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Influence of the Electron-Phonon Iinteraction on Phonon Heat Conduction in a Molecular Nanowire

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Abstract:

A model for phonon heat conduction in a molecular nanowire is developed. The calculation takes into account modification of the acoustic phonon dispersion relation due to the electron-phonon interaction. The results obtained are compared with models based upon a simpler, Callaway formula.

Keywords: *Molecular nanowire, Phonon heat conduction, Modeling.*

Introduction

In some systems a strong electron-phonon interaction could cause the appearance of small polarons. As discussed in many experimental and theoretical studies in recent years, the presence of small polarons in these systems could be of great importance for all processes of charge and energy transfer through different mechanisms in various materials such as polymers with a large electrical conductivity, molecular chains, organic macromolecules, etc. [1,2]. Moreover, a strong electron-phonon interaction can to a certain degree change oscillatory properties of a lattice [1,2]. Having in mind the modification of the dispersion relation for acoustic phonons caused by the polaron effect, the flow of thermal energy and thermal conductivity of one-dimensional structures are the subject of this paper. Investigation of thermal properties of one dimensional structures has become one of the very interesting problems in recent years due to its theoretical importance and also application of these structures in different areas of science and technology [3,4,5]. Existing theoretical studies of the above-mentioned problem discard a possible polaron effect. Our results are compared with the results obtained using other models and they show that the existence of a small polaron changes the dispersion relation and, in this way, changes thermal conductivity in a certain temperature range.

Theoretical analysis

Heat current is the energy flux due to the transport of phonons, carrying an energy of $\hbar\omega$. The energy flux in the direction of a small temperature gradient is given by:

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$$\vec{J}_Q = \sum_s \sum_{\vec{q}} \widetilde{N}_{\vec{q},s} \hbar \omega_s(\vec{q}) \frac{\vec{v}_s(\vec{q}) \cdot \nabla T}{\left| \nabla T \right|^2} \nabla T \qquad (1)$$

where subscript s refers to a particular phonon polarization type, $\vec{q}$ is the phonon wave vector, ω is the phonon frequency, $\vec{v}_s(\vec{q})$ is the phonon group velocity, and $\widetilde{N}_{\vec{q},s} = N_{\vec{q},s}^0 - N_{\vec{q},s}$ is the deviation of the phonon distribution, $N_{\vec{q},s}$, from its equilibrium value, $N_{\vec{q},s}^0$. The equilibrium phonon distribution $N_{\vec{q},s}^0$ is given as by the Bose-Einstein distribution, and the deviation of the phonon distribution, $N_{\vec{q},s}$ is given as a solution of Boltzmann's equation [6,7]:

$$\widetilde{N}_{\vec{q},s} = N_{\vec{q},s} - N_{\vec{q},s}^0 = -\frac{\partial N_{\vec{q},s}^0}{\partial T} \nabla T \vec{v}_s(\vec{q}) \tau_c, \qquad (2)$$

where τ_c is the combined phonon relaxation time. By definition, heat current is

$$\vec{J}_Q = -\kappa_{latt} \nabla T , \qquad (3)$$

for isotropic media where κ_{latt} is the thermal conductivity coefficient [7]. Substituting Eq (2) in Eq (1) and comparing the results with Eq (3), we obtained a regular three-dimensional formula for lattice thermal conductivity:

$$\kappa_{latt} = \sum_s \sum_{\vec{q}} \frac{\partial N_{\vec{q},s}^0}{\partial T} \frac{\vec{v}_s(\vec{q}) \cdot \nabla T}{\left| \nabla T \right|^2} \nabla T \hbar \omega_s(\vec{q}) \tau_c . \qquad (4)$$

The density of states in $\vec{q}$ spaces is sufficient by large so the sum in Eq (4) may be replaced by an integral according to the standard procedure. We supposed that the optical modes would not be excited at the low temperatures we are interested in [8]. In the other case their contribution to thermal conductivity is limited by their low group velocity [9]. In the1D case we obtain

$$\kappa_{latt} = \frac{3}{2\pi} \frac{\hbar^2}{k_B T^2} \int_0^{\pi/a_0} n_q \omega^2(q) \frac{\exp(\hbar\omega(q)/k_B T)}{(\exp(\hbar\omega(q)/k_B T)-1)^2} v^2(q) \tau_c \, dq . \qquad (5)$$

The factor 3 originates from the three contributing branches of the vibrational spectrum and n_q is the density of phonon states. Eq. (5) could be transformed into equations that were used in literature [5].

