order parameter reduces and concentration of free carriers increases. In particular, phonon-phonon umklapp scattering grows faster than phonon-electron scattering due to large mobility of carriers in the normal state ( $T > T_c$ ). In this respect for all temperatures above  $T_c$ , the phonon-impurity scattering saturates for higher  $\xi$  values in  $K(Rb)_3C_{60}$ .

We now qualitatively discuss the phonon drag thermoelectric power ( $S_{ph}^{drag}$ ) in the presence of various scattering mechanisms for  $K(Rb)_3C_{60}$  (please see Fig. 7). At low temperatures through  $T_c$ , the quasiparticle excitations condensed into the ground state of  $K(Rb)_3C_{60}$  and they cannot scatter phonons.  $S_{ph}^{drag}$ , thus, increases exponentially with temperature in the vicinity of transition temperature of  $K(Rb)_3C_{60}$ . Various scatterings of phonons contribute to reduce in the thermal conductivity that leads to increase in thermoelectric power. The individual effect on thermoelectric power due to different scattering mechanisms is discerned in Fig. 7 for  $K(Rb)_3C_{60}$ . The results show that the effect of scatterings on thermoelectric power is additive and the final variation depends on the relative magnitude of different scattering processes available. It is worth to mention that  $S$  in the superconducting state of  $K(Rb)_3C_{60}$  is zero ( $T \rightarrow 0$  K) and that every non-zero value is an artifact due to the model.

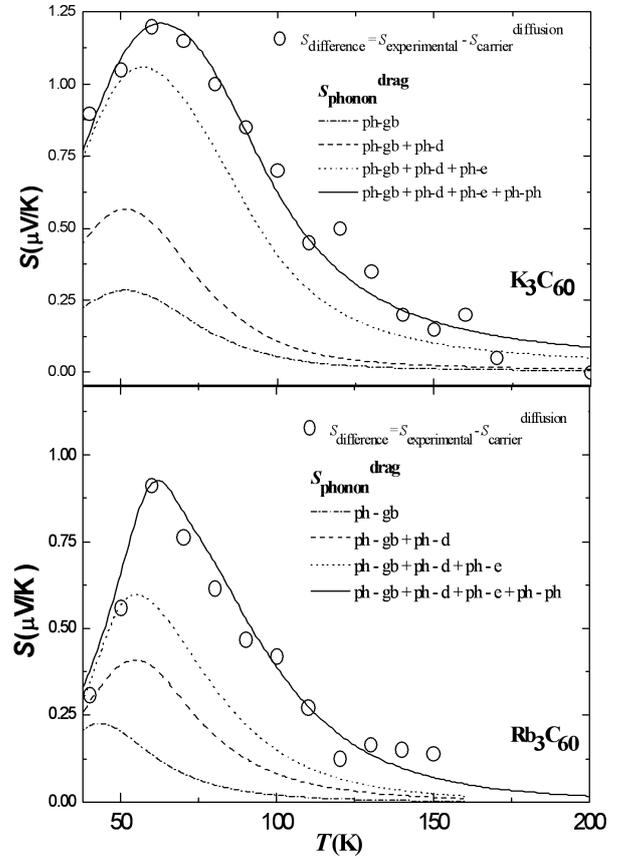


Fig. 7. Variation of phonon drag thermoelectric power as function of temperature in presence of various phonons scattering mechanism. A comparison is being made with the data obtained from Fig. 1 as  $S_{experimental} - S_{carrier}^{diffusion}$  for  $K(Rb)_3C_{60}$ .

To ascertain the physical significance of the density of impurities, we evaluate the transport coefficients  $D_{phd}$  appearing in Eqs. (10)–(11). For  $K(Rb)_3C_{60}$ , we estimate the product of density of impurities and square of relative

ionic mass difference,  $n_i R^2 = 4.12 (4.91) \times 10^{-3}$  from the value of coefficient  $D_{\text{phd}}$ . Due to the fact that the transport parameter  $D_{\text{phd}}$  is determined by the magnitude of the phonon–impurity interaction, we are able to roughly estimate the density of impurity scatterers which may point to the fact that the quasiparticles in the metallic state are essentially localized. By this way, one can set a limit to the concentration of impurities if the impurities as scatterers are of isotope in origin. Herein, we believe that the density of impurity is constant with respect to temperature.

It is worth to refer to the work of Erwin and Pickett [21] who work out the lowest order variational solution for the  $S(T)$ . Herein, for  $\text{K(Rb)}_3\text{C}_{60}$  the energy dependence of scattering rate  $1/\tau$  is considered (a) the electron–phonon coupling strength  $\lambda(\varepsilon)$  as constant leading to a hole-like thermoelectric power with positive slope and linear behaviour and (b)  $\lambda(\varepsilon) = N(\varepsilon)$  resulting electron behaviour up to  $\approx 200$  K and a slow transition to positive slope thereafter.

The  $S(T)$  behavior depends on the competition among the various scattering mechanisms for the heat carriers and balance between the electron and phonon competition. It is worth stressing that the  $S(T)$  increases linearly above 70 K and is well reproduced from the present theoretical model, this phenomenon is attributed to shortened phonon mean free path as compared to that at low temperatures. It may be seen that the slope change in  $S_{\text{ph}}^{\text{drag}}$  is much more pronounced than that in  $S_c^{\text{diff}}$  below 150 K. The reason for being this change is due to the fact that the phonon–impurity scattering dominates and electron–impurity scattering is weaker. Below  $T_c$  the opening of superconducting gap rapidly reduces the phonon–electron scattering rate, and the competition in between phonon–impurity and phonon–electron scattering mechanism leads to faster change of slope in  $S_{\text{ph}}^{\text{drag}}$  in alkali intercalated trivalent fullerenes  $\text{K(Rb)}_3\text{C}_{60}$ .

The reason is further related to the fact that the mean free path of both electrons and phonons change below  $T_c$ , because the scattering of phonons on electrons is reduced when electron is condensed in the superconducting state. Deduced results on temperature dependence of thermoelectric power of  $\text{K(Rb)}_3\text{C}_{60}$  from the present model are consistent qualitatively with the experimental data [9, 11, 12]. Apart from the qualitative agreement at low temperature at room temperature the diffusive thermoelectric power improves on phonon drag thermoelectric power. The reason for being this is the shorter mean free path of carriers in the normal state. However, below  $T_c$  where the concentration of charge carrier is decreased by forming a Cooper pair and the phonon mean free path becomes longer,  $S_c^{\text{diff}}$  continue to play an important role even near the room temperature.

It is customary to mention that a change in slope of  $S_{\text{ph}}^{\text{drag}}$  is obtained at about  $T \approx \theta_D$  as in the normal metals [8]. Indeed below  $T \approx \theta_D$  the temperature dependence of the phonon drag contribution is attributed to be a competitive process in which  $S(T)$  decreases on lower-

ing the temperature and slightly improves on increasing temperature is attributed to phonon–phonon scattering. To an end, a comparison of the computed data, a consistent fit with the reported data was obtained by choosing a reasonable set of parameters. It is instructive to compare the observation with conventional superconductors where the thermally excited quasiparticles of the electron system are dominant carriers of heat; similar situation is revealed in  $\text{K(Rb)}_3\text{C}_{60}$ .

#### 4. Conclusions

Either carrier diffusion or phonon drag have primarily been the concern of thermal conduction in alkali intercalated trivalent fullerenes  $\text{K(Rb)}_3\text{C}_{60}$ . Any discussion of the non-cuprate superconductors, organic materials as alkali metal intercalated fullerenes  $\text{M}_3\text{C}_{60}$  rests on the vital information on the structural aspects. The developed theory inevitably entails certain complications due to scattered experimental information and one really needs to find suitable data for the test of approximations. Special attention is paid in this approach to address the issue regarding the molecular vibrations that are at the origin of the substantial properties of the alkali intercalated trivalent fullerenes  $\text{K(Rb)}_3\text{C}_{60}$ .