To obtain thermal conductivity we must compute both complete dispersion relations for the 1D system, $\omega(q)$, enabling calculation of the group velocity using $v(q) = d\omega(q)/dq$ and the total relaxation time $\tau_c(\omega)$. The total relaxation time is commonly given by Matheissen's rule, expressing the total inverse lifetime as a sum of the inverse lifetimes corresponding to each scattering mechanism [10]. The expression used for boundary, anharmonic and impurity scattering are [5,8]:

$$\frac{1}{\tau_c} = \frac{1}{\tau_b} + \frac{1}{\tau_a} + \frac{1}{\tau_i} = A\omega^4 + (B_1 + B_2)T^3\omega^2 + \frac{c}{L} , \qquad (6)$$

where the values of the A, B_1, B_2 and c/L are obtained from the literature [8]:

$$A = 2{,}57 \cdot 10^{-44} \text{ s}^{-3}, \ B_1 + B_2 = 2{,}77 \cdot 10^{-23} \text{ s/deg}^3, \ c = 3{,}5 \cdot 10^3 \text{ m/s}, \ L = 1{,}8 \cdot 10^{-3} \text{ m}$$

In order to take into account the possible influence of the small polaron effect on the problem of heat conduction we shall use Eqs. (5) and (6), by simply replacing phonon frequency with the renormalized dispersion relation [1, 2]:

$$\widetilde{\omega}_q^2 = \omega_q^2 [1 + 4.5 \pi \overline{v} \, S \, B \, e^{-S(T)} \cos(qa_0/2)], \qquad (7)$$

where $\omega_q = \omega_B \sin|qa_0/2|$, ω_B is the phonon bandwidth, $S = \dfrac{8}{3\pi}\dfrac{E_B}{\hbar\omega_B}$ and

$B = \dfrac{8}{3\pi}\dfrac{2J}{\hbar\omega_B}$ denote the zero-temperature coupling constant and adiabatic parameter

respectively, E_B is small-polaron binding energy, $\bar{v} = (2/N)\sum_k \bar{n}_k \cos ka_0$ is the effective

the small-polaron concentration, where $\bar{n} = \{\exp[(E_k - E_F)/k_B T]+1\}^{-1}$ denotes the small-polaron mean number. In order to calculate the effective carrier concentration we supposed that the polaron zone is half-full, so $k_f = \pi/(2a_0)$ and $\bar{v} = 4\bar{n}/\pi$ [1,2]. We assumed that $\bar{n} = \bar{n}_k = 1$ for a small temperature range [1,2].

Results and discussion

The results we obtained are shown in Figs 1 (a,b) and 2 (a,b).
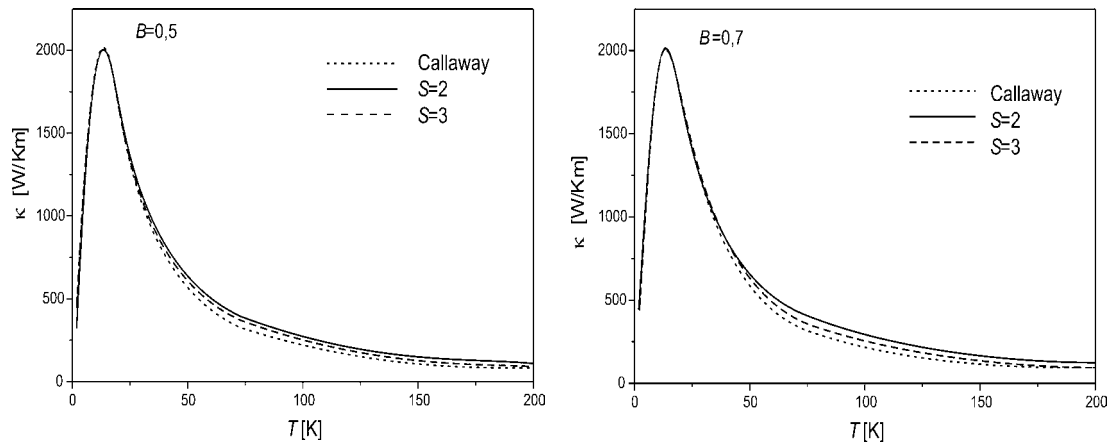
Fig. 1. Coefficient of thermal conductivity for A=0.5 (a) and 0.7 (b)