The thermoelectric power  $S(T)$  behaviour is an instructive probe to reveal the lattice effects and carrier diffusion as well the interaction of these excitations with one another with impurities, grain boundaries and defects. Among various transport probes it brings information about available subsystems and the measurements are fairly simple. The present study intends to contribute towards a thorough understanding of the scattering processes taking place in this fascinating material. The thermoelectric power behaviour of alkali intercalated trivalent fullerenes  $\text{K(Rb)}_3\text{C}_{60}$  exhibits nearly  $T$ -linear dependence above  $T_c$ , a broad peak around 70 K, and further deviation from  $T$ -linear dependence above 200 K. In order to simulate the actual situation occurring in the temperature dependent behaviour of  $S(T)$  in trivalent fullerenes  $\text{K(Rb)}_3\text{C}_{60}$ , we consider two channels to  $S(T)$ : carrier diffusion thermoelectric power ( $S_c^{\text{diff}}$ ) and phonon drag thermoelectric power ( $S_{\text{ph}}^{\text{drag}}$ ).

The phonon drag thermoelectric power ( $S_{\text{ph}}^{\text{drag}}$ ) is discussed within the Debye-type relaxation rate approximation in terms of the acoustic phonon frequency, a relaxation time  $\tau$  and the sound velocity. The total phonon relaxation rate is the sum of terms corresponding to independent scattering mechanism, like defects, grain boundaries, phonons and holes as carriers dominating in different temperature intervals. We have made a careful analysis taking into account several different processes that can exist in this material whose interaction can yield the observed dependence.

The quasiparticles cause an increase of the carrier heat and a slow increase of the phonon contribution below  $T_c$ . The rapid increase in thermoelectric power  $S(T)$  is attributed to increase in phonon mean free path due to

carrier condensation in the superconducting state limited by various impurity scattering mechanism. The physical entities in the present scheme that characterize the strengths of the phonon–defect, phonon–electron, and phonon–phonon scattering leads to a result that successfully retrace the experimental curve.

The anomalous behaviour around 70 K is attributed to electron–phonon interactions. The model calculations assume electrons as carriers for thermoelectric power and negative behaviour of thermoelectric power up to room temperature with a value of 12.4 (18.9)  $\mu\text{V}/\text{K}$  is in good agreement with the room temperature values in the range 10–20  $\mu\text{V}/\text{K}$ . It is known that the satisfactory explanation of these peculiar properties is constrained as electron and the lattice contributes to the thermoelectric power and because both contributions shall be limited by various scattering mechanisms. Despite of the limitations and use of material parameters for the estimation of transport coupling strengths, the present theoretical model on the thermoelectric power of the high- $T_c$  aromatic organic fullerenes  $\text{K}(\text{Rb})_3\text{C}_{60}$  consistently reveals the interesting behaviour reported experimentally. Herein, we notice that the intermolecular acoustic phonons are solely responsible for thermoelectric power behaviour, however electron–intramolecular phonon interaction is a key for superconductivity.

To conclude, the present model calculations thus lead to both qualitative and quantitative agreement between the calculated and experimental results. The thermoelectric power is one of those important transport entity which exhibits non-zero values in both the normal and superconducting state, its behavior is determined by competition among the several operating scattering rates for the heat carriers and a balance between diffusive carriers and phonon drag contributions with acoustic phonons are effectively scattered by various scatterers for the thermoelectric power. Moreover, the scatterings of quasiparticles are constrained by impurities as clearly evidenced in orientationally disordered trivalent fullerenes  $\text{K}(\text{Rb})_3\text{C}_{60}$  superconductors. Despite the limitations, the present approach successfully describes the nearly  $T$ -linear dependence above  $T_c$ , a broad peak around 70 K, and further deviation from  $T$ -linear dependence above 200 K of thermoelectric power in alkali intercalated trivalent fullerenes  $\text{K}(\text{Rb})_3\text{C}_{60}$  superconductors. Although we have provided a simple phenomenological explanation of this effect, there is clearly a need for a good theoretical understanding of the transport.

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