On Fig. 1 we plotted the temperature dependence of thermal conductivity, for several values of the adiabatic parameter and coupling constant. Dotted lines present the results obtained by the Callaway formula. As it could be seen from Fig. 1, the results obtained using Callaway are in agreement with our calculation for the lower range of temperatures.

Above the inflection point, the change of the dispersion relation caused by the polaron effect yields an increase of thermal conductivity (the difference is about 20 percent and it is the function of adiabatic parameters and constants in the expression for the relaxation time). This difference decreases when the temperature and coupling constants increase and increases when the adiabatic parameter increases.
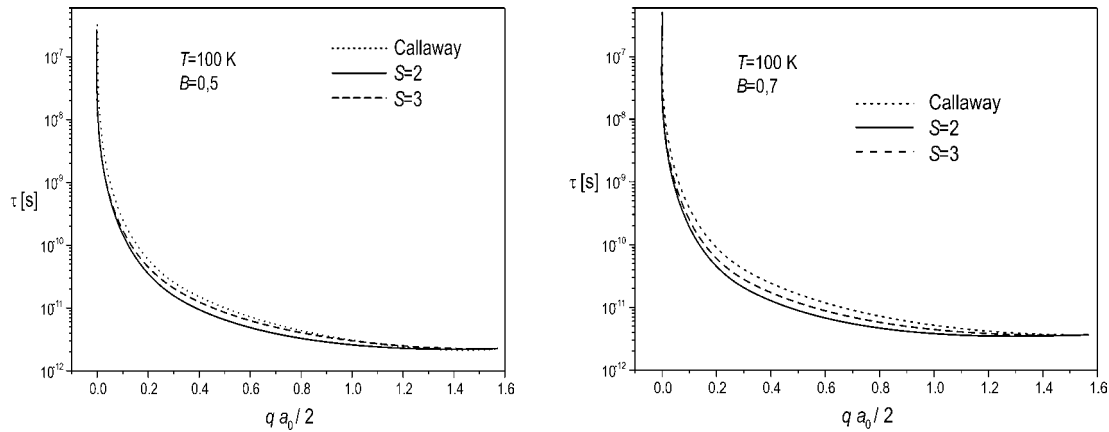
Fig. 2. Relaxation time for B=0.5 (a) and 0.7 (b)

The total relaxation time, including the renormalized dispersion relation (eq. 7), and total relaxation time obtained using the approximative linear dispersion relation are both shown in Fig. 2.

The dotted line presents the total relaxation time obtained by the simple linear dispersion law $\vec{q} = \vec{v}\,\omega/v^2$. As it can be seen, renormalization of the dispersion law causes decrease of the total relaxation time. The decreasing effect is also more noticeable for small values of S and in this case it increases when B increases.

Conclusion

Changes of the phonon spectrum caused by the polaron effect produce a larger coefficient of thermal conductivity in the area above the temperature on which the thermal conductivity becomes maximal. The results obtained are in good agreement with predictions made, using Callaway's formula at lower temperatures. The influence of the change of dispersion law also disappeared at higher temperatures that is in agreement with our previos results. The influence of the change of the dispersion relation caused by the polaron effect is more noticeable for lower values of the coupling constant and it disappears when this constant increases. This influence also increases when the adiabacy of the system increases. The total influence of the polaron effect on heat flow and thermal conductivity requires an additional study of the relaxation time and derivation of expressions for terms, which should describe phonon scattering on polarons, and will the subject of further research.

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Садржај: *У раду је развијен модел провођења топлоте у молекуларним наножицама заснован на транспорту фонона. При прорачуну је узета у обзир модификација дисперзионог закона за акустички фононски спектар која је последица електрон-фононске интеракције. Добијени резултати упоређени су са резултатима који се добијају применом једноставније Калвејеве формуле.*
Кључне речи*: молекуларне нано жице, фононско провођење топлоте, моделовање.